ORGANIC IDENTIFICATION

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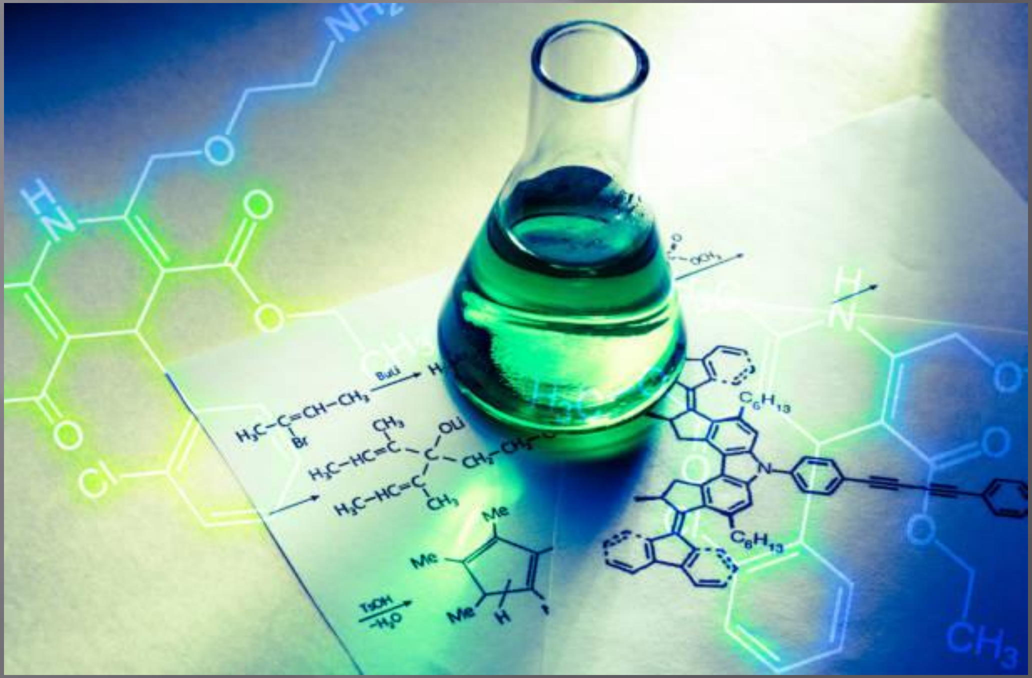
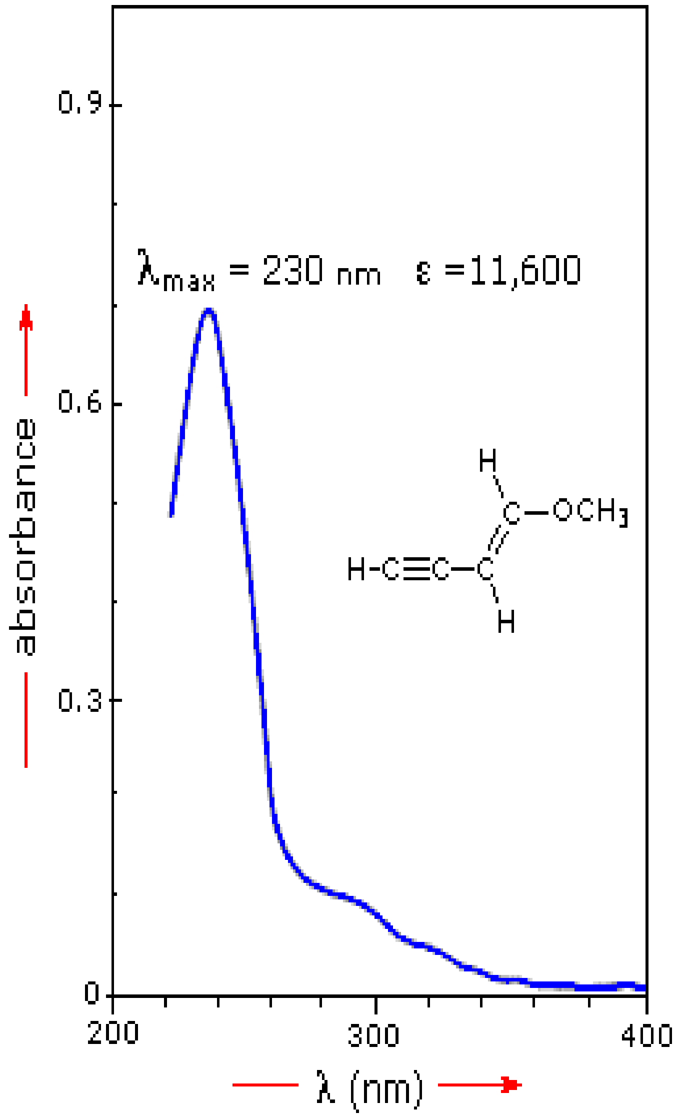


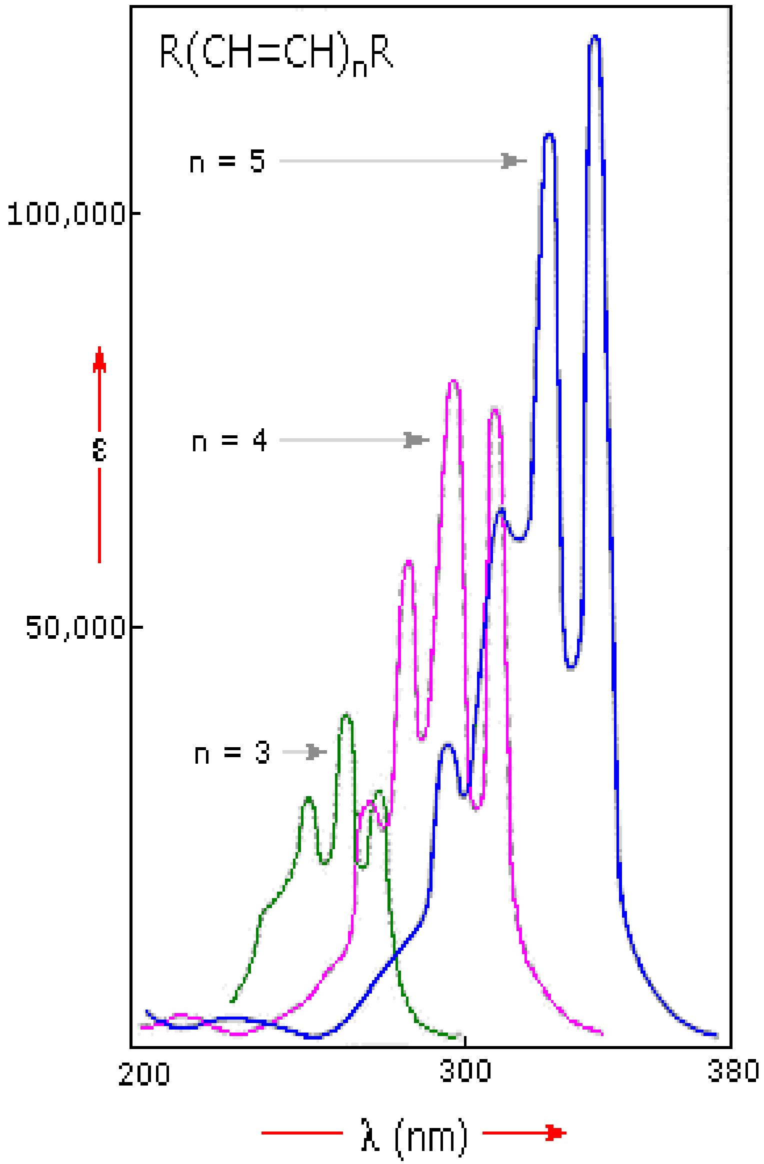
The Importance of Conjugation

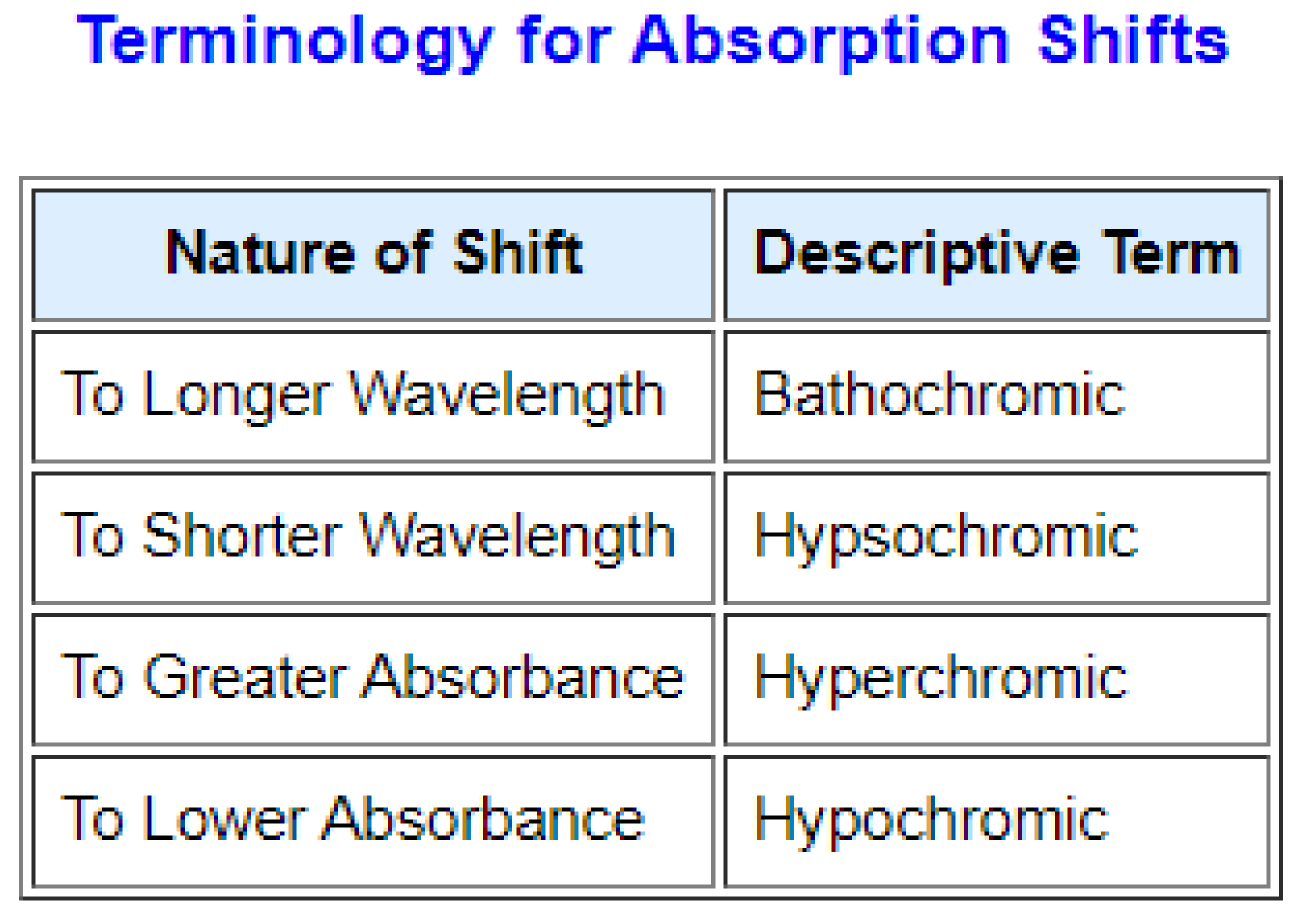
- A comparison of the absorption spectrum of 1-pentene, λ_{max} = 178 nm, with that of isoprene (above) clearly demonstrates the importance of chromophore conjugation. Further evidence of this effect is shown below. The spectrum on the left illustrates that conjugation of double and triple bonds also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

- 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. Vibrational fine structure of this kind is most pronounced in vapor phase spectra, and is increasingly broadened and obscured in solution as the solvent is changed from hexane to methanol.


λmax = 230 nm ε =11,600
H
C—OCH3
H-C≡C—C
H
absorbance
0.9
0.6
0.3
0
200
300
400
λ (nm)


R(CH=CH)nR
n = 5
n = 4
n = 3
ε
100,000
50,000
200
300
380
λ (nm)

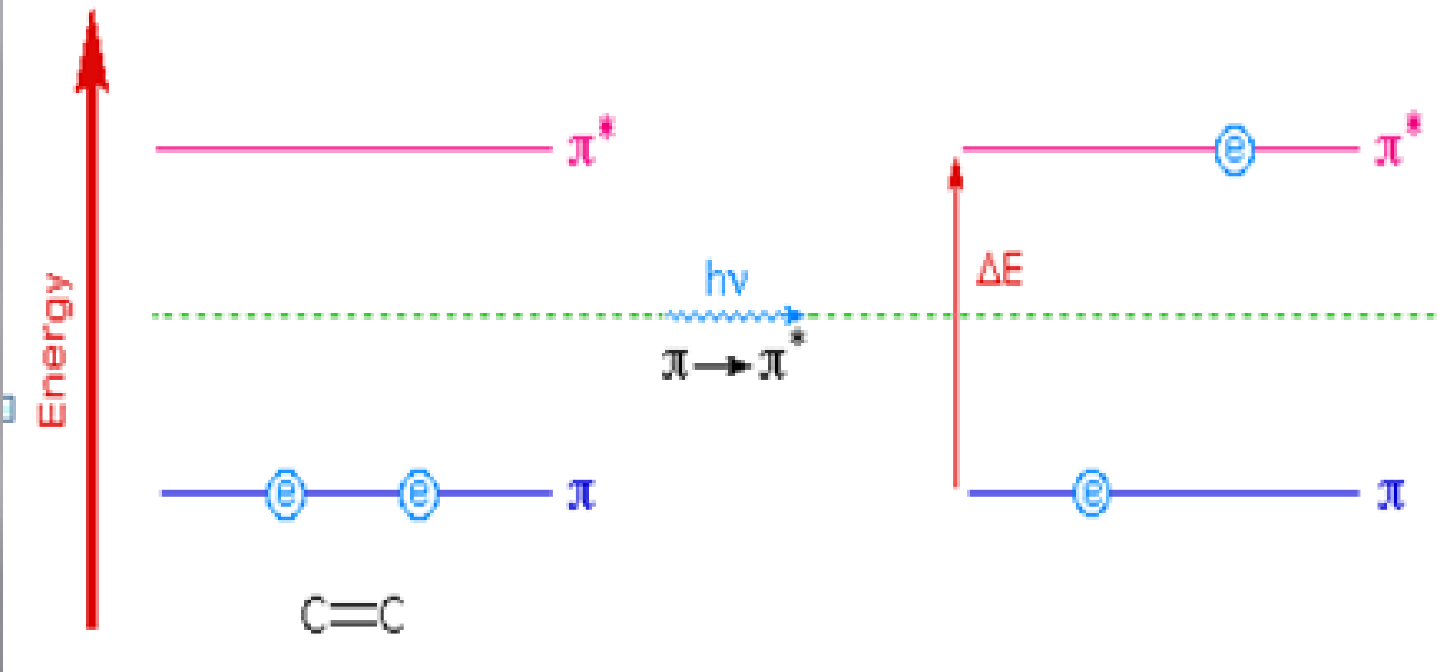


Terminology for Absorption Shifts

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

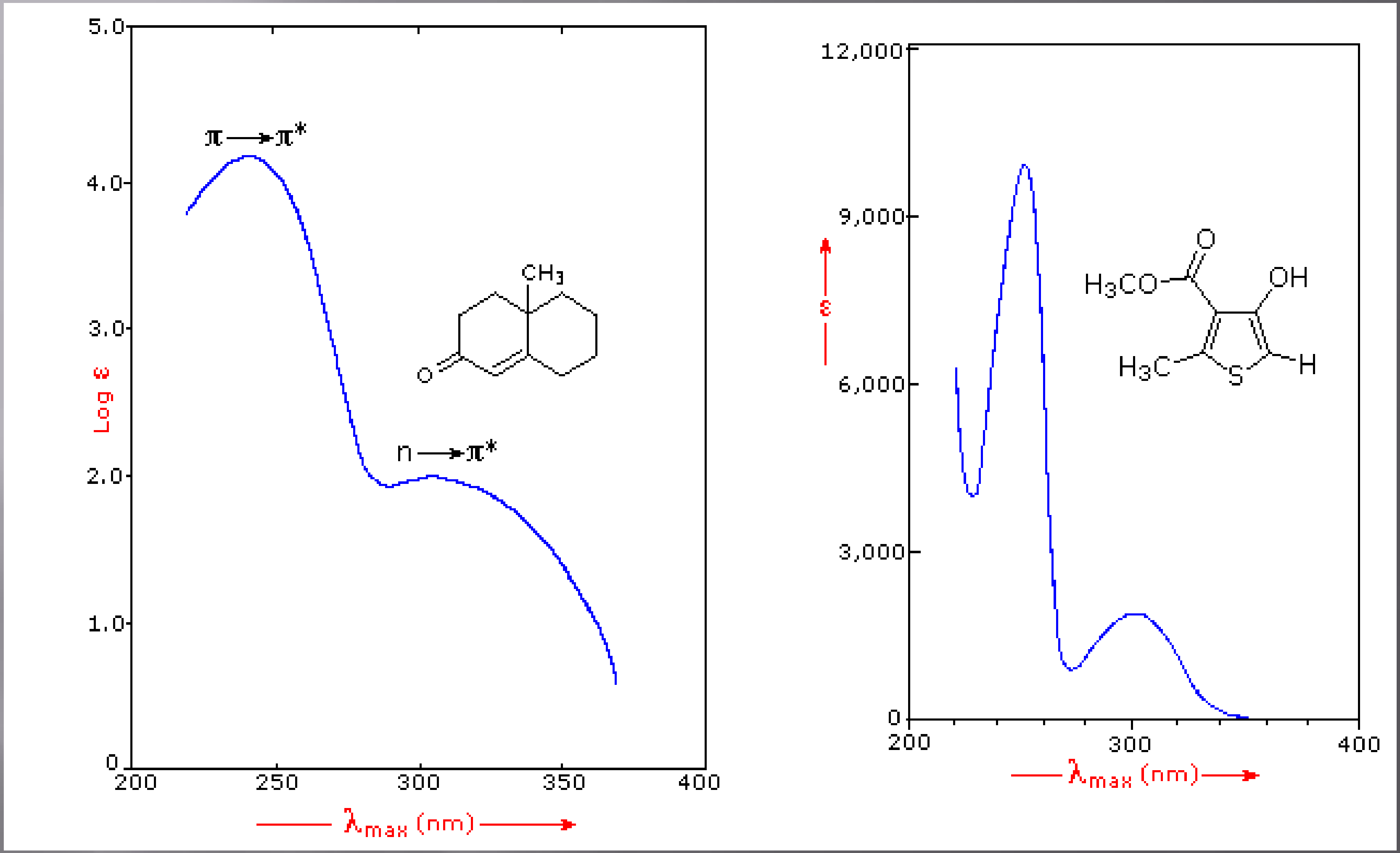
- To understand why conjugation should cause bathochromic shifts in the absorption maxima of chromophores, we need to look at the relative energy levels of the pi-orbitals. When two double bonds are conjugated, the four p-atomic orbitals combine to generate four pi-molecular orbitals (two are bonding and two are antibonding). This was described earlier in the section concerning diene chemistry. 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 π —> π* 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, on clicking the diagram, for a conjugated diene and triene. 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 **$\lambda = h \bullet c/\Delta E$**)

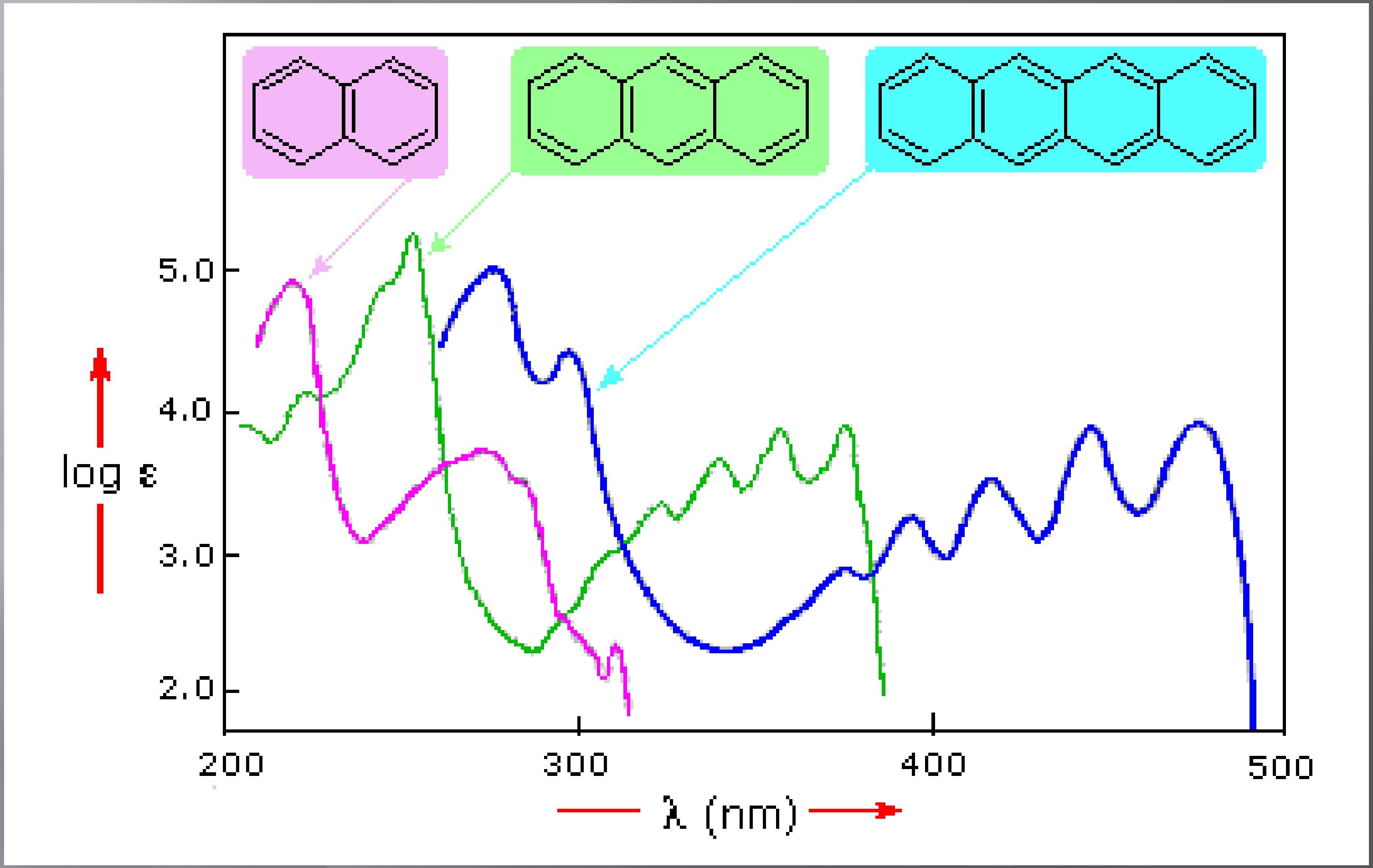


Examples of π —> π* Excitation

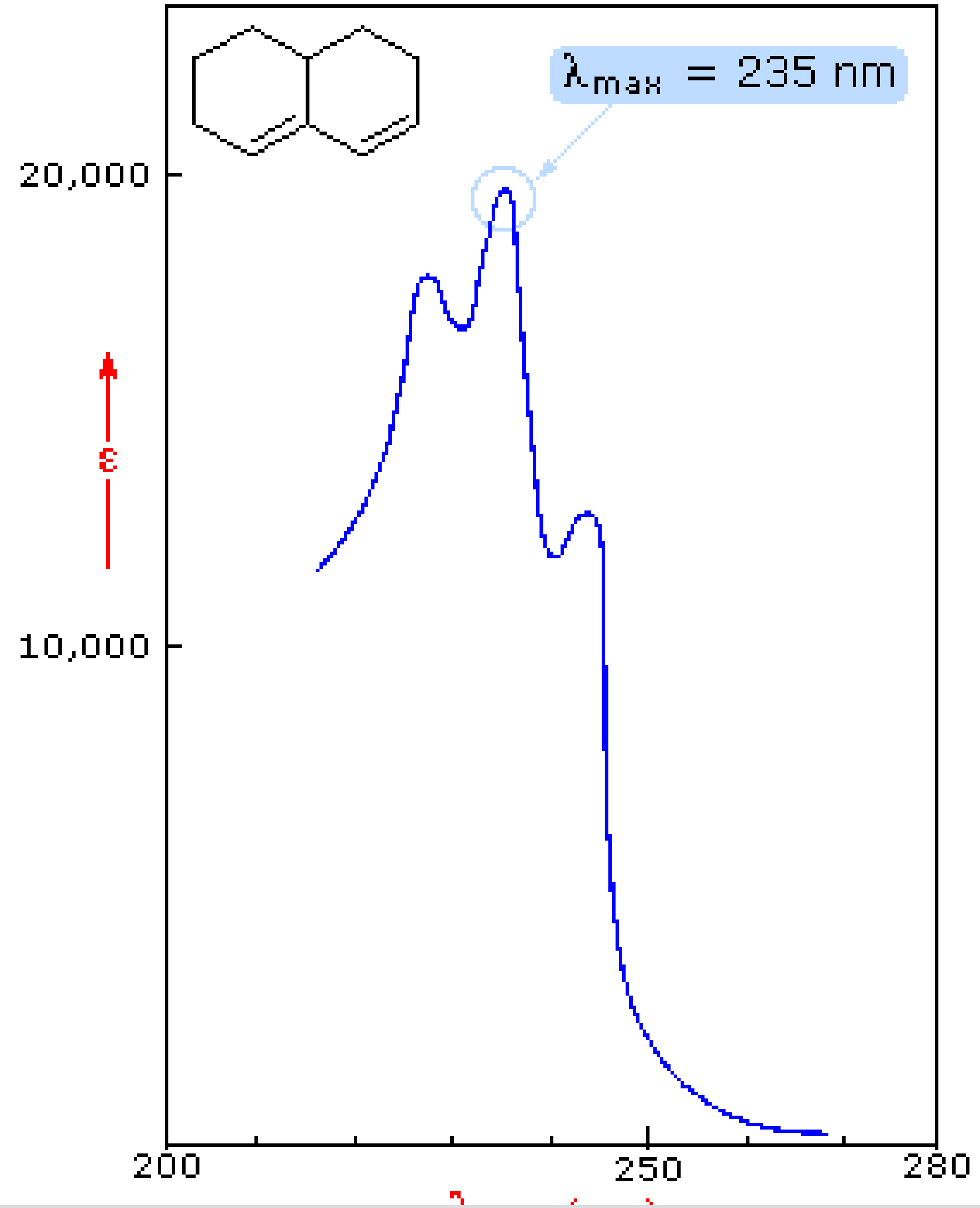
- Many other kinds of conjugated pi-electron systems act as chromophores and absorb light in the 200 to 800 nm region. These include unsaturated aldehydes and ketones and aromatic ring compounds. A few examples are displayed below. The spectrum of the unsaturated ketone (on the left) illustrates the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


5.0
4.0
3.0
2.0
1.0
0
Log ε
200
250
300
350
400
λmax (nm)
π → π*
n → π*
CH3
O
12,000
9,000
6,000
3,000
0
ε
200
300
400
λmax (nm)
H3CO
O
OH
H3C
S
H

- Benzene exhibits very strong light absorption near 180 nm (ε > 65,000) , weaker absorption at 200 nm (ε = 8,000) and a group of much weaker bands at 254 nm (ε = 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.

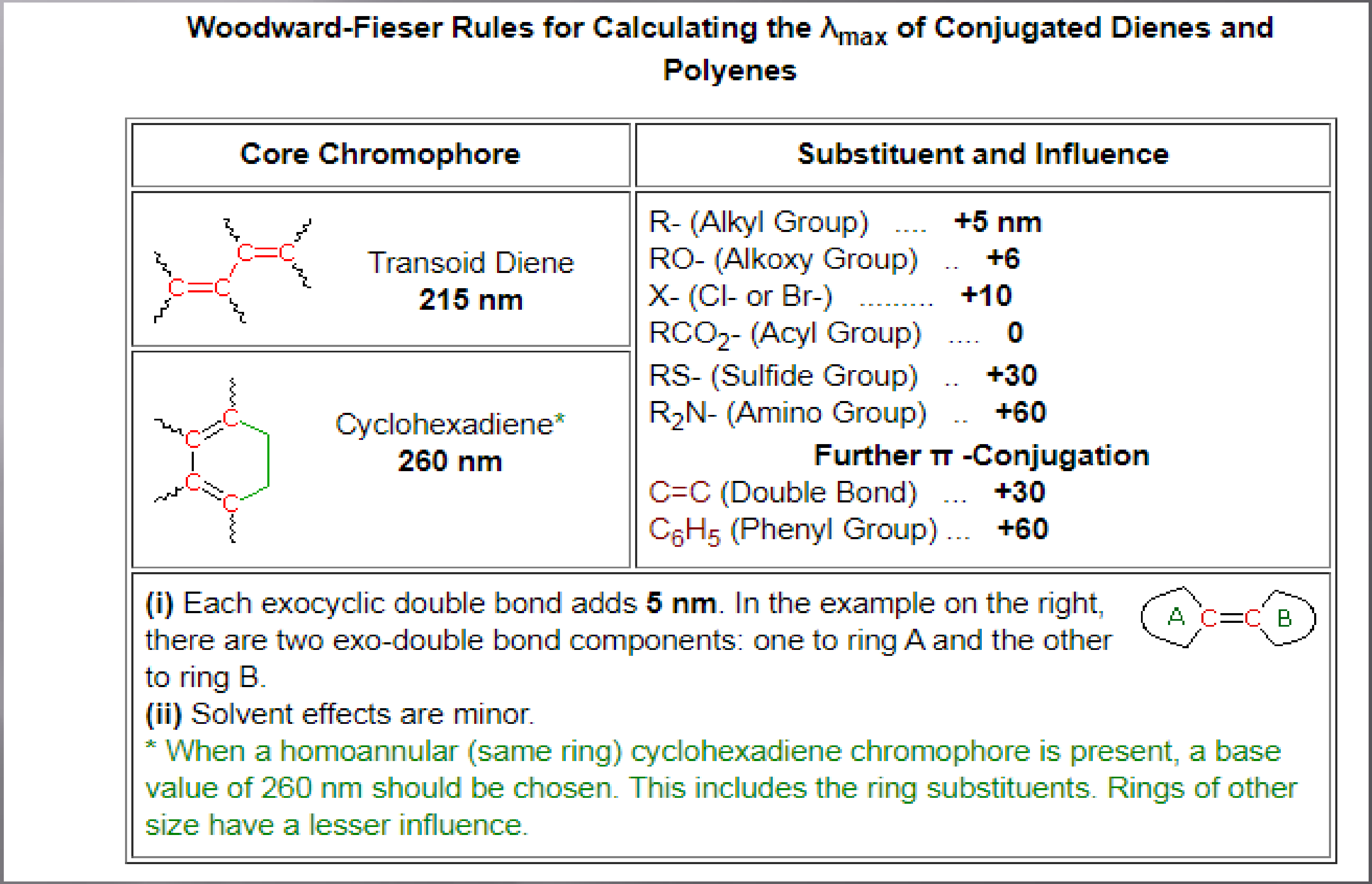


5.0
4.0
3.0
2.0
log ε
200
300
400
500
λ (nm)


λmax = 235 nm
20,000
10,000
ε
200
250
280

- The spectrum of the bicyclic diene (above right) shows some vibrational fine structure, but in general is similar in appearance to that of isoprene, shown above. 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** **Further π -Conjugation** C=C (Double Bond) ... **+30** C_6H_5 (Phenyl Group) ... **+60**
Cyclohexadiene* **260 nm**	

(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.