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SHORT COMMUNICATION

SINGLET-TRIPLET GAP STUDIES ON ARYL-CYCLOPENTADIENYLIDENES: INDIRECT ELECTRONIC EFFECTS

E. Vessally*

Payame Noor University (PNU), Zanjan, Iran

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ABSTRACT. Energy gaps, $\Delta X_{S\text{–}t}$ (X = E, H and G) ($\Delta X_{s\text{-}t} = X_{(singlet)}\text{-}X_{(triplet)}$) between singlet (s) and triplet (t) states of aryl substituted cyclopentadienylidenes, Ar-C_4H_3C, were calculated at B3LYP/6-311++G**. 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_3C. The results of the singlet-triplet gap calculations were fully supported by HOMO-LUMO gaps.

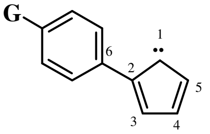
KEY WORDS: Carbene, Cyclopentadienylidenes, Singlet-triplet gap, Electronic effects

INTRODUCTION

Divalent carbenes and their analogues are strongly reactive [1]. The cyclic completely 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 have found minimum energy for the most of these singlet cyclic conjugated carbenes through semi-empirical studies [4]. The isolation of the stable five membered cyclic conjugated carbene has firstly been reported by Arduengo [5]. Since most of divalent carbenes and their analogues are unstable, theoretical calculation was required to analyze the carbene properties. As a continuation of our studies [2, 6], in this manuscript, 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_3C was investigated.

CALCULATION METHOD

Full geometry optimizations of Ar-C_4H_3C (G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3 and -NO_2) were carried out by Density Functional Theory, DFT, method using 6-311++G** basis set of the GAUSSIAN 98 program [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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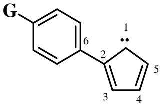
*Corresponding author. E-mail: e_vesali@yahoo.com

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 for obtaining more accurate values of thermal energies (E) enthalpies (H) and Gibbs free energies (G). "Freq" keyword was used for obtaining thermal energies (E), enthalpies (H) and Gibbs free energies (G). All calculations were carried out for gas phase at 298 K temperature and 1 atm pressure.

RESULTS AND DISCUSSION

The total energies, E_T, thermal energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for the singlet and triplet states of substituted aryl divalent five membered cyclic compound Ar-C_4H_3C (G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3 and -NO_2) at B3LYP/6-31+G* and B3LYP/6-311++G** levels of theory. Considering the size of molecules probed, and the consistency of the results obtained, these *ab initio* levels proved to be appropriate. For the sake of brevity, only the data acquired through the highest level of theory (B3LYP/6-311++G**) are reported (Scheme 1 and Table 1). Total energy gaps, $\Delta E_{T(s\text{-}t)}$, thermal energy gaps, $\Delta E_{s\text{–}t}$, enthalpy gaps, $\Delta H_{s\text{–}t}$, Gibbs free energy gaps, $\Delta G_{s\text{–}t}$, between singlet (s) and triplet (t) states of Ar-C_4H_3C were calculated at B3LYP/6-311++G** (Table 2). For facility, the Gibbs free energy gaps, $\Delta G_{s\text{–}t}$, was selected to discussion of the data.

Table 1. Sum of total energy, ET; 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-C4H3C.

				
Compound	Singlet state			
	E_T kcal/mol	E kcal/mol	H kcal/mol	G kcal/mol
G = -NH_2	-300664.770	-300555.492	-300554.899	-300584.125
G = -OH	-313140.845	-313039.531	-313038.939	-313067.886
G = -CH_3	-290586.575	-290460.681	-290460.089	-290490.863
G = -F	-328221.282	-328127.919	-328127.327	-328155.915
G = -Cl	-554344.482	-554251.723	-554251.130	-554280.541
G = -Br	-1880829.451	-1880736.933	-1880736.340	-1880766.608
G = -H	-265925.150	-265827.162	-265826.569	-265853.839
G = -CF_3	-477483.876	-477372.091	-477371.498	-477405.345
G = -NO_2	-394287.832	-394178.270	-394177.677	-394209.309
Compound	Triplet state			
	E_T	E	H	G
G = -NH_2	-300675.569	-300566.270	-300565.677	-300595.460
G = -OH	-313150.951	-313049.753	-313049.160	-313078.771
G = -CH_3	-290596.375	-290470.381	-290469.789	-290500.462
G = -F	-328230.926	-328137.763	-328137.171	-328166.433
G = -Cl	-554353.987	-554261.384	-554260.792	-554290.812
G = -Br	-1880838.953	-1880746.614	-1880746.021	-1880776.929
G = -H	-265934.631	-265836.809	-265836.216	-265864.107
G = -CF_3	-477492.728	-477380.844	-477380.251	-477414.098
G = -NO_2	-394296.463	-394186.802	-394186.209	-394217.842

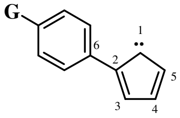
The DFT calculations indicate that all the singlet state of Ar-C_4H_3C is ground state with non-planar conformer while all the triplet state of Ar-C_4H_3C is ground state with planar conformer (Table 1).

DFT calculations specify that all triplet states of Ar-C_4H_3C (G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3 and -NO_2) is more stable than those corresponding singlet states. Calculated $\Delta G_{s\text{–}t}$ shows that the electron donating substituents (G = -NH_2, -OH, -CH_3, -F, -Cl and -Br) at phenyl group cause to increase $\Delta G_{s\text{–}t}$ and the electron withdrawing substituents (G = -CF_3 and -NO_2) lead to decrease the $\Delta G_{s\text{–}t}$ of Ar-C_4H_3C. Therefore, changing substituents at phenyl groups from an electron donating toward an electron withdrawing groups lead to decrease the $\Delta G_{s\text{–}t}$. Relative energy analysis reveals that the substitution of the electron donating groups at phenyl group leads to the stability of the triplet state (respect to those corresponding singlet state) while the substitution of the electron withdrawing groups leads to the stability of the singlet state (respect to those corresponding triplet state).

The electron withdrawing groups at phenyl groups enforce a higher percentage of *s*-character on nonbonding electrons at the carbenic center of Ar-C_4H_3C. The higher *s*-character of nonbonding electrons leads to the stability of the singlet state as well as decrease the singlet-triplet gap $\Delta G_{s\text{–}t}$. Furthermore, the electron withdrawing groups at phenyl groups cause a high polarity of :C-C in the direction :C^+-C^-. Strongly polarized bond leads to more stability of the singlet state as well as decrease the singlet-triplet gap $\Delta G_{s\text{–}t}$.

The HOMO-LUMO gaps of Ar-C_4H_3C were calculated at B3LYP/6-311++G** level. The HOMO-LUMO gaps could be explained the energy changes of the singlet and triplet states [10, 11]. The results of the singlet-triplet gap $\Delta G_{s\text{–}t}$ calculations are fully supported by HOMO-LUMO gaps (Table 2). HOMO-LUMO gaps were increased with the substitution of the electron withdrawing groups at phenyl group. In contrast, the HOMO-LUMO gaps are decreased with the substitution of the electron donating groups at phenyl group. Higher HOMO-LUMO gaps lead to increase the stability of singlet state as well as decrease of the singlet-triplet gap $\Delta G_{s\text{–}t}$.

Table 2. Total energy gaps, ΔET(s-t), thermal energy gaps, ΔEs-t, thermal enthalpy gaps, ΔHs-t, thermal free energy gaps, ΔGs-t, between singlet (s) and triplet (t) states and LUMO-HOMO gaps of Ar-C4H3C at B3LYP/6-311++G**.



Compound	$\Delta E_{T(s\text{-}t)}$ kcal/mol	$\Delta E_{s\text{-}t}$ kcal/mol	$\Delta H_{s\text{-}t}$ kcal/mol	$\Delta G_{s\text{-}t}$ kcal/mol	HOMO (eV)	LUMO (eV)	$\Delta_{LUMO\text{-}HOMO}$ (eV)
G = -NH_2	10.799	10.777	10.778	11.335	-5.279	-3.048	2.231
G = -OH	10.106	10.222	10.222	10.885	-5.606	-3.211	2.422
G = -CH_3	9.800	9.700	9.700	9.599	-5.714	-3.184	2.531
G = -F	9.644	9.844	9.844	10.518	-5.959	-3.347	2.585
G = -Cl	9.506	9.662	9.662	10.271	-5.987	-3.401	2.585
G = -Br	9.502	9.680	9.681	10.321	-5.987	-3.429	2.585
G = -H	9.481	9.647	9.647	10.268	-5.878	-3.238	2.612
G = -CF_3	8.852	8.753	8.753	8.753	-6.286	-3.592	2.694
G = -NO_2	8.631	8.532	8.532	8.533	-6.504	-3.810	2.694

CONCLUSIONS

Calculated ΔG_{s-t} show that the electron donating substituents (G = $-NH_2$, -OH, $-CH_3$, -F, -Cl and -Br) at phenyl group cause to increase ΔG_{s-t} and the electron withdrawing substituents (G = $-CF_3$ and $-NO_2$) lead to decrease the ΔG_{s-t} of Ar-C_4H_3C. Relative energy analysis reveals that the substitution of the electron donating groups at phenyl group leads to the stability of the triplet state (respect to those corresponding singlet state) while the substitution of the electron withdrawing groups leads to the stability of the singlet state (respect to those corresponding triplet state).

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