Substituent Effects on Carbonyl Stretching Frequency of β-Naphthyl Styryl Ketones

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The s-cis carbonyl stretching frequencies of two series of substituted β-naphthyl styryl ketones have been measured in chloroform and carbon tetrachloride. One series contains substituents in benzene ring (Series-A) and the other contains substituents in naphthalene ring (Series-B). Substituent effects have been analysed in terms of Hammett equation. Good correlations have been obtained with σ + constants in both the solvents. The low p-value for Series-A as compared to that of chalcones is explained on the basis of non-coplanarity of the styryl group and the carbonyl group in the ketones of Series-A.

In recent years much attention has been paid to correlate the infrared group frequencies of related group of organic molecules with substituent constants. Good correlations have been obtained for νC = O with the substituent constants, σ + in the case of acetophenones, benzophenones, chalcones and benzalacetones. However, similar studies in polynuclear aromatic system are lacking. With a view to understanding the extent of transmission of electronic effects of the substituents in naphthalene system, several 6'-substituted β-naphthyl styryl ketones (Series-B) and 4-substituted β-naphthyl styryl ketones (Series-A) were prepared and their carbonyl stretching frequencies were measured in chloroform and carbon tetrachloride.

The 6-substituted 2-acetonaphthones were prepared by literature method. The benzaldehydes were commercial samples (Fluka, AR). β-Naphthyl styryl ketones were prepared by Claisen-Schmidt condensation of appropriate aldehydes and ketones and recrystallised from benzene-pet ether (60-80°).

Spectral grade chloroform was passed through alumina before use and carbon tetrachloride was dried over anhydrous potassium carbonate and distilled in an all glass apparatus. The νC = O were measured at 25° with a Perkin-Elmer IR-783 double beam grating spectrophotometer using CsI cells of 1 mm path length. The IR spectra of the compounds were recorded in CHCl 3 and CCl 4 at concentrations of 0.5% and 0.2% respectively. The β-naphthyl styryl ketones exhibited a shoulder on the lower frequency side of the band. The height of each band was taken as the distance from shoulder to the point of maximum absorption. The band frequencies were then measured at the half-width of the half-height of the band. The frequencies were directly read from the digital display corresponding to this position. The values reported here are average of three scans which are accurate within ±0.2 cm⁻¹.

The α,β-unsaturated ketones exist in two different conformations namely s-cis and s-trans. The carbonyl stretching frequencies of these conformers (1665 cm⁻¹ for s-cis and 1639 cm⁻¹ for s-trans conformer) have been assigned for chalcone in chloroform. In the present study the assignments have been made by analogy. In chloroform all β-naphthyl styryl ketones exhibited an intense band near 1662 cm⁻¹ with a shoulder at the lower frequency side of the band. This band was assigned to the s-cis conformer. It was difficult to identify the non-s-cis band for various substituted β-naphthyl styryl ketones since the intensity and shape of this band was similar to the aromatic hydrogen overtone bands in the 1600 cm⁻¹ region. The parent ketone exhibited a broad, weak band at 1629 cm⁻¹ which was assigned to the s-trans conformer. A shift of approximately 6 cm⁻¹ was observed for the s-cis carbonyl band on changing the solvent from chloroform to carbon tetrachloride. This may be due to weak hydrogen bonding between carbonyl group and the solvent molecules (chloroform).

Effect of substituents in benzene ring (Series-A)

The νC = O modes of the s-cis conformers of several 4-substituted β-naphthyl styryl ketones are presented in Table 1. These modes were correlated with σ p/σ p + constants. The results of statistical analysis are presented in Table 2. The νC = O modes were found to correlate better with σ p + constants. The low p-values obtained in both the solvents do not differ much. Apparently, weak hydrogen bonding in chloroform does not have a large influence on the transmission of substituent effects. Analysis of the data in Table 2 reveals that the p-values in both solvents are lower...
Table 1—s-cis Carbonyl Stretching Frequencies of Substituted \( \beta \)-Naphthyl Styryl Ketones

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Series-A</th>
<th>Series-B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( v_C = \text{O(cm}^{-1} )</td>
<td>( v_C = \text{O(cm}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3)</td>
<td>CCl(_4)</td>
</tr>
<tr>
<td>4-N(CH(_2)(_2))</td>
<td>1653.7</td>
<td>1660.5</td>
</tr>
<tr>
<td>4-OCH(_3)</td>
<td>1658.4</td>
<td>1665.3</td>
</tr>
<tr>
<td>4-CH(_3)</td>
<td>1660.5</td>
<td>1666.7</td>
</tr>
<tr>
<td>4-H</td>
<td>1662.0</td>
<td>1668.0</td>
</tr>
<tr>
<td>4-F</td>
<td>1662.5</td>
<td>1668.3</td>
</tr>
<tr>
<td>4-Cl</td>
<td>1663.8</td>
<td>1669.0</td>
</tr>
<tr>
<td>4-Br</td>
<td>1663.0</td>
<td>1668.6</td>
</tr>
<tr>
<td>4-NO(_2)</td>
<td>1665.5</td>
<td>1671.2</td>
</tr>
</tbody>
</table>

Table 2—Results of Statistical Analysis of Carbonyl Stretching Frequencies with \( \sigma_p/\sigma_p^+ \) Constants

<table>
<thead>
<tr>
<th>( \sigma )-constants</th>
<th>( p )</th>
<th>( a(\text{cm}^{-1}) )</th>
<th>( r )</th>
<th>S.O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series-A: Solvent CHCl(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sigma_p )</td>
<td>7.50</td>
<td>1661.0</td>
<td>0.966</td>
<td>1.01</td>
</tr>
<tr>
<td>( \sigma_p^+ )</td>
<td>4.86</td>
<td>1662.2</td>
<td>0.996</td>
<td>0.36</td>
</tr>
<tr>
<td>Series-A: Solvent CCl(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sigma_p )</td>
<td>6.68</td>
<td>1667.2</td>
<td>0.970</td>
<td>0.85</td>
</tr>
<tr>
<td>( \sigma_p^+ )</td>
<td>4.30</td>
<td>1668.3</td>
<td>0.994</td>
<td>0.37</td>
</tr>
<tr>
<td>Series-B: Solvent CHCl(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sigma_p )</td>
<td>5.64</td>
<td>1661.3</td>
<td>0.891</td>
<td>0.85</td>
</tr>
<tr>
<td>( \sigma_p^+ )</td>
<td>3.98</td>
<td>1662.3</td>
<td>0.987</td>
<td>0.30</td>
</tr>
<tr>
<td>Series-B: Solvent CCl(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sigma_p )</td>
<td>4.66</td>
<td>1667.5</td>
<td>0.904</td>
<td>0.65</td>
</tr>
<tr>
<td>( \sigma_p^+ )</td>
<td>3.21</td>
<td>1668.3</td>
<td>0.977</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Chalcone*: Solvent CHCl\(_3\)

\( \sigma_p \) | 6.24 | 1666.7 |
| \( \sigma_p^+ \) | 6.24 | 1666.7 |

Chalcone: Solvent CCl\(_4\)

\( \sigma_p \) | 5.36 | 1670.5 |
| \( \sigma_p^+ \) | 5.36 | 1670.5 |

(a) Ref. 4

Effect of substituents in naphthalene ring (Series-B)

In order to understand the extent of transmission of electronic effects of the substituents across the naphthalene ring, the \( v_C = O \) modes of the s-cis conformers of several 6'-substituted \( \beta \)-naphthyl styryl ketones were measured (Table 1). The 2'- and 6'-positions in naphthalene ring are analogous to the para-position in benzene system and hence \( v_C = O \) were correlated with \( \sigma_p/\sigma_p^+ \) constants (Table 2). For s-cis conformers of 3'- and 4'-substituted chalcones\(^4\), the \( p \)-value was 5.44 in chloroform solvent. The \( p \)-value for naphthalene system is lower and this may be due to the fact that the electronic effects of the substituents are to be transmitted from one ring to another ring. Unlike in the case of chalcones, the correlation with \( \sigma_p^+ \) constants is fairly good. This may be due to the fact that for \( \beta \)-naphthyl styryl ketones, there may be a constant average conformation, i.e. the extent of coplanarity may not be changing with substituents, unlike for chalcones where coplanarity of the styryl group and the carbonyl group may be affected by the introduction of substituents.

Good correlation with \( \sigma_p^+ \) constants implies that there is significant resonance interaction between the substituents and the carbonyl group and hence the carbonyl frequencies were analysed in terms of Yukawa-Tsuno equation\(^8\). Multiple linear regression analysis gave the following equations.

For Series-A in CCl\(_4\) and CHCl\(_3\) respectively

\[ v_C = O = 4.25\sigma_p + 4.38(\sigma_p^+ - \sigma_p) \]
\[ + 1668.2 \text{ cm}^{-1}(r = 0.992) \]

For Series-B in CCl\(_4\) and CHCl\(_3\) respectively

\[ v_C = O = 4.39\sigma_p + 5.43(\sigma_p^+ - \sigma_p) \]
\[ + 1662.3 \text{ cm}^{-1}(r = 0.994) \]

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References