Woodward-Fieser Rules for Calculating the $\lambda_{\text{max}}$ of Conjugated Dienes and Polyenes

<table>
<thead>
<tr>
<th>Core Chromophore</th>
<th>Substituent and Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transoid Diene</td>
<td></td>
</tr>
<tr>
<td>215 nm</td>
<td>R- (Alkyl Group) .... +5 nm</td>
</tr>
<tr>
<td></td>
<td>RO- (Alkoxy Group) .. +6</td>
</tr>
<tr>
<td></td>
<td>X- (Cl- or Br-) .......... +10</td>
</tr>
<tr>
<td></td>
<td>RCO$_2$- (Acyl Group) .... 0</td>
</tr>
<tr>
<td></td>
<td>RS- (Sulfide Group) .. +30</td>
</tr>
<tr>
<td></td>
<td>R$_2$N- (Amino Group) .. +60</td>
</tr>
</tbody>
</table>

Further $\pi$-Conjugation

C=C (Double Bond) ... +30

C$_6$H$_5$ (Phenyl Group) ... +60

(i) Each exocyclic double bond adds 5 nm. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.

(ii) Solvent effects are minor.

* When a homoannular (same ring) cyclohexadiene chromophore is present, a base value of 260 nm should be chosen. This includes the ring substituents. Rings of other size have a lesser influence.

$\lambda_{\text{max}}$ (calculated) = Base (215 or 260) + Substituent Contributions

Examples

Woodward-Fieser Rules for Calculating the $\pi \rightarrow \pi^*$ $\lambda_{\text{max}}$ of Conjugated Carbonyl Compounds

<table>
<thead>
<tr>
<th>Core Chromophore</th>
<th>Substituent and Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substituent</td>
<td>Contribution (nm)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>R = Alkyl</td>
<td>215</td>
</tr>
<tr>
<td>R = H</td>
<td>210</td>
</tr>
<tr>
<td>R = OR'</td>
<td>195</td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>202</td>
</tr>
</tbody>
</table>

α-Substituent
- R- (Alkyl Group) +10
- Cl- (Chloro Group) +15
- Br- (Chloro Group) +25
- HO- (Hydroxyl Group) +35
- RO- (Alkoxyl Group) +35
- RCO₂- (Acyl Group) +6

β-Substituent
- R- (Alkyl Group) +12
- Cl- (Chloro Group) +12
- Br- (Chloro Group) +30
- HO- (Hydroxyl Group) +30
- RO- (Alkoxyl Group) +30
- RCO₂- (Acyl Group) +6
- RS- (Sulfide Group) +85
- R₂N- (Amino Group) +95

γ & δ-Substituents
- R- (Alkyl Group) +18 nm (both γ & δ)
- HO- (Hydroxyl Group) +50 nm (γ)
- RO- (Alkoxyl Group) +30 nm (γ)

Further π-Conjugation
- C=C (Double Bond) ... +30
- C₆H₅ (Phenyl Group) ... +60

(i) Each exocyclic double bond adds 5 nm. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.
(ii) Homoannular cyclohexadiene component adds +35 nm (ring atoms must be counted separately as substituents)
(iii) Solvent Correction: water = −8; methanol/ethanol = 0; ether = +7; hexane/cyclohexane = +11

λ_max (calculated) = Base + Substituent Contributions and Corrections

Examples
Contributors