Substituent Effects on the Geometrical Properties of 1-Phenylallyl Alcohol

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Optimized geometrical parameters, electron densities, heats of formation and stabilization energies have been obtained on X-substituted phenylallyl alcohols, where X is H, OCH\(_3\), NH\(_2\), CN, F and CH\(_3\) at \textit{ortho}, \textit{meta}, and \textit{para} positions, using MINDO-Forces SCF-molecular orbital calculations. The substituent effects on the geometrical parameters and the electron density are discussed.

Key words: Phenylallyl Alcohols; Substituent Effects; Allyl System; MINDO-Forces.

1. Introduction

Pyrolysis of unsymmetrically substituted allyl alcohols involving migration of the hydroxyl group is known as oxotropy rearrangement [1]. Much attention has been paid to the chemistry of phenylallyl alcohols because of their utilities [2]. Approximate molecular orbital theories are based on a scheme developed within the molecular orbital theory, but with several simplifications. Often experimental data on atoms and prototype molecules are used to estimate values of quantities entering the calculations as parameters, and for this reason the procedures are known as semi-empirical methods [3]. There are various approximation methods in the literature, which differ mainly in the degree of approximation [3].

The present work deals with the electronic structure of substituted 1-phenylallyl alcohols (Fig. 1), using MINDO-Forces SCF-molecular orbital calculations [4], whereby the molecular energy of the alcohols was completely minimized by the Murtagh-Sargent technique [5]. The derivative of the energy was calculated according to Pulay’s force method. The program allows the variation of the \(\beta\)-parameter with the geometrical change in a consistent way. A full description of the program and its application is given in [4]. The substituent effects on the calculated results is discussed by means of the correlation analysis.

2. Calculations

The MINDO-Forces program was carried out on a HYUNDAI personal computer Model No. HCM-1420. Cartesian coordinates are obtained from polar coordinates. Final geometrical parameters are obtained from an improved set of Cartesian coordinates (MINDO-Forces) using the Dewar program on a Hewlett-Pakard 9830 A calculator. Standard bond lengths and angles are used as initial input data. For CH\(_3\)-group substituents different conformations were completely optimized and the most stable conformation data are recorded, in which one hydrogen atom of CH\(_3\)-group was placed in the phenyl ring plane, similarly for the OCH\(_3\)-group where the most stable conformation data are recorded.

3. Results and Discussion

The complete optimized geometrical parameters, electron densities, heats of formation and stabilization energies of substituted 1-phenylallyl alcohols (Fig. 1) are listed in Tables 1, 2, 3 and 4, respectively.

3.1. Stabilization by Substituent Groups

The effect of substituents on the energy of substituted 1-phenylallyl alcohols has been assessed from the depicted isodesmic reaction [6, 7].
Effects of the Fluoro Substituent Group

Introduction of a fluorine atom into the ortho, meta or para positions of the phenyl ring causes a slight decrease in the electron density on the carbon atom directly attached to the substituent, and slightly increases the electron density on the adjacent carbon atoms. The C8-C9 bond length was not affected by the substituent group. The C7-C8 bond length was slightly increased by the substituent group at ortho and para positions, and not affected by meta substitution, while the C7-C8 bond angle was increased by the substituent group at ortho and para positions, and not affected by para substituents (Tables 1 and 2).

3.3. Effect of the Methyl Substituent Group

Introduction of the CH3-group into the ortho, meta or para positions of the phenyl ring causes a slight decrease in the electron density on the carbon atom directly attached to the substituent, and slightly increases the electron density on the adjacent carbon atoms. The C8-C9 bond length was not affected by the substituent group. The C7-C8 bond angle was slightly increased by the substituent group at ortho and para positions, and not affected by meta substitution, while the C7-C8 bond angle was increased by the substituent group (Tables 1 and 2, Fig. 2).

3.4. Effect of the Cyano Substituent Group

Introduction of a cyano group into the ortho, meta or para positions of the phenyl ring causes a slight decrease in the electron density on the carbon atom directly attached to the substituent, and slightly increases the electron density on the adjacent carbon atoms. The C8-C9 bond length was not affected by the substituent group. The C7-C8 bond angle was slightly increased by the substituent group at ortho and para positions, and not affected by meta substitution, while the C7-C8 bond angle was increased by the substituent group (Tables 1 and 2, Fig. 2).

The calculated heats of formation indicate that ortho-, meta- and para-substituted isomers have almost the same stability (Table 4).

The C7-C2 bond length is not affected by the substituent at different positions, the C1-C7, C7-C8, and C8-C9 bond lengths are not affected by the substituent at para position, while bond lengthenings were observed on substitution at ortho and meta positions. The C6-C7-C2 bond angle was decreased by the substituent group at the ortho position, while substitution at the meta or para position did not affect the angle. The C1-C7-C8 bond angle was not affected by the substituent, while the C7-C8-C9 bond angle was increased by the substituent group at ortho and meta positions, and not affected by para substituents (Tables 1 and 2).

The published results [6, 8–10] suggested amphielectronic behavior of π-electron acceptor groups such as CF3, CN, CHO. Thus these groups donate π-electrons when attached to a system that has electron demand, such as CH2X and acceptors in the case of electron rich systems.

Introduction of the CN-group into the ortho, meta or para positions of the phenyl ring was found to have
Table 2. The bond angles (°) of selected angles of substituted 1-phenylallyl alcohols. The atom numbers as shown in Figure 1.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Bond angles (°)</th>
<th>X</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>X*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1-C-2, C-7-C-8 and C-6-C-9 bond lengths are not affected by the substituent at different positions, while the substituent causes shortening of the C-1-C-7 bond. The C-6-C-2 bond angle was not affected by substituents. The C-1-C-7 bond angle was slightly increased by the substituent group, while the C-7-C-6-C-9 bond angle increases by substitution at different positions (Tables 1 and 2, Fig. 2).</td>
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<td></td>
</tr>
</tbody>
</table>

3.5. Effect of the Amino Substituent Group

Introduction of the NH₂-group into the ortho, meta or para position of the phenyl ring causes a decrease in the electron density on the carbon atom directly attached to the substituent, and an increase in the electron density on the adjacent carbon atoms (Table 3), i.e. it acts as electron donating group, in agreement with similar published results [6–8–10].

The calculated heats of formation (Table 4) indicate that ortho-, meta- and para-substituted isomers have nearly the same stability.

Table 3. Electron density distributions in substituted 1-phenylallyl alcohols. For atom numbers see Figure 1.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Electron density on atom number</th>
<th>X*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1-C-2, C-7-C-8 and C-6-C-9 bond lengths are not affected by the substituent at different positions, while the substituent causes shortening of the C-1-C-7 bond. The C-6-C-2 bond angle was not affected by substituents. The C-1-C-7 bond angle was slightly increased by the substituent group, while the C-7-C-6-C-9 bond angle increases by substitution at different positions (Tables 1 and 2, Fig. 2).</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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The calculated heats of formation (Table 4) indicate that the para-substituted isomer is the most stable isomer.

The C-1-C-2 bond is lengthened by substitution at ortho position. Meta substitution causes a small short-
Fig. 2. Optimized geometries of substituted 1-phenylallyl alcohols; bond lengths in Å and bond angles in degrees.
Shortening, while para substitution has no effect. Substitution at different positions causes lengthening of the C1-C7 bond. The C7-C8 and C8-C9 bond lengths were not affected by meta substitution, while substitution at ortho and para positions causes small lengthening and small shortening in bond lengths, respectively. The C6C1C2 bond angle was not affected by ortho or meta substituents but the para substituent causes a small decrease. The C1C7C8 bond angles were slightly affected by the substituent, while the C7C8C9 bond angle increases by the substituent (Tables 1 and 2).

3.6. Effect of the Methoxy Substituent Group

Introduction of the OCH3-group into the ortho, meta, or para positions of the phenyl ring causes a decrease in the electron densities on the carbon atoms directly attached to the substituent, and an increase in the electron densities on the adjacent carbon atoms (Table 3), i.e. it acts as electron donating group, in agreement with similar published results [6, 8–10].

The calculated heats of formation (Table 4) indicate that the para-substituted isomer is the most stable isomer.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>ΔHf</th>
<th>S. E.</th>
<th>Substituent</th>
<th>ΔHf</th>
<th>S. E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>63.23</td>
<td>0</td>
<td>m-OCH3</td>
<td>−114.25</td>
<td>31.84</td>
</tr>
<tr>
<td>α-CH3</td>
<td>56.33</td>
<td>−49.59</td>
<td>p-OCH3</td>
<td>−133.16</td>
<td>50.76</td>
</tr>
<tr>
<td>m-CH3</td>
<td>30.04</td>
<td>−23.31</td>
<td>α-F</td>
<td>−205.94</td>
<td>81.27</td>
</tr>
<tr>
<td>p-CH3</td>
<td>2.67</td>
<td>4.05</td>
<td>m-F</td>
<td>−196.98</td>
<td>72.31</td>
</tr>
<tr>
<td>α-NH3</td>
<td>21.05</td>
<td>6.61</td>
<td>p-F</td>
<td>−198.36</td>
<td>73.86</td>
</tr>
<tr>
<td>m-NH3</td>
<td>4.10</td>
<td>23.56</td>
<td>α-CN</td>
<td>141.95</td>
<td>−12.59</td>
</tr>
<tr>
<td>p-NH3</td>
<td>−4.47</td>
<td>32.14</td>
<td>m-CN</td>
<td>140.90</td>
<td>−11.55</td>
</tr>
<tr>
<td>α-OCH3</td>
<td>−113.66</td>
<td>31.26</td>
<td>p-CN</td>
<td>135.63</td>
<td>−6.27</td>
</tr>
</tbody>
</table>

Taft’s dual parameter equation [11] was applied on all molecular properties. For meta- and para-substituted compounds, the following were the best correlations:

E.D at (C1)m = 4.05 ± 0.006 + 0.127 σR ± 0.02, r = 0.95,
E.D at (C4)m = 3.98 ± 0.015 − 0.29 σR ± 0.05, r = 0.94,
E.D at (C7)m = 3.56 ± 0.000 − 0.012 σR ± 0.002, r = 0.92,
E.D at (C1)p = 4.05 ± 0.001 − 0.10 σR ± 0.034, r = 0.92,
E.D at (C7)p = 3.67 ± 0.001 + 0.037 σR ± 0.000, r = 0.97.

In general the Hammett and extended Hammett substituent constants (σ, σI and σR) are poor parameters for measuring the substituent effects on molecule geometry.

4. Conclusion

All substituents have an effect on the geometrical parameters, and the electron density distribution. The best correlation obtained between the electron density and σR or the extended Hammett equation clearly indicates that the major affecting ability of substituents on the electron density distribution is through resonance effects. The poor correlation between the substituent constants and the geometrical properties (bond length and bond angle) indicates that there must be consistent parameters which measure the substituent effects on the geometrical properties.