Spectroscopic Methods in Organic Chemistry

CHEM-6124, Organic Chemistry (Minor)

Online Lectures (UV-Vis)

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UV-Vis Spectroscopy

Frequency (ν) = 4.0×10^{14} to 8.6×10^{14} Hz (Vis)

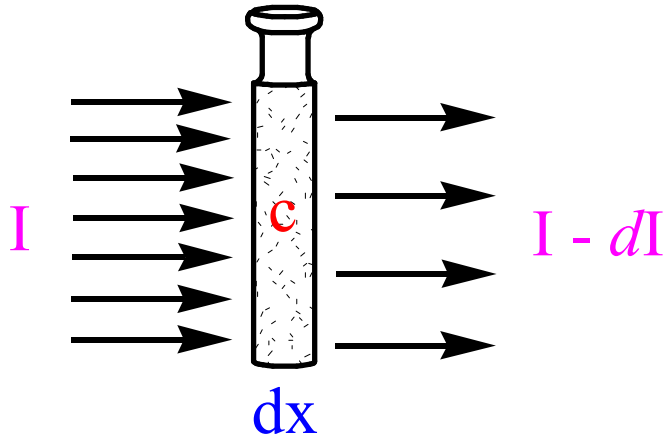
8.6×10^{14} to 1.5×10^{15} Hz (UV)

Wavelength (λ) = 750 to 350 nm (Vis)

350 to 200 nm (UV)

Wave Number ($\acute{\upsilon}$) = 1.33×10^{6} to 2.9×10^{6} m^{-1} (Vis)

2.9×10^{6} to 5.0×10^{6} m^{-1} (UV)



I = Intensity of EMR

dI = Absorbed EMR

dx / l = Path length

c = Concentration of analyte

Lambert-Beer's Law

$$\left.\begin{array}{l} -dI \;\alpha\; I \\ -dI \;\alpha\; c \\ -dI \;\alpha\; dx \end{array}\right\} \quad -dI \;\alpha\; I \,.\, c.\, dx$$

$$-dI = k \,.\, I \,.\, c.\, dx \quad \Rightarrow \quad \frac{-dI}{I} = k \,.\, c.\, dx$$

$$\frac{dI}{I} = -\,k \,.\, c.\, dx$$

$$\ln I - \ln I_o = -\,k \,.\, c \,.\, l \quad \Rightarrow \quad \ln\left(\frac{I}{I_o}\right) = -\,k \,.\, c.\, l$$

$$\log\left(\frac{I}{I_o}\right) = \frac{-\,k \,.\, c.\, l}{2.303} \quad \Rightarrow \quad \log\left(\frac{I}{I_o}\right) = -\,\varepsilon \,.\, c.\, l$$

$$\left(\frac{I}{I_o}\right) = 10^{-\,\varepsilon\, c\, l} \quad \Rightarrow \quad T = 10^{-A}$$

$$A = \varepsilon \,.\, c.\, l \qquad \varepsilon = \frac{A}{c.\, l} = \frac{1}{\text{mol / L} \,.\, \text{cm}} = \text{L} \,.\, \text{mol}^{-1} \,.\, \text{cm}^{-1}$$

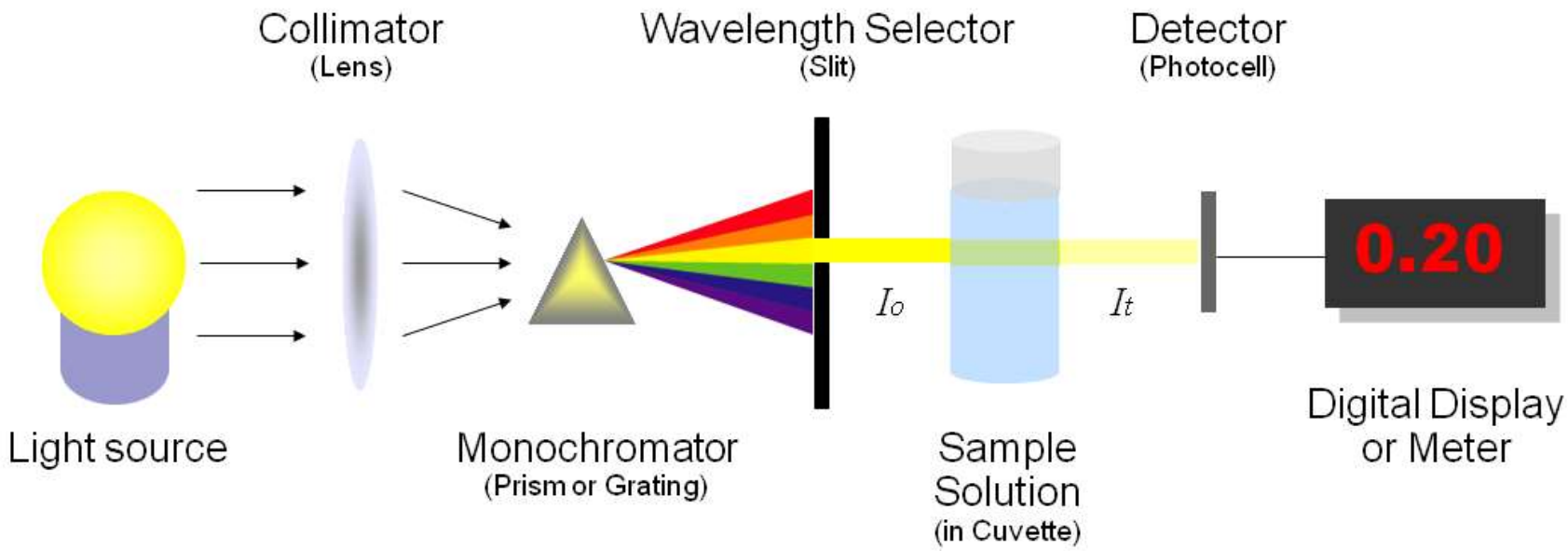
Absorbance Vs Transmittance

$T = 10^{-\varepsilon c l}$ $\log T = -A$

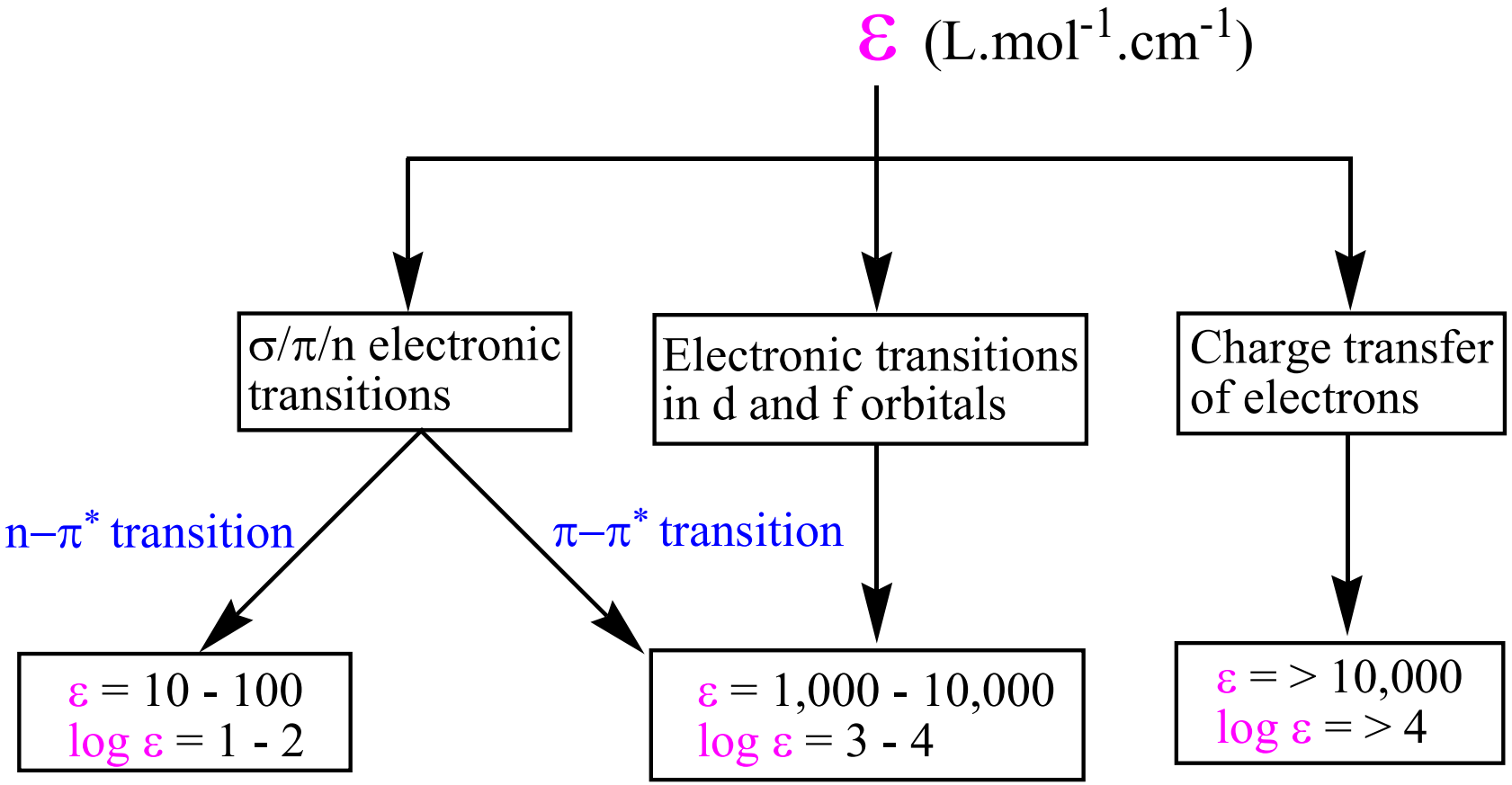
$T = 10^{-A}$ $A = -\log T$

A	T	T	A
0.1	0.79	0.1	1
0.2	0.63	0.2	0.70
0.25	0.56	0.25	0.60
0.3	0.50	0.3	0.52
0.4	0.39	0.4	0.40
0.5	0.32	0.5	0.30

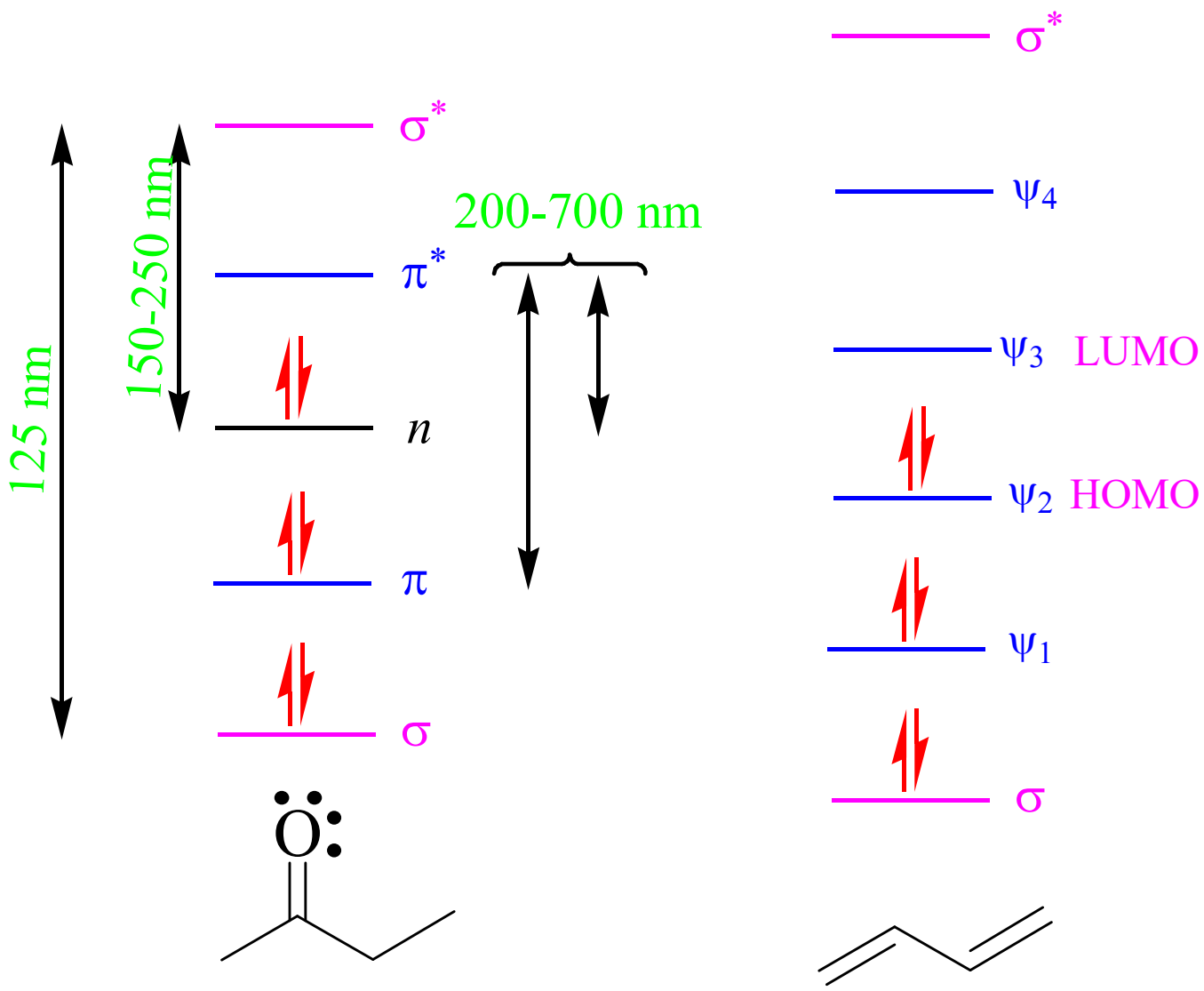
Source of Radiation



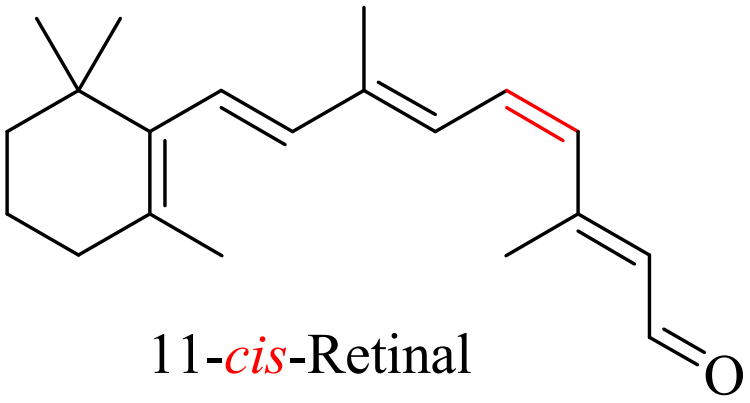
Importance of ε



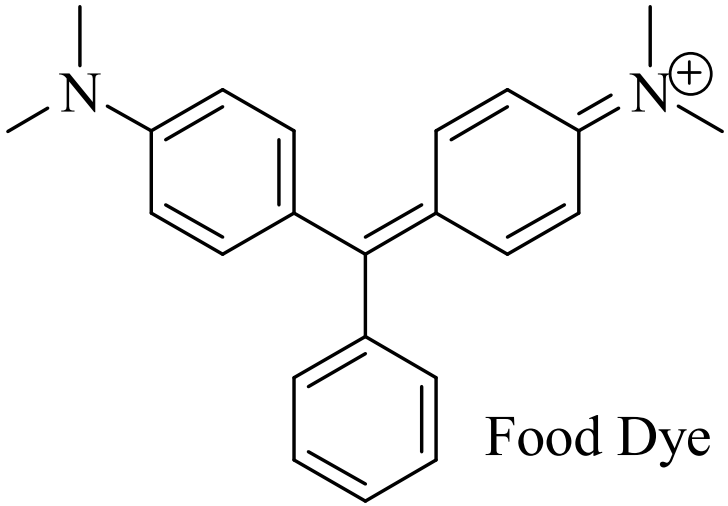
Electronic Transitions *vs* ε



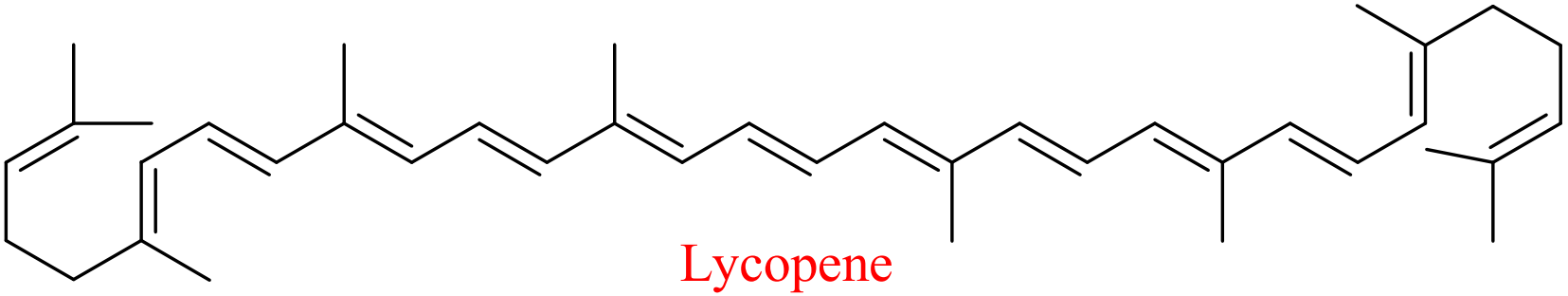
Chromophores



11-*cis*-Retinal

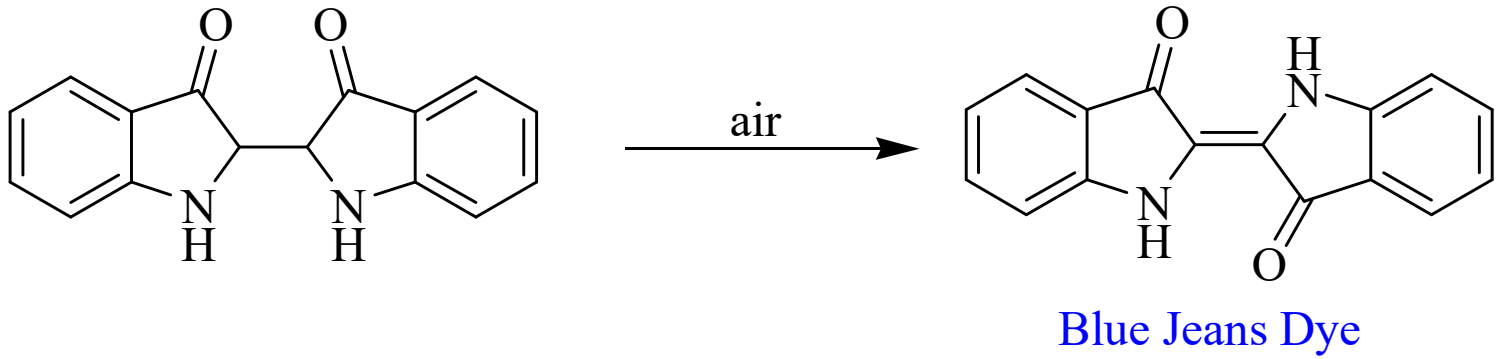


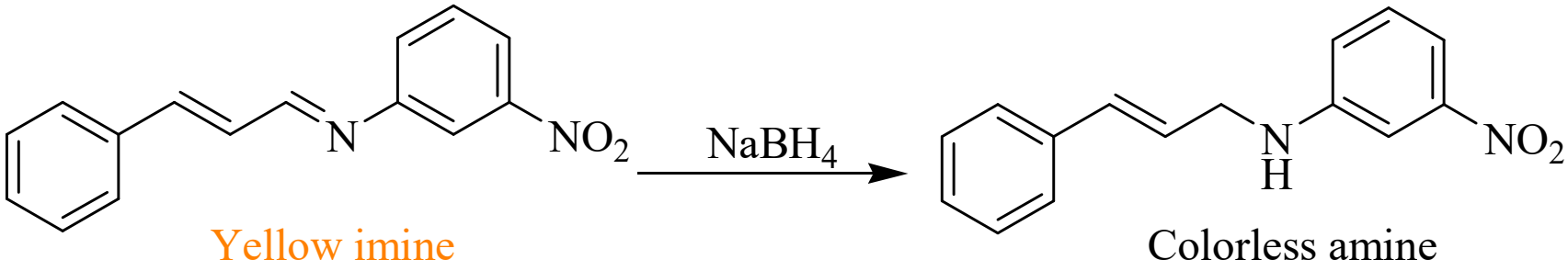
Food Dye (Blue)



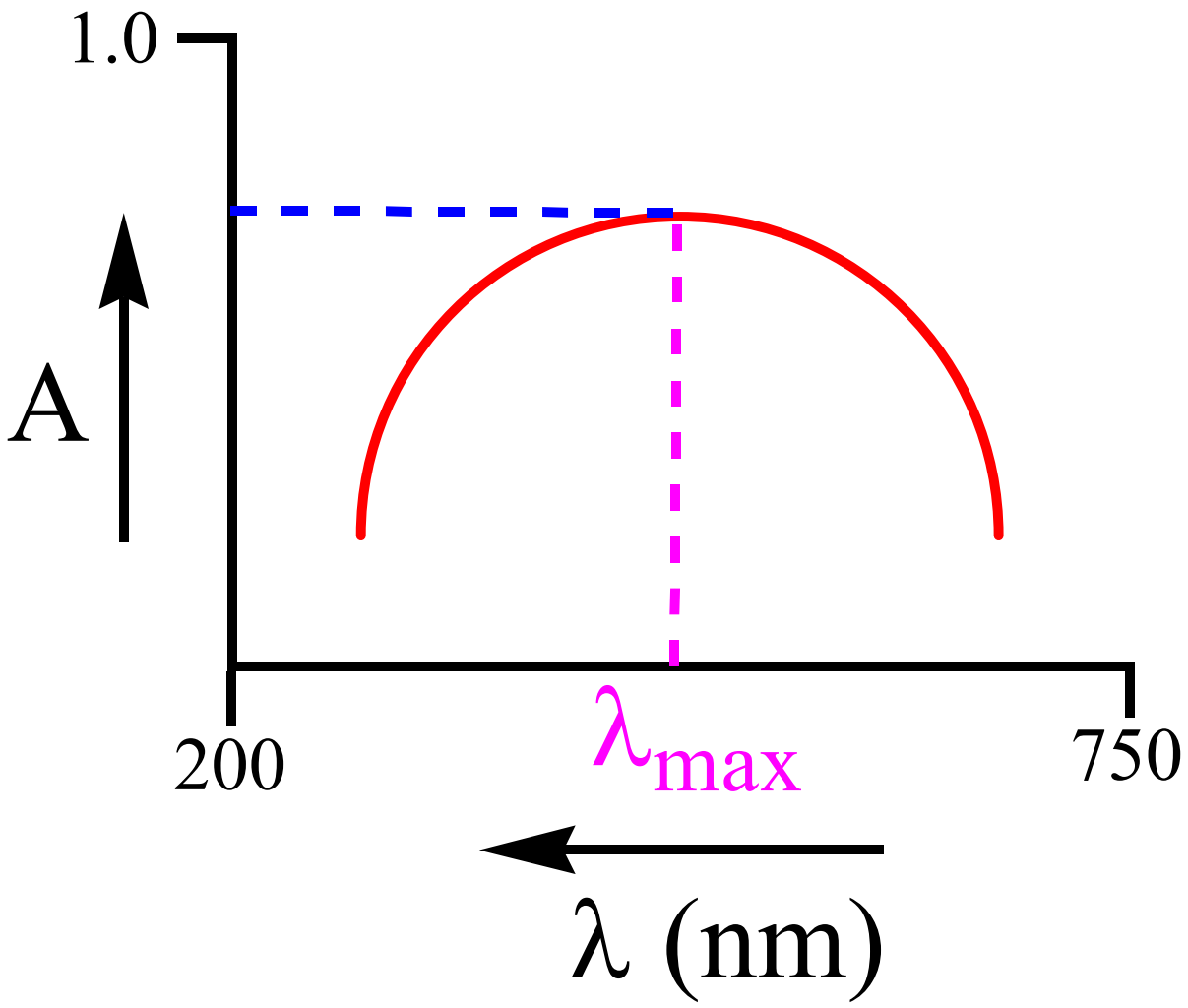
Lycopene

Chromophores

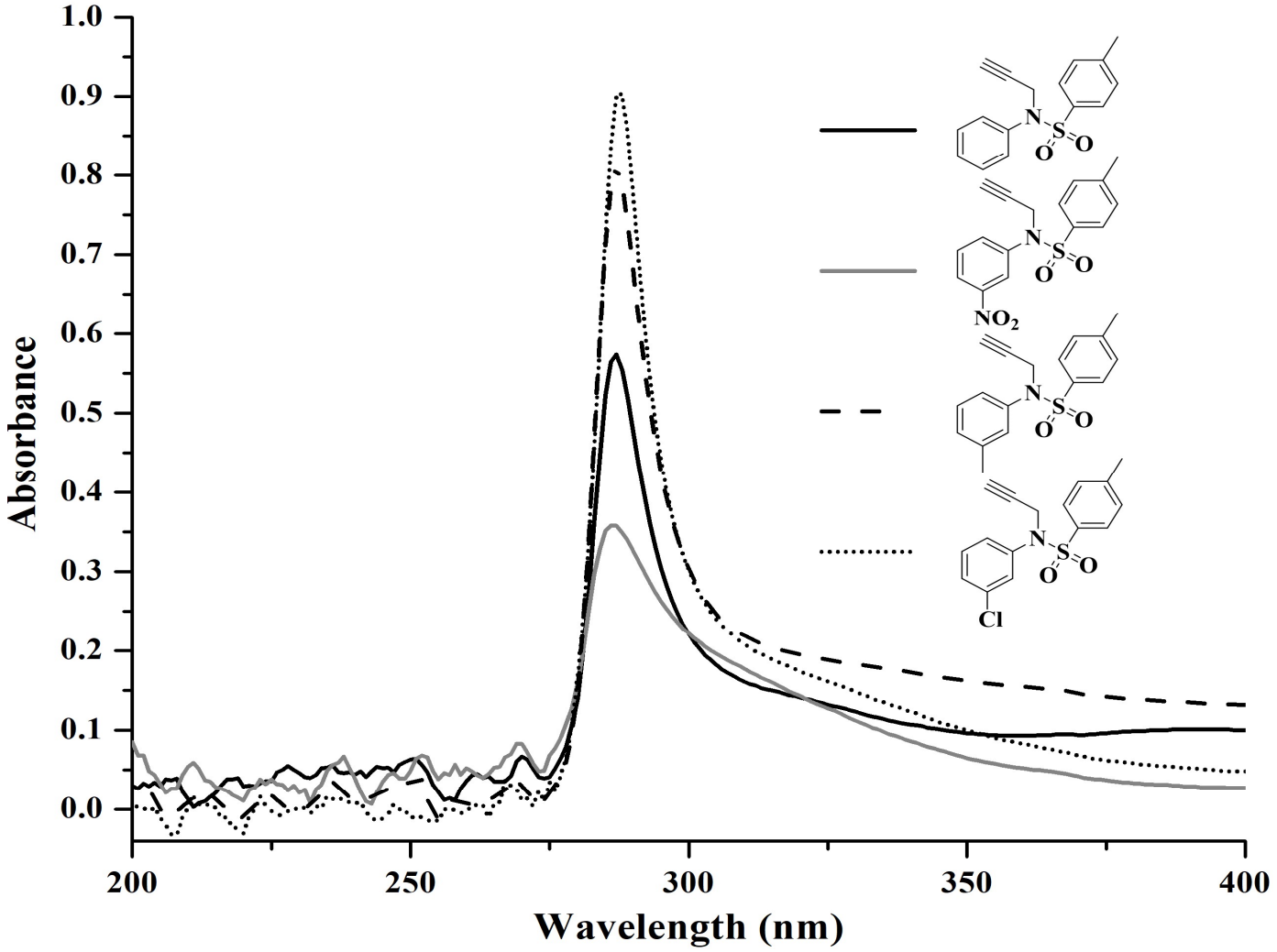




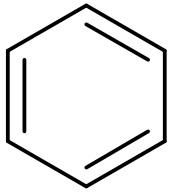
λ_{max}



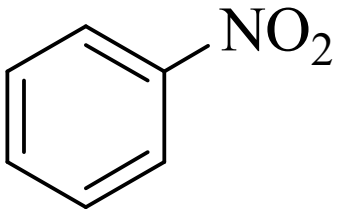
UV Spectra


Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
200
250
300
350
400
Wavelength (nm)
NO2
Cl

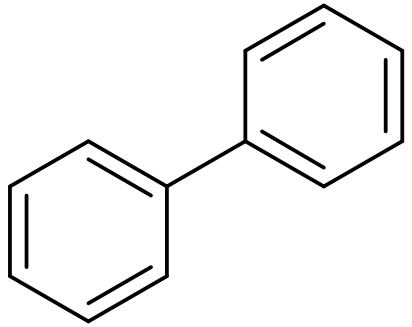
Importance of λ_{max}



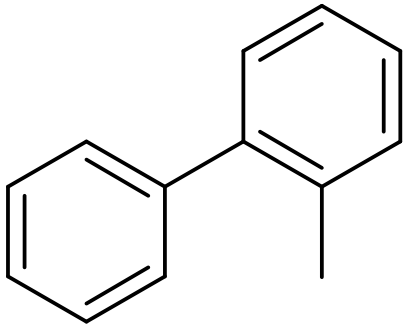
1 λ_{max} = 203 nm



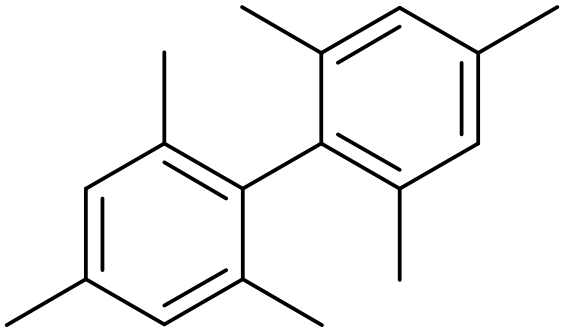
2 λ_{max} = 268 nm



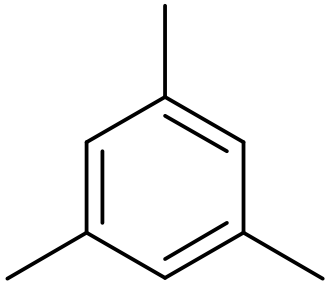
3 λ_{max} = 250 nm



4 λ_{max} = 237 nm

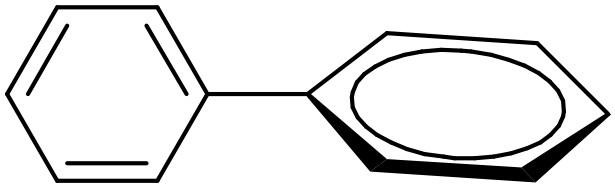


5 λ_{max} = 266 nm

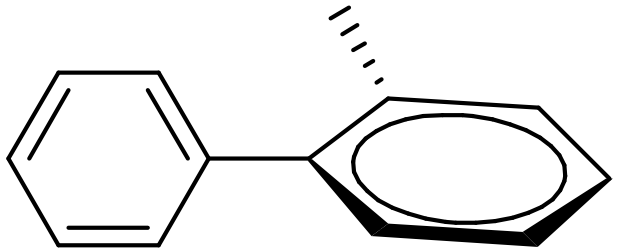


6 λ_{max} = 266 nm

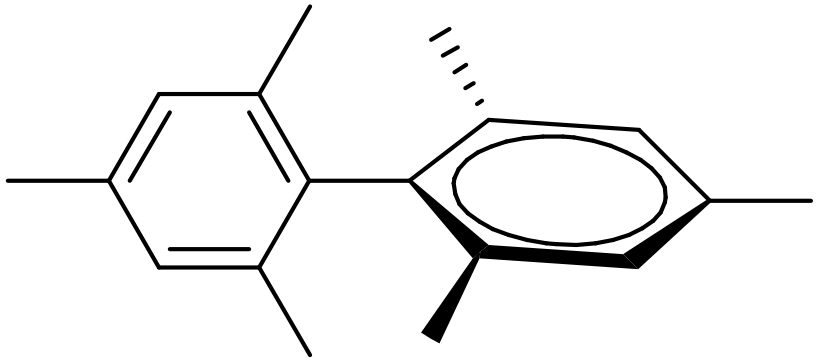
Importance of λ_{max}



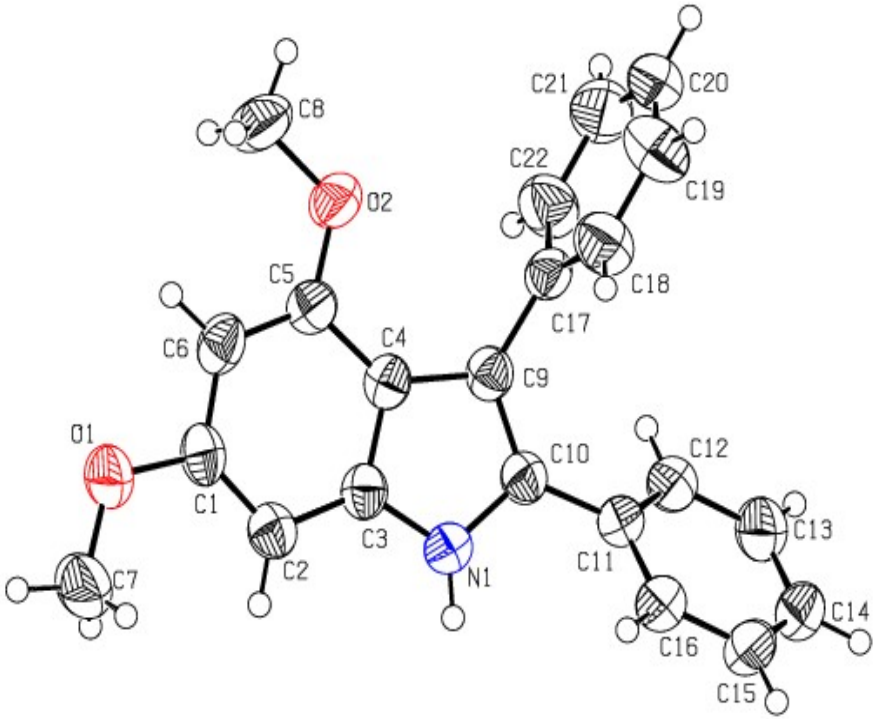
3 λ_{max} = 250 nm

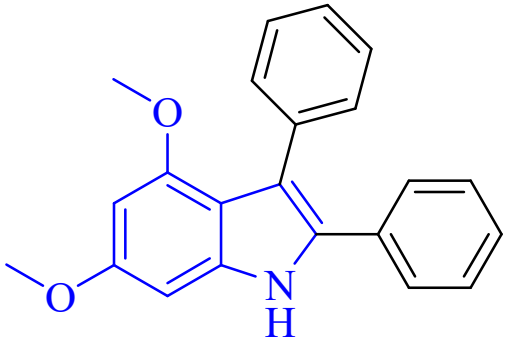


4 λ_{max} = 237 nm

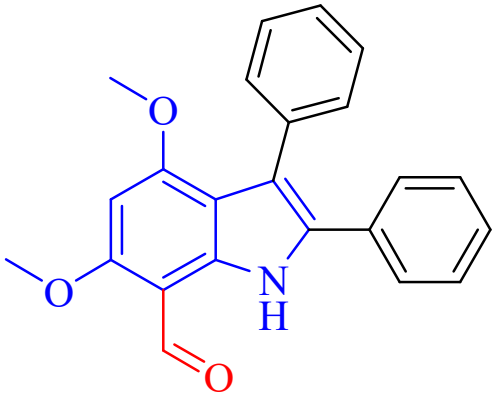


5 λ_{max} = 266 nm

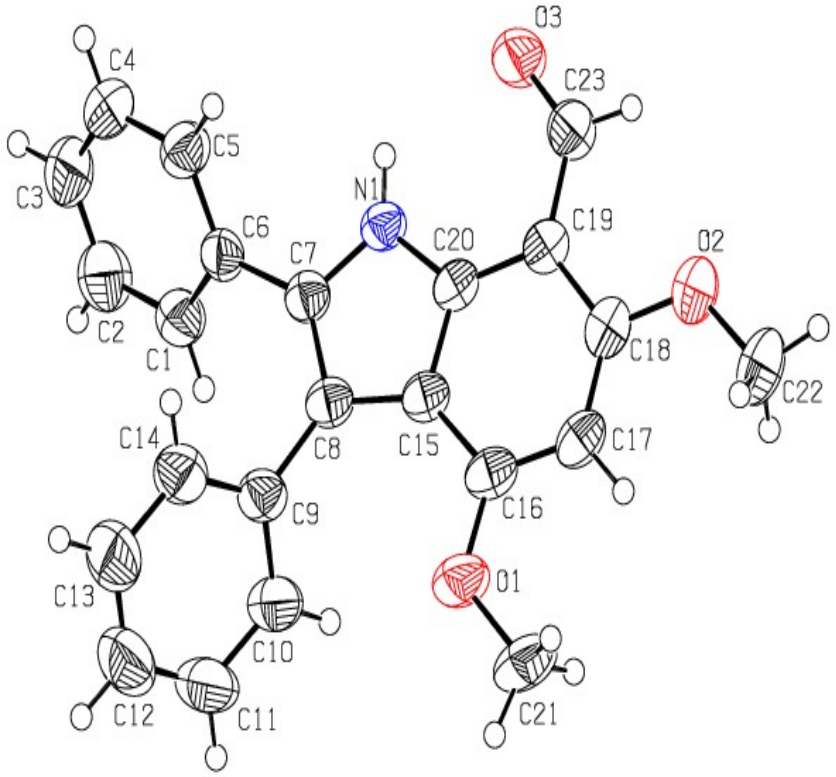


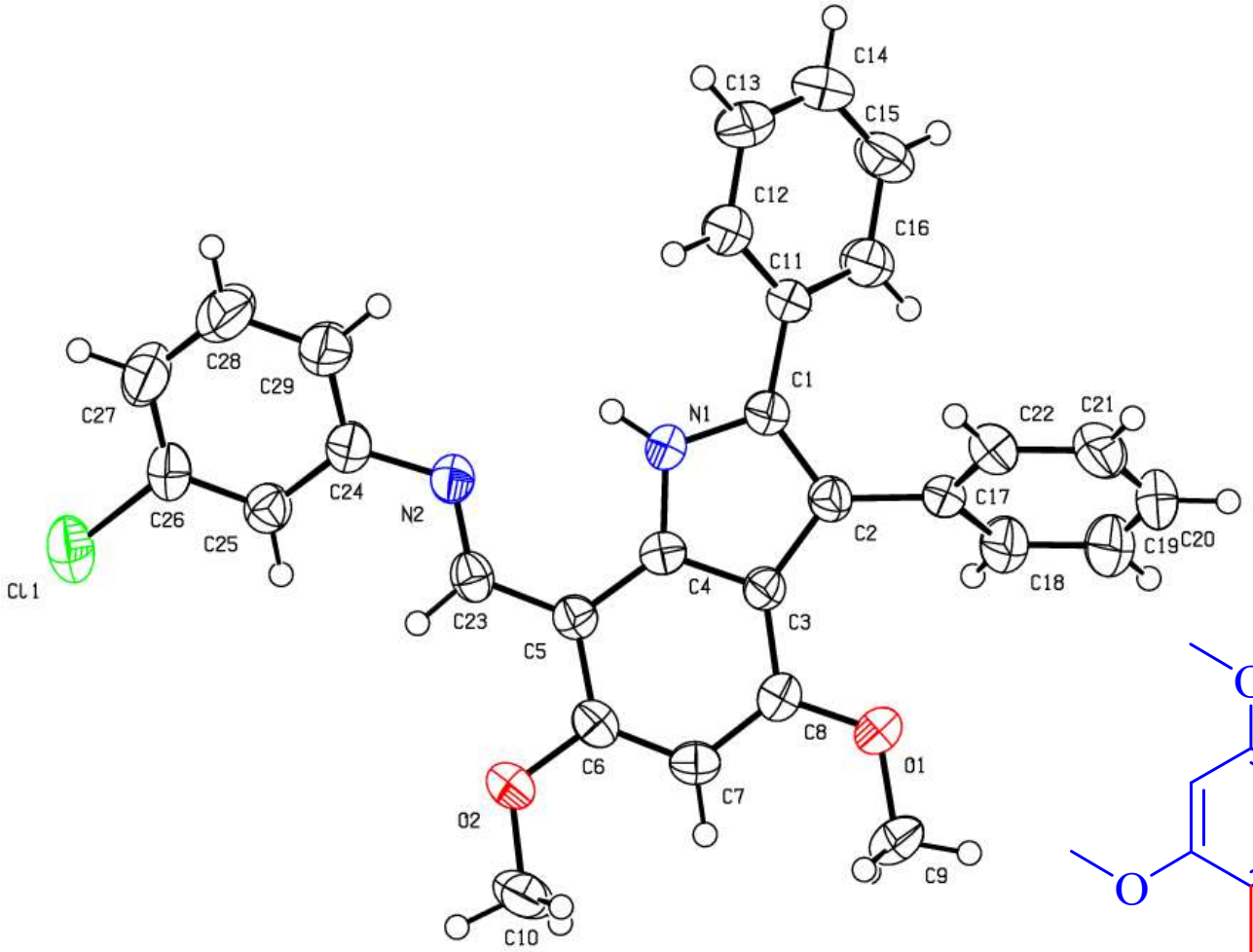


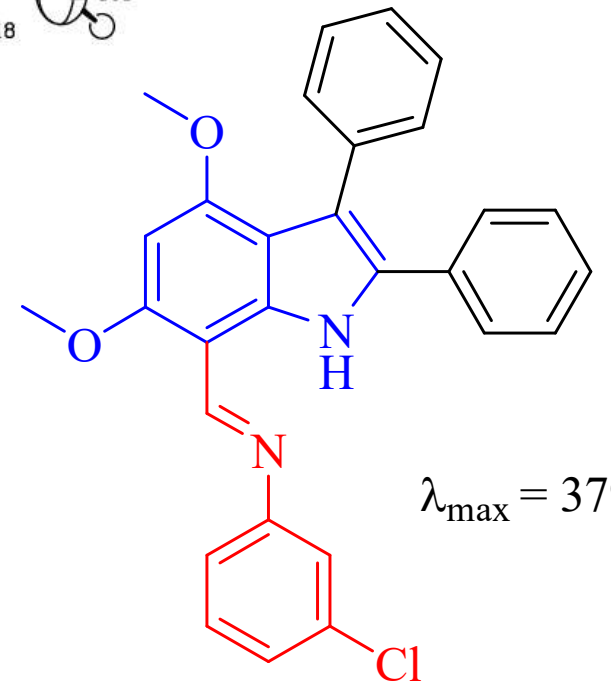
λ_{max} = 324 nm



λ_{max} = 372 nm

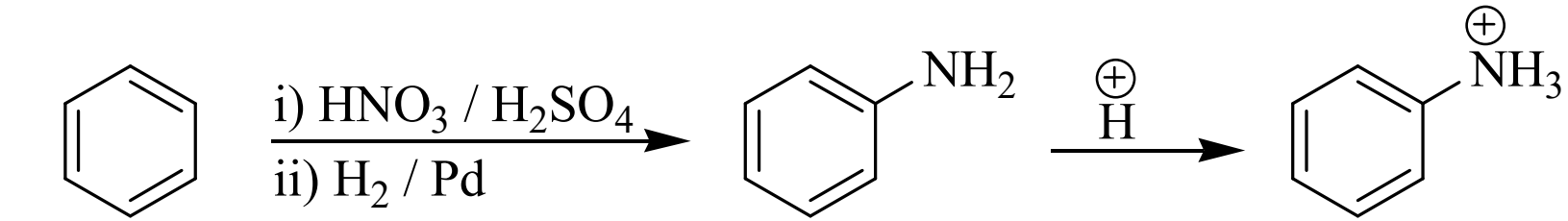






λ_{max} = 379 nm

Red / Blue Shifts



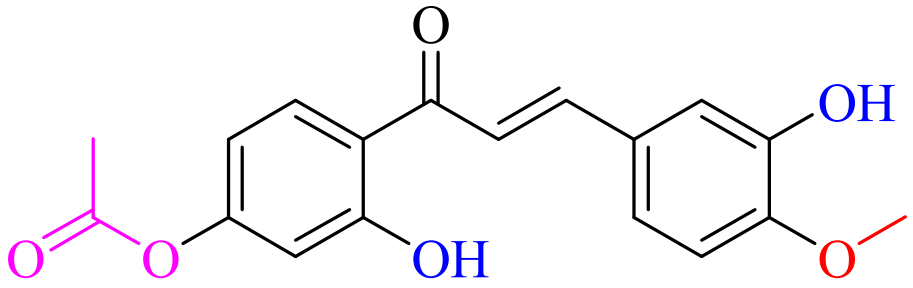
λ_{max} = 203 nm

λ_{max} = 230 nm

λ_{max} = 221 nm

Red / Bathochromic Shift

Blue / Hypsochromic Shift



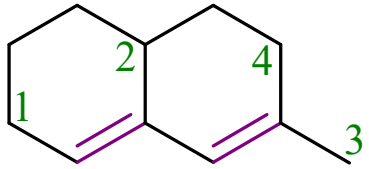
OH, OMe, OAc etc

Auxochromes

Absorbed *vs* Transmitted Colour

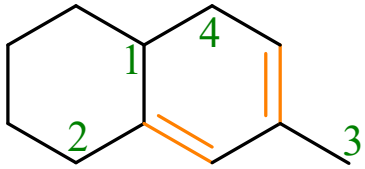
Colour (Absorbed)	Colour (Transmitted)	λ (nm)
UV	-	200-350
Violet	Yellow-Green	350-425
Indigo-Blue	Yellow	425-450
Blue	Orange	450-490
Blue-Green	Red	490-510
Green	Purple	510-530
Yellow-Green	Violet	530-550
Yellow	Indigo-Blue	550-590
Orange	Blue	590-640
Red	Blue-Green	640-720
Purple	Green	720-750

Calculating λ_{max} (Woodward-Fieser's Rule)



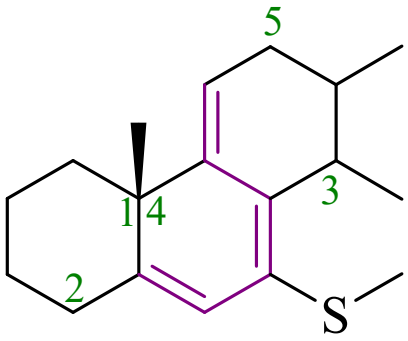
Heteroannular diene (**A**) = 214 nm
Double bond extension (**C**) = +30 nm
Exocyclic double bond (**D**) = +5 nm

λ_{max} (nm) = **A**/**B** + **C** + **D** + Substituents

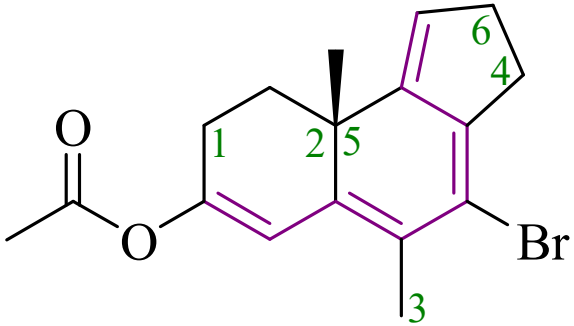


Homoannular diene (**B**) = 253 nm
Double bond extension (**C**) = +30 nm
Exocyclic double bond (**D**) = +5 nm
Substituents
Sec. aminic group = +60 nm
Alkylthio (-SR) group = +30 nm
Alkoxy (-OR) group = +6 nm
Halo / alkyl (-R) group = +5 nm
Acetato (-OCOR) group = 0 nm

Calculating λ_{max}

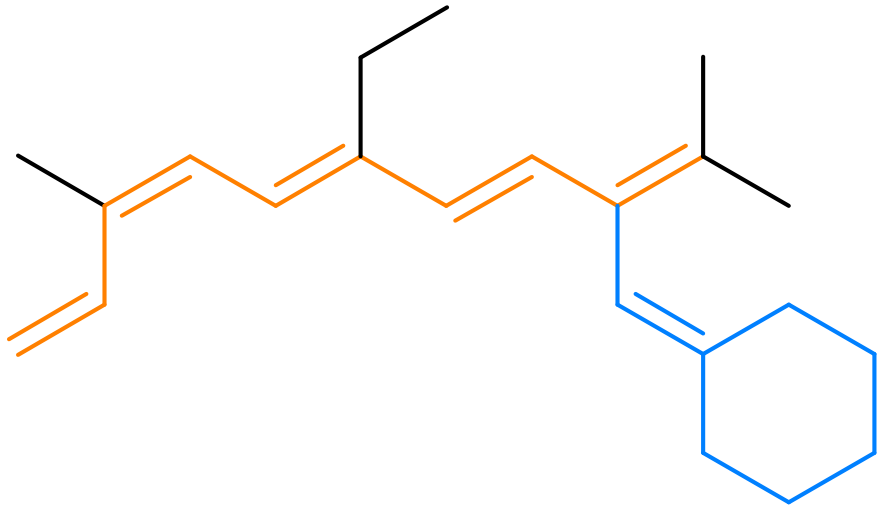


λ_{max} (nm) = **A**/**B**+**C**+**D**+Substituents
λ_{max} (nm) = 253+30+3(5)+[30+5x5)
λ_{max} (nm) = 353 nm
if -SR group is replaced by -NR_2 group
λ_{max} (nm) = 383 nm



λ_{max} (nm) = **A**/**B**+**C**+**D**+Substituents
λ_{max} (nm) = 253+60+3(5)+[0+5+(6x5)]
λ_{max} (nm) = 363 nm

Calculating λ_{max}



λ_{max} (nm) = 114 + 5*S* + *n* (48 - 1.7*n*) - 16.5 R_{endo} - 10 R_{exo}

λ_{max} (nm) = 114 + 5 (4) + 5 [48 - (1.7x5)] - 16.5 (0) - 10 (1)

λ_{max} (nm) = 114 + 20 + 197.5 - 0 - 10

λ_{max} (nm) = 321.5 nm

Calculating λ_{max}

β-carotene

λ_{max} (nm) = 114 + 5*S* + *n* (48 - 1.7*n*) - 16.5 R_{endo} - 10 R_{exo}

λ_{max} (nm) = 114 + 5 (10) + 11 [48 - (1.7x11)] - 16.5 (2) - 10 (0)

λ_{max} (nm) = 114 + 50 + 322.3 - 33 - 0

λ_{max} (nm) = 453.3 nm

Calculating λ_{max}

Lycopene

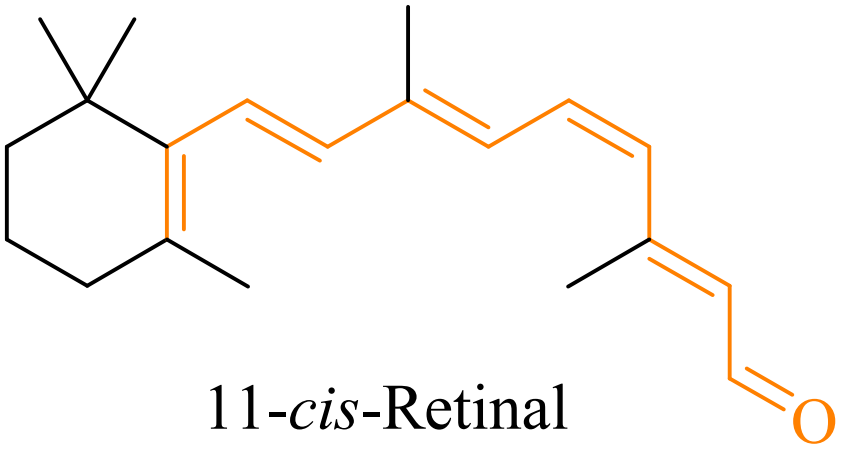
λ_{max} (nm) = 114 + 5*S* + *n* (48 - 1.7*n*) - 16.5 R_{endo} - 10 R_{exo}

λ_{max} (nm) = 114 + 5 (8) + 11 [48 - (1.7x11)] - 16.5 (0) - 10 (0)

λ_{max} (nm) = 114 + 40 + 322.3 - 0 - 0

λ_{max} (nm) = 476.3 nm

Calculating λ_{max}



11-*cis*-Retinal

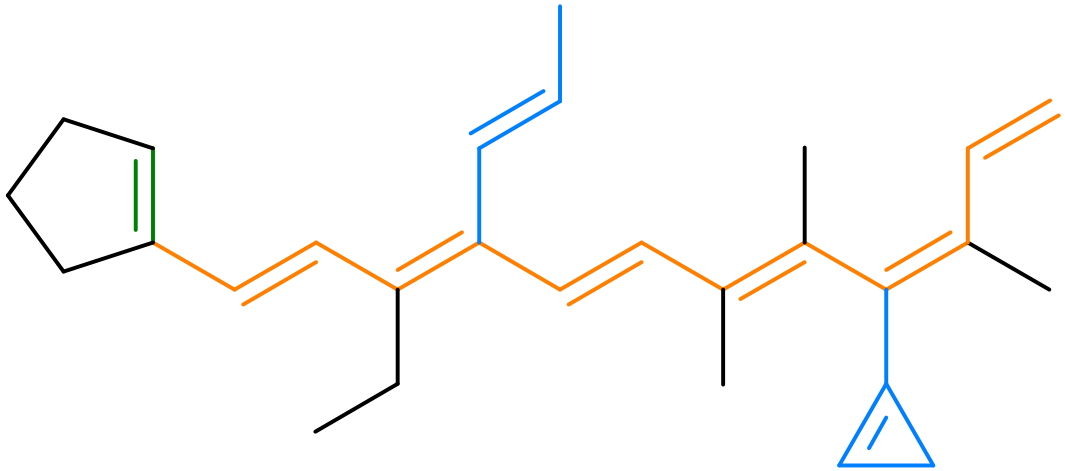
λ_{max} (nm) = 114 + 5*S* + *n* (48 - 1.7*n*) - 16.5 R_{endo} - 10 R_{exo}

λ_{max} (nm) = 114 + 5 (5) + 6 [48 - (1.7x6)] - 16.5 (1) - 10 (0)

λ_{max} (nm) = 114 + 25 + 210.3 - 16.5 - 0

λ_{max} (nm) = 349.3 nm

Calculating λ_{max}



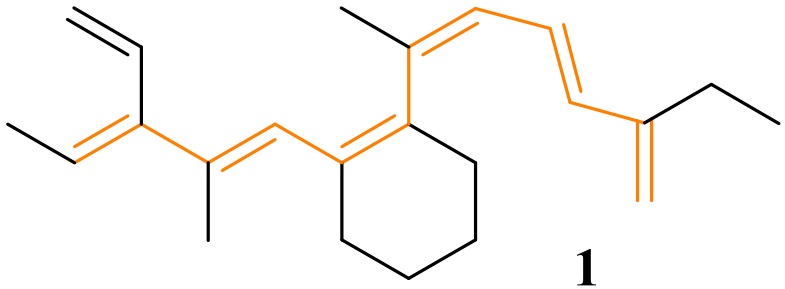
λ_{max} (nm) = 114 + 5*S* + *n* (48 - 1.7*n*) - 16.5 R_{endo} - 10 R_{exo}

λ_{max} (nm) = 114 + 5 (6) + 7 [48 - (1.7x7)] - 16.5 (1) - 10 (2)

λ_{max} (nm) = 114 + 30 + 252.7 - 16.5 - 20

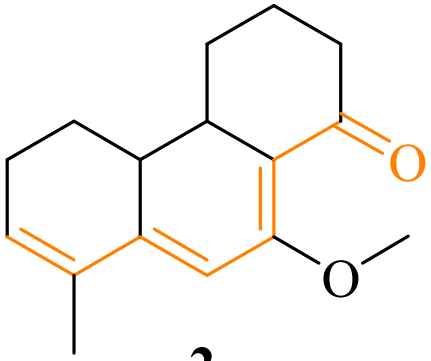
λ_{max} (nm) = 360.2 nm

Calculating λ_{max}



1

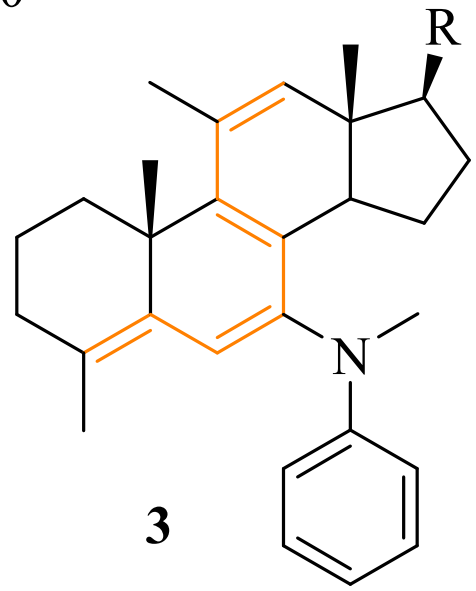
λ_{max} = 114 + 5 (6) + 6 (48 - 1.7x6) - 16.5 - 10
114 + 30 + 226.8 - 16.5 - 10
344.3 nm



2

λ_{max} = 443 nm

215	Base Value
39	Homoannular
60	2 (C=C) extension
10	Exocyclic C=C
25	Alkyl substituents
10	α-Alkyl group
30	β-OMe group
18	δ-Alkyl group
36	ω-Alkyl group

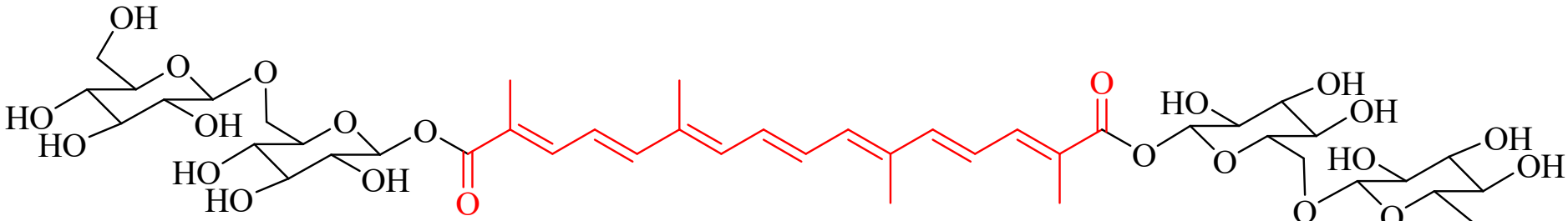


3

253	
60	
35	
60	
5	

λ_{max} = 413 nm

Crocus sativus (Saffron)



Crocin λ_{max} = 441 nm