

## Electronic effects on singlet-triplet energy splittings in aryl-cyclopentadienylidenes

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### ABSTRACT

Energy gaps,  $\Delta X_{S-T}$  ( $X=E, H$  and  $G$ ) ( $\Delta X_{S-T} = X_{(singlet)} - X_{(triplet)}$ ) between singlet (s) and triplet (t) states were calculated at B3LYP/6-311++G\*\* level of theory. Our results showed that electron donating substituents ( $G = -NH_2, -OH, -CH_3, -F, -Cl$  and  $-Br$ ) at phenyl group cause to increase and electron withdrawing substituents ( $G = -CF_3$  and  $-NO_2$ ) lead to decrease the singlet-triplet energy gaps of  $Ar - C_4H_3\dot{C}$ .

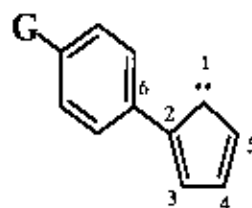
**Keywords:** Carbenes; Cyclopentadienylidenes; Singlet-Triplet gap; Electronic effects

### INTRODUCTION

Divalent carbenes and their analogues are strongly reactive [1]. The cyclic conjugated species are important in the chemistry of divalent carbene intermediates [2]. These divalent structures were formerly described in terms of the Huckel  $4n + 2$  rule [3]. However, non-planar isomers are found to have energy minima for most of these singlet cyclic conjugated carbenes through semi-empirical studies [4]. The isolation of the stable five membered cyclic conjugated carbene was first reported by Arduengo [5]. As a continuation of our studies [2,6], the effects of electron donating substituents ( $G = -NH_2, -OH, -CH_3, -F, -Cl$  and  $-Br$ ) and electron withdrawing substituents ( $G = -CF_3$  and  $-NO_2$ ) of aryl groups on the singlet-triplet energy gaps in cyclopentadienylidenes  $Ar - C_4H_3\dot{C}$  were investigated.

### COMPUTATIONAL METHODS

Full geometry optimizations of  $Ar - C_4H_3\dot{C}$  ( $G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3$  and  $-NO_2$ ) were carried out by DFT method using 6-311++G\*\* basis set of the GAUSSIAN 98 system of programs [7-9] (Scheme 1).



$G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, CF_3$  and  $-NO_2$

**Scheme 1.** Electron donating substituents ( $G = -NH_2, -OH, -CH_3, -F, -Cl$  and  $-Br$ ) and electron withdrawing substituents ( $G = -CF_3$  and  $-NO_2$ ) of cyclopentadienylidenes.

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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. This was to obtain more accurate values of thermal energies (E) enthalpies (H) and Gibbs free energies (G). "Freq" keyword was used for obtaining zero-point energies (ZPE), thermal energies (E), enthalpies (H) and Gibbs free energies (G).

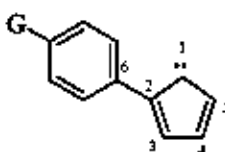
## RESULTS AND DISCUSSION

The total energy,  $E_T$ ; zero-point energy, thermal energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for aryl substituted divalent five membered cyclic compounds  $Ar - C_4H_3\dot{C}$

( $G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3$  and  $-NO_2$ ) at B3LYP/6-311++G\*\* level of theory (Scheme 1 and Table 1). Total energy gaps,  $\Delta E_{T(s-t)}$ ; zero-point energy gaps,  $\Delta ZPE_{s-t}$ ; thermal energy gaps,  $\Delta E_{s-t}$ ; enthalpy gaps,  $\Delta H_{s-t}$ ; Gibbs free energy gaps,  $\Delta G_{s-t}$ , between singlet (s) and triplet (t) states of  $Ar - C_4H_3\dot{C}$  were calculated at B3LYP/6-311++G\*\* (Table 2). For facility, Gibbs free energy gaps,  $\Delta G_{s-t}$ , was selected to discuss the data.

The DFT calculations indicate that all singlet states of  $Ar - C_4H_3\dot{C}$  are ground states with non-planar conformer while all triplet states of  $Ar - C_4H_3\dot{C}$  are ground state with planar conformer (Tables 1).

**Table 1.** Sum of total energy,  $E_T$ ; zero point energy, ZPE; thermal energy, (E); thermal enthalpy (H); thermal free energy (G) at B3LYP/6-311++G\*\* for both singlet (s) and triplet (t) states of  $Ar - C_4H_3\dot{C}$



Compound	Singlet state				
	$E_T$ kcal/mol	ZPE kcal/mol	E kcal/mol	H kcal/mol	G kcal/mol
G=-NH <sub>2</sub>	-300664.770	-300561.822	-300555.492	-300554.899	-300584.125
G=-OH	-313140.845	-313045.675	-313039.531	-313038.939	-313067.886
G=-CH <sub>3</sub>	-290586.575	-290467.262	-290460.681	-290460.089	-290490.863
G=-F	-328221.282	-328133.808	-328127.919	-328127.327	-328155.915
G=-Cl	-554344.482	-554257.854	-554251.723	-554251.130	-554280.541
G=-Br	-1880829.45	-1880743.23	-1880736.93	-1880736.34	-1880766.60
G=-H	-265925.150	-265832.531	-265827.162	-265826.569	-265853.839
G=-CF <sub>3</sub>	-477483.876	-477379.765	-477372.091	-477371.498	-477405.345
G=-NO <sub>2</sub>	-394287.832	-394185.263	-394178.270	-394177.677	-394209.309
Compound	Triplet state				
	$E_T$	ZPE	E	H	G
G=-NH <sub>2</sub>	-300675.569	-300572.565	-300566.270	-300565.677	-300595.460
G=-OH	-313150.951	-313055.897	-313049.753	-313049.160	-313078.771
G=-CH <sub>3</sub>	-290596.375	-290476.962	-290470.381	-290469.789	-290500.462
G=-F	-328230.926	-328143.661	-328137.763	-328137.171	-328166.433
G=-Cl	-554353.987	-554267.501	-554261.384	-554260.792	-554290.812
G=-Br	-1880838.95	-1880752.911	-1880746.614	-1880746.021	-1880776.929
G=-H	-265934.631	-265842.168	-265836.809	-265836.216	-265864.107
G=-CF <sub>3</sub>	-477492.728	-477388.518	-477380.844	-477380.251	-477414.098
G=-NO <sub>2</sub>	-394296.463	-394193.795	-394186.802	-394186.209	-394217.842

DFT calculations specify that all triplet states of  $Ar-C_4H_3\dot{C}$  ( $G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3$  and  $-NO_2$ ) are more stable than their corresponding singlet states. Calculated  $\Delta G_{s-t}$  shows that electron donating substituents ( $G = -NH_2, -OH, -CH_3, -F, -Cl$  and  $-Br$ ) at phenyl group cause to increase  $\Delta G_{s-t}$  and electron

withdrawing substituents ( $G = -CF_3$  and  $-NO_2$ ) lead to decrease the  $\Delta G_{s-t}$  of  $Ar-C_4H_3\dot{C}$ . Therefore, changing substituents at phenyl groups from electron donating toward electron withdrawing groups lead to decrease the  $\Delta G_{s-t}$ . Relative energy analysis reveal that substitution of electron donating groups at phenyl group

**Table 2.** Total energy gaps,  $\Delta E_{T(s-t)}$ ; zero point energy gaps,  $\Delta ZPE_{s-t}$ ; thermal energy gaps,  $\Delta E_{s-t}$ ; thermal enthalpy gaps  $\Delta H_{s-t}$ ; thermal free energy gaps  $\Delta G_{s-t}$  between singlet (s) and triplet (t) states and LUMO-HOMO gaps of  $Ar-C_4H_3\dot{C}$  at B3LYP/6-311++G\*\*

Compound	$\Delta E_{T(s-t)}$ kcal/mol	$\Delta ZPE_{s-t}$ kcal/mol	$\Delta E_{s-t}$ kcal/mol	$\Delta H_{s-t}$ kcal/mol	$\Delta G_{s-t}$ kcal/mol	HOMO (eV)	LUMO (eV)	$\Delta_{LUMO-HOMO}$ (eV)
G=-NH <sub>2</sub>	10.799	10.743	10.777	10.778	11.335	-0.194	-0.112	0.082
G=-OH	10.106	10.222	10.222	10.222	10.885	-0.206	-0.118	0.089
G=-CH <sub>3</sub>	9.800	9.700	9.700	9.700	9.599	-0.210	-0.117	0.093
G=-F	9.644	9.853	9.844	9.844	10.518	-0.219	-0.123	0.095
G=-Cl	9.506	9.647	9.662	9.662	10.271	-0.220	-0.125	0.095
G=-Br	9.502	9.677	9.680	9.681	10.321	-0.220	-0.126	0.095
G=-H	9.481	9.637	9.647	9.647	10.268	-0.216	-0.119	0.096
G=-CF <sub>3</sub>	8.852	8.753	8.753	8.753	8.753	-0.231	-0.132	0.099
G=-NO <sub>2</sub>	8.631	8.532	8.532	8.532	8.533	-0.239	-0.140	0.099

leads to stability of triplet state (respect to their corresponding singlet state) while substitution of electron withdrawing groups leads to stability of singlet state (respect to their corresponding triplet state).

Electron withdrawing groups at phenyl groups enforce a higher percentage of *s*-character on nonbonding electrons at carbonic center of  $Ar-C_4H_3\dot{C}$ . The higher *s*-character of nonbonding electrons leads stability of singlet state as well as decrease the singlet-triplet gap  $\Delta G_{s-t}$ . Furthermore, Electron withdrawing groups at phenyl groups cause a high polarity of :C-C in the direction :C<sup>+</sup>-C<sup>-</sup>. Strongly polarized bond leads to more stability of singlet state as well as decrease singlet-triplet gap  $\Delta G_{s-t}$ .

The HOMO-LUMO gaps of  $Ar-C_4H_3\dot{C}$  were calculated at B3LYP/6-311++G\*\* level. The HOMO-LUMO gaps could be explained the energy changes of singlet and triplet states [10,11]. The results of singlet-triplet gap  $\Delta G_{s-t}$  calculation are fully supported by HOMO-LUMO gaps (Table 1). HOMO-LUMO gaps are increased with substitution of electron withdrawing groups at phenyl group. In contrast,

HOMO-LUMO gaps are decreased with substitution of electron donating groups at phenyl group. Higher HOMO-LUMO gaps lead to increase stability of the singlet state as well as decrease of the singlet-triplet gap  $\Delta G_{s-t}$ .

## CONCLUSION

Calculated  $\Delta G_{s-t}$  show that electron donating substituents ( $G = -NH_2, -OH, -CH_3, -F, -Cl$  and  $-Br$ ) at phenyl group cause to increase  $\Delta G_{s-t}$  and electron withdrawing substituents ( $G = -CF_3$  and  $-NO_2$ ) lead to decrease the  $\Delta G_{s-t}$  of  $Ar-C_4H_3\dot{C}$ . Relative energy analysis reveals that substitution of electron donating groups at phenyl group lead to stability of triplet state (respect to their corresponding singlet state) while substitution of electron withdrawing groups lead to stability of singlet state (respect to their corresponding triplet state).

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