Theoretical study of [1,5]-hydrogen shift in substituted 1,8a-dihydronaphthalene

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Introduction

The [1,5]-hydrogen shift stimulated many mechanistic studies [1,2] and has found numerous applications in organic synthesis[3,4]. This reaction usually proceeds by concerted pathway involving an aromatic transition state[5,6,7]. The effect of aromatic stabilization on the rates of [1,5]-hydrogen shift were previously estimated experimentally and theoretically. Not only the activation energy but also the shape and the position of the reaction barrier can be efficiently controlled by change in aromaticity.

In the present work, we wish to study the effect of substituents on the aromaticity of transition state and product in [1,5]-hydrogen shift of 1,8a-dihydronaphthalene ring (Scheme 1). Nature of transition state has also been studied by population analysis using atoms in molecules (AIM) method[8]. As a result, relation between Hammett constants and energy barriers was also investigated to determine a quantitative scale for substituents.

![Scheme 1](image_url)

X = H, O’, OH, CH₃, NH₂, NO₂, F, CN, N(CH₃)₂, NH(CH₃)

Scheme 1. Different substituted 1,8a-dihydronaphtalene.

Computational methods

Computations were performed by B3LYP density functional with 6-31G(d,p) basis set using Gaussian03 package[9]. AIM analyses were performed on the wave functions.
obtained at the mentioned level by AIM2000 program [10].

Results and discussion

The most important structural parameters corresponding to reactants (see Scheme 1), and also the change in C1C2 bond length at steps 1 and 2 (O₁ and O₂, respectively) are reported in Table 1. The positive values of O₁ and O₂ are in agreement with increasing the aromaticity of ring A at both steps. This result is in a good agreement with the changes of nuclear independent chemical shift (NISC) calculated at the center of ring A at B3LYP/6-31G (d,p) level of theory by GIAO method.

Table 1. Energy data (in kcal/mol) and the most important geometrical parameters of reactants, transition states, and products. Bond lengths are in angstroms and bond angles are in degrees

<table>
<thead>
<tr>
<th></th>
<th>ΔE₁</th>
<th>ΔE₂</th>
<th>ΔE</th>
<th>Δ₀(C1C2)</th>
<th>Δ²(C1C2)</th>
<th>r(C1H)</th>
<th>r(C5H)</th>
<th>C1HC5</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>28.17</td>
<td>59.21</td>
<td>31.04</td>
<td>0.1154</td>
<td>0.0506</td>
<td>1.409</td>
<td>1.604</td>
<td>97.48</td>
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<tr>
<td>F</td>
<td>28.66</td>
<td>59.11</td>
<td>30.45</td>
<td>0.1176</td>
<td>0.0513</td>
<td>1.411</td>
<td>1.600</td>
<td>97.65</td>
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<tr>
<td>O</td>
<td>31.83</td>
<td>50.51</td>
<td>27.24</td>
<td>0.1157</td>
<td>0.0486</td>
<td>1.455</td>
<td>1.554</td>
<td>99.59</td>
</tr>
<tr>
<td>NO₂</td>
<td>29.25</td>
<td>59.06</td>
<td>29.81</td>
<td>0.1117</td>
<td>0.0497</td>
<td>1.405</td>
<td>1.594</td>
<td>97.29</td>
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<tr>
<td>OH</td>
<td>30.01</td>
<td>58.94</td>
<td>28.93</td>
<td>0.1187</td>
<td>0.0531</td>
<td>1.412</td>
<td>1.599</td>
<td>97.81</td>
</tr>
<tr>
<td>NH₂</td>
<td>29.36</td>
<td>57.93</td>
<td>28.57</td>
<td>0.1167</td>
<td>0.0495</td>
<td>1.419</td>
<td>1.591</td>
<td>98.04</td>
</tr>
<tr>
<td>CN</td>
<td>29.00</td>
<td>59.21</td>
<td>30.21</td>
<td>0.1129</td>
<td>0.0498</td>
<td>1.406</td>
<td>1.596</td>
<td>97.36</td>
</tr>
<tr>
<td>N(CH₃)₂</td>
<td>29.50</td>
<td>58.06</td>
<td>28.55</td>
<td>0.1154</td>
<td>0.0489</td>
<td>1.418</td>
<td>1.592</td>
<td>98.03</td>
</tr>
<tr>
<td>NHCH₃</td>
<td>28.68</td>
<td>58.59</td>
<td>29.91</td>
<td>0.1134</td>
<td>0.0483</td>
<td>1.415</td>
<td>1.597</td>
<td>98.01</td>
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<tr>
<td>CH₃</td>
<td>28.75</td>
<td>58.60</td>
<td>29.85</td>
<td>0.1141</td>
<td>0.0480</td>
<td>1.413</td>
<td>1.599</td>
<td>97.64</td>
</tr>
</tbody>
</table>

As can be seen, in TS structure, C1H bond length is shorter than C5H bond length. Thus TS can be considered a reactant like transition state. The plots of OE₁ (Eₜₛₜ- Eᵣᵢｃｔᵃｎｔ) and OE₂ (Eₜₛₜ- Eₚᵣᵢᵈᵘᵗ) versus r(C1H) (and r(C5H)) show that the correlation of OE₂ vs. r is better than OE₁ vs. r. Although the electron withdrawing substituents decrease slightly C1H bond length in TS structure (with the exception of F), but the
electron donating substituents increase that. Therefore, the aromaticity of ring A increases with the electron donating substituents in TS structures.

In addition, effect of substituents on the transition state makes an obvious show on C1HC5 angle. Thus, this angle can be considered as an important geometrical parameter in TS structure. With some exceptions, increasing C1HC5 angle (causes to decrease the angle strain of TS) is accompanied by the reduction of energy barrier OE2. This behavior is not absolutely observed between energy barrier OE1 and C1HC5 angle. As a result, not only electron donating substituents increase C1HC5 angle, but also decrease energy barrier OE2.

Furthermore, there is not a good relationship between Hammett constants of substituents and OE1. This behavior is expected, because the ring A is not aromatic in reactant. Although along the process the aromaticity of ring A can be change, but the aromaticity of both TS and product is higher than reactant and a liner relationship between OE2 and Hammett constants σ is observed (R = 0.77). The low correlation coefficient could be attributed to the change in the aromaticity of ring A.

Our calculations indicated that there is a linear relationship between Hammett constants and some geometrical parameters of TS structures (C1HC5 bond angle and C1H bond length, Figure1). This relationship decreases with enhancement of the distance between structural parameters and ring A (the aromaticity of TS is higher than reactant). It is obvious that this behavior is never observed between Hammett constants and C5H bond length.

The topological properties of electronic charge density were determined by AIM analysis. Contour maps of electron density illustrate interaction of migrating H atom with different parts of reactant, especially C6 carbon atom.

![Graphs showing the relationship between Hammett constants and C1HC5 bond angle, C1H bond length](image)

Figure 1. (a) Hammett constant vs. C1HC5 bond angle, (b) Hammett constant vs. C1H bond length.
Conclusions

Our results indicated that TS structure is reactant like. Also, electron donating substituents reduced energy barrier between TS and product ($\Delta E_2$). Furthermore, a good relationship between Hammett constants, $\Delta E_2$, and some geometrical parameters of TS structures was observed. But, there was never a quantitative relationship between OE$_1$ and different properties of substituents.

References
