

**Steric effects on the Singlet–Triplet Energy Gaps of Seven Membered Ring silylenes,
 $R_2C_6H_6Si$**

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ABSTRACT

With the aim of recognizing the steric effects on the silylenic $R_2C_6H_6Si$ structures, DFT calculations are carried out on 8 structures of $R_2C_6H_6Si$ (where R is hydrogen (H), methyl (Me), isopropyl (i-pro), and tert-butyl (tert-Bu)). These species are at either triplet (t) or singlet (s) states. Singlet–triplet energy separations (ΔG_{t-s}) and relative energies for the above structures are acquired at B3LYP/6-31G** levels of theory. The ΔG_{t-s} of $R_2C_6H_6Si$ was increased in the order (in kcal/mol): H (23.73) > i-Pr (20.56) > Me (20.32) > t-Bu (15.92). all singlet states of $R_2C_6H_6Si$, are more stable than their corresponding triplet states. linear correlations are encountered between the LUMO–HOMO energy gaps of the singlet(stable) states of $R_2C_6H_6Si$ compounds, and their corresponding singlet–triplet energy separations are calculated at B3LYP/6-311++G** level of theory. Other geometrical parameters such as bond angles, dihedral angles, bond lengths, NBO charge at atoms, dipole moments (D), (HOMO), (LUMO), chemical hardness (η), chemical potential (μ), electrophilicity (ω) and the maximum amount of electronic charge, ΔN_{max} were calculated and discussed.

Keywords: Silylenes; Energy gaps; Seven-memebered; DFT method

INTRODUCTION

Many workers have addressed interesting questions concerning the generation, reactivity, substituent effects, singlet–triplet energy gaps, relative stabilities and usages of silylenes [1–7].the ground state of silylene (SiH_2) is singlet and Singlet–Triplet Energy Gaps of it is 20 kcal/mol [8]. the most important factor in the stabilization of singlet silylene is the p-electron donation from the substituent to the formally empty p-orbital of silicon. This effect is the largest if the substituent

is in α -position to the divalent center. On the other hand, triplet silylenes can be stabilized by electropositive substituents [9, 10]. steric effects on C_3H_2 isomers due to dialkyl substitutions has been studied and reported [11]. 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

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atom with heavier group 14 elements as well as steric effects on the singlet-triplet energy gaps of five membered ring $R_2C_4H_2M$ [12-18]. Follow up on our works [12-18], in this paper, we have studied the Steric effects on the Singlet-Triplet Energy Gaps of Seven Membered Ring $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$) using computational DFT method (Fig 1).

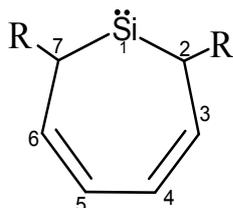


Fig. 1. Singlet-triplet states of $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$).

MODEL OF EQUATIONS

The global electrophilicity power (ω), has been defined by Parr et al [19]. The electrophilicity index has been successfully applied in the theoretical studies of many systems [20-28] and a useful review has also published by Chattaraj and Roy [29]. It has been successfully used to describe reactivity in the different organic systems. For instance, the global electrophilicity values obtained from ω have been used to rank the electrophilicity of reagents participating in Diels Alder and 1, 3-dipolar cycloaddition reactions [30,31]. The global electrophilicity index which measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment, has been given in the following expressions [19] in terms of the electronic chemical potential, μ , or the electronegativity, χ , and the chemical hardness, η .

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}$$

For an N-electron system with η and χ were defined as [19,32]:

$$\eta \approx E_{LUMO} - E_{HOMO}$$

$$\chi = -\mu \approx -\frac{1}{2}(E_{LUMO} + E_{HOMO})$$

The ω index establishes an absolute scale of electrophilicity in the sense that the hierarchy of electrophilicity is built up from the electronic structure of molecules, independent of the nucleophilic partner, which is replaced by an unspecified environment viewed as a sea of electrons [19]. This index has been found to be almost insensitive to solvent effects for neutral electrophiles [33]. Thus, gas phase calculations suffice to establish the electrophilic power of molecules. A high value of μ and a low value of η therefore characterize a good electrophile. On the other hand, the maximum amount of electronic charge that the electrophile system may accept is given by:

$$\Delta N_{max} = -\frac{\mu}{\eta}$$

Thus, while the quantity of ω describes the propensity of the system to acquire additional electronic charge from the environment, the quantity of ΔN_{max} describes the charge capacity of the molecule.

COMPUTATIONAL METHODS

All the structures considered here, were fully optimized within the symmetry constraints using the hybrid density functional B3LYP [34-36] method using the 6-311++G** basis set. GAUSSIAN 98 program package was employed for all the calculations carried out in the study [37]. All the calculations were carried out for gas phase at 298K temperature and 1 atm pressure.

RESULTS AND DISCUSSION

Thermal internal energy (E), enthalpies (H) and Gibbs free energies (G) were calculated for the singlet (s) and triplet (t) states of $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$) via B3LYP/6-311++G** level

(Table 1), also Thermal internal energy gaps, ΔE_{t-s} ; enthalpy gaps, ΔH_{t-s} ; Gibbs free energy gaps ΔG_{t-s} , in kcal/mol between singlet and triplet states, were calculated at same the level (Table1).

Other geometrical parameters such as bond angles and dihedral angles are given in degrees, bond lengths in angstroms. the NBO charge at atoms and dipole moments (D) are given in Debyes, and the positions of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and chemical hardness (η), chemical potential (μ), electrophilicity (ω) are given in electron volt (e.v) and the maximum amount of electronic charge, ΔN_{max} , electron volt (e.v) were calculated and discussed.

Rationalizations free energy gaps $\Delta G(t-s)$ for substitution effects at 2,7 α -position of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu)
The ΔG_{t-s} between the singlet and triplet states of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu) were increased at B3LYP/6-311++G** level in the order (in kcal/mol): H (23.73) > *i*-Pr (20.56) > Me (20.32) > *t*-Bu (15.92) (Table1).

DFT calculations indicated that all the singlet states of $R_2C_6H_6Si$ are more stable than the related triplet states. also The calculated ΔG_{t-s} indicated that the effect of bulky substituent (R = *t*-Bu) on free energy gap (ΔG_{t-s}) is mor than other groups. the triplet states of $R_2C_6H_6Si$ were generally stabilized or the singlet state were generally unstabilized when the bulky substituent (R = *t*-Bu) was used at 2,7 α - position of seven membered ring $R_2C_6H_6Si$.

Rationalizations bond lengths (A°) bond angle and dihedral angle (degree) for substitution effects at 2,7 α -position of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu)
The triplet states of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu) have a larger bond

lengths Si₁-C₂ and Si₁-C₇ respect to corresponding to singlet states (Table 2). larger bond lengths for the triplet state of $R_2C_6H_6Si$ led to *p* character of nonbonding electron (Table 2).

The $\angle C_2-Si_1-C_7$ angles of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu) is larger for their triplet than their singlet states. decrease in the bond angle of $R_2C_6H_6Si$ for the singlet states led to *s* character of nonbonding electron; stabilizing the singlet states. Also from -H substituent to bulky substituent (R = *t*-Bu) the bond angles were increased for both singlet and triplet states led to *p* character of nonbonding electron and distabilizing the singlet states (Table 2).

Calculated dihedral angles indicated a nonplanar structure for both singlet and triplet states of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu) (Table2).

Rationalizations NBO charge and dipole Moment (D) for substitution effects at 2,-7 α -position of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu)

Calculated NBO charge indicated that NBO charge at heteroatomic center of $R_2C_6H_6Si$ (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 2,7 α - position of seven membered ring (table3) This shows that bulky substituent (R = *t*-Bu) decrease the electron density of heteroatomic center. The highest dipole moment (D) was Obtained for the -H group in both singlet and triplet states of $R_2C_6H_6Si$ (Table3).

Rationalizations the (HOMO) and (LUMO), chemical hardness (η), chemical potential (μ), electrophilicity (ω), the maximum amount of electronic charge, ΔN_{max} , in electron volt for substitution effects at 2,7 α -position of $R_2C_6H_6Si$ (R= -H, -CH₃, *i*-Pr, *t*-Bu)
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 $R_2C_6H_6Si$ ($R = -H, -CH_3, i\text{-Pr}, t\text{-Bu}$) were larger than the corresponding singlet states (Table 3). Thus kinetic stability of all triplet states in $R_2C_6H_6Si$ ($R = -H, -CH_3, i\text{-Pr}, t\text{-Bu}$) is more than their corresponding singlet states. the lowest kinetic stability and highest chemical reactivity of $R_2C_6H_6Si$ ($R = -H, -CH_3, i\text{-Pr}, t\text{-Bu}$) were reasonably obtained for bulky substituent ($R = t\text{-Bu}$) in singlet state.

Also linear correlations are encountered between the LUMO–HOMO energy gaps of the singlet(stable) states of $R_2C_6H_6Si$ compounds, and their corresponding singlet–triplet energy separations are calculated at B3LYP/6-311++G** level of theory (Fig 2). Correlation coefficient (R^2) value of $R_2C_6H_6Si$ compounds is $R^2 = 0.81$.

chemical potential (μ) value for all triplet states were larger than the corresponding singlet states. The lowest

chemical potential (μ) for triplet states were reasonably obtained for bulky substituent ($R = t\text{-Bu}$) but for triplet states were obtained for -H substituent.

The electrophilicity (ω) values for all singlet states were larger than the corresponding triplet states. The lowest electrophilicity value (ω) for both singlet and triplet states of $R_2C_6H_6Si$ ($R = -H, -CH_3, i\text{-Pr}, t\text{-Bu}$) were reasonably obtained for Methyl substituent ($R = -Me$).

The electrophilicity (ω) values for all singlet and triplet states of $R_2C_6H_6Si$ were increased at B3LYP/6-311++G** level in the order (in e.v):

For singlet states: $H (0.097) > t\text{-Bu} (0.092) > i\text{-Pr} (0.089) > Me (0.087)$ (Table 3).

For triplet states: $i\text{-Pr} (0.041) > H (0.040) > t\text{-Bu} (0.039) = Me (0.039)$ (Table 3).

The maximum charge transfer (ΔN_{\max}) for all singlet states were larger than the corresponding triplet states. The lowest maximum charge transfer (ΔN_{\max}) for both singlet and triplet states of $R_2C_6H_6Si$ ($R = -H, -CH_3, i\text{-Pr}, t\text{-Bu}$) were reasonably obtained for Methyl substituent ($R = -Me$).

Table 1. Calculated Thermal internal energy (E), enthalpy (H), Gibbs energies (G), Thermal internal energy gaps, ΔE_{t-s} ; enthalpy gaps, ΔH_{t-s} ; Gibbs free energy gaps, ΔG_{t-s} , (in kcal/mol) between triplet(t) and singlet(s) states of $R_2C_6H_6Si$ ($R = -H, -CH_3, i\text{-Pr}, t\text{-Bu}$) at B3LYP/6-311++G** level of theory

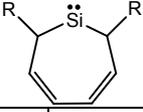
							
	R	E	H	G	ΔE_{t-s}	ΔH_{t-s}	ΔG_{t-s}
singlet	H	-327997.58	-327996.99	-328020.45	25.14	25.14	23.73
	Me	-377266.88	-377266.29	-377295.48	20.24	20.24	20.32
	i-Pr	-475821.74	-475821.15	-475856.22	21.67	21.67	20.56
	t-Bu	-525098.84	-525098.24	-525136.13	17.95	17.95	15.92
	triplet	H	-327972.44	-327971.85	-327996.72	X	X
Me	-377246.64	-377246.05	-377275.16				
i-Pr	-475800.06	-475799.47	-475835.65				
t-Bu	-525080.88	-525080.29	-525120.20				

Table 2. Calculated bond lengths (Å) bond angle and dihedral angle (degree), for the singlet (s) and triplet (t) states of $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$) at B3LYP/6-311++G** level of theory

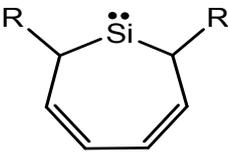
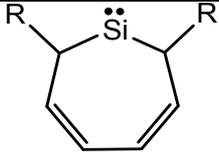
						
		R	Si ₁ -C ₂	Si ₁ -C ₇	A _{7,1,2}	D _{7,1,2,3}
singlet	H		1.923	1.923	102.020	-67.220
	Me		1.937	1.937	101.471	-32.905
	i-Pr		1.934	1.934	108.832	-23.303
	t-Bu		1.948	1.948	108.781	-26.384
triplet	H		1.960	1.960	105.492	72.570
	Me		1.959	1.959	112.269	-35.573
	i-Pr		1.948	1.948	118.617	-28.910
	t-Bu		1.951	1.951	119.430	-28.946

Table 3. Calculated HOMO, LUMO, chemical hardness (η), chemical potential (μ), electrophilicity (ω), maximum amount of electronic charge transfer, ΔN_{max} , in electron volt, dipole moments (D) in debye, for the singlet and triplet states of 2,7 α -position divalent seven-membered $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$) at B3LYP/6-311++G** level of theory

									
	R	HOMO	LUMO	η	μ	ω	ΔN_{max}	D	Charg on hetroatom
singlet	H	-0.199	-0.091	0.108	-0.145	0.097	1.342	1.545	0.835
	Me	-0.193	-0.084	0.109	-0.138	0.087	1.270	0.629	1.062
	i-Pr	-0.195	-0.085	0.110	-0.140	0.089	1.272	0.769	1.076
	t-Bu	-0.189	-0.086	0.102	-0.137	0.092	1.348	0.826	1.096
triplet	H	-0.157	-0.038	0.118	-0.097	0.040	0.826	1.198	0.724
	Me	-0.158	-0.037	0.120	-0.097	0.039	0.812	1.021	0.792
	i-Pr	-0.155	-0.040	0.114	-0.097	0.041	0.855	0.942	0.825
	t-Bu	-0.154	-0.038	0.116	-0.096	0.039	0.827	0.971	0.851

CONCLUSION

The ΔG_{t-s} between singlet and triplet states of $R_2C_6H_6Si$ was determined. The lowest ΔG_{t-s} were reasonably obtained when bulky substituent ($R = t-Bu$) were used at 2 and 7 (α -position) of $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$). DFT calculations indicated that all the singlet states of $R_2C_6H_6Si$ are more stable than the corresponding triplet states. According to chemical hardness (η) value The kinetic stability of all triplet states in $R_2C_6H_6Si$ is more than their corresponding singlet states. the lowest kinetic stability and highest chemical reactivity of $R_2C_6H_6Si$ ($R = -H, -CH_3, i-Pr, t-Bu$) were reasonably obtained for bulky substituent ($R = t-Bu$) in singlet state. Correlation coefficient (R^2) value for seven membered ring $R_2C_6H_6Si$ showed linear relationships between singlet(stable states) LUMO-HOMO energy gaps, and their corresponding singlet-triplet energy separations $\Delta G_{(t-s)}$.

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