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Quantum-chemical study of stability, aromaticity and reactivity properties on O- and S-heterocyclic divalent five-memberedRings $C_2H_2X_2M$ (X=O and S; M=C, Si, Ge, Sn and Pb)

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Abstract: In the present work, Density functional theory computations have been carried out at B3LYP/LANL2DZ level of theory to obtain the singlet-triplet energy, stability, aromaticity and reactivity properties of O- and S-heterocyclic five-membered divalent carbenes $C_2H_2X_2M$ (X = O and S; M = C, Si, Ge, Sn and Pb). The stabilization energies (SEs) are calculated using five isodesmic reactions. All calculations were carried out in the gas phase at room temperature and 1 atm pressure. The results indicate that the singlet states of molecules are more stable than their triplet states. All molecules have a planar conformer. The stability of $C_2H_2X_2M$ decreases from M = C to M = Pb. In contrast, the reactivity of heterocyclic carbenes is increases from M = C to M = Pb. The nucleus-independent chemical shift calculations have not effect in the stabilizing of molecules.

Keywords: Density functional theory, O-heterocyclic carbenes, S-heterocyclic carbenes, Stability, Aromaticity.

Introduction

More than 55 years ago Doering et al. and Dvoretzky et al. showed the mechanism of C-H insertion reactions of methylene [1, 2]. Hine proved dichlorocarbene as an intermediate in the chloroform hydrolysis [3]. The simple type of carbene (CR_2) has been studies by chemists for decades [4]. The carbene term refers to the specific compound methylene [5]. Carbenes are classified to singlet carbenes and triplet carbenes by their electronic structure [6]. Most of them are very short lived [7]. The spin of singlet carbenesis paired but the triplet carbenes have two unpaired electrons [8]. The triplet carbenes are paramagnetic and they could be analyzed by electron spin resonance spectroscopy, but the total spine of singlet carbenes is zero [9]. It should be noted thatthe carbenes have linear or bent geometry.

The linear and bent carbenes are formed from sp and sp^2 (or nearly pure s) orbital hybridizations, respectively [10]. These divalent carbenes and their analogues show divergent reactivity. Singlet carbenes participate in reactions as electrophiles or nucleophiles, whiles triplet carbenes participate in stepwise radical addition reactions as diradicals [11]. The first stable five-membered cyclic carbene was reported by Arduengo [12]. Later, many five-membered cyclic carbenes were prepared or studied theoretically [13-16]. Until now, many N-heterocyclic carbenes have been reported [17] but few O- and S-heterocyclic carbenes were prepared. So far, only dioxolecarbenes and dithiazolecarbenes have been synthesized [18, 19]. In the present work, we report the theoretical study of O- and S-heterocyclic five-memberedcarbenes: $C_2H_2X_2M$ (X = O and S; M = C, Si, Ge, Sn and Pb). The density functional theory (DFT) methods are used for the estimation of structural properties of different

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molecules. We have successfully used B3LYP (Becke, 3 parameter, Lee-Yang-Parr) method with LANL2DZ basis set for computing geometries, natural bond orbital populations, nucleus-independent chemical shifts (NICS), frontier orbitals energies and stabilization energies through five isodesmic reactions.

Results and discussion

The present work studies important properties containing thermal energies (E), enthalpies (H), Gibbs free energies (G), stabilization energies (SEs), aromaticity, stability and reactivity of O- and S-containing carbenes $C_2H_2X_2M$ (X = O and S; M = C, Si, Ge, Sn and Pb) (Figure **1**) by density functional theory.

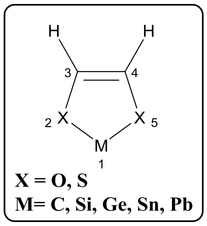


Figure 1: Divalent species of group 14 in the periodic table: Singlet and triplet of cyclic carbenes

All divalent five-membered heterocyclic molecules were optimized using the B_3LYP method in combination with the LANL2DZ basis set and the frequency calculations were carried out.
The calculated thermal energies, enthalpies and Gibbs free energies for singlet (s) and triplet (t) states of the molecules are shown in Table **1**.

Thermal energies differences (ΔE_{s-t}), enthalpy differences (ΔH_{s-t}) and Gibbs free energy differences (ΔG_{s-t}) were calculated and collected in Table **2**. We know that the compounds with negative energies are stable [21]. The DFT calculations indicate the singlet state of carbenes is more stable than the triplet state of carbenes. The change order of singlet-triplet splitting (ΔE_{s-t}, ΔH_{s-t} and ΔG_{s-t}) of $C_2H_2O_2M$ is decreased from M = C to M = Pb. The interaction of p orbital of M atom with p orbital of O atoms decreases when the size of M atom increases. The interaction between p orbitals in the singlet state of dioxolecarbene ($C_3H_2O_2$) is more than other O-heterocyclic five-membered carbenes. And also, we see the energy differences order in S-heterocyclic divalent molecules is M: Si >Ge> C >Sn>Pb. The interaction of d orbital of sulfur atoms with d orbital of silicon atom and germanium atom is more than the interaction between sulfur and carbon atoms. The strongly polarized bonds (Table **3**) of S-Sn (2.532 and 2.808 angstrom in singlet and triplet states, respectively) and S-Pb (2.575 and 2.847 angstrom in singlet and triplet states, respectively) lead to low energy differences of singlet-triplet states of $C_2H_2S_2$Snand $C_2H_2S_2$Pb.

The dihedral angles data indicate all O- and S-heterocyclic divalent compounds are planar. For determination of the stability of the carbenes, we use five isodesmic reactions (Scheme **1**).

In an isodesmic reaction, the type of chemical bonds broken in the reactant is the same as the type of bonds formed in the product [22].In the following discussion, all calculated stabilization energies (SE) were performed at the B3LYP/LANL2DZ level of theory, the same method we used in the previous sections. The values of calculated SEs for all five isodesmic equations are collected in Table 4. We concluded from previous section the singlet state of each heterocyclic carbene is more stable than the triplet state of that compound. For this reason, the isodesmic equations 1-3 are not suitable for investigation of stabilization energies. As we know, the molecules with negative stabilization energy are stabilized but the compounds with positive stabilization energy are destabilized. The dependence between isodesmic reactions, SE (Eq. 4) vs. SE (Eq. 5) is showed for both singlet and triplet states of all O- and S-heterocyclic divalent carbenes in Figure **2.**

Higher correlation coefficient ($R^2 = 0.9921$) for these two equations indicates a great convergence. As can be seen from the data of Table **4**, the stabilization energies (SEs) order in both O-heterocyclic and S-heterocyclic divalent carbenes is M: Pb>Sn>Ge> Si > C. This stabilization energies order shows the stability of heterocyclic five-membered divalent molecules is related to the size of M atom. The larger size of the lone pair orbital leads to the stability of both spin states of heterocyclic carbenes because of electron-electron repulsion factor. It can be deduced from the SEs the singlet state of $C_2H_2X_2M$ is more stable than their corresponding triplet state. For singlet states of the compounds, the lone pair electrons of M could share in electron resonance of the five-membered rings.

Aromaticity is an important character in determination of stable nature of flat rings of atoms [23]. The aromatic compounds are formed easily and after the formation, participated difficulty in reactions [24]. They show highly chemical stability, compared to similar non-aromatic compounds [25]. The nucleus-independent chemical shift (NICS) is a theoretical method for computing the aromaticity character of molecules. This theory is described by Schleyer in 1996 [26]. In this method, the chemical shift of a ghost atom is computed at various distances above the center of rings. Negative and positive NICS show the aromatic and antiaromatic character, respectively [27]. Here, we calculated this character at distances 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8 and 2 angstrom above the center of O- and S-heterocyclic divalent carbenes. The data of the NICS computations are collected in Table 5. The reliable results for aromaticity property of molecules are related to the NICS (1) calculations. As can be seen from the data, the singlet and triplet carbenes are aromatic and non-aromatic, respectively. In triplet state of compounds, the M atom could not share the lone pair electrons in electron resonance of rings. We can see this in HOMO orbital images of the molecules (Figure **3**). In contrast, the lone pair electrons of singlet carbenes could participate in electron resonance of rings. The images related to the HOMO orbital of singlet carbenes indicate the electron resonance of the rings.

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/LANL2DZ for singlet (s) and triplet (t) states of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb)

Compound	E (kcal.mol^{-1})	H (kcal.mol^{-1})	G (kcal.mol^{-1})
X=O, M=C$_{(s)}$	-166743.649	-166743.057	-166762.454
X=O, M=C$_{(t)}$	-166676.778	-166676.186	-166696.168
X=O, M=Si$_{(s)}$	-145354.451	-145353.859	-145374.197
X=O, M=Si$_{(t)}$	-145300.971	-145300.379	-145322.673
X=O, M=Ge$_{(s)}$	-145296.043	-145295.450	-145316.699
X=O, M=Ge$_{(t)}$	-145251.209	-145250.617	-145273.732
X=O, M=Sn$_{(s)}$	-145059.685	-145059.093	-145080.946
X=O, M=Sn$_{(t)}$	-145022.448	-145021.856	-145045.458
X=O, M=Pb$_{(s)}$	-145118.421	-145117.828	-145140.311
X=O, M=Pb$_{(t)}$	-145087.186	-145086.593	-145110.771
X=S, M=C$_{(s)}$	-85029.545	-85028.952	-85050.157
X=S, M=C$_{(t)}$	-84987.656	-84987.064	-85008.669
X=S, M=Si$_{(s)}$	-63630.140	-63629.548	-63652.008
X=S, M=Si$_{(t)}$	-63584.842	-63584.249	-63607.419
X=S, M=Ge$_{(s)}$	-63579.987	-63579.394	-63602.782
X=S, M=Ge$_{(t)}$	-63536.395	-63535.803	-63561.848
X=S, M=Sn$_{(s)}$	-63346.244	-63345.652	-63369.670
X=S, M=Sn$_{(t)}$	-63305.745	-63305.152	-63331.327
X=S, M=Pb$_{(s)}$	-63413.162	-63412.570	-63437.157
X=S, M=Pb$_{(t)}$	-63374.099	-63373.506	-63400.052

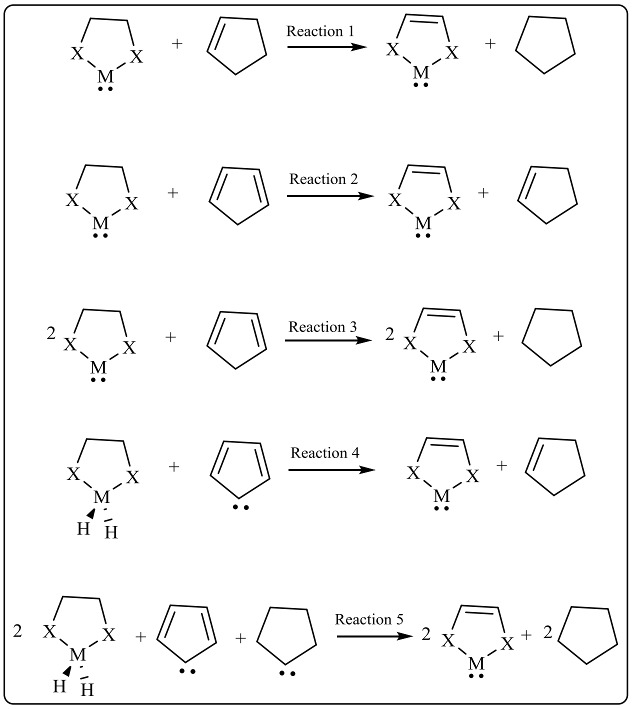
Table 2: Sum of electronic and thermal energy differences between singlet and triplet states (ΔE_{s-t}), electronic and thermal enthalpy differences (ΔH_{s-t}), electronic and thermal free energy differences (ΔG_{s-t}) at B3LYP/LANL2DZ for $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb)

Compound	ΔE_{S-T}	ΔH_{S-T}	ΔG_{S-T}
X=O, M=C	-66.871	-66.871	-66.286
X=O, M=Si	-53.480	-53.480	-51.524
X=O, M=Ge	-44.834	-44.833	-42.967
X=O, M=Sn	-37.237	-37.237	-35.488

X=O, M=Pb	-31.235	-31.235	-29.540
X=S, M=C	-41.889	-41.888	-41.488
X=S, M=Si	-45.298	-45.299	-44.589
X=S, M=Ge	-43.592	-43.591	-40.934
X=S, M=Sn	-40.499	-40.500	-38.343
X=S, M=Pb	-39.063	-39.064	-37.105

It can be concluded the aromatic character does not play an important role in the stabilizing of triplet divalent carbenes. The NICS order for singlet O- and S-heterocyclic carbenes is: M: C > Si >Ge>Sn>Pb.

Scheme 2: Five isodesmic formal reactions for stabilization energies estimation of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb)



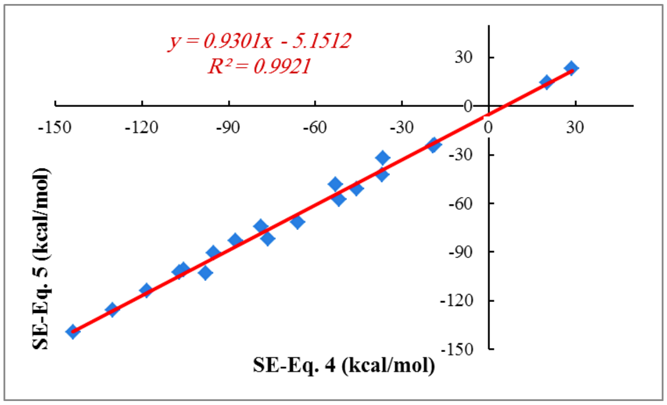
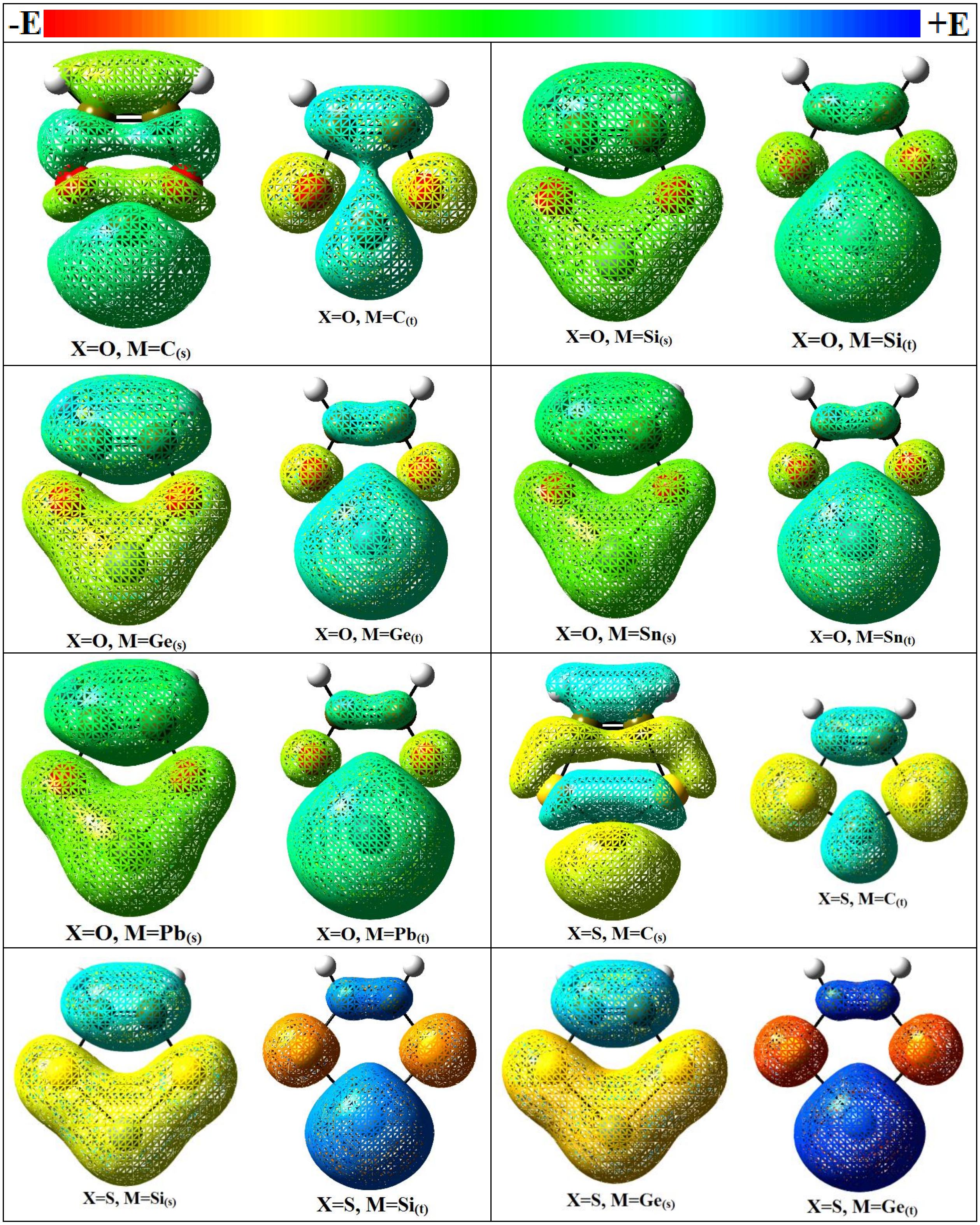


Figure 2: The dependence between SE (4) and SE (5)


-E
+E
X=O, M=C(s)
X=O, M=C(t)
X=O, M=Si(s)
X=O, M=Si(t)
X=O, M=Ge(s)
X=O, M=Ge(t)
X=O, M=Sn(s)
X=O, M=Sn(t)
X=O, M=Pb(s)
X=O, M=Pb(t)
X=S, M=C(s)
X=S, M=C(t)
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X=S, M=Si(t)
X=S, M=Ge(s)
X=S, M=Ge(t)

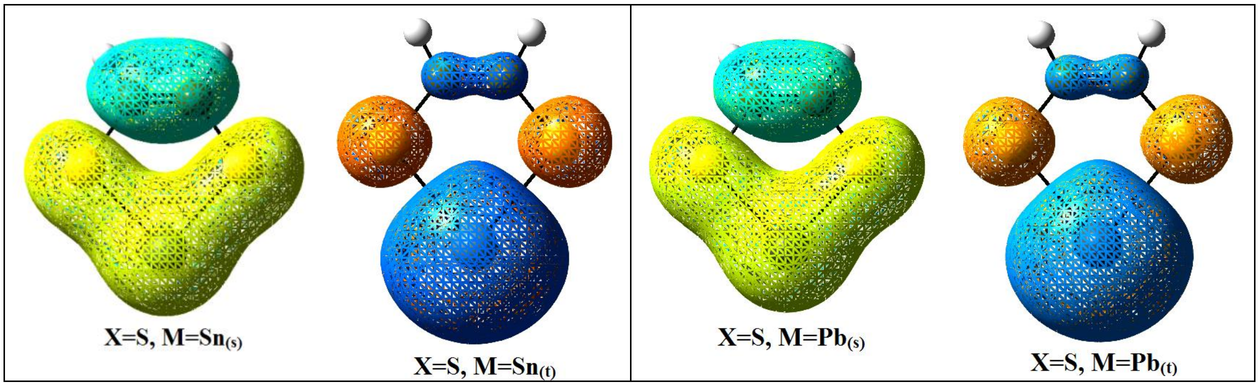

Figure 3: HOMOs for singlet (s) and triplet (t) states of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb).

Table 3: Bond lengths (angstrom), bond angles (degree) and dihedral angles (degree) at B3LYP/LANL2DZ for $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb)

Compound	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	$A_{2,1,5}$	$A_{3,2,1}$	$A_{4,3,2}$	$D_{3,2,1,5}$	$D_{4,3,2,1}$	$D_{2,3,4,5}$
X=O, M=$C_{(s)}$	1.396	1.431	1.347	103.295	111.232	107.121	0.002	-0.001	0.000
X=O, M=$C_{(t)}$	1.425	1.434	1.350	112.276	103.100	110.762	0.003	-0.002	0.000
X=O, M=$Si_{(s)}$	1.764	1.401	1.361	87.369	113.726	112.589	0.000	0.000	0.000
X=O, M=$Si_{(t)}$	2.016	1.322	1.426	80.956	112.735	116.788	0.000	0.000	0.000
X=O, M=$Ge_{(s)}$	1.861	1.394	1.364	84.436	113.505	114.177	0.000	0.000	0.000
X=O, M=$Ge_{(t)}$	2.111	1.320	1.426	78.621	112.479	118.210	0.000	0.000	0.000
X=O, M=$Sn_{(s)}$	2.011	1.389	1.368	80.000	114.013	115.986	-0.001	0.001	0.000
X=O, M=$Sn_{(t)}$	2.240	1.319	1.428	74.511	113.619	119.125	0.000	0.000	0.000
X=O, M=$Pb_{(s)}$	2.081	1.385	1.370	78.760	113.299	117.321	-0.001	0.001	0.000
X=O, M=$Pb_{(t)}$	2.317	1.318	1.428	73.315	112.822	120.520	0.000	0.000	0.000
X=S, M=$C_{(s)}$	1.797	1.833	1.352	108.997	100.104	115.439	0.000	0.000	0.000
X=S, M=$C_{(t)}$	1.824	1.834	1.350	118.715	91.456	119.191	0.000	0.000	0.000
X=S, M=$Si_{(s)}$	2.282	1.810	1.356	92.209	101.610	122.286	0.000	0.000	0.000
X=S, M=$Si_{(t)}$	2.583	1.754	1.397	85.174	100.652	126.761	-0.004	0.003	0.000
X=S, M=$Ge_{(s)}$	2.369	1.809	1.357	89.959	101.596	123.425	0.034	-0.029	0.000
X=S, M=$Ge_{(t)}$	2.659	1.754	1.397	83.279	100.847	127.513	0.077	-0.073	0.000
X=S, M=$Sn_{(s)}$	2.532	1.811	1.357	85.947	101.691	125.335	0.000	0.000	0.000
X=S, M=$Sn_{(t)}$	2.808	1.754	1.398	79.335	101.763	128.570	0.000	0.000	0.000
X=S, M=$Pb_{(s)}$	2.575	1.810	1.358	85.199	101.410	125.996	0.000	0.000	0.000
X=S, M=$Pb_{(t)}$	2.847	1.754	1.399	78.660	101.611	129.060	0.000	0.000	0.000

This armaticity character order is consistent with the stability order of O-heterocyclic singlet carbenes but is not consistent with the stability order of S-heterocyclic five-membered divalent carbenes. The only conclusion that is received from the NICS data is the more stability of singlet carbenes to the triplet carbenes.

Natural bond orbital (NBO) analysis of M atoms in studied carbenes is performed at the B3LYP/LANL2DZ level of theory. The natural bond orbital data are collected in Table 6. As can be seen from the data, the M atom participates in all structures with s or nearly s hybrids.

Table 4: Stabilization energies (SE) estimation for singlet and triplet states of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb) through five isodesmic equations (eq.) at B3LYP/LANL2DZ level of theory

Compound	Stabilization Energy (kcal.mol^{-1}) B3LYP/LANL2DZ				
	Eq. 1	Eq. 2	Eq. 3	Eq. 4	Eq. 5
X=O, M=C$_{(s)}$	3.904	5.399	4.652	-52.852	-48.432
X=O, M=C$_{(t)}$	5.466	6.961	6.214	28.761	23.253
X=O, M=Si$_{(s)}$	-3.215	-1.720	-2.467	-87.504	-83.084
X=O, M=Si$_{(t)}$	-27.621	-26.126	-26.873	-19.282	-24.790
X=O, M=Ge$_{(s)}$	-5.930	-4.435	-5.182	-105.356	-100.936
X=O, M=Ge$_{(t)}$	-40.180	-38.098	-39.432	-45.780	-51.288
X=O, M=Sn$_{(s)}$	-9.424	-7.929	-8.676	-118.155	-113.735
X=O, M=Sn$_{(t)}$	-37.536	-36.041	-36.788	-66.176	-71.684
X=O, M=Pb$_{(s)}$	-11.435	-9.940	-10.687	-143.771	-139.351
X=O, M=Pb$_{(t)}$	-38.861	-37.366	-38.113	-97.794	-103.302
X=S, M=C$_{(s)}$	1.736	3.231	2.484	-36.529	-32.109
X=S, M=C$_{(t)}$	5.320	6.815	6.068	20.102	14.594
X=S, M=Si$_{(s)}$	-2.626	-1.131	-1.878	-78.628	-74.208
X=S, M=Si$_{(t)}$	-8.151	-6.656	-7.403	-18.588	-24.096
X=S, M=Ge$_{(s)}$	-2.986	-1.491	-2.238	-95.256	-90.836
X=S, M=Ge$_{(t)}$	-15.579	-14.084	-14.831	-36.922	-42.430
X=S, M=Sn$_{(s)}$	-3.137	-1.642	-2.389	-107.047	-102.627
X=S, M=Sn$_{(t)}$	-10.546	-9.051	-9.798	-51.806	-57.314
X=S, M=Pb$_{(s)}$	-3.565	-2.070	-2.817	-130.070	-125.65
X=S, M=Pb$_{(t)}$	-11.293	-9.798	-10.545	-76.265	-81.773

Table 5: NICS calculations for singlet and triplet states of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb) at B3LYP/LANL2DZ level of theory

Compound	NICS (0)	NICS (0.2)	NICS (0.4)	NICS (0.6)	NICS (0.8)	NICS (1)	NICS (1.2)	NICS (1.4)	NICS (1.6)	NICS (1.8)	NICS (2)
X=O, M=C$_{(s)}$	-11.326	-11.441	-11.540	-11.211	-10.328	-9.061	-7.660	-6.315	-5.131	-4.142	-3.341
X=O, M=C$_{(t)}$	-8.246	-7.679	-6.305	-4.773	-3.526	-2.659	-2.078	-1.665	-1.342	-1.074	-0.847
X=O, M=Si$_{(s)}$	-9.129	-9.111	-8.976	-8.589	-7.916	-7.039	-6.078	-5.134	-4.272	-3.524	-2.896
X=O, M=Si$_{(t)}$	1.235	1.075	0.684	0.239	0.145	-0.439	-0.650	-0.785	-0.846	-0.843	-0.792
X=O, M=Ge$_{(s)}$	-8.394	-8.397	-8.326	-8.042	-7.492	-6.733	-5.870	-5.001	-4.194	-3.486	-2.887
X=O, M=Ge$_{(t)}$	1.293	1.121	0.702	0.229	-0.172	-0.471	-0.682	-0.817	-0.882	-0.886	-0.845
X=O, M=Sn$_{(s)}$	-7.781	-7.778	-7.705	-7.453	-6.979	-6.326	-5.576	-4.808	-4.081	-3.430	-2.869
X=O, M=Sn$_{(t)}$	1.595	1.419	0.987	0.493	0.066	-0.264	-0.512	-0.691	-0.803	-0.853	-0.849
X=O, M=Pb$_{(s)}$	-7.246	-7.256	-7.225	-7.038	-6.643	-6.073	-5.400	-4.697	-4.022	-3.408	-2.872
X=O, M=Pb$_{(t)}$	1.769	1.589	1.149	0.643	0.204	-0.138	-0.398	-0.591	-0.719	-0.786	-0.798
X=S, M=C$_{(s)}$	-10.659	-10.811	-11.110	-11.235	-10.943	-10.197	-9.122	-7.894	-6.669	-5.548	-4.578

X=S, M=$C_{(t)}$	-8.665	-8.348	-7.488	-6.310	-5.063	-3.925	-2.975	-2.222	-1.643	-1.208	-0.886
X=S, M=$Si_{(s)}$	-10.164	-10.169	-10.119	-9.886	-9.383	-8.617	-7.668	-6.641	-5.631	-4.707	-3.903
X=S, M=$Si_{(t)}$	-0.215	-0.283	-0.434	-0.564	-0.606	-0.564	-0.476	-0.382	-0.304	-0.250	-0.218
X=S, M=$Ge_{(s)}$	-9.807	-9.805	-9.740	-9.499	-9.006	-8.268	-7.361	-6.380	-5.417	-4.534	-3.766
X=S, M=$Ge_{(t)}$	-0.116	-0.188	-0.349	-0.494	-0.554	-0.527	-0.452	-0.368	-0.298	-0.251	-0.223
X=S, M=$Sn_{(s)}$	-9.477	-9.452	-9.335	-9.046	-8.535	-7.820	-6.967	-6.057	-5.166	-4.347	-3.632
X=S, M=$Sn_{(t)}$	0.097	0.027	-0.133	-0.283	-0.358	-0.355	-0.309	-0.257	-0.220	-0.203	-0.201
X=S, M=$Pb_{(s)}$	-9.093	-9.069	-8.957	-8.683	-8.200	-7.526	-6.720	-5.859	-5.014	-4.235	-3.550
X=S, M=$Pb_{(t)}$	0.197	0.127	-0.037	-0.194	-0.277	-0.284	-0.249	-0.209	-0.183	-0.176	-0.182

Table 6: NBO analysis for singlet and triplet states of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb) at B3LYP/LANL2DZ level of theory

Compound	NBOs	Hybrids	Geometry
X=O, M=$C_{(s)}$	LP (C_s)	$sp^{0.44}$	Bent
X=O, M=$C_{(t)}$	LP (C_t)	p, $sp^{0.70}$	Bent
X=O, M=$Si_{(s)}$	LP (Si_s)	$sp^{0.17}$	Bent
X=O, M=$Si_{(t)}$	LP (Si_t)	p, $sp^{0.06}$	Bent
X=O, M=$Ge_{(s)}$	LP (Ge_s)	$sp^{0.13}$	Bent
X=O, M=$Ge_{(t)}$	LP (Ge_t)	$sp^{0.06}$	Bent
X=O, M=$Sn_{(s)}$	LP (Sn_s)	$sp^{0.11}$	Bent
X=O, M=$Sn_{(t)}$	LP (Sn_t)	$sp^{0.06}$	Bent
X=O, M=$Pb_{(s)}$	LP (Pb_s)	$sp^{0.07}$	Bent
X=O, M=$Pb_{(t)}$	LP (Pb_t)	$sp^{0.03}$	Bent
X=S, M=$C_{(s)}$	LP (C_s)	$sp^{0.49}$	Bent
X=S, M=$C_{(t)}$	CR (C_t)	s	Bent
X=S, M=$Si_{(s)}$	LP (Si_s)	$sp^{0.14}$	Bent
X=S, M=$Si_{(t)}$	LP (Si_t)	$sp^{0.05}$	Bent
X=S, M=$Ge_{(s)}$	LP (Ge_s)	$sp^{0.10}$	Bent
X=S, M=$Ge_{(t)}$	LP (Ge_t)	$sp^{0.04}$	Bent
X=S, M=$Sn_{(s)}$	LP (Sn_s)	$sp^{0.08}$	Bent
X=S, M=$Sn_{(t)}$	LP (Sn_t)	$sp^{0.04}$	Bent
X=S, M=$Pb_{(s)}$	LP (Pb_s)	$sp^{0.06}$	Bent
X=S, M=$Pb_{(t)}$	LP (Pb_t)	$sp^{0.02}$	Bent

Then, it can be deduced the M atom has bent geometry in all heterocyclic carbenes.

Table **7** indicates the frontier orbitals (HOMO and LUMO) energies of singlet and triplet carbenes.

The energy gaps of the frontier orbitals could explain the energy changes of singlet and triplet states [28]. The larger HOMO-LUMO energy gap shows more stability to lower energy gaps [29]. According to the data, all singlet carbenes are more stable than the triplet states of carbenes. The HOMO-LUMO energy gaps order for both singlet and triplet states of O- and S-heterocyclic divalent molecules is M: C > Si >Ge>Sn>Pb. We can deduce that the frontier orbitals energies gap increases when the size of M atom decreases. This energy gaps order is precisely consistent with the stability order that described in previous sections. The chemical hardness of a molecule is obtained by following equation [30]:

$$n = \frac{\text{LUMO} - \text{HOMO}}{2}$$

As we know, the reactivity of a compound increases when the chemical hardness character of the molecule decreases [31]. From the data of the Table 7, we can see the reactivity of the triplet carbenes is more than the reactivity of the singlet carbenes. And also, the reactivity order for both singlet and triplet carbenes is M: Pb>Sn>Ge> Si > C.

Table 7: LUMO-HOMO gaps (eV) of $C_2H_2X_2M$ (where X = O and S; M = C, Si, Ge, Sn and Pb) at B3LYP/LANL2DZ level of theory

Compound	ε_{HOMO} (a.u.)	ε_{LUMO} (a.u.)	$GAP_{L\text{-}H}$ (eV)	η (eV)
X=O, M=$C_{(s)}$	-0.28007	-0.05101	6.233	3.117
X=O, M=$C_{(t)}$	-0.16776	-0.01572	4.137	2.069
X=O, M=$Si_{(s)}$	-0.25150	-0.07797	4.722	2.361
X=O, M=$Si_{(t)}$	-0.15950	-0.03553	3.373	1.687
X=O, M=$Ge_{(s)}$	-0.23424	-0.07974	4.204	2.102
X=O, M=$Ge_{(t)}$	-0.15621	-0.04391	3.056	1.528
X=O, M=$Sn_{(s)}$	-0.21584	-0.08405	3.586	1.793
X=O, M=$Sn_{(t)}$	-0.14986	-0.05503	2.580	1.290
X=O, M=$Pb_{(s)}$	-0.20211	-0.08068	3.304	1.652
X=O, M=$Pb_{(t)}$	-0.14631	-0.05635	2.448	1.224
X=S, M=$C_{(s)}$	-0.25639	-0.08053	4.785	2.393
X=S, M=$C_{(t)}$	-0.17127	-0.03839	3.616	1.808
X=S, M=$Si_{(s)}$	-0.25618	-0.10316	4.164	2.082
X=S, M=$Si_{(t)}$	-0.17564	-0.06568	2.992	1.496
X=S, M=$Ge_{(s)}$	-0.24496	-0.10149	3.904	1.952
X=S, M=$Ge_{(t)}$	-0.16958	-0.06763	2.774	1.387
X=S, M=$Sn_{(s)}$	-0.23301	-0.10279	3.543	1.772
X=S, M=$Sn_{(t)}$	-0.16226	-0.07468	2.383	1.192
X=S, M=$Pb_{(s)}$	-0.22366	-0.09745	3.434	1.717
X=S, M=$Pb_{(t)}$	-0.15598	-0.07098	2.313	1.157

Conclusions

The above computational study of O- and S-heterocyclic five-membered carbenes in gas phase yielded good results about the stability, aromaticity and reactivity characters. All calculations are carried out at B3LYP/LANL2DZ level of theory. For all molecules, both singlet and triplet states show a planar conformer with a singlet ground state. The M atom geometry is bent in all singlet and triplet carbenes. The calculations results indicate the stability order and reactivity order of the divalent molecules are M: C > Si >Ge>Sn>Pb and Pb>Sn>Ge> Si > C, respectively. NICS data indicate the aromaticity has not effect in the stability of heterocyclic carbenes.

Computational methods

All geometry optimizations of O- and S-heterocyclic five-membered carbenes are performed at B3LYP/LANL2DZ level of theory by the GAUSSIAN 03 software [20]. All optimized structures were determined to be true local energy minima on potential energy surfaces without imaginary frequencies.Stabilization energy (SE) has been calculated by designing five isodesmic reactions for the compounds. The nucleus-independent chemical shift (NICS) has been computed for prediction of aromaticity property of molecules. All computations are performed without restrictions in gas phase at room temperature and 1 atm pressure.

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