COMPUTATIONAL METHODS
Full geometry optimizations of Ar-C_414_3C (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).

Scheme 1. Electron donating substituents (G = -NH_2, -OH, -CH_3, -F, -Cl, -Br, -H, -CF_3 and -NO_2) and electron withdrawing substituents (G = -CF_3 and -NO_2) of aryl groups on the singlet-triplet energy gaps in cyclopentadienylidene Ar-C_414_3C were investigated.
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 tool energy, $E_T$, zero-point energy, thermal energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for aryl substituted divalent five membered (Ache) compounds $\text{Ar - C}_4\text{H}_3$ and $\text{Ar - C}_4\text{F}_3$ at B3LYP/6-311++G** level of theory (Scheme I and Table I).

### 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 $\text{Ar - C}_4\text{H}_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_T$ (kcal/mol)</th>
<th>ZPE (kcal/mol)</th>
<th>$E$ (kcal/mol)</th>
<th>$H$ (kcal/mol)</th>
<th>$G$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G=\text{NH}_2$</td>
<td>-300666.770</td>
<td>-300516.822</td>
<td>-300555.492</td>
<td>-300554.899</td>
<td>-300584.125</td>
</tr>
<tr>
<td>$G=\text{OH}$</td>
<td>-313140.845</td>
<td>-313045.675</td>
<td>-313039.531</td>
<td>-313038.939</td>
<td>-313067.886</td>
</tr>
<tr>
<td>$G=\text{CH}_3$</td>
<td>-290586.575</td>
<td>-290467.262</td>
<td>-290460.691</td>
<td>-290460.089</td>
<td>-290490.663</td>
</tr>
<tr>
<td>$G=F$</td>
<td>-328221.282</td>
<td>-328133.808</td>
<td>-328127.919</td>
<td>-328127.327</td>
<td>-328155.915</td>
</tr>
<tr>
<td>$G=\text{Cl}$</td>
<td>-554344.482</td>
<td>-554257.854</td>
<td>-554251.723</td>
<td>-554251.130</td>
<td>-554280.541</td>
</tr>
<tr>
<td>$G=\text{Br}$</td>
<td>-1880829.45</td>
<td>-1880743.23</td>
<td>-1880736.93</td>
<td>-1880736.34</td>
<td>-1880766.60</td>
</tr>
<tr>
<td>$G=\text{CF}_3$</td>
<td>-477483.876</td>
<td>-477379.763</td>
<td>-477372.091</td>
<td>-477371.498</td>
<td>-477405.345</td>
</tr>
<tr>
<td>$G=\text{NO}_2$</td>
<td>-394287.832</td>
<td>-394185.263</td>
<td>-394178.270</td>
<td>-394177.677</td>
<td>-394209.309</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_T$ (kcal/mol)</th>
<th>ZPE (kcal/mol)</th>
<th>$E$ (kcal/mol)</th>
<th>$H$ (kcal/mol)</th>
<th>$G$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G=\text{NH}_2$</td>
<td>-300675.569</td>
<td>-300572.565</td>
<td>-300566.270</td>
<td>-300565.677</td>
<td>-300595.460</td>
</tr>
<tr>
<td>$G=\text{OH}$</td>
<td>-313159.952</td>
<td>-313055.897</td>
<td>-313049.753</td>
<td>-313049.160</td>
<td>-313078.771</td>
</tr>
<tr>
<td>$G=\text{CH}_3$</td>
<td>-290596.375</td>
<td>-290476.962</td>
<td>-290470.381</td>
<td>-290470.789</td>
<td>-290500.462</td>
</tr>
<tr>
<td>$G=F$</td>
<td>-328230.926</td>
<td>-328143.661</td>
<td>-328137.763</td>
<td>-328137.171</td>
<td>-328166.433</td>
</tr>
<tr>
<td>$G=\text{Cl}$</td>
<td>-554353.987</td>
<td>-554267.501</td>
<td>-554261.384</td>
<td>-554260.792</td>
<td>-554290.812</td>
</tr>
<tr>
<td>$G=\text{Br}$</td>
<td>-1880838.95</td>
<td>-1880752.911</td>
<td>-1880746.614</td>
<td>-1880746.021</td>
<td>-1880776.929</td>
</tr>
<tr>
<td>$G=\text{CF}_3$</td>
<td>-477492.728</td>
<td>-477388.518</td>
<td>-477380.844</td>
<td>-477380.251</td>
<td>-477414.098</td>
</tr>
<tr>
<td>$G=\text{NO}_2$</td>
<td>-394296.463</td>
<td>-394193.795</td>
<td>-394186.892</td>
<td>-394186.209</td>
<td>-394217.842</td>
</tr>
</tbody>
</table>
DFT calculations specify that all triplet states of 
Ar - C6H3 C (G = -NH2, -OH, -CH3, -F, -Cl, -Br, -H, -CF3 and -NO2) are more stable than their 
corresponding singlet states. Calculated AGs show that electron donating substituents (G = - 
NH2, -OH, -CH3, -F, -Cl and -Br) at phenyl group cause to increase ΔGₘ⁺ and electron 
withdrawing substituents (G = -CF3 and -NO2) lead to decrease the ΔGₘ⁺ of Ar - C6H3 C. 
Therefore, changing substituents at phenyl groups from electron donating toward electron 
withdrawing groups lead to decrease the ΔGₘ⁺. Relative energy analysis reveal that substitution 
of electron donating groups at phenyl group lead to stability of triplet state (respect to their 
corresponding singlet state) while substitution of 

### Table 2. Total energy gaps, ΔE (eV), zero point energy gaps, ΔZPE (eV), thermal 
enthalpy gaps ΔH (eV), thermal free energy gaps ΔG (eV) between singlet (s) and triplet (1) states and HOMO-LUMO 
gaps of Ar - C6H3 C at B3LYP/6-311++G** 

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔE (eV)</th>
<th>ΔZPE (eV)</th>
<th>ΔE (eV)</th>
<th>ΔH (eV)</th>
<th>ΔG (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>ΔHOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G = -NH2</td>
<td>10.799</td>
<td>10.743</td>
<td>10.777</td>
<td>10.778</td>
<td>11.335</td>
<td>-0.194</td>
<td>-0.112</td>
<td>0.082</td>
</tr>
<tr>
<td>G = -OH</td>
<td>10.106</td>
<td>10.222</td>
<td>10.222</td>
<td>10.222</td>
<td>10.885</td>
<td>-0.206</td>
<td>-0.118</td>
<td>0.089</td>
</tr>
<tr>
<td>G = -CH3</td>
<td>9.800</td>
<td>9.700</td>
<td>9.700</td>
<td>9.700</td>
<td>9.599</td>
<td>-0.210</td>
<td>-0.117</td>
<td>0.093</td>
</tr>
<tr>
<td>G = -F</td>
<td>9.644</td>
<td>9.833</td>
<td>9.844</td>
<td>9.844</td>
<td>10.518</td>
<td>-0.219</td>
<td>-0.123</td>
<td>0.095</td>
</tr>
<tr>
<td>G = -Cl</td>
<td>9.408</td>
<td>9.647</td>
<td>9.662</td>
<td>9.662</td>
<td>10.171</td>
<td>-0.220</td>
<td>-0.125</td>
<td>0.095</td>
</tr>
<tr>
<td>G = -CF3</td>
<td>9.481</td>
<td>9.637</td>
<td>9.647</td>
<td>9.647</td>
<td>10.258</td>
<td>-0.215</td>
<td>-0.121</td>
<td>0.096</td>
</tr>
<tr>
<td>G = -NO2</td>
<td>8.852</td>
<td>8.753</td>
<td>8.753</td>
<td>8.753</td>
<td>8.753</td>
<td>-0.231</td>
<td>-0.132</td>
<td>0.099</td>
</tr>
<tr>
<td>G = -C6H3</td>
<td>8.631</td>
<td>8.552</td>
<td>8.532</td>
<td>8.532</td>
<td>8.532</td>
<td>-0.239</td>
<td>-0.140</td>
<td>0.099</td>
</tr>
</tbody>
</table>

leaves 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 - C6H3 C. The higher s-character of 
nonbonding electrons leads stability of singlet 
state as well as decrease the single-triplet gap 
ΔGₘ⁺. Furthermore, Electron withdrawing groups 
at phenyl groups cause a high polarity of σ-C in 
the direction: C-C. Strongly polarized bond 
leads to more stability of singlet state as well as 
decrease single-triplet gap ΔGₘ⁺.

The HOMO-LUMO gaps of Ar - C6H3 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 ΔGₘ⁺ 
calculations 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 ΔGₘ⁺.

CONCLUSION

Calculated ΔGₘ⁺ show that electron donating 
substituents (G = -NH2, -OH, -CH3, -F, -Cl and 
-Br) at phenyl group cause to increase ΔGₘ⁺ and 
electron withdrawing substituents (G = -CF3 and 
-NO2) lead to decrease the ΔGₘ⁺ of Ar - C6H3 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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REFERENCES


(c) E. Vessally, et. al. Asian J. Chem. 19, 5000, (2007); 


