

Electronic Transitions to Probe Bonding Orbital Energies

- Electronic transitions as a source of bonding information,
- $h\nu$ absorption leads to excitation of electrons from a ground state to an excited one
- The wavelength (λ_{\max}) of an absorption (in nm) can be used to deduce details of the structure of the *chromophore*.
- Most important in the structural analysis of compounds containing π electrons, and particularly highly conjugated systems.

Beer-Lambert Law

$$A = \log(I/I_0) = \epsilon \cdot c \cdot l$$

where I = transmitted light intensity

I_0 = incident light intensity

c = concentration (M)

l = path length of cell (cm)

ϵ = molar extinction coefficient (usually in the range $0-10^5$, with $<10^3$ considered to be a weak absorption)

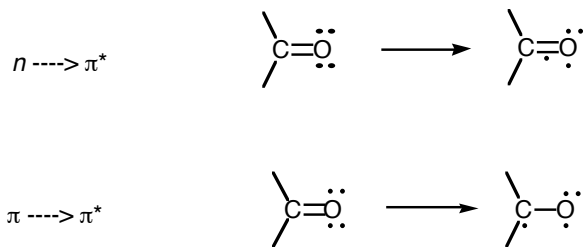
- In characterization λ_{\max} and ϵ normally reported for each maximum

Sample Preparation

| <i>Solvent</i> | <i>Minimum wavelength for 1 cm cell, nm</i> |
|----------------------|---|
| Acetonitrile | 190 |
| Water | 191 |
| Cyclohexane | 195 |
| Hexane | 201 |
| Methanol | 203 |
| Ethanol | 204 |
| Ether | 215 |
| Methylene dichloride | 220 |
| Chloroform | 237 |
| Carbon tetrachloride | 257 |

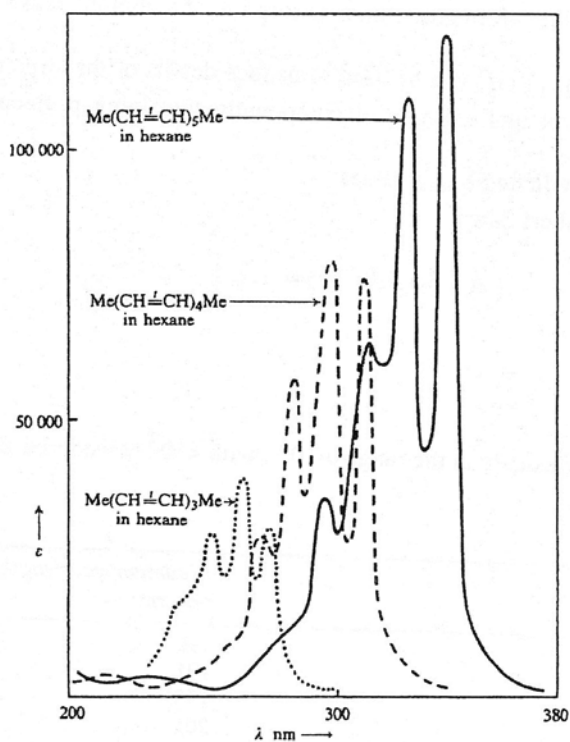
Common Transitions and Functional Groups

- Most frequently observed, most important transitions involve 'loosely held' n and π electrons



| Chromophore | Transition notation† | λ_{\max} , nm |
|---|-------------------------------|-----------------------|
| σ -bonded electrons | | |
| $\text{>C-C<} \text{ and } \text{>C-H}$ | $\sigma \rightarrow \sigma^*$ | ~ 150 |
| Lone-pair electrons | | |
| $\text{-}\ddot{\text{O}}\text{-}$ | $n \rightarrow \sigma^*$ | ~ 185 |
| $\text{-}\ddot{\text{N}}\text{<}$ | $n \rightarrow \sigma^*$ | ~ 195 |
| $\text{-}\ddot{\text{S}}\text{-}$ | $n \rightarrow \sigma^*$ | ~ 195 |
| $\text{>C=}\ddot{\text{O}}$ | $n \rightarrow \pi^*$ | ~ 300 |
| $\text{>C=}\ddot{\text{O}}$ | $n \rightarrow \sigma^*$ | ~ 190 |
| π -bonded electrons | | |
| >C=C< (isolated) | $\pi \rightarrow \pi^*$ | ~ 190 |

Conjugation



Woodward-Fieser Rules

- Empirical rules for predicting λ_{\max}

$\overset{\delta}{\text{C}}=\overset{\gamma}{\text{C}}-\overset{\beta}{\text{C}}=\overset{\alpha}{\text{C}}-\text{C}=\text{O}$ ϵ values are usually above 10 000 and increase with the length of the conjugated system.

| | |
|--|--------|
| Value assigned to parent $\alpha\beta$ -unsaturated six-ring or acyclic ketone | 215 nm |
| Value assigned to parent $\alpha\beta$ -unsaturated five-ring ketone | 202 nm |
| Value assigned to parent $\alpha\beta$ -unsaturated aldehyde | 207 nm |
| Increments for | |
| (a) a double bond extending the conjugation | 30 nm |
| (b) each alkyl group or ring residue α | 10 nm |
| β | 12 nm |
| γ and higher | 18 nm |
| (c) auxochromes | |
| (i) —OH α | 35 nm |
| β | 30 nm |
| δ | 50 nm |
| (ii) —OAc α, β, δ | 6 nm |
| (iii) —OMe α | 35 nm |
| β | 30 nm |
| γ | 17 nm |
| δ | 31 nm |
| (iv) —SAlk β | 85 nm |
| (v) —Cl α | 15 nm |
| β | 12 nm |
| (vi) —Br α | 25 nm |
| β | 30 nm |
| (vii) —NR ₂ β | 95 nm |
| (d) the exocyclic nature of any double bond | 5 nm |
| (e) homodiene component | 39 nm |

$\lambda_{\text{calc}}^{\text{EtOH}}$

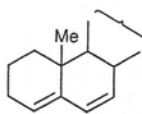
Total

For $\lambda_{\text{max}}^{\text{calc}}$ in other solvents a solvent correction (Table 1.7) must be subtracted from the above value.

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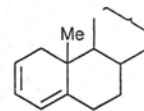
- Ring variant

Woodward's rules for diene and triene absorptions (as modified by Fieser & Scott)



Heteroannular diene

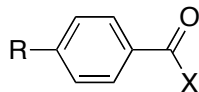
| | |
|--|--------|
| Value assigned to parent heteroannular or open chain diene | 214 nm |
| Value assigned to parent homoannular diene | 253 nm |
| Increment for | |
| (a) each alkyl substituent or ring residue | 5 nm |
| (b) the exocyclic nature of any double bond | 5 nm |
| (c) a double bond extension | 30 nm |
| (d) auxochrome —OAcyl | 0 nm |
| —OAlkyl | 6 nm |
| —SAlkyl | 30 nm |
| —Cl, —Br | 5 nm |
| —NAlkyl ₂ | 60 nm |
| λ_{calc} | Total |



Homoannular diene

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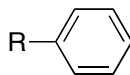
• Benzene rules



| | Orientation | $\lambda_{\text{calc}}^{\text{EtOH}}$, nm |
|---------------------------------|-------------|---|
| Parent chromophore: | | |
| X = alkyl or ring residue | | 246 |
| X = H | | 250 |
| X = OH or OAlkyl | | 230 |
| Increment for each substituent: | | |
| R = alkyl or ring residue | <i>o, m</i> | 3 |
| | <i>p</i> | 10 |
| R = OH, OMe, OAlkyl | <i>o, m</i> | 7 |
| | <i>p</i> | 25 |
| R = O ⁻ | <i>o</i> | 11 |
| | <i>m</i> | 20 |
| | <i>p</i> | 78 |
| R = Cl | <i>o, m</i> | 0 |
| | <i>p</i> | 10 |
| R = Br | <i>o, m</i> | 2 |
| | <i>p</i> | 15 |
| R = NH ₂ | <i>o, m</i> | 13 |
| | <i>p</i> | 58 |
| R = NHAc | <i>o, m</i> | 20 |
| | <i>p</i> | 45 |
| R = NHMe | <i>p</i> | 73 |
| R = NMe ₂ | <i>o, m</i> | 20 |
| | <i>p</i> | 85 |

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and actual...



| R | λ_{max} , nm (ϵ) (solvent H ₂ O or MeOH) | | | |
|---------------------------------------|--|-------|---------|-------------|
| -H | 203.5 (7 400) | 254 | (204) | |
| -NH ₃ ⁺ | 203 (7 500) | 254 | (160) | |
| -Me | 206.5 (7 000) | 261 | (225) | |
| -I | 207 (7 000) | 257 | (700) | |
| -Cl | 209.5 (7 400) | 263.5 | (190) | |
| -Br | 210 (7 900) | 261 | (192) | |
| -OH | 210.5 (6 200) | 270 | (1 450) | |
| -OMe | 217 (6 400) | 269 | (1 480) | |
| -SO ₂ NH ₂ | 217.5 (9 700) | 264.5 | (740) | |
| -CN | 224 (13 000) | 271 | (1 000) | |
| -CO ₂ ⁻ | 224 (8 700) | 268 | (560) | |
| -CO ₂ H | 230 (11 600) | 273 | (970) | |
| -NH ₂ | 230 (8 600) | 280 | (1 430) | |
| -O ⁻ | 235 (9 400) | 287 | (2 600) | |
| -NHAc | 238 (10 500) | | | |
| -COMe | 245.5 (9 800) | | | |
| -CH=CH ₂ | 248 (14 000) | 282 | (750) | 291 (500) |
| -CHO | 249.5 (11 400) | | | |
| -Ph | 251.5 (18 300) | | | |
| -OPh | 255 (11 000) | 272 | (2 000) | 278 (1 800) |
| -NO ₂ | 268.5 (7 800) | | | |
| -CH ¹ =CHCO ₂ H | 273 (21 000) | | | |
| -CH ¹ =CHPh | 295.5 (29 000) | | | |

(Most values taken with permission from H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.)

Examples

(a) Biphenyl (1) and 2,6,2',6'-tetramethylbiphenyl (2) have the ultraviolet absorption spectra shown. What may be deduced from this information?

