Electronic effects at 2 and 7 α–position of divalent unsaturated seven membered ring R₂C₆H₆M (M=C, Si, Ge, Sn, Pb)

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ABSTRACT

Electronic effects were investigated on the singlet–triplet energy gaps of divalent unsaturated seven-membered ring R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr , t-Bu) at B3LYP/6-311++G** level. All the triplet states of R2C6H6C were more stable than the related the singlet states while all the singlet states of R2C6H6M (M= Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr , t-Bu) were more stable than the related triplet states. The ∠C2-M1-C7 angle of all the triplet states of R2C6H6M is larger than their singlet states. Calculated dihedral angles indicated a nonplanar structure for both singlet and triplet states of R2C6H6M. The NBO charge at heteroatom center (M) of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, *i*-Pr , t-Bu) for both singlet and triplet states were generally increased when the bulky substituent (R = t-Bu) were placed at 2 and 7 (α–position) of seven membered ring. The chemical hardness (η) value for triplet states of R2C6H6M (M=C, Si, Ge, Sn R= –H, -CH3, *i*-Pr , t-Bu) were larger than the corresponding singlet states. A linear correlation was found between the LUMO–HOMO energy gaps of the singlet species, and their corresponding ∆Gt–s..

Keywords: carbenes; energy gaps; NBO charge; Seven-memebered; DFT method

INTRODUCTION

Compounds of carbenes possessing a neutral divalent carbon atom with six electrons on its valence shell have enjoyed a long and fruitful history in the field of chemical sciences that started almost a 150 years ago [1].

Divalent carbenes and their analogues remained simple proposals for a long time and generated numerous theoretical and experimental interrogations. Among the most noticeable questions, their electronic configuration − singlet or triplet − along with the geometry around the carbenic carbon took a prominent place. Carbenes and their analogues are strongly reactive and have played important roles as transient intermediate and powerful reagents [2-3]. These compounds are found with both the singlet and triplet ground electronic states, each with a distinctive chemistry [4].

The influence of the substituents on the carbene ground-state multiplicity can be easily analyzed in terms of electronic and steric effects.

It is now well established that the σ-electron withdrawing substituents favor the singlet versus the triplet state [5-7]. In particular, Harrison et. al [5a,c] showed that the ground state goes from triplet to

singlet when the substituents changed from electropositive lithium to hydrogen and to electronegative fluorine for methelenes compounds. The σ-electron withdrawing substituents inductively stabilize the σ nonbonding orbital by increase its *s* character and leave the *p*π orbital unchanged. The σ-pπ gap is thus increased and the singlet state is favored. In contrast, the σ-electron-donating substituents induce a small σ-pπ gap which favors the triplet state. Bulky substituents clearly kinetically stabilize all types of carbenes. Moreover, if electronic effects are negligible, the steric effects may also dictate the ground-state spin multiplicity. Increase the steric bulk of carbene substituents broadens the carbene bond angle and therefore favors the triplet state [8].

We have already reported the halogens, electron donating and electron withdrawing substituents effects on the stability, multiplicity, the singlet–triplet splitting and geometrical parameters of different three, five and seven membered ring of divalent carbon atom with heavier group 14 elements as well as steric effects on the singlet-triplet energy gaps of five membered ring R2C4H2M [9-15]. Follow up on our works [9-15], in this paper, we will focus on the energies of the singlet and triplet state as well as the energy splitting of the singlet-triplet state of the carbenes and their analogues. thus the density functional theory (DFT) calculations were carried out due to study the electronic effects at α-position on the singlet-triplet splitting R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, *i*-Pr , t-Bu) (Fig. 1).

COMPUTATIONAL METHODS
All the structures considered here, were fully optimized within the symmetry constraints using the hybrid density functional B3LYP [16-18] method using

the 6-311++G** basis set. GAUSSIAN 98 program package was employed for all the calculations carried out in the study [19]. For Sn and Pb atoms, the calculations were done using LANL2DZ basis set [20]. All the calculations were carried out for gas phase at 298K temperature and 1 atm. pressure.
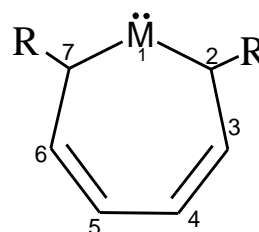
Fig. 1. Singlet-triplet states of R2C6H6M. M=C,Si,Ge,Sn,Pb and R = -H, -CH3, i-Pr, t-Bu.

RESULTS AND DISCUSSION
Gibbs free energies (G) and Gibbs free energy gaps ΔGt–s , in kcal/mol between the singlet (s) and triplet (t) states were calculated for R2C6H6M (M=C, Si, Ge, Sn, Pb; R= –H, -CH3, *i*-Pr , t-Bu) *via* B3LYP/6-311++G** level (Table 1).
Other geometrical parameters such as bond angles and dihedral angles are given in degrees, bond lengths in angstrom. The NBO charge at atoms and chemical hardness (η) in electron volte (e.v) were calculated and discussed (Table 2-4).

Rationalizations free energy gaps ΔG(t-s) for substitution effects at 2 and 7 (α –position) of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr , t-Bu).
The ΔGt–s between the singlet and triplet states of R2C6H6M (M = C, Si, Ge, Sn, Pb, R= –H, -CH3, *i*-Pr, t-Bu) were increased at B3LYP/6-311++G** level in the order (in kcal/mol):
For M = C H (-0.26) > Me (-3.77) > *i*-Pr (-4.55) > *tert*-Bu (-8.08)
For M= Si H (23.73) > *i*-pr (20.56) > Me (20.32) > *tert*-Bu (15.92)

For M= Ge H (27.69) > *i*-pr (21.25) > Me (20.25) > *tert*-Bu (18.34)
For M= Sn *i*-pr (19.38) > H (18.69) > *tert*-Bu (18.25) > Me (14.66)
For M= Pb Me (29.43) > *tert*-Bu (18.85) > *i*-pr (18.31) > H (16.86)

DFT calculations indicated that all the triplet states of R2C6H6M (M=C, R= –H, -CH3, *i*-Pr, t-Bu) are more stable than the related singlet states while for M= Si, Ge, Sn and Pb all the singlet states are more stable than the related triplet states.

The calculated ΔG(t-s) for R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, *i*-Pr, t-Bu) indicated that the triplet states of R2C6H6M were generally stabilized or the singlet state were generally unstabilized when the bulky substituent (R = *t*-Bu) was used at 2 and 7 (α –position) of seven membered ring R2C6H6M. The singlet-triplet gaps ΔGt–s, for R2C6H6M (M = C, Si, Ge, Sn and Pb) were generally increased in the order : R2C6H6Ge > R2C6H6Si > R2C6H6Sn > R2C6H6Pb > R2C6H6C.

The determined ΔGt–s between the singlet and triplet states of R2C6H6M indicate that the ΔGt–s was increased from M = C to M = Ge. The stability of the singlet state of R2C6H6M with replacement of the heavy atom (from M = C to M = Ge) could reasonably be explained by atomic radius of heteroatom. The higher atomic radius of a heteroatom (M) decreases the lone pair electron repulsion for the singlet state and hence increases the stability of the singlet state. The unpredicted decrease of ΔGt–s for R2C6H6M from M = Ge to M = Pb is related to triplet state structures obtained through full optimizations. Triplet state structure tends to break out from strained seven membered ring during optimizations. Therefore, the triplet state of these structures is not actually a seven membered rings. Thus, the triplet states of R2C6H6M (M = Ge to M = Pb) achieve more stability and decrease of ΔGt–s.

Rationalizations bond lengths (A•), bond angle and dihedral angle (degree) for substitution effects at 2 and 7 (α–position) of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= – H, -CH3, i-Pr , t-Bu)

The triplet states of R2C6H6C (R= –H) have a larger bond lengths C1-C2 respect to the corresponding to the singlet states (Table 2). Larger bond lengths C1-C2 for the triplet state of R2C7H6 (R= –H) led to *p* character of nonbonding electron. However, the singlet states of R2C6H6C (R= -CH3, *i*-Pr, t-Bu) have larger bond lengths C1-C2 and C1-C7 than corresponding triplet states. Larger bond lengths C1-C2 and C1-C7 for the singlet state of R2C6H6C (R= -CH3, *i*-Pr, t-Bu) led to *p* character of nonbonding electron (Table 2).

In contrast to R2C6H6C, the triplet states of R2C6H6M (M= Si, Ge, Sn and Pb, R= –H, -CH3, *i*-Pr, t-Bu) have a larger bond angle C7–M:1–C2 respect to corresponding to triplet state; stabilizing the singlet state (Table 2). Larger bond lengths M1-C2 and M1-C7 for the triplet state of R2C6H6M led to *p* character of nonbonding electron.

The ∠C2-M1-C7 angles of R2C6H6M (M = C, Si, Ge, Sn, Pb, R= –H, -CH3, *i*-Pr, t-Bu) is larger for their triplet than their singlet states. Decrease in the bond angle of R2C6H6C for the singlet states led to s character of nonbonding electron; stabilizing the singlet states.

Calculated dihedral angles indicated a non-planar structure for both singlet and triplet states of R2C6H6C (R= –H, -CH3, *i*-Pr, t-Bu) (Table 2).

Rationalizations chemical hardness (η) and NBO charge on heteroatom for substitution effects at 2 and 7 (α–position)

**of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr , t-Bu).**

Calculated NBO charge indicated that NBO charge at heteroatom center of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr, t-Bu) for both singlet and triplet states were generally increased when the bulky substituent (R = t-Bu) were placed at 2 and 7 (α–position) of seven membered ring (Table 3). This show that the bulky substituent (R = t-Bu) decrease the electron density of heteroatom center.

The chemical hardness (η) value is equal to HOMO-LUMO energy separation. The chemical hardness (η) value is a simple indicator of kinetic stability. A large chemical hardness (η) implies high kinetic stability and low chemical reactivity. The chemical hardness (η) value

for all triplet states of R2C6H6M (M=C, Si, Ge, Sn; R= –H, -CH3, *i*-Pr , t-Bu) were larger than the corresponding singlet states. Thus kinetic stability of all triplet states in R2C6H6M (M=C, Si, Ge, Sn) is more than their corresponding singlet states.

Also linear correlations are encountered between the LUMO–HOMO energy gaps of the singlet(stable) states of R2C6H6M (M= Si, Ge, Sn, Pb) compounds, and their corresponding singlet–triplet energy separations are calculated at B3LYP/6-311++G∗∗ level of theory (Fig 2). Correlation coefficient (R2) values of R2C6H6M compounds is R2 =0.81 for M= Si, R2 =0.96 for M= Ge, R2 =0.82 for M= Sn and R2 =0.99 for M= Pb respectively.
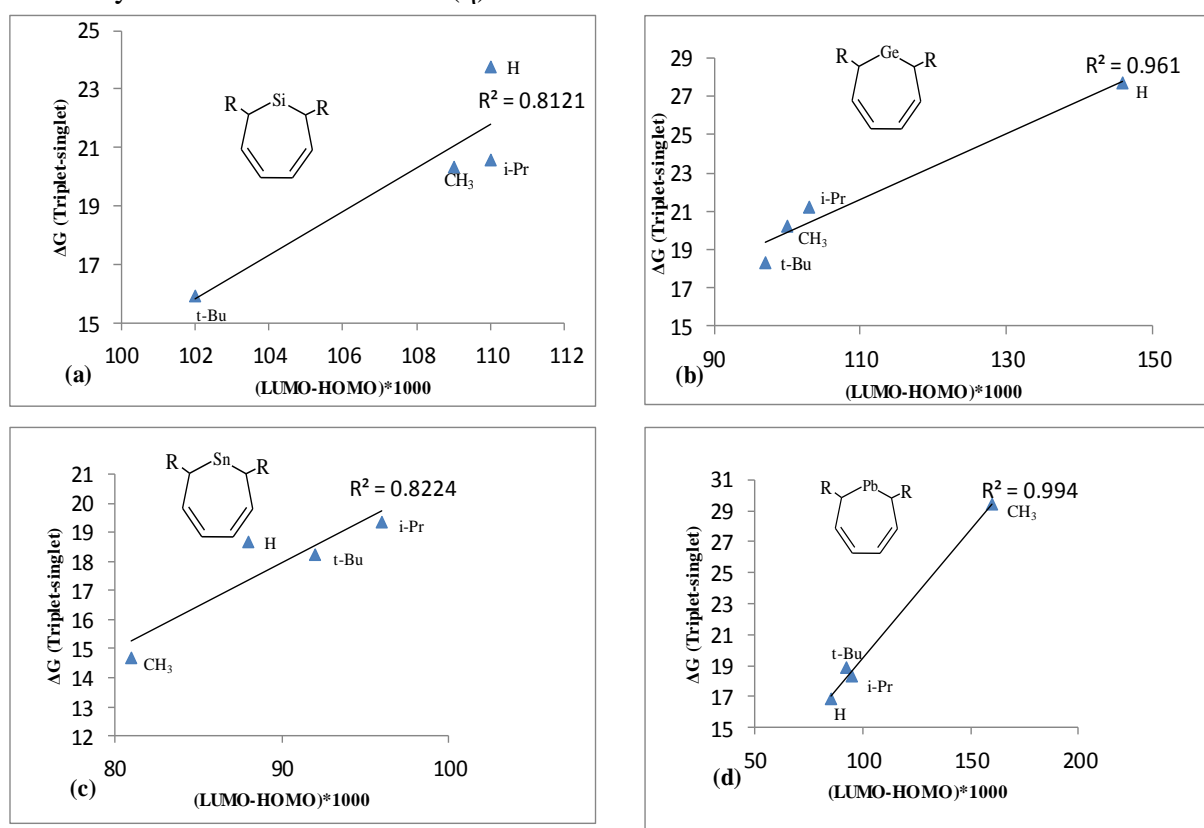
Fig. 2. Linear relationships between singlet LUMO–HOMO energy gaps, and their corresponding singlet–triplet energy separations ΔG(triplet–singlet), for $R_2C_6H_6M$ compounds : silylenes (a), germylenes (b), stanylenes (c), plumbylenes (d); with correlation coefficient(R^2), respectively.

CONCLUSIONS

The ΔGt–s between singlet and triplet states of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr, t-Bu) was determined. The calculated ΔGt–s for R2C6H6M (M=C, Si, Ge, Sn, Pb) indicated that the triplet states of R2C6H6M were stabilized when the bulky substituent (R = t-Bu) was used. DFT calculations indicated that all the triplet states of R2C6H6C are more stable than the related singlet states but for R2C6H6M (M= Si, Ge, Sn, Pb) all the singlet states are more stable than the related triplet states.

The bond angle A7,1.2 of R2C6H6M (M=C, Si, Ge, Sn, Pb, R= –H, -CH3, i-Pr, t-Bu) is larger for the triplet than those singlet states. Calculated dihedral angles indicated a nonplanar structure for both the singlet and triplet states of R2C6H6M.

Calculated NBO charge indicated that NBO charge at heteroatomic center of R2C6H6M (R= –H, -CH3, i-Pr, t-Bu) for both singlet and triplet states were generally increased when the bulky substituent (R = t-Bu) were placed at 2 and 7 (α –position) of seven membered ring.

According to chemical hardness (η) value The kinetic stability of all triplet states in R2C6H6M (M=C, Si, Ge, Sn) is more than their corresponding singlet states.

Correlation coefficient (R2) value for seven membered ring R2C6H6M (M= Si, Ge, Sn, Pb) showed linear relationships between singlet(stable states) LUMO–HOMO energy gaps, and their corresponding singlet–triplet energy separations ΔG(t-s).

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