

NOTE

Studies on Electronic Effects on the Singlet-Triplet Gap of Aryl-C₄H₃Si

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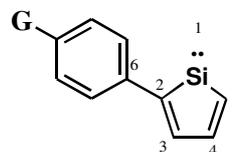
The thermal energies (E), enthalpies (H) and Gibbs free energies (G) and their gap energies between singlet (s) and triplet (t) states including ΔE_{s-t} , ΔH_{s-t} and ΔG_{s-t} of Ar-C₄H₃Si (G = -NH₂, -OH, -CH₃, -F, -Cl, -Br, -H, -CF₃ and -NO₂) were studied at B3LYP/6-311++G** level of theory.

Key Words: Silylene, Singlet-triplet gap, Electronic effects.

Divalent carbenes and their analogues are strongly reactive¹. The cyclic completely conjugated species are important in the chemistry of divalent carbene intermediates². These divalent structures were formerly described in terms of the Huckel $4n + 2$ rule³. However, non-planar isomers are found energy minima for most of these singlet cyclic conjugated carbenes through semi-empirical studies⁴. The isolation of the stable five membered cyclic conjugated carbene is firstly reported by Arduengo *et al.*⁵ and then Su and Chu⁵. Since most of divalent carbenes and their analogues are unstable, theoretical calculation was required for analysis of their properties. In continuation of our studies^{2,6}, in this manuscript, the singlet-triplet gap energies were studied on Ar-C₄H₃Si (G = -NH₂, -OH, -CH₃, -F, -Cl, -Br, -H, -CF₃ and -NO₂).

Full geometry optimizations of Ar-C₄H₃Si were carried out by density functional theory, DFT, method using 6-311++G** basis set of the GAUSSIAN 98 program⁷⁻⁹ (**Scheme-I**). To find a global minimum on a specific surface, all possible conformations of the given species were examined through scanning the specific dihedral angles at B3LYP/6-311++G** level. All calculations were carried out for gas phase at 298 K temperature and 1 atm pressure.

The thermal energies (E), enthalpies (H), Gibbs free energies (G) and their gap energies between singlet (s) and triplet (t) states including ΔE_{s-t} , ΔH_{s-t} and ΔG_{s-t} of Ar-C₄H₃Si (G = -NH₂, -OH, -CH₃, -F, -Cl, -Br, -H, -CF₃ and -NO₂) were calculated at B3LYP/6-311++G** level of theory (**Scheme-I** and Table-1). The gap free energies, ΔG_{s-t} , for various substituents were changed in the followed order: -Br > -CF₃ > -NO₂ > -H > -Cl > -CH₃ > -F > -NH₂ > -OH.



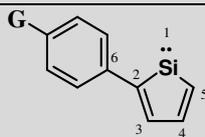
G = -NH₂, -OH, -CH₃, -F, -Cl, -Br, -H, -CF₃ and -NO₂

Scheme-I: Electron donating substituents (G = -NH₂, -OH, -CH₃, -F, -Cl and -Br) and electron withdrawing substituents (G = -CF₃ and -NO₂) of Ar-C₄H₃Si

Calculated ΔG_{s-t} shows that the electron donating substituents (G = -NH₂, -OH, -CH₃, -F, -Cl and -Br) at phenyl group cause to increase ΔG_{s-t} while the electron withdrawing substituents (G = -CF₃ and -NO₂) lead to decrease the ΔG_{s-t} of Ar-C₄H₃Si. Therefore, changing substituents at phenyl groups from an electron donating toward an electron withdrawing groups lead to increase of the ΔG_{s-t} . Relative energy analysis reveals that the substitution of the electron donating groups at phenyl group leads to the instability of the singlet state while the substitution of the electron withdrawing groups leads to the stability of the singlet state.

The electron withdrawing groups at phenyl groups enforce a higher percentage of s-character on nonbonding electrons at the silylenic center of Ar-C₄H₃Si. The higher s-character of nonbonding electrons leads to the stability of the singlet state as well as increase the singlet-triplet gap ΔG_{s-t} . Furthermore, the electron withdrawing groups at phenyl groups cause a high polarity of: Si-C in the direction: Si⁺-C⁻. Strongly polarized bond leads to more stability of the singlet state as well as increase the singlet-triplet gap ΔG_{s-t} .

TABLE-1
THERMAL ENERGY, (E); THERMAL ENTHALPY (H); THERMAL FREE ENERGY (G) at
B3LYP/6-311++G** FOR BOTH SINGLET (s) AND TRIPLET (t) STATES OF Ar-C₄H₃Si



Compound	Singlet state			$\Delta E_{s,t}$ (kcal/mol)	$\Delta H_{s,t}$ (kcal/mol)	$\Delta G_{s,t}$ (kcal/mol)
	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)			
G=-NH ₂	-458340.873	-458340.908	-458370.265	-14.526	-15.149	-14.426
G=-OH	-470824.890	-470824.297	-470855.049	-14.333	-14.333	-13.506
G=-CH ₃	-448259.659	-448259.067	-448289.868	-14.886	-14.886	-14.770
G=-F	-485917.313	-485916.721	-485947.041	-15.335	-15.335	-14.585
G=-Cl	-712043.277	-712042.684	-712073.811	-15.602	-15.602	-14.882
G=-Br	-2038529.041	-2038528.448	-2038560.428	-14.935	-14.935	-16.478
G=-H	-423616.956	-423617.581	-423646.010	-14.303	-15.520	-14.936
G=-CF ₃	-635267.957	-635267.706	-635267.957	-15.237	-14.986	-15.237
G=-NO ₂	-551974.086	-551973.494	-552006.653	-15.279	-15.279	-15.119
Compound	Triplet state			$\Delta E_{s,t}$ (kcal/mol)	$\Delta H_{s,t}$ (kcal/mol)	$\Delta G_{s,t}$ (kcal/mol)
	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)			
G=-NH ₂	-458326.347	-458325.759	-458355.839			
G=-OH	-470810.557	-470809.965	-470841.544			
G=-CH ₃	-448244.774	-448244.181	-448275.098			
G=-F	-485901.979	-485901.386	-485932.456			
G=-Cl	-712027.675	-712027.082	-712058.929			
G=-Br	-2038514.105	-2038513.513	-2038543.950			
G=-H	-423602.654	-423602.061	-423631.074			
G=-CF ₃	-635252.720	-635252.720	-635252.720			
G=-NO ₂	-551958.807	-551958.215	-551991.534			

The B3LYP/6-311++G** calculations indicated that the bond length Si₁-C₂ for the singlet states of Ar-C₄H₃Si increase with substitution of the electron donating groups while decrease with substitution of electron withdrawing groups at phenyl group. The bond length of Si₁-C₂ is higher respect to Si₁-C₅ for both singlet and triplet states of Ar-C₄H₃Si. Therefore, it could be concluded that a carbenic character was constructed instead of an allenic character for both singlet and triplet states of Ar-C₄H₃Si. Carbenic character was not significantly affected by substitution of electron withdrawing or electron donating groups at phenyl group.

The bond angle $\angle A_{2,1,5}$ for singlet states of Ar-C₄H₃Si is more than for triplet state (Table-1). This is inconsistent for acyclic carbenes. The DFT calculations indicated that bond angle $\angle A_{2,1,5}$ for both singlet and triplet states of Ar-C₄H₃Si was increased through replacement of electron withdrawing groups at phenyl group.

DFT calculations specified that the dihedral angle $\angle D_{2,1,5,4}$ for both singlet and triplet states of Ar-C₄H₃Si were not changed with substitution of the electron donating groups while increase with substitution of electron withdrawing groups at phenyl group.

Conclusion

B3LYP/6-311++G** calculations indicated that a carbenic character was constructed instead of an allenic character for both singlet and triplet states of Ar-C₄H₃Si. Calculated $\Delta G_{s,t}$ shows that the electron donating substituents at phenyl group cause to increase of the $\Delta G_{s,t}$ while the electron withdrawing substituents lead to decrease the $\Delta G_{s,t}$ of Ar-C₄H₃Si.

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