**UV-Vis Lesson 3 - Woodward-Fieser Rules**

As you look over the rules below, you will notice a striking feature. Making the chromophore more conjugated significantly increases the value of $\lambda_{\text{max}}$. *Greater conjugation leads to a longer $\lambda_{\text{max}}*$.

**CONJUGATED DIENE CORRELATIONS**  \[ R_2C=CR-CR=CR_2 \]

*Base:* (chose the highest appropriate base value)
- for acyclic 214, or
- for heteroannular 214, or
- for homoannular 253

*Auxochrome Corrections:*
- +60 for each dialkylamino
- +30 for each extending olefin
- +30 for each alkylthio
- +5 for each Cl, Br, or alkoxy
- +5 for each exocyclic olefin
- +5 for each alkyl (cyclic or acyclic)

**ENONE CORRELATIONS**  \[ \beta \alpha \]

*Base:*
- for acyclic or cyclohexenone 215, or
- for cyclopentenone 202

*Auxochromes:*
- +30 for each extending olefin
- +5 for each exocyclic olefin

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>Auxochrome</th>
<th>$\beta$</th>
<th>$\gamma, \delta, \text{etc.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+35</td>
<td>-OH or -OR</td>
<td>+30</td>
<td></td>
</tr>
<tr>
<td>+25</td>
<td>-Br</td>
<td>+30</td>
<td></td>
</tr>
<tr>
<td>+15</td>
<td>-Cl</td>
<td>+12</td>
<td></td>
</tr>
<tr>
<td>+10</td>
<td>aliphatic</td>
<td>+12</td>
<td>+18</td>
</tr>
<tr>
<td>+6</td>
<td>-OCOR</td>
<td>+6</td>
<td>+6</td>
</tr>
</tbody>
</table>
**BENZOYL CORRELATIONS**

\[ X-C_6H_4-CO-Z \]

**Base:**
- where \( Z = H, 250; \) or \( X-C_6H_4-COH \) (benzaldehydes)
- where \( Z = \) aliphatic, 246; or \( X-C_6H_4-COR \) (acetophenones, \( \alpha \)-tetralones, etc.)
- where \( Z = O-H / O-R, 230 \) \( X-C_6H_4-COOH / X-C_6H_4-COOR \) (acids / esters)

**Auxochromes:**

<table>
<thead>
<tr>
<th>( R )</th>
<th>( o-, m- )</th>
<th>( p- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR_2</td>
<td>20</td>
<td>85</td>
</tr>
<tr>
<td>O-H, O-R</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>aliphatic</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Br</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>Cl</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

The rules listed above apply only to diene, enone or benzoyl containing compounds. If a compound does not contain one of these three chromophores, you will not be able to predict or calculate a diagnostic \( \lambda_{max} \) value using these tables. Also, if a compound contains one of the listed chromophores, but it has an auxochrome that is not listed, then, the best that you will be able to do is to predict a minimum value for the diagnostic \( \lambda_{max} \). In these cases, the diagnostic \( \lambda_{max} \) will be greater than the predicted \( \lambda_{max} \) using the tables. In the event that you have a compound that fits the rules, the calculated \( \lambda_{max} \) should be within \((+/-)\) 3 nm of the \( \lambda_{max} \) observed in the UV-Vis spectrum.

Work through each of the examples listed in the following application notes to see how the rules are applied. As you work through them double-check the identification of chromophores, auxochromes, and special corrections (homoannular, heteroannular, exocyclic, etc.) that are applied to each case. You should NOT memorize the data tables.
Application Examples for Woodward’s Rules

**Diene Example #1:**

![Diene Example #1 Diagram]

Calc. $\lambda_{\text{max}} = 214$ (acyclic base) + 5 (alkyl auxochrome at C$_3$) + 5 (alkyl auxochrome at C$_4$) = 224 nm

One way to identify an auxochrome is to draw a loop around the entire conjugated system (including extending olefins) and then add hash marks across all bonds attached to the loop. The hash marks define auxochrome attachments.

**Diene Example #2:**

![Diene Example #2 Diagram]

Calc. $\lambda_{\text{max}} = 214$ (heteroannular since two pi bonds are not in the same ring) + 20 (5 + 5 + 5 + 5 = 20, for each of the alkyl or ring auxochromes attached to C$_1$, C$_2$, C$_4$, and C$_4$) + 5 (pi bond of C$_1$-C$_2$ is exocyclic to ring B) = 239 nm
Diene Example #3:

Calc. $\lambda_{\text{max}} = 253$ (choose diene with highest base value, pi bonds C\textsubscript{1-2} and C\textsubscript{3-4} are within same ring, so homoannular base should be selected) + 30 (C\textsubscript{5-6} pi bond is conjugated to diene and is therefore an extending diene) + 5 (C\textsubscript{5-6} is exocyclic to ring B) + 30 (5 + 5 + 5 + 5 + 5 = 30, for the alkyl or ring auxochromes at C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{5}, and C\textsubscript{6}) = 318 nm

Enone Example #1:

Calc. $\lambda_{\text{max}} = 215$ (cyclohexenone base) + 30 (extending conjugation) + 5 ($\alpha,\beta$ olefin is exocyclic to ring B) + 12 ($\beta$ auxochrome) + 36 (2 $\delta$ auxochromes) = 298 nm
Benzoyl Example #1:

\[ \text{Calc. } \lambda_{\text{max}} = 246 \text{ (Benzoyl Base, where } Z \text{ is the aliphatic methyl group)} + 3 \text{ (} o \text{ auxochrome)} + 3 \text{ (} m \text{ auxochrome)} = 252 \text{ nm} \]

Benzoyl Example # 2:

\[ \text{Calc. } \lambda_{\text{max}} = 230 \text{ (Benzoyl Base, where } Z \text{ is O-R in this ester functionality)} + ? \]

(There is no value listed for a meta nitro group.)

> 230 nm. The rules are not perfect. They do not allow you to make predictions for all compounds, not even all the simple ones. The best you can predict in this situation is that the observed $\lambda_{\text{max}}$ should be greater than 230 nm. After all, the nitro group contains a $\pi$ bond that extends the length of the conjugated $\pi$ system. And if nothing else, you know that greater conjugation means longer wavelength $\lambda_{\text{max}}$.}

\[ \text{O} \]

\[ \text{N}^{+} \]

\[ \text{O} \]

\[ \text{OCH}_3 \]
<table>
<thead>
<tr>
<th>Question</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>QUVVis3-1.</strong> What is the predicted $\lambda_{\text{max}}$ for the compound drawn below?</td>
<td><img src="image" alt="Compound" /></td>
</tr>
<tr>
<td><strong>QUVVis3-2.</strong> Calculate the predicted $\lambda_{\text{max}}$ for the compound drawn below.</td>
<td><img src="image" alt="Compound" /></td>
</tr>
<tr>
<td><strong>QUVVis3-3.</strong> What is the chromophore in the compound drawn below?</td>
<td><img src="image" alt="Compound" /></td>
</tr>
<tr>
<td><strong>QUVVis3-4.</strong> What is the predicted $\lambda_{\text{max}}$ for the compound drawn in QUVVis3-3?</td>
<td><img src="image" alt="Compound" /></td>
</tr>
<tr>
<td><strong>QUVVis3-5.</strong> What is the predicted $\lambda_{\text{max}}$ for the compound drawn below?</td>
<td><img src="image" alt="Compound" /></td>
</tr>
<tr>
<td><strong>QUVVis3-6.</strong> Suppose you have the two compounds listed below and a UV-Vis instrument, but no access to tables or rules for calculation of $\lambda_{\text{max}}$ values. How could you use UV-Vis to differentiate between these two compounds?</td>
<td><img src="image" alt="Compounds" /></td>
</tr>
</tbody>
</table>