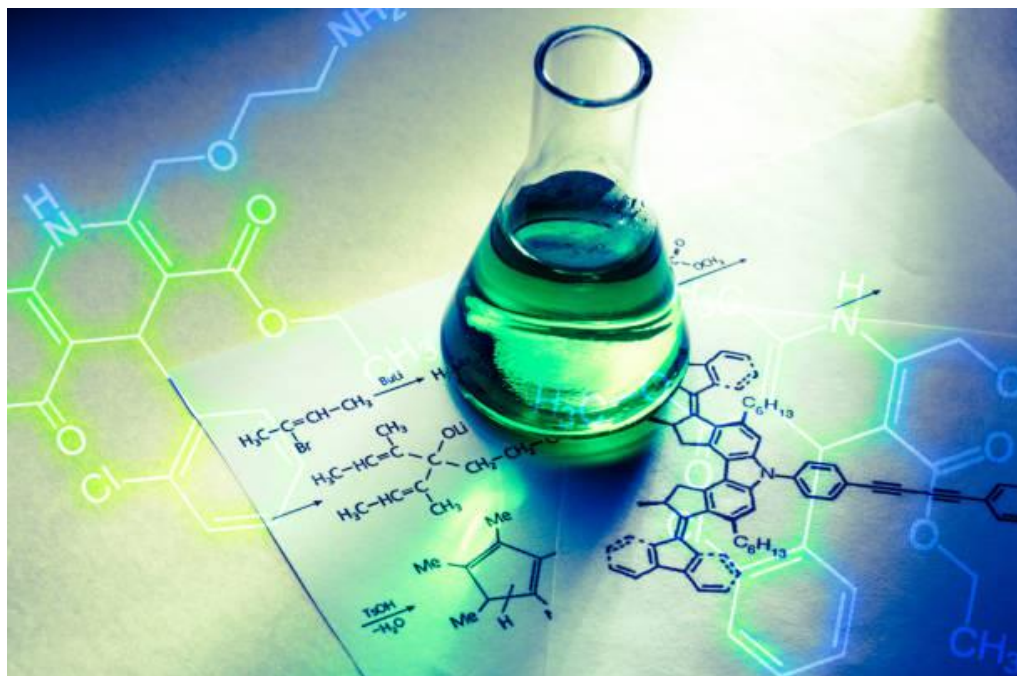# Organic identification

Lecturer : Shaymaa Adil Mohammed

The Importance of Conjugation

- A comparison of the absorption spectrum of 1-pentene, λ_{max} = 178 nm, with that of isoprene (above) clearly demonstrates the importance of chromophore conjugation. Further evidence of this effect is shown below. The spectrum on the left illustrates that conjugation of double and triple bonds also shifts the absorption maximum to longer wavelengths.

- From the polyene spectra displayed in the center diagram, it is clear that each additional double bond in the conjugated pi-electron system shifts the absorption maximum about 30 nm in the same direction. Also, the molar absorptivity (ε) roughly doubles with each new conjugated double bond. Spectroscopists use the terms defined in the table on the right when describing shifts in absorption. Thus, extending conjugation generally results in bathochromic and hyperchromic shifts in absorption.

$\lambda_{max} = 230$ nm $\varepsilon = 11,600$

$R(CH=CH)_n R$

n = 5

n = 4

n = 3

100,000

50,000

ε

absorbance

λ (nm)

λ (nm)
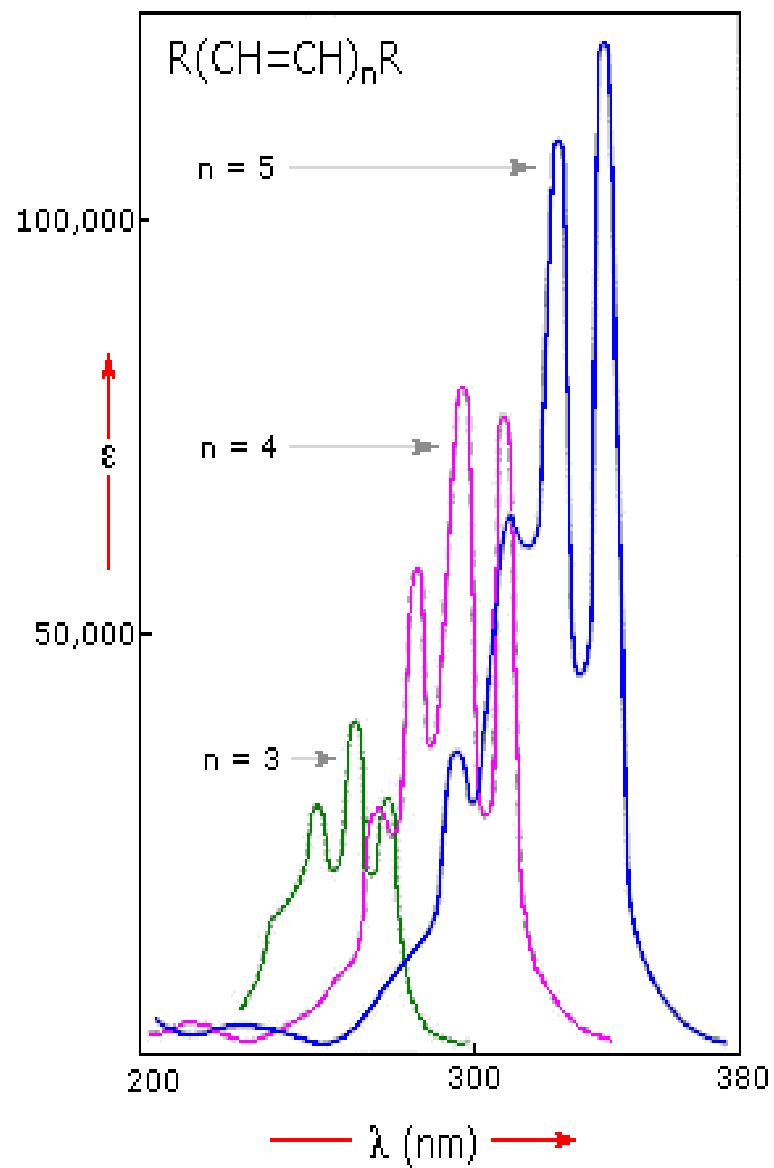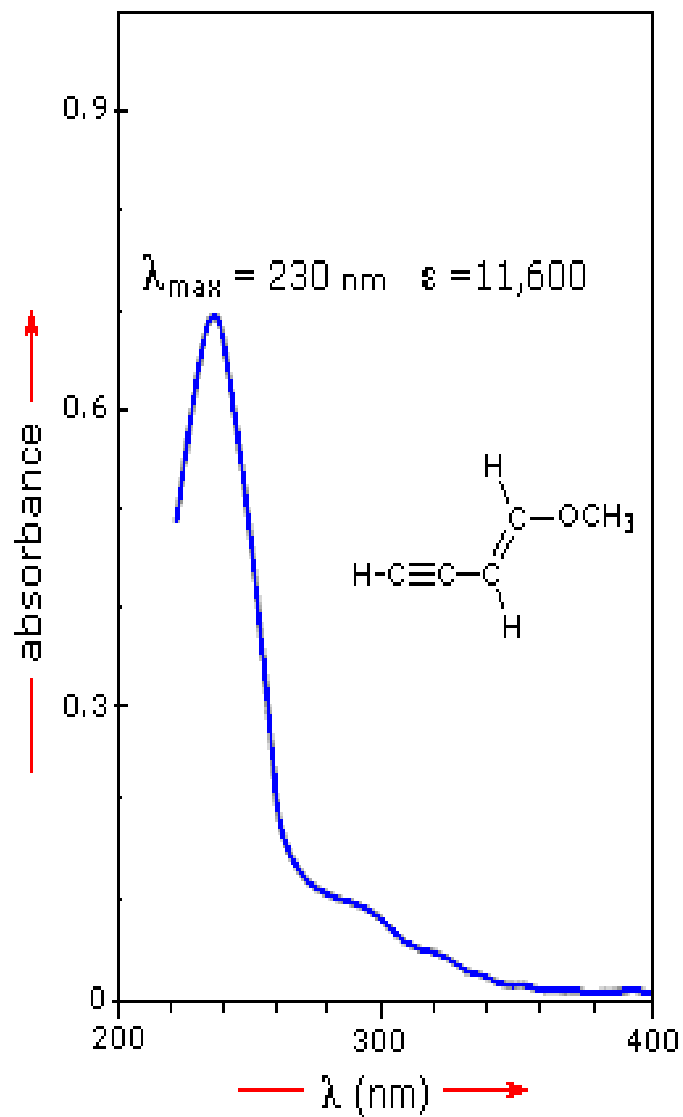
- The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only the different conformations such systems may assume, but also electronic transitions between the different vibrational energy levels possible for each electronic state.

Terminology for Absorption Shifts

Nature of Shift	Descriptive Term
To Longer Wavelength	Bathochromic
To Shorter Wavelength	Hypsochromic
To Greater Absorbance	Hyperchromic
To Lower Absorbance	Hypochromic

- To understand why conjugation should cause bathochromic shifts in the absorption maxima of chromophores, we need to look at the relative energy levels of the pi-orbitals. When two double bonds are conjugated, the four p-atomic orbitals combine to generate four pi-molecular orbitals (two are bonding and two are antibonding). In a similar manner, the three double bonds of a conjugated triene create six pi-molecular orbitals, half bonding and half antibonding. The energetically most favorable $\pi \longrightarrow \pi^*$ excitation occurs from the highest energy bonding pi-orbital (**HOMO**) to the lowest energy antibonding pi-orbital (**LUMO**).

- The following diagram illustrates this excitation for an isolated double bond (only two pi-orbitals) and, In each case the HOMO is colored blue and the LUMO is colored magenta. Increased conjugation brings the HOMO and LUMO orbitals closer together. The energy (ΔE) required to effect the electron promotion is therefore less, and the wavelength that provides this energy is increased correspondingly (remember **λ = h • c/ΔE**)
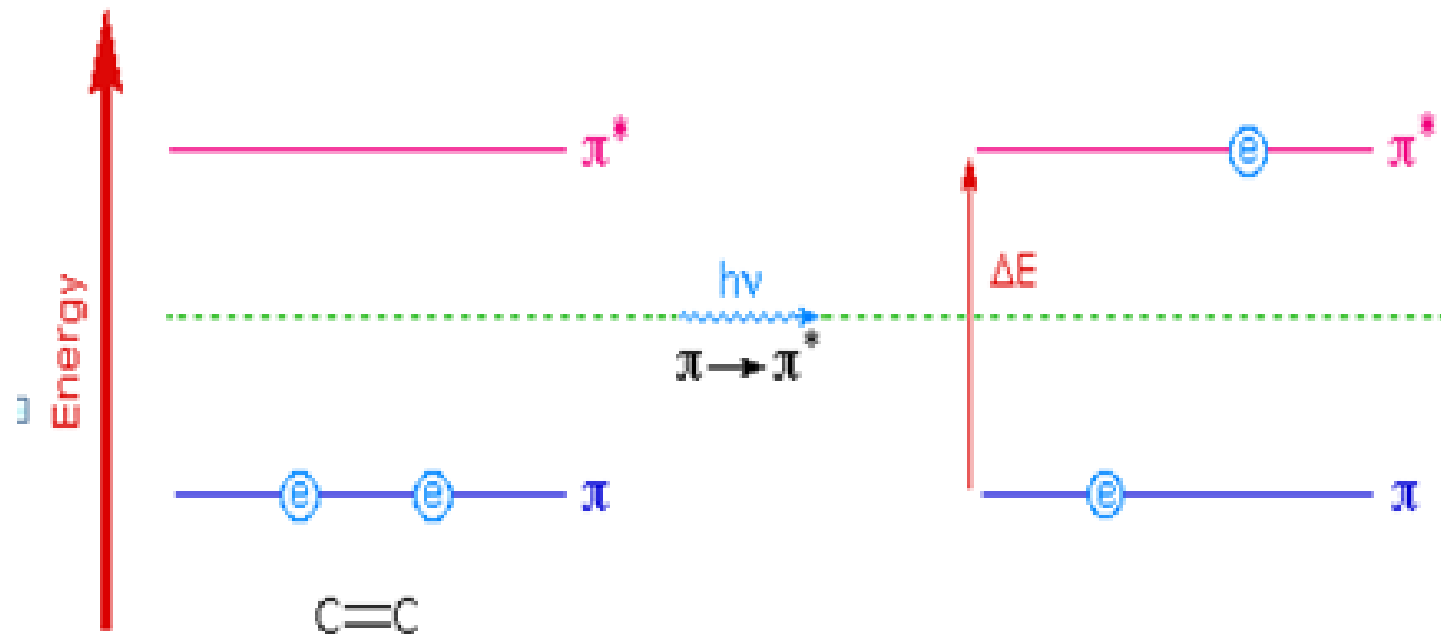
Examples of π —> π* Excitation

- Many other kinds of conjugated pi-electron systems act as chromophores and absorb light in the 200 to 800 nm region. These include unsaturated aldehydes and ketones and aromatic ring compounds. A few examples are displayed below. The spectrum of the unsaturated ketone (on the left) illustrates the advantage of a logarithmic display of molar absorptivity. The $\pi \longrightarrow \pi^*$ absorption located at 242 nm is very strong, with an $\varepsilon = 18{,}000$. The weak n $\longrightarrow \pi^*$ absorption near 300 nm has an $\varepsilon = 100$.

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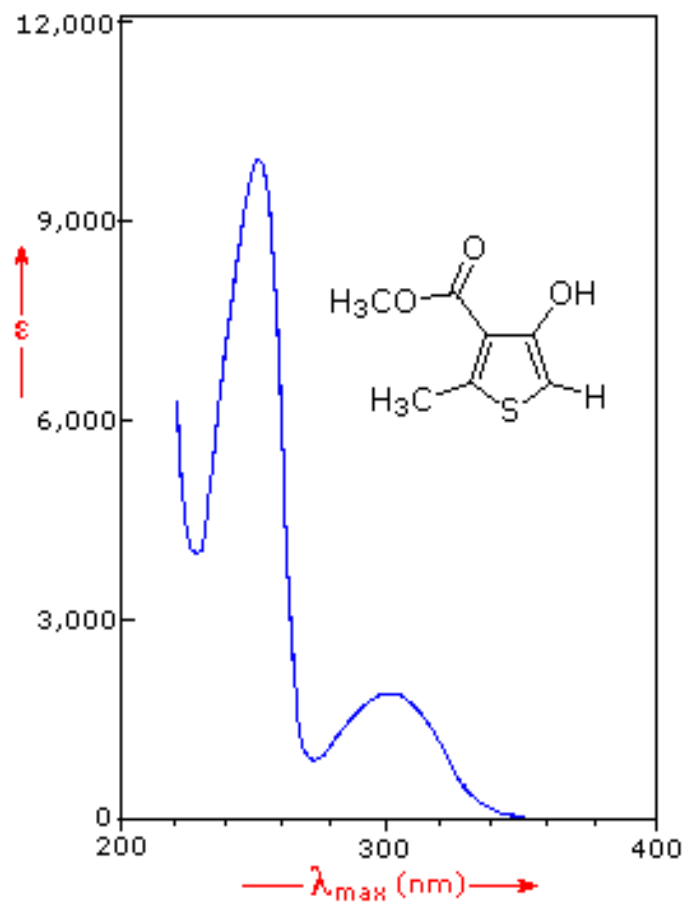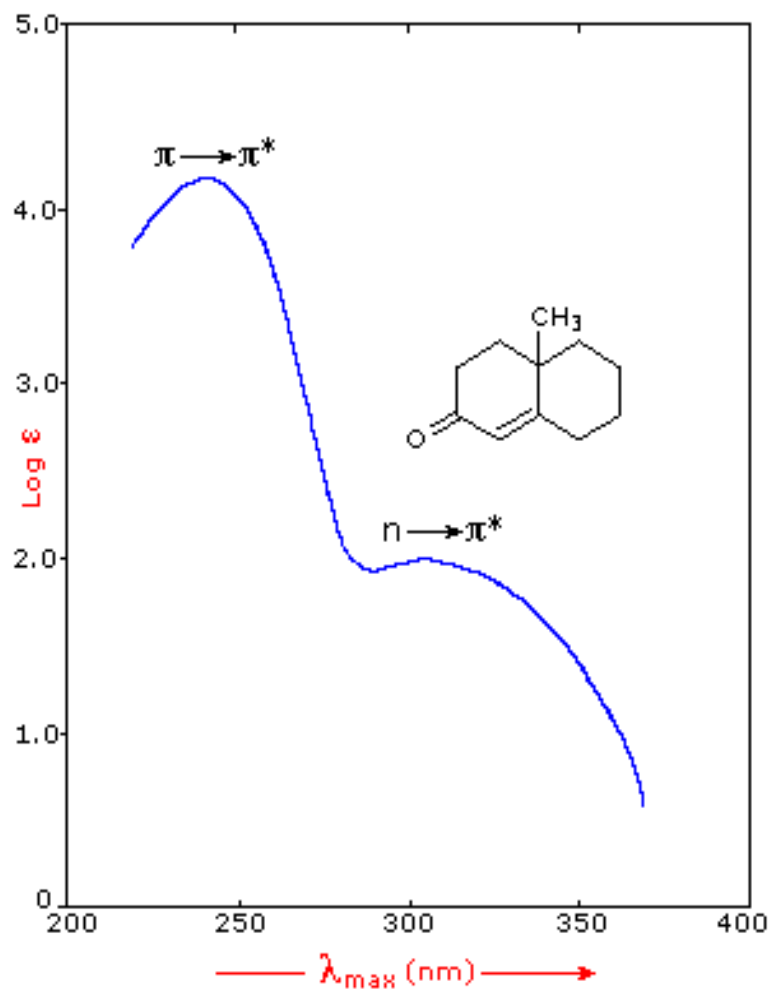
- Benzene exhibits very strong light absorption near 180 nm ($\varepsilon > 65,000$) , weaker absorption at 200 nm ($\varepsilon = 8,000$) and a group of much weaker bands at 254 nm ($\varepsilon = 240$). Only the last group of absorptions are completely displayed because of the 200 nm cut-off characteristic of most spectrophotometers. The added conjugation in naphthalene, anthracene and tetracene causes bathochromic shifts of these absorption bands, as displayed in the chart on the left below. All the absorptions do not shift by the same amount, so for anthracene (green shaded box) and tetracene (blue shaded box) the weak absorption is obscured by stronger bands that have experienced a greater red shift. As might be expected from their spectra, naphthalene and anthracene are colorless, but tetracene is orange.
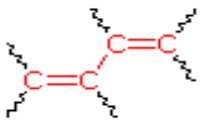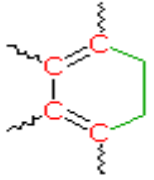
$\lambda_{max} = 235$ nm
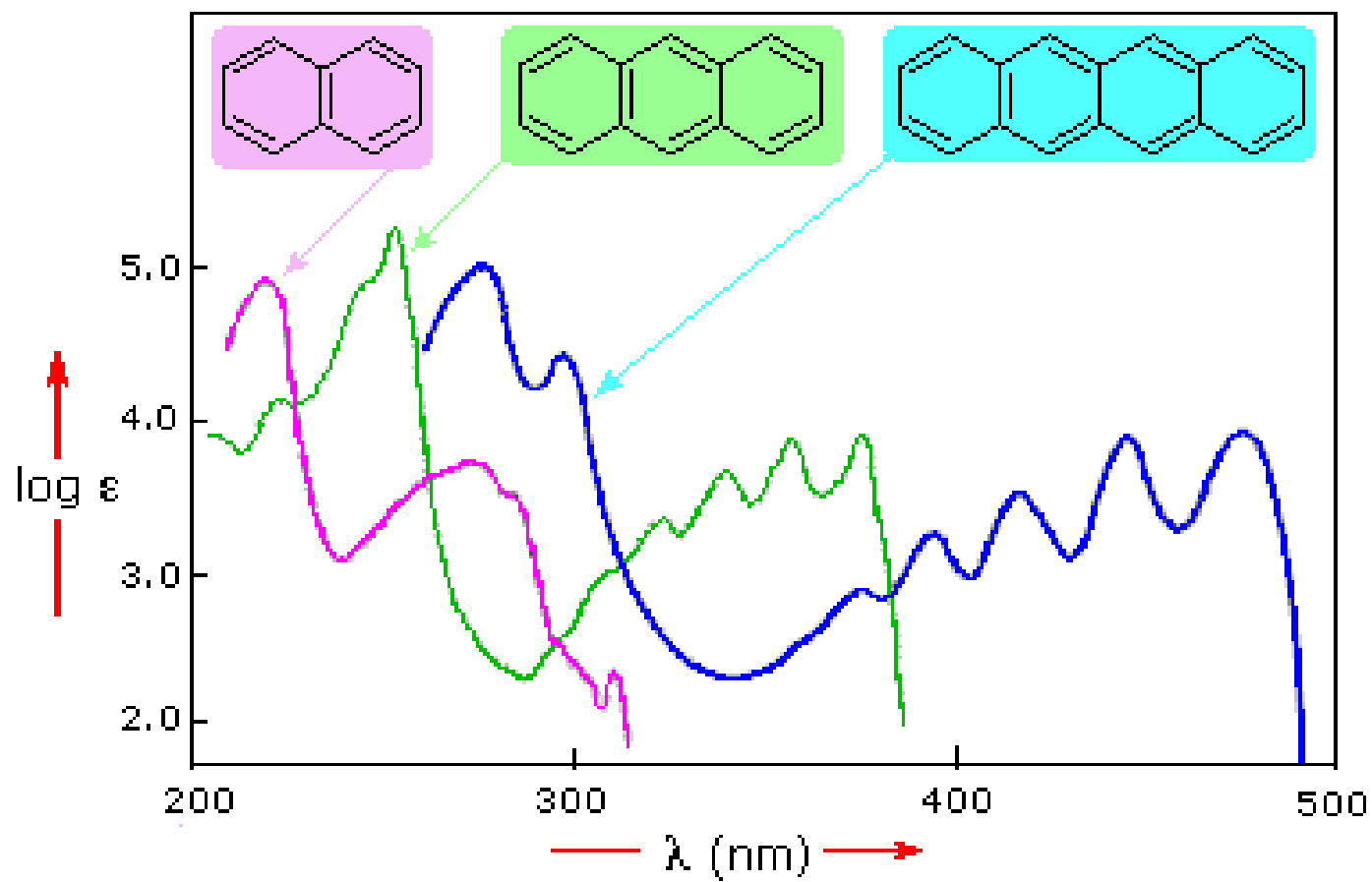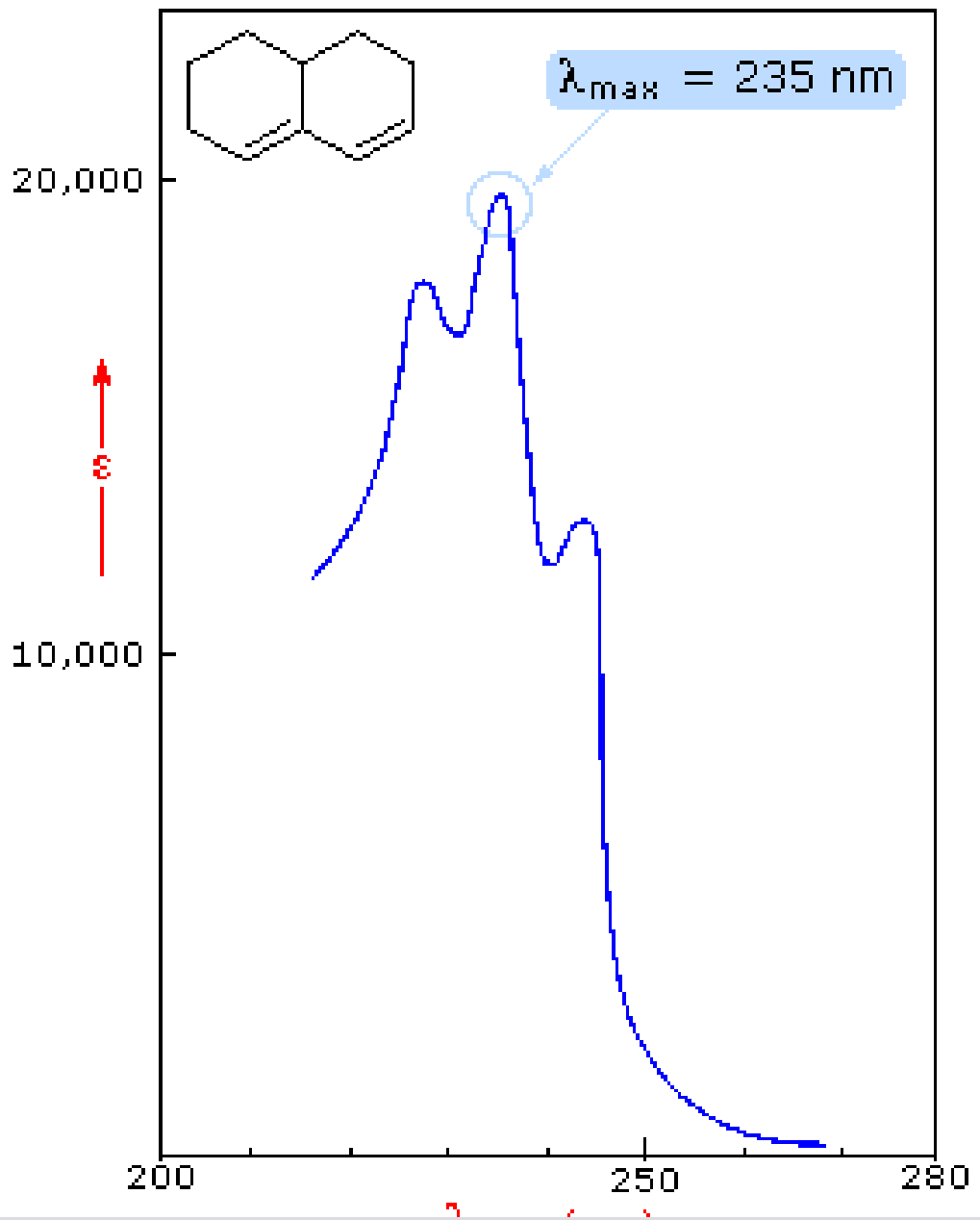
- The spectrum of the bicyclic diene (above right) shows some vibrational fine structure, but in general is similar in appearance to that of isoprene. Closer inspection discloses that the absorption maximum of the more highly substituted diene has moved to a longer wavelength by about 15 nm. This "substituent effect" is general for dienes and trienes, and is even more pronounced for enone chromophores.

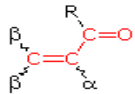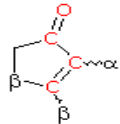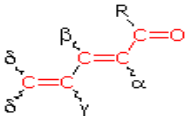# Empirical Rules for Absorption Wavelengths of Conjugated Systems

Woodward-Fieser Rules for Calculating the λ_{max} of Conjugated Dienes and Polyenes

Core Chromophore	Substituent and Influence
Transoid Diene **215 nm**	R- (Alkyl Group) .... **+5 nm** RO- (Alkoxy Group) .. **+6** X- (Cl- or Br-) .... **+10** RCO_2- (Acyl Group) .... **0** RS- (Sulfide Group) .. **+30** R_2N- (Amino Group) .. **+60**
Cyclohexadiene* **260 nm**	**Further π -Conjugation** C=C (Double Bond) ... **+30** C_6H_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.
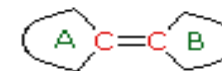
λ_{max} (calculated) = **Base + Substituent Contributions and Corrections**

Woodward-Fieser Rules for Calculating the π —> π* λ_{max} of Conjugated Carbonyl Compounds

Core Chromophore	Substituent and Influence
R = Alkyl 215 nm R = H 210 nm R = OR' 195 nm	**α- Substituent** R- (Alkyl Group) +10 nm Cl- (Chloro Group) +15 Br- (Chloro Group) +25 HO- (Hydroxyl Group) +35 RO- (Alkoxyl Group) +35 RCO_2- (Acyl Group) +6
Cyclopentenone **202 nm**	**β- Substituent** R- (Alkyl Group) +12 nm Cl- (Chloro Group) +12 Br- (Chloro Group) +30 HO- (Hydroxyl Group) +30 RO- (Alkoxyl Group) +30 RCO_2- (Acyl Group) +6 RS- (Sulfide Group) +85 R_2N- (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 C_6H_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) 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**

Some of example

H

H₃C

$C=O$

C

C

Cl

OCH_3

H_3CO

H_3CO

$C=O$

C

C

H_3C

Br