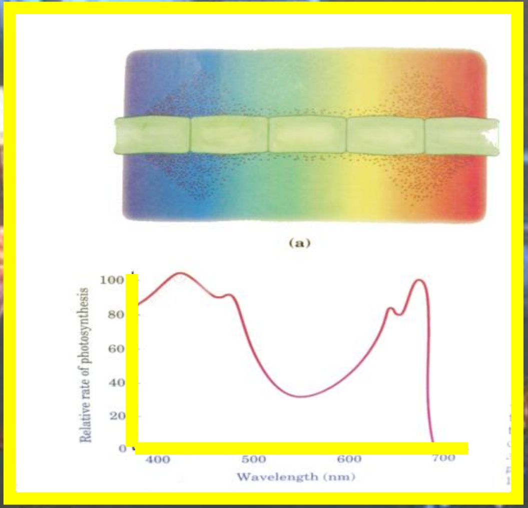


Disciplina: QFL0341

Estrutura e Propriedades de Compostos Orgânicos

01/outubro/2019

Propriedades físicas de dienos e
compostos conjugados:

Espectroscopia no UV-VIS

Literatura

Bruice (4a ed, 2006)
p. 260: deslocalização eletrônica e ressonância – teoria do OM; reações de dienos, p. 298: espectroscopia na região do UV-VIS, Diels-Alder;

McMurry (5a ed, 2000)
p. 522: Conjugated dienes and UV spectroscopy;
p. 1235: Orbitals and organic chemistry – Pericyclic reactions (vide somente cicloadições)

Solomons (8a ed, 2005)
p. 549: Sistemas insaturados conjugados (UV e Diels-Alder)

Vollhardt (6a ed, 2011)
p. 28: Orbitais moleculares e ligações covalentes;
p. 609: Sistemas p deslocalizados (exceto benzeno e reações eletrocíclicas);

Clayden (2001)
p. 95: Molecular orbitals;
p. 151: Delocalization and conjugation;
p. 905: Pericyclic reaction 1 - cycloaddition

Determination of functional groups

Chemical Properties:

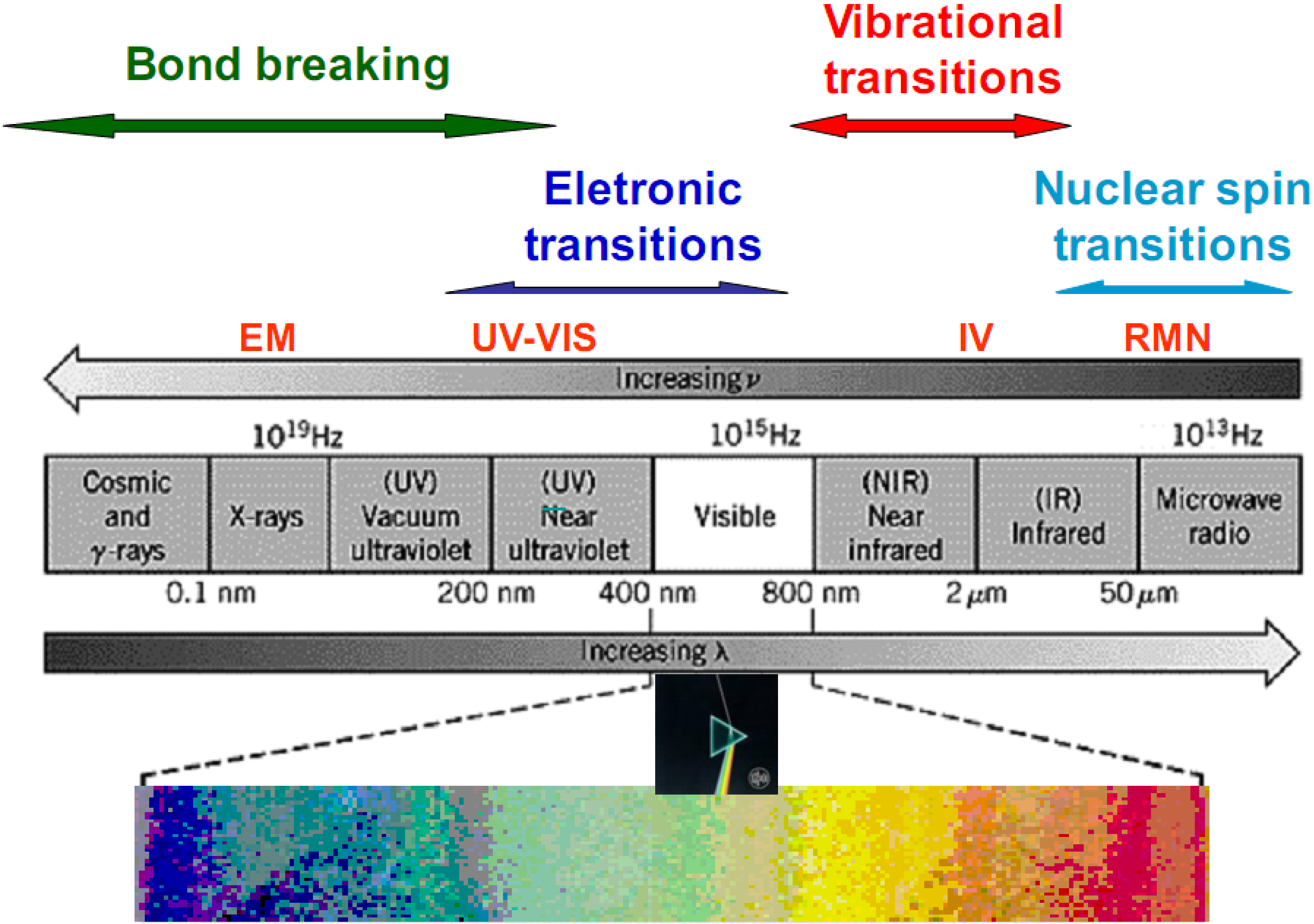
Solubility,
organic
Reactions
(colorimetric,
precipitation)

Spectrophotometric data:

Infrared
Ultraviolet

Spectroscopic data:

^{1}H and ^{13}C NMR



Bond breaking

Vibrational transitions

Eletronic transitions

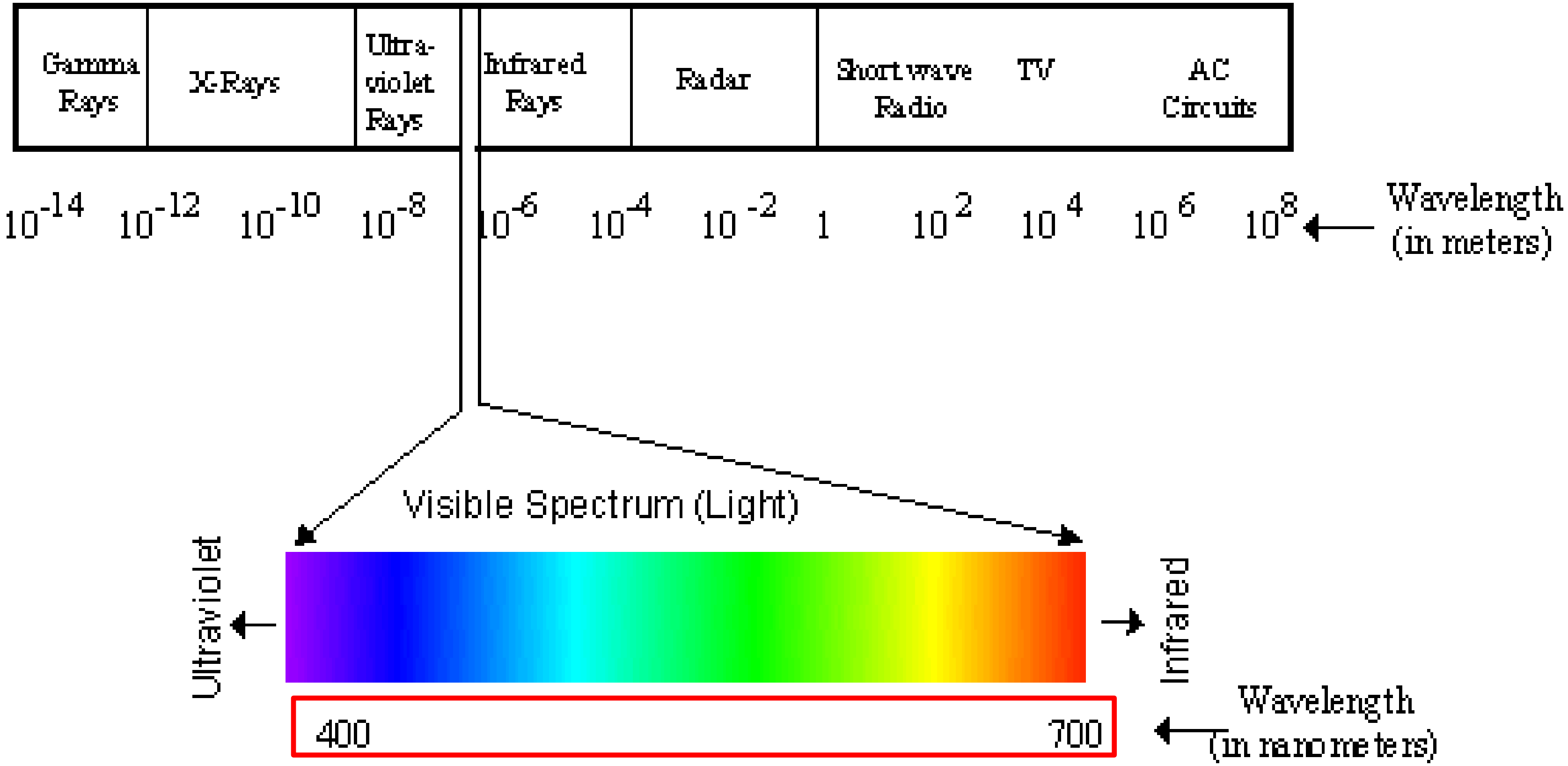
Nuclear spin transitions

EM

UV-VIS

IV

RMN



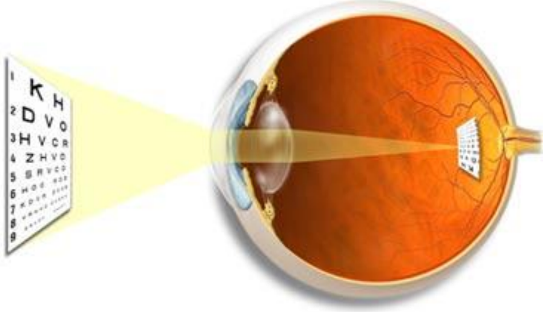
Gamma Rays | X-Rays | Ultra-violet Rays | Infrared Rays | Radar | Short wave Radio | TV | AC Circuits

10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 1 10^{2} 10^{4} 10^{6} 10^{8} ← Wavelength (in meters)

Visible Spectrum (Light)

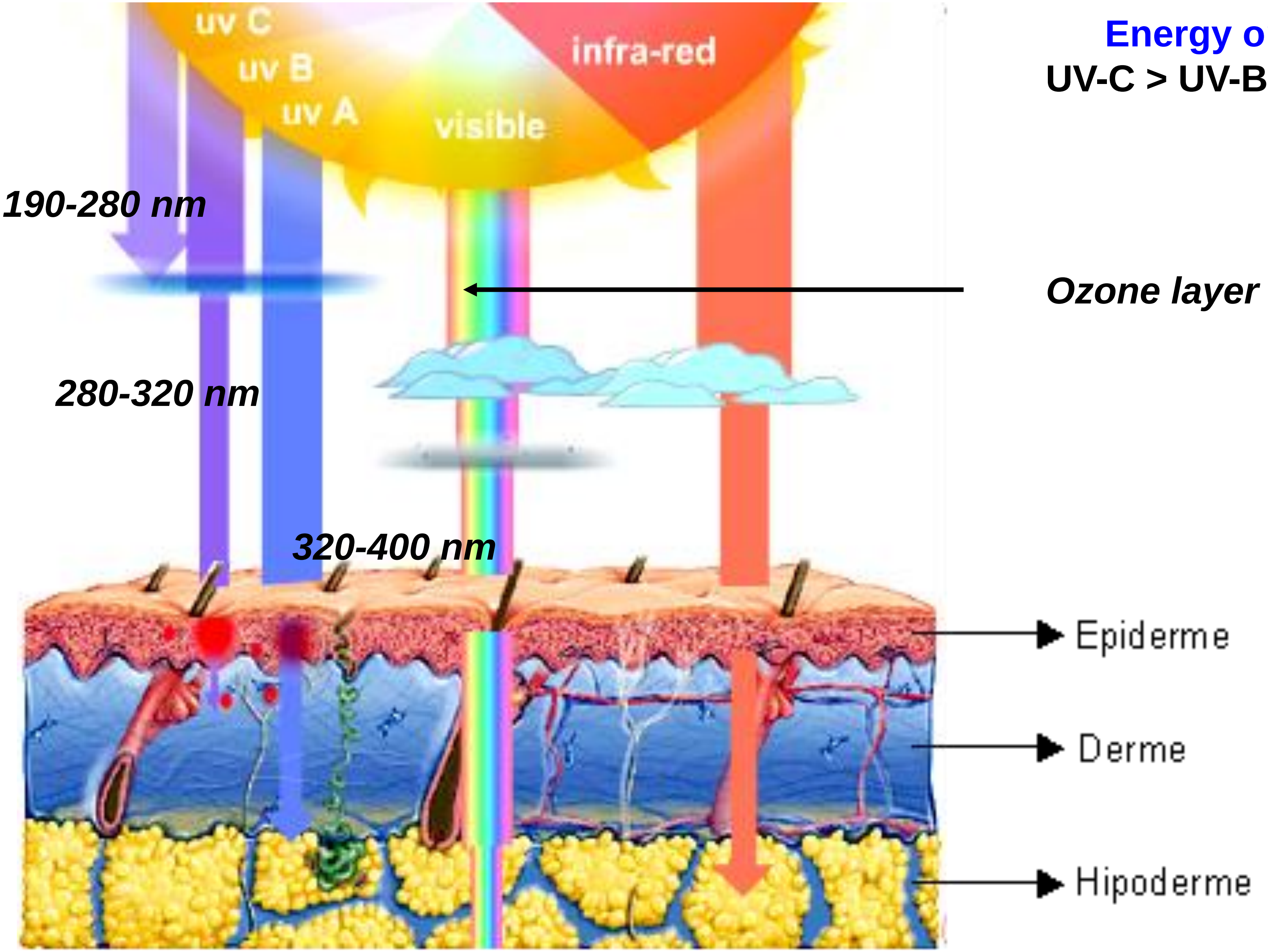
Ultraviolet ← → Infrared

400 700 ← Wavelength (in nanometers)



Energy order:

UV-C > UV-B > UV-A



190-280 nm

280-320 nm

320-400 nm

Ozone layer

Epiderme

Derme

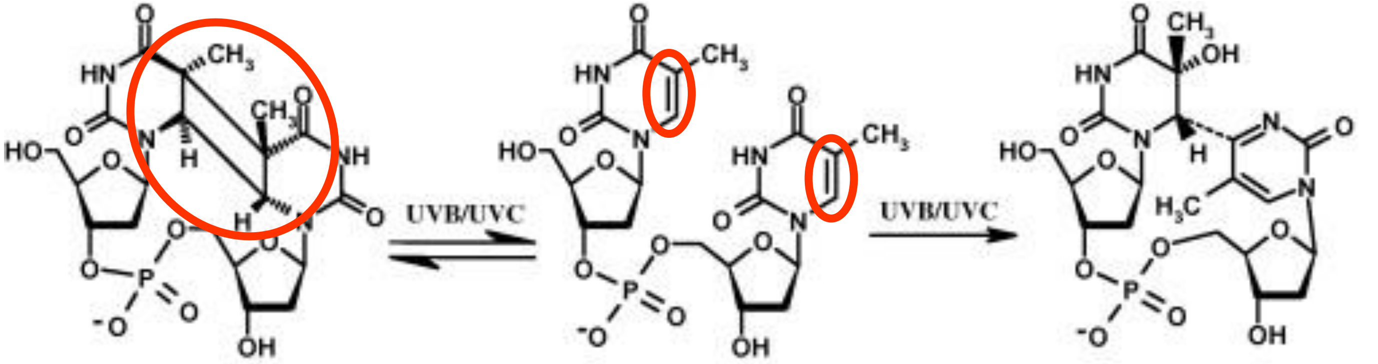
Hipoderme

UV-C: (100 a 280 nm) são potencialmente mais carcinogênicos, mas são bloqueados pela camada de ozônio (poderá agravar-se pela destruição desta).

UV-B: (280 a 320 nm) é filtrada pela camada de ozônio e não chega a camadas profundas da pele, mas possui mais energia e pode causar queimaduras e câncer.

UV-A: (320 a 400 nm) penetra até a derme e não é filtrada pela camada de ozônio, é um dos principais causadores do envelhecimento precoce e câncer de pele.

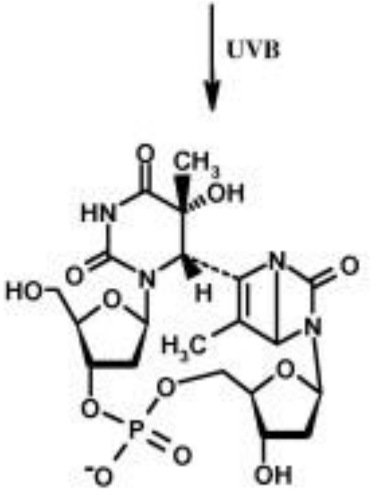
UV-radiation induced thymine dimeric photoproducts (causing ultimately mutations)



cyclobutane thymine dimer (2)

dithymine (1)

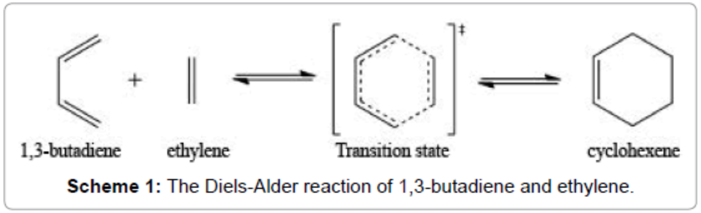
thymine (6-4) thyminone adduct (3)



Dewar valence isomer (4)

Pericyclic reactions (cyclic transition state):

[2+2]

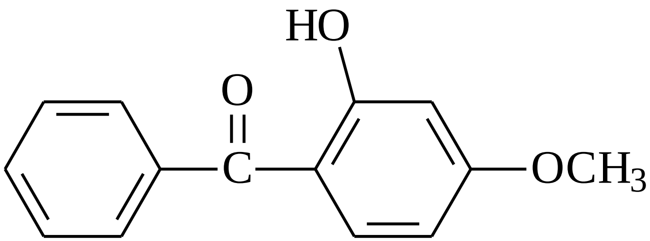


Scheme 1: The Diels-Alder reaction of 1,3-butadiene and ethylene.

[4+2]

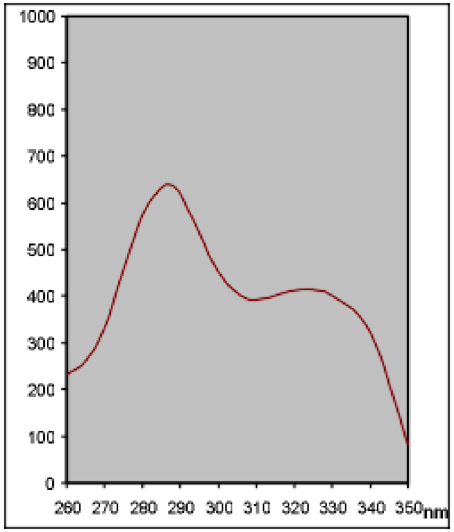
Estruturas de fotoprotetores comerciais

2-hidróxi-4-metóxibenzofenona



Nome comercial: Benzofenona 3

CAS: 131-57-7

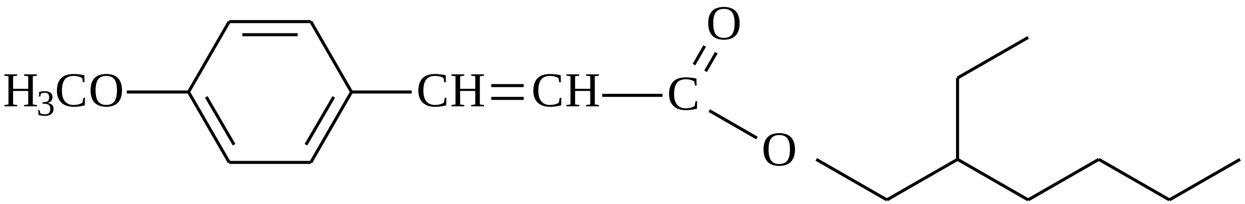


Características:
Pureza: maior de 98%
Ponto de fusão: 62,5 ºC
Absorbância máx.: 290 e 324nm

É um pó cristalino, praticamente inodoro e lipossolúvel. Apresenta boa absorção de radiação UV-A e UV-B.

Estruturas de fotoprotetores comerciais

p-metóxicinamato de octila



CAS: 5466-77-3

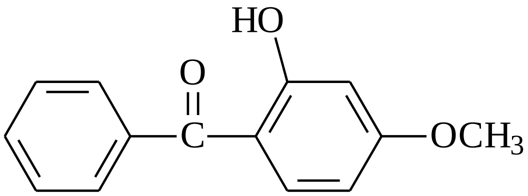
Nome comercial: Metóxicinamato de etil-hexila

Características:
Pureza: maior de 98%
Ponto de ebulição: 100 ºC
Ponto de congelamento: -30 ºC
Comp. de onda máx.: 307-308 nm

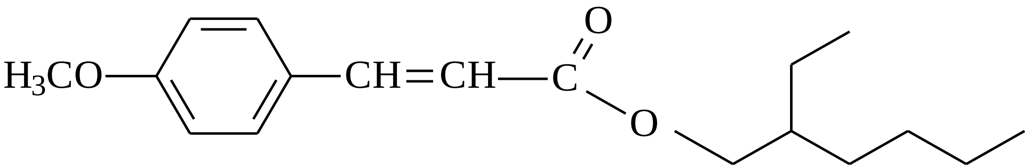
É um líquido claro, praticamente inodoro, lipossolúvel, resistente à luz e dermatologicamente testado.

Composição de um bloqueador Solar comercial FPS 30 - à prova d`água

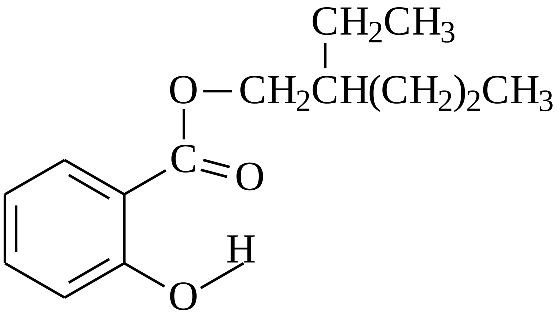
Benzofenona 3 - 4,0%



Metoxicinamato de octila - 7,5%



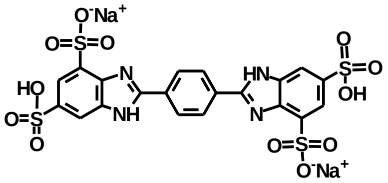
Salicilato de octila - 2,0%



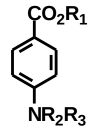
Dióxido de Titânio - 2,85%

Main constituents of commercial UV-screens and their corresponding range of protection

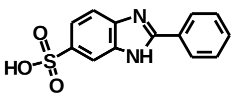
UVB (290 - 320 nm) and UVA- II (320 - 340 nm)



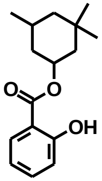
bisdisulizole disodium
(Neo Heliopan AP)



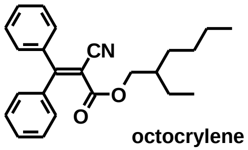
4-amino benzoic acid (R_1=R_2=R_3=H)
(290-320 nm)
padimate O (R=2-ethylhexane; R_2=R_3=Me)
(295-330 nm)



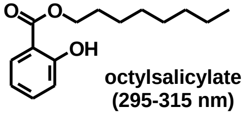
phenylbenzimidazole
sulfonic acid (Ensulizole)
(290, 340 nm)



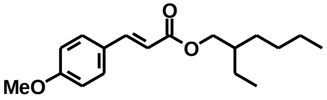
homosalate
(295-315 nm)



octocrylene
(280-310 nm)

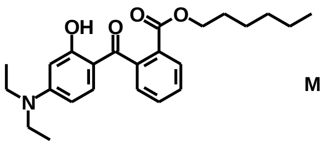


octylsalicylate
(295-315 nm)

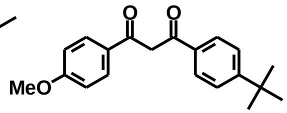


octyl methoxycinnamate (Eusolex 2291,
Tinosorbo OMC)

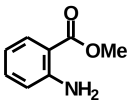
UVA- I (340 - 400 nm)



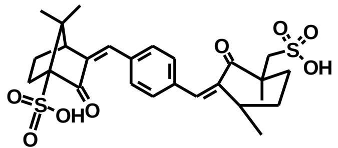
diethylamino hydroxybenzoyl hexyl
benzoate (Uvinul A Plus) (354 nm)



avobenzone (Parsol 1789)
(357 nm)



methyl anthranilate
(452 nm)

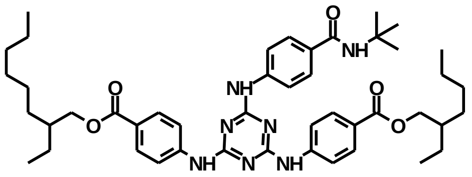


Ecamsule (Mexoryl SX)
(280, 320, 400 nm)

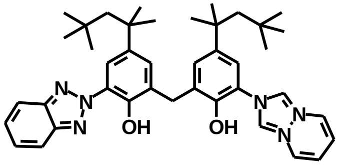
UVA + UVB

Titanium dioxide

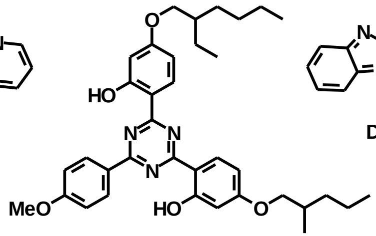
Zinc oxide



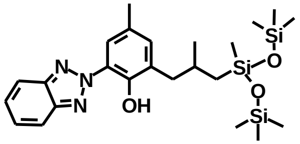
Iscotrizinol (Uvasorb HEB)



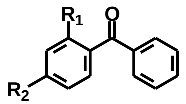
bisoctrizole (Tinosorb M)
(UVA and UVB)



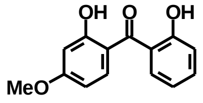
bemotrizinol (Tinosorb S, Escalol S)
(310, 340 nm)



Drometrizole trisiloxane
(303 and 344 nm)



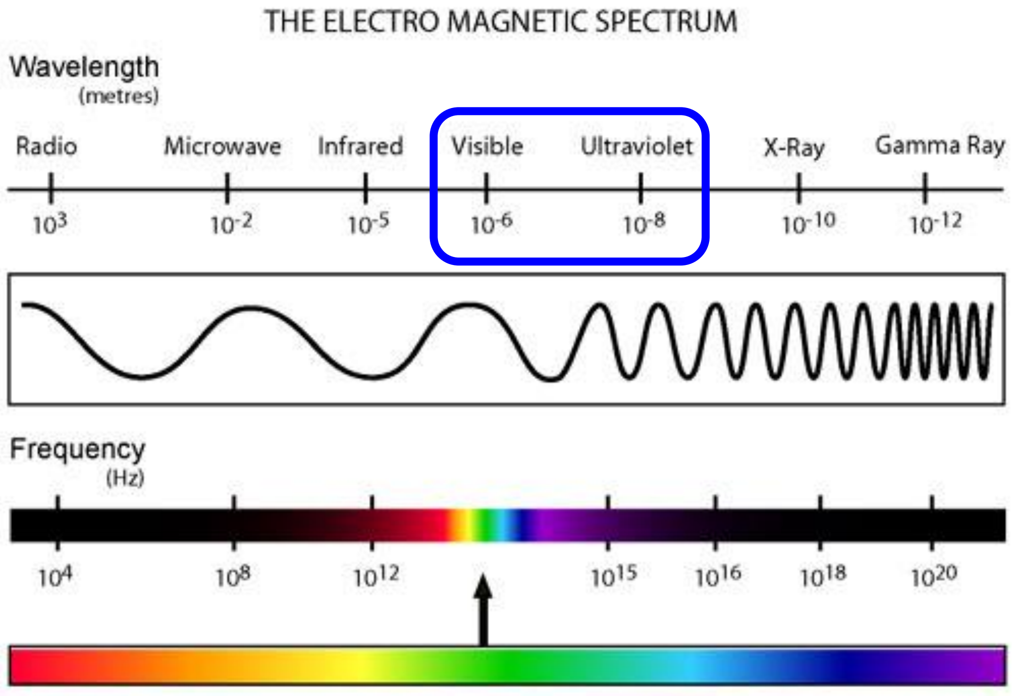
benzophenones 1-12
(202, 250, 345 nm)



dioxybenzone
(benzophenone-8)

Spectrophotometry

- a quantitative method of studying matter
- studies amount of light transmitted/absorbed by matter



Spectrophotometer

- measures absorbance or transmittance of light, as a function of wavelength

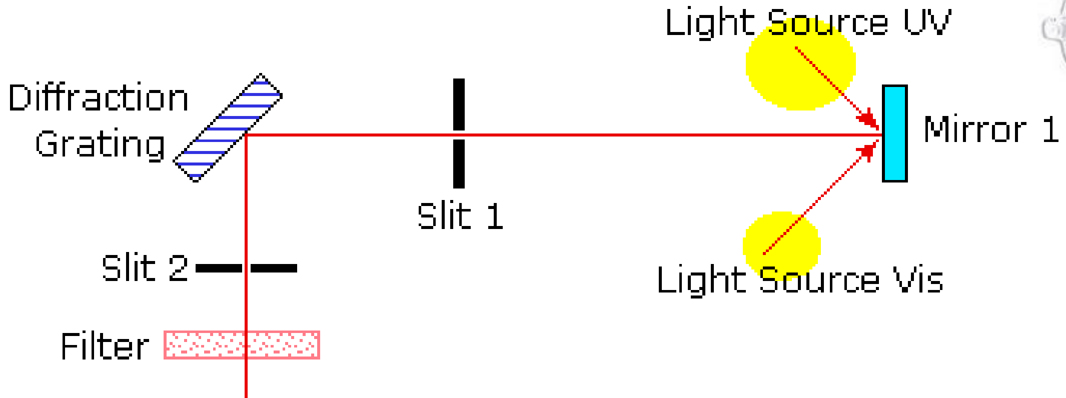
General procedure:

- sample is placed into cuvette
- light of selected wavelength (λ_{max}) is passed through sample
- instrument measures the amount of light absorbed by the sample

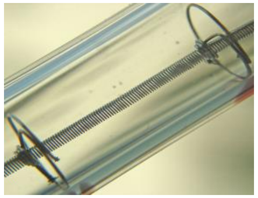
a cuvette

spectrophotometer

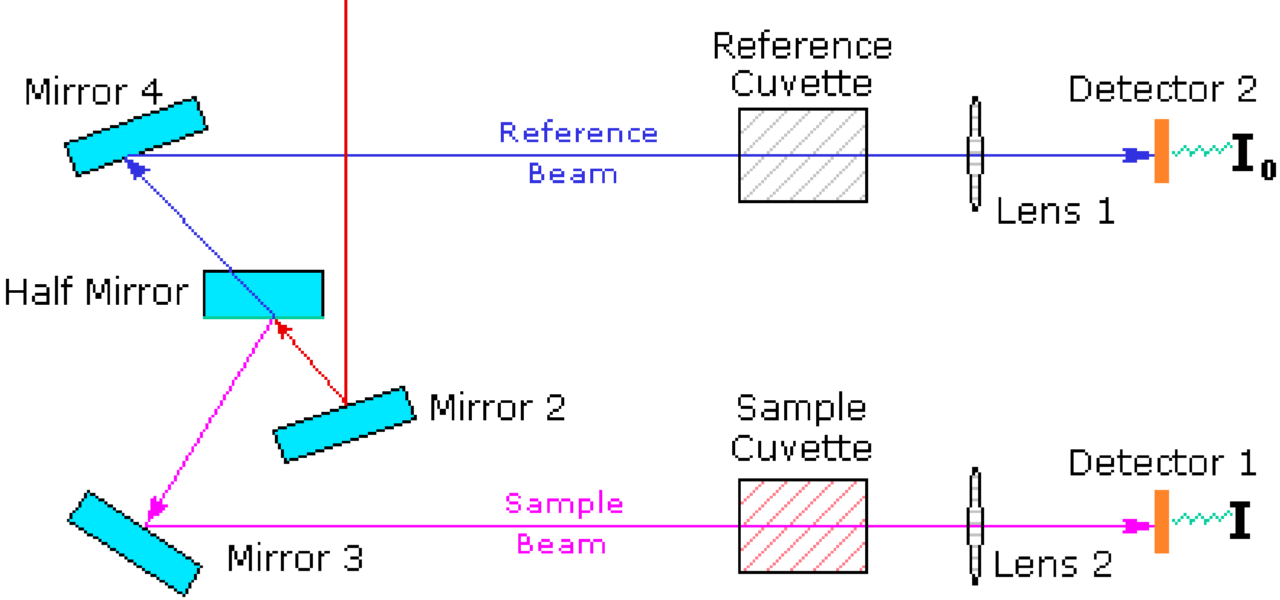
UV-VIS light absorption instrumentation (spectrophotometer)

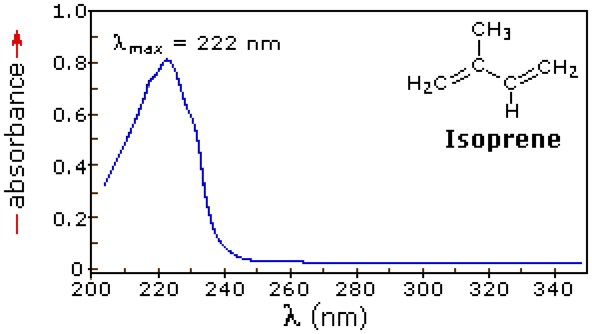


Deuterium lamp

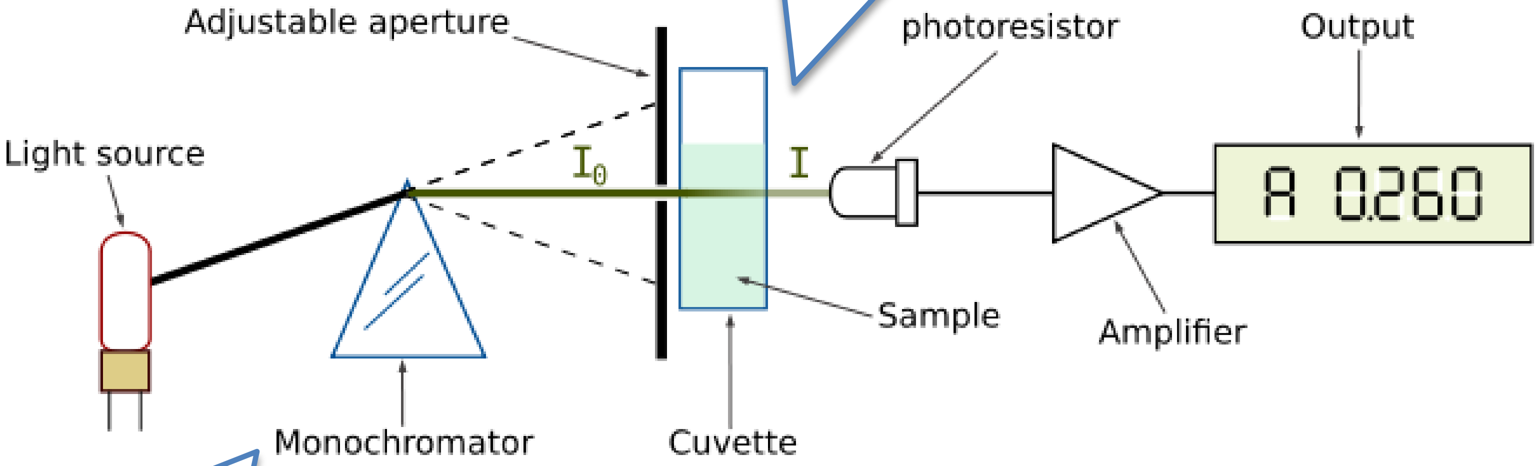


W lamp





- **I_o** = Original intensity of light
- **I** = Intensity of transmitted light



Monochromator separates and transmits a particular wavelength (colour) of light

Two ways of Reporting:

1. Transmission, **$T = I/I_o$**

   or **$\%T = I/I_o \times 100\%$**

2. Absorbance, **$A = 2\text{-}\log(\%T)$**

LEI DE LAMBERT - BEER OU LEI DE BEER

$$A = \varepsilon \times b \times c$$

A = ABSORBÂNCIA

ε = COEFICIENTE DE ABSORTIVIDADE MOLAR ($cm^{-1}\ mol^{-1}\ L$)

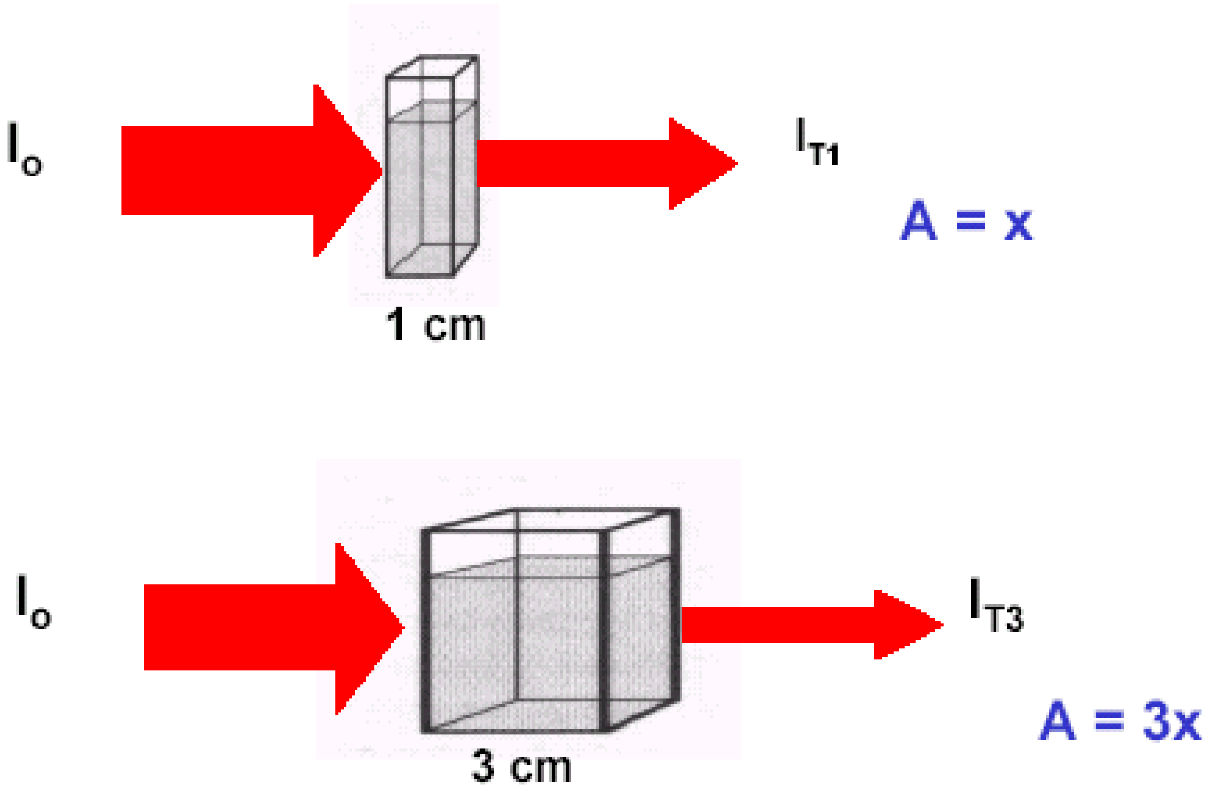
b = CAMINHO ÓTICO, cm

c = CONCENTRAÇÃO DA ESPÉCIE ABSORVENTE ($mol\ L^{-1}$)

ε - coeficiente de absortividade molar é a absorbância medida para uma concentração de 1 mol L^{-1} do analito para uma célula de 1 cm de largura (1 cm de caminho ótico).

Influência da largura do caminho ótico (b)

$$A = \varepsilon \times b \times c$$



I_o

I_{T1}

A = x

1 cm

feixe de luz de intensidade I_o

I_o

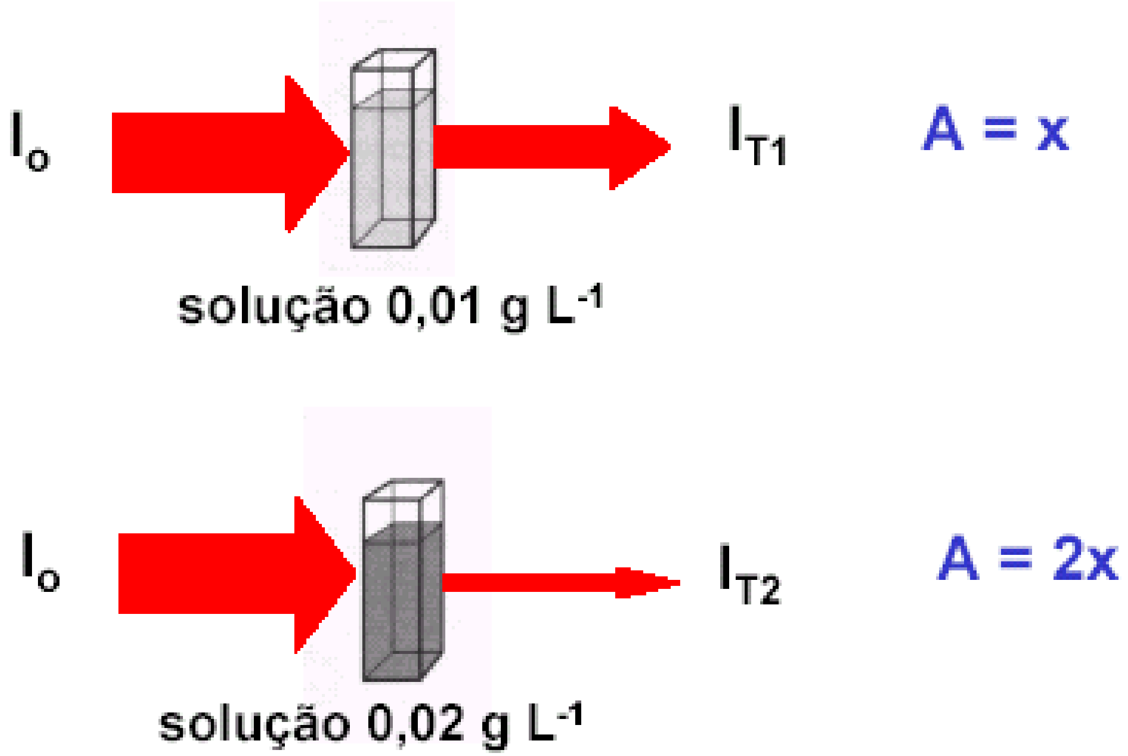
I_{T3}

A = 3x

3 cm

Influência da concentração da solução (c)

$$A = \varepsilon \times b \times c$$



I_o

I_{T1}

$A = x$

solução 0,01 g L^{-1}

feixe de luz de intensidade I_o

I_o

I_{T2}

$A = 2x$

solução 0,02 g L^{-1}

Practical application of UV spectroscopy

1. UV was the first organic spectral method, however, nowadays it is rarely used as a primary method for structure determination

2. It is most useful in combination with NMR and IR data to elucidate unique electronic features;

3. It can be used to assay (via λ_{max} and molar absorptivity) the proper irradiation wavelengths for **photochemical experiments**, the design of UV resistant paints and coatings, or simulate ageing in materials.

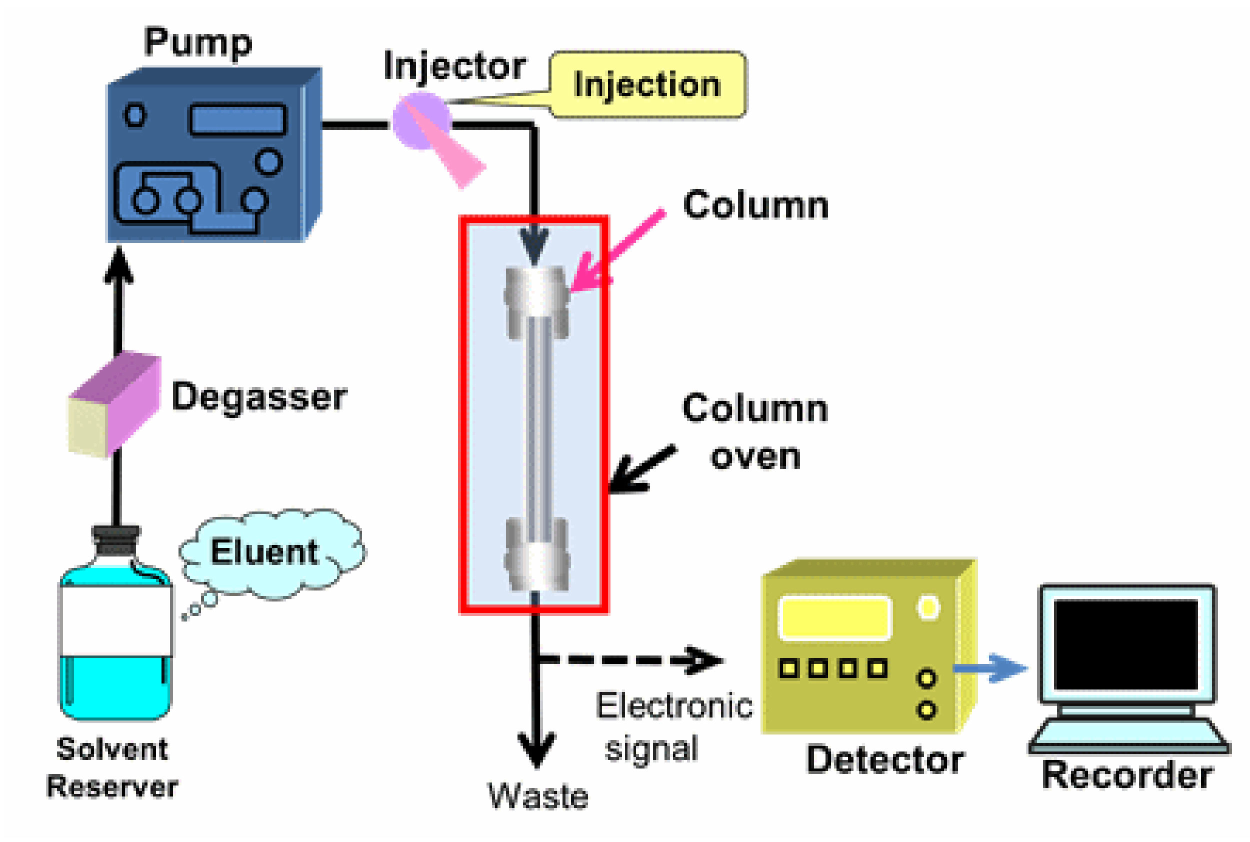
4. The most ubiquitous use of UV is as a **detection device** for HPLC; since UV is utilized for solution phase samples vs. a reference solvent this is easily incorporated into LC design

Detectors for:

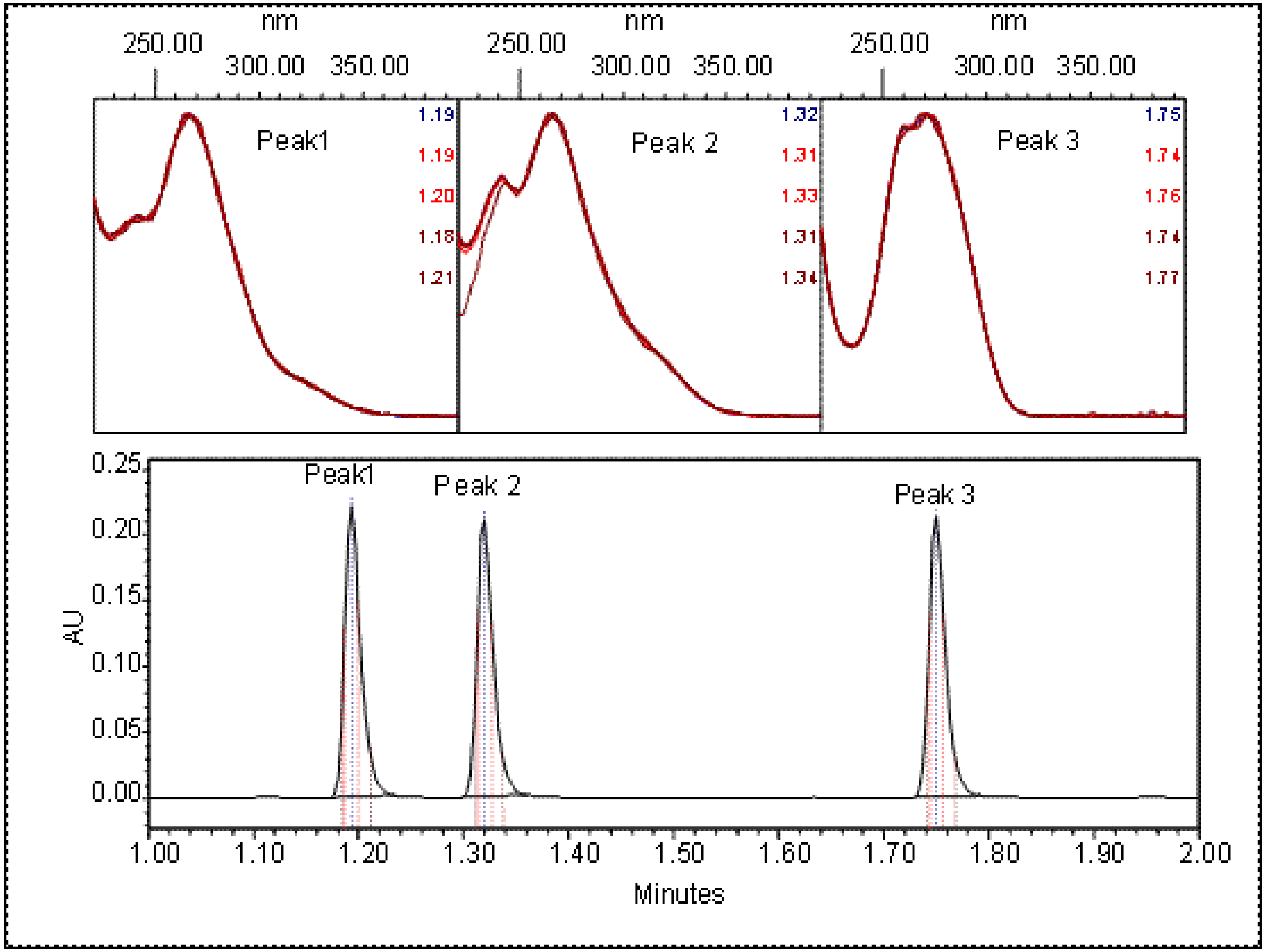
HPLC (UV-VIS, Fluorescence, refractor Index, MS, CD)

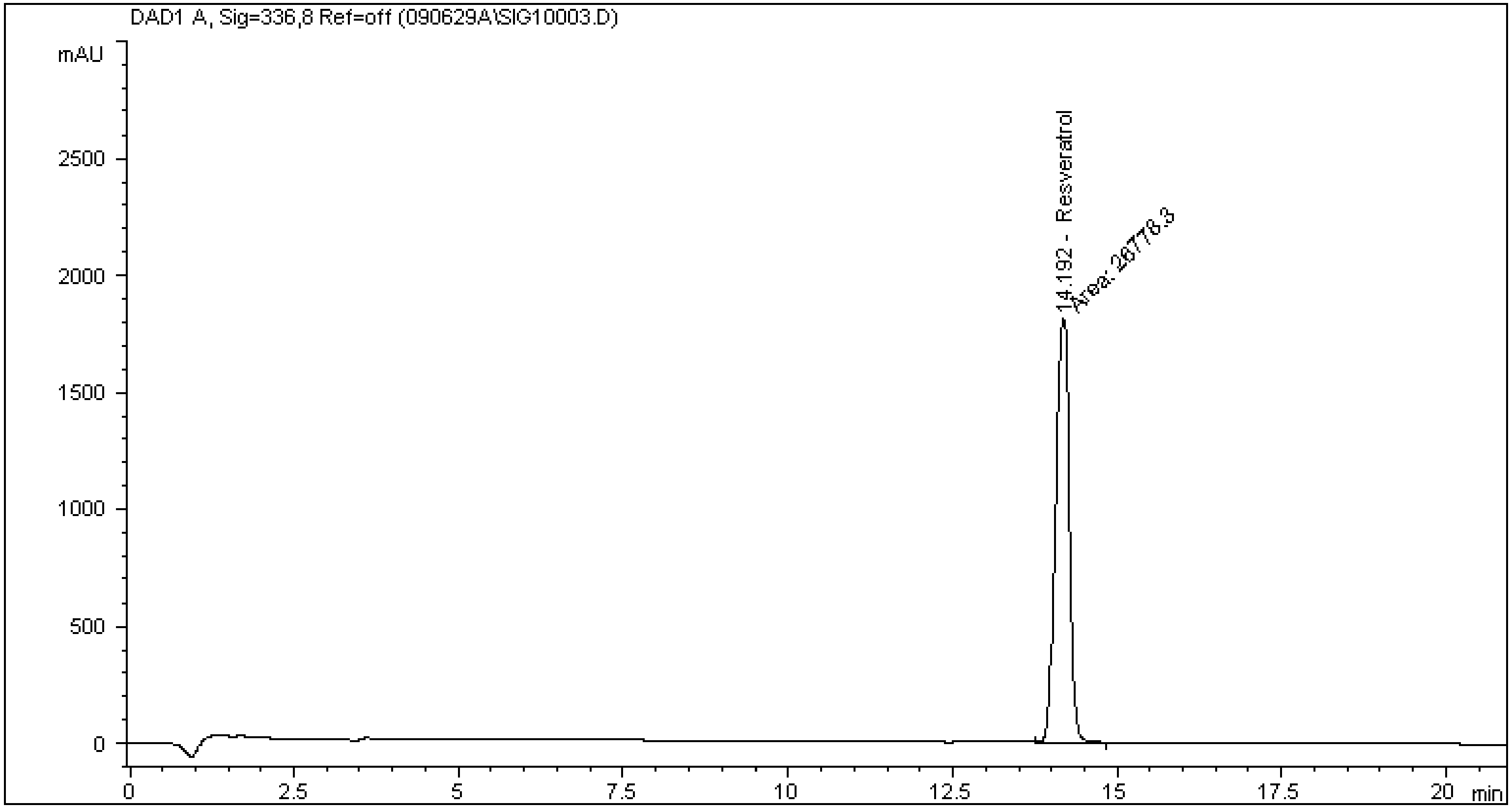
GC (FID, ECD, IV, MS, EAD)

Diagram for the components of an HPLC instrument



Chromatogram with spectrophotometric HPLC detection



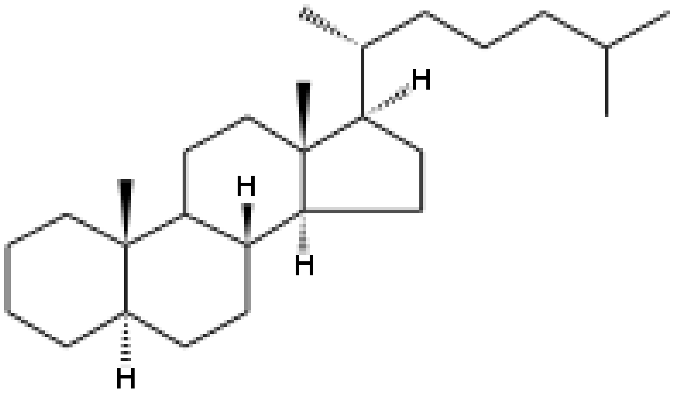


Cromatograma obtido por CLAE com detecção espectrofotométrica:

Qual a pureza da substância?

(é possível dizer que nessa detecção pelo menos uma substância foi detectada)

Analysis of cholestane by HPLC (?)



It is invisible under UV (200-600 nm) light:

No chromophore groups at this range of UV light !!

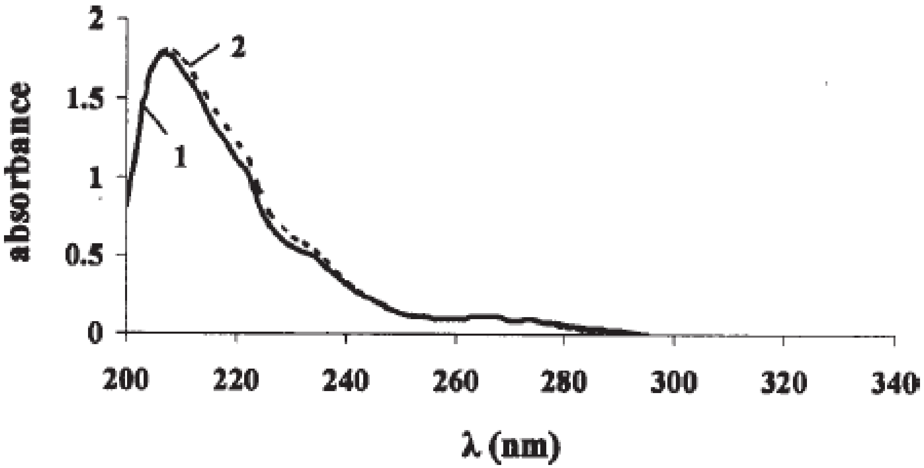
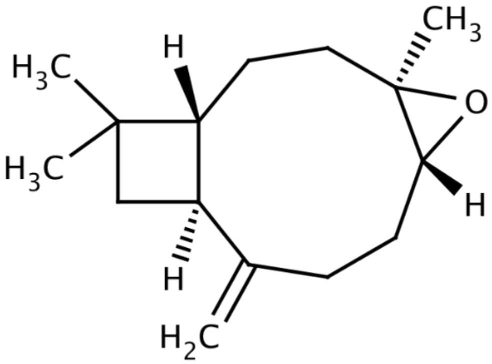
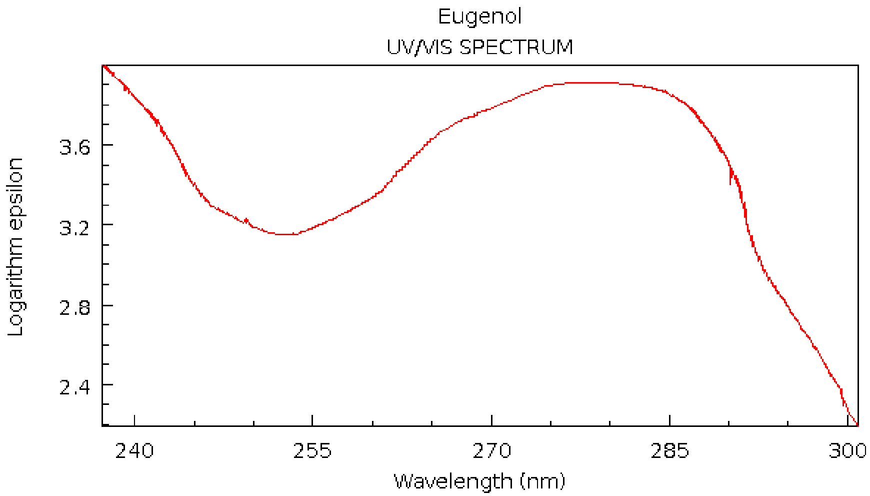


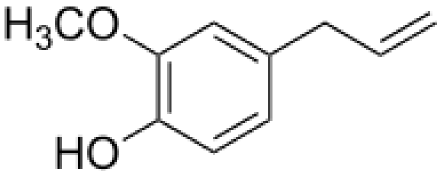
Fig. 4. Ultraviolet-visible spectra of *Eucalyptus globulus* essential oil samples: **1** – EG1; **2** – EG2



Caryophyllene oxide



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)



eugenol

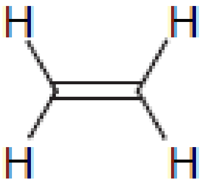
Principles of UV-VIS absorption

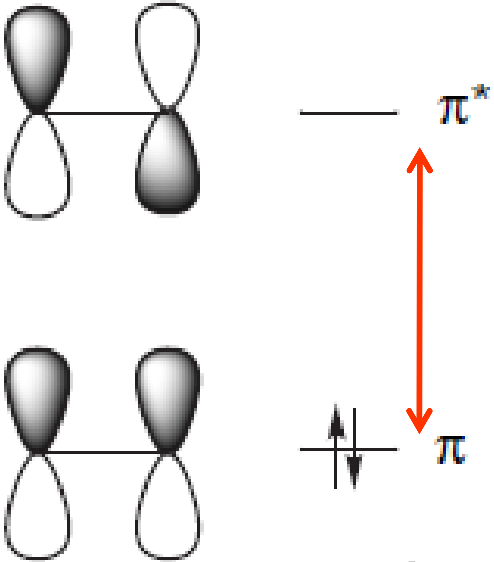
Electronic transition between different

HOMO and LUMO orbitals

Molecular Orbital Description for ethylene (frontiers orbitals)

Ethene:





ground state

LUMO

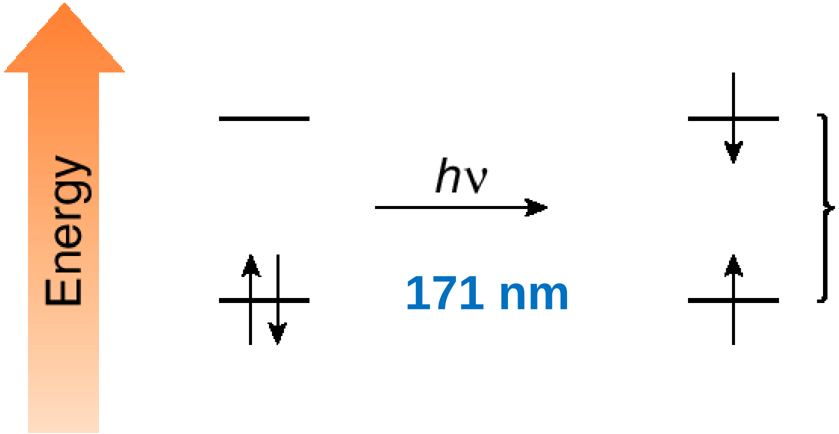
(lowest unoccupied Molecular orbital)

HOMO

(highest occupied Molecular orbital)

The excitation process:

absorption of energy (photon) by a chromophore



This energy difference depends on the location of the electron.

ground state

lower energy state

excited state

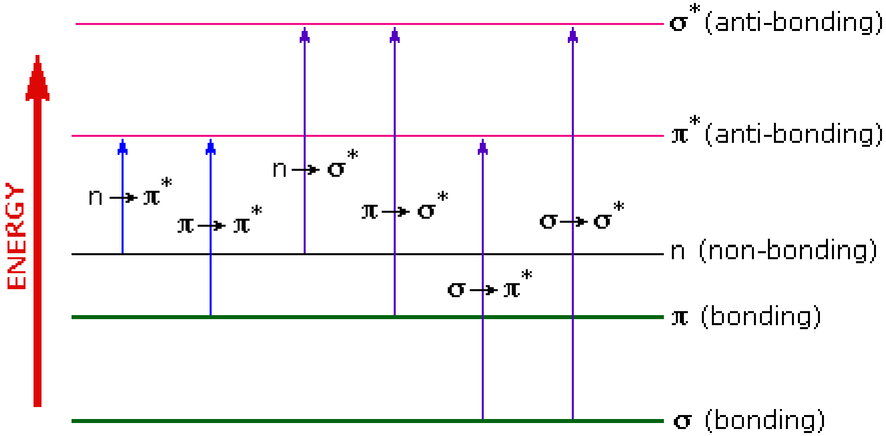
higher energy state

For ethylene:

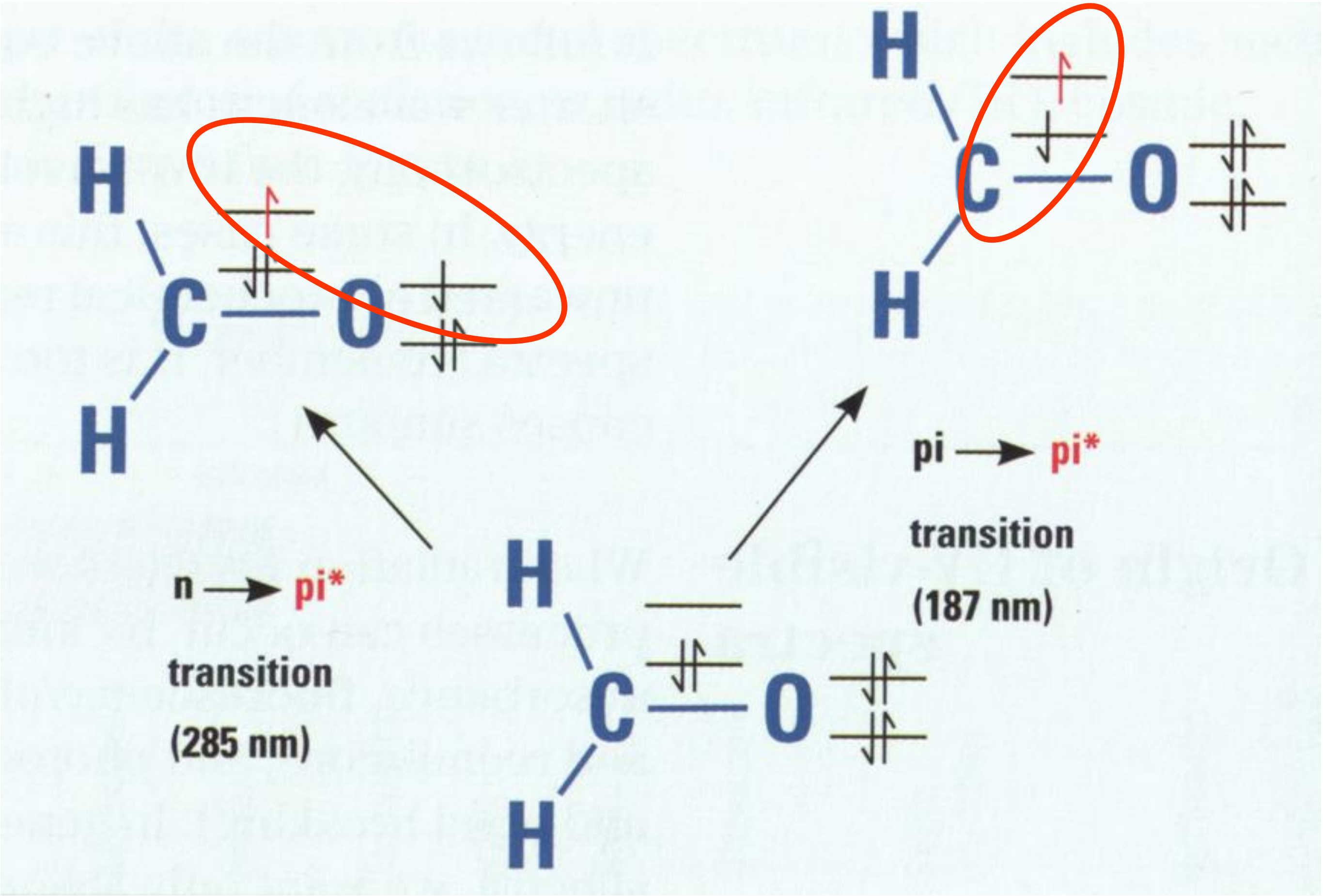
a band at 171 nm (ε 17000)

Examples of electronic transitions for organic functional groups:

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	π —> π*	171	15,000	hexane
C≡C	1-Hexyne	π —> π*	180	10,000	hexane
C=O	Ethanal	n —> π* π —> π*	290 180	15 10,000	hexane hexane
N=O	Nitromethane	n —> π* π —> π*	275 200	17 5,000	ethanol ethanol
C-X X=Br	Methyl bromide	n —> σ*	205	200	hexane
X=I	Methyl Iodide	n —> σ*	255	360	hexane

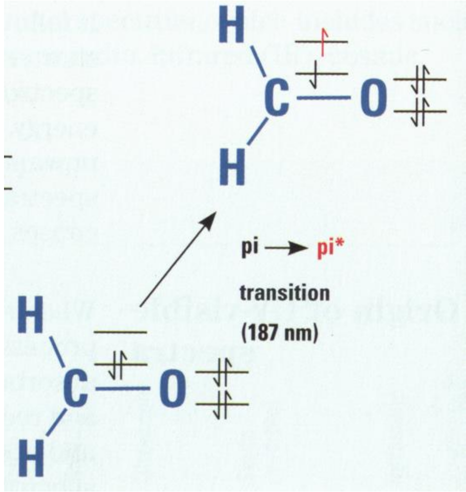


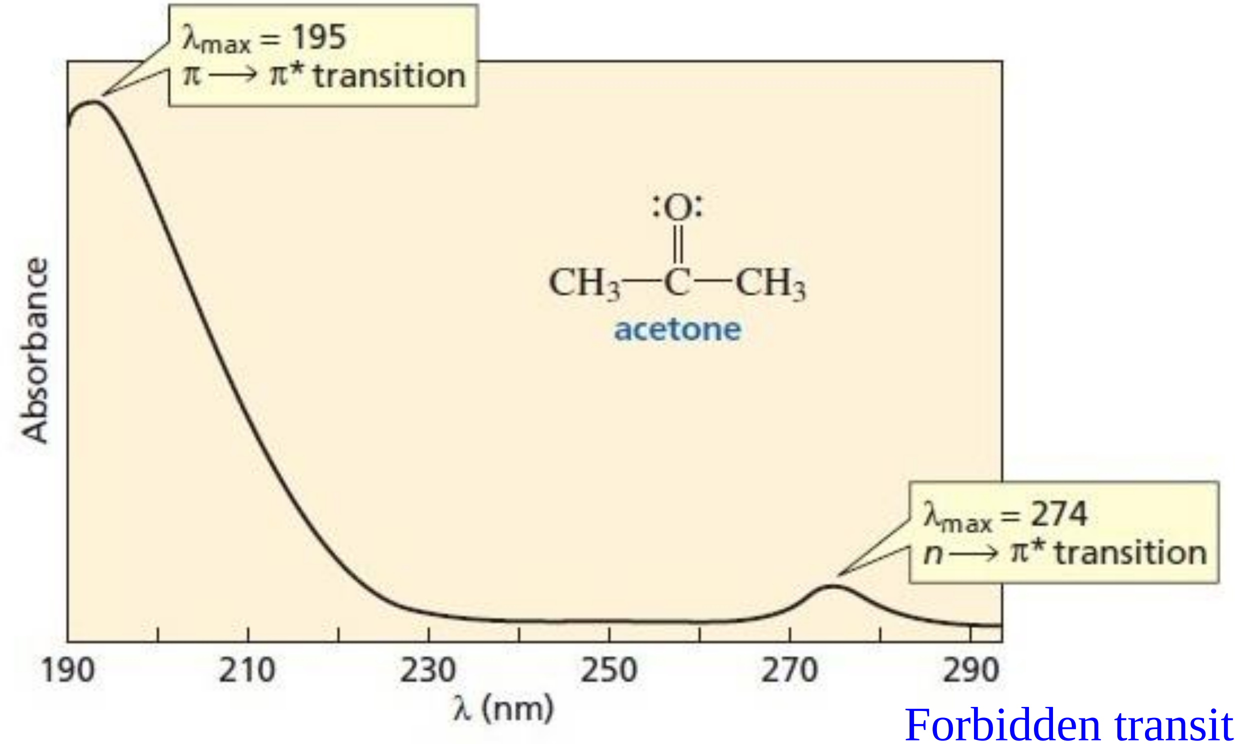
Carbonyl chromophores



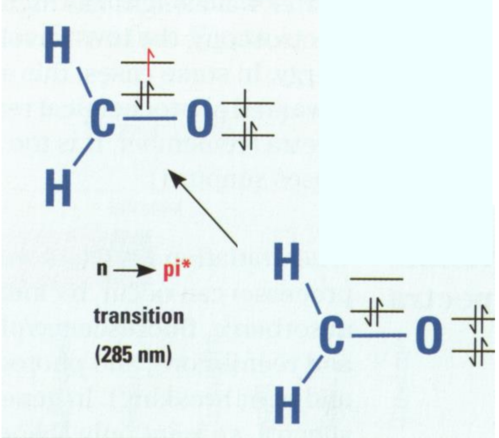
Forbidden transition (Transição proibida):
transições de energia não permitidas normalmente pelas regras de seleção da mecânica quântica

UV absorption of acetone



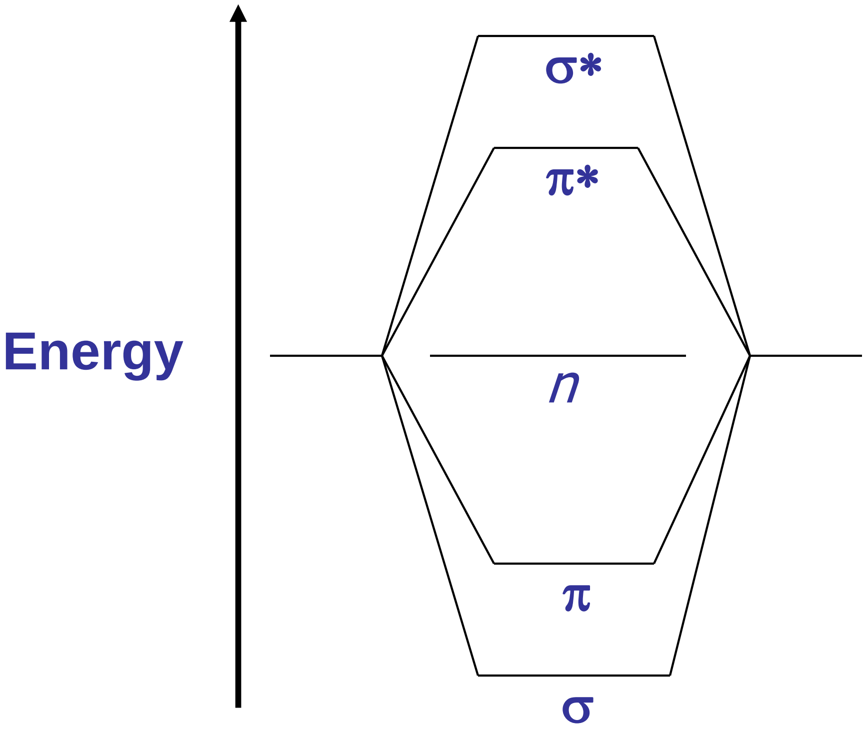


Forbidden transition
(low intensity)



Intensity of absorption is associated
to the probability of transition to occur!

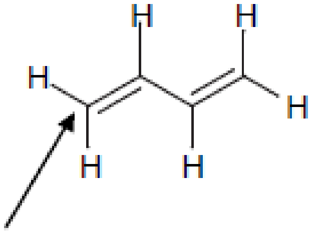
Possible electronic transitions for common organic compounds:



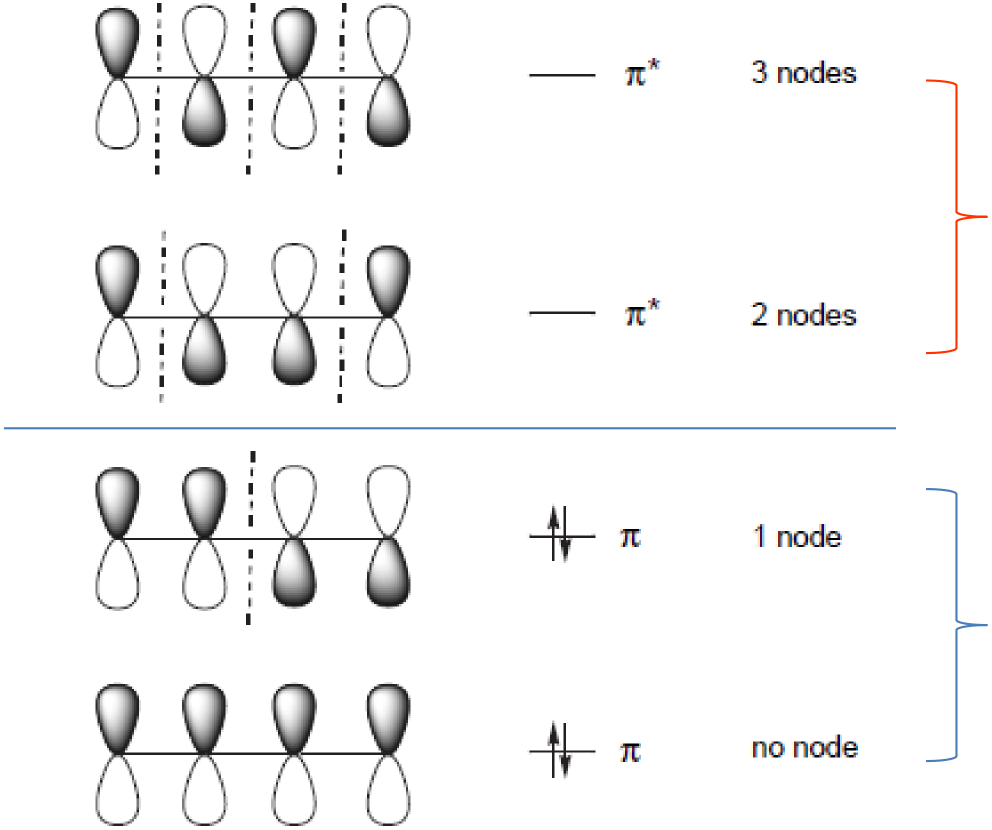
$\sigma \longrightarrow \sigma^*$	alkanes
$\sigma \longrightarrow \pi^*$	carbonyls
$\pi \longrightarrow \pi^*$	unsaturated cmpds.
$n \longrightarrow \sigma^*$	O, N, S, halogens
$n \longrightarrow \pi^*$	carbonyls

Molecular Orbital Description for 1,3-butadiene

- Butadiene:



Carbon: sp^2 hybridized



π^* 3 nodes

π^* 2 nodes

antibonding MO´s

π 1 node

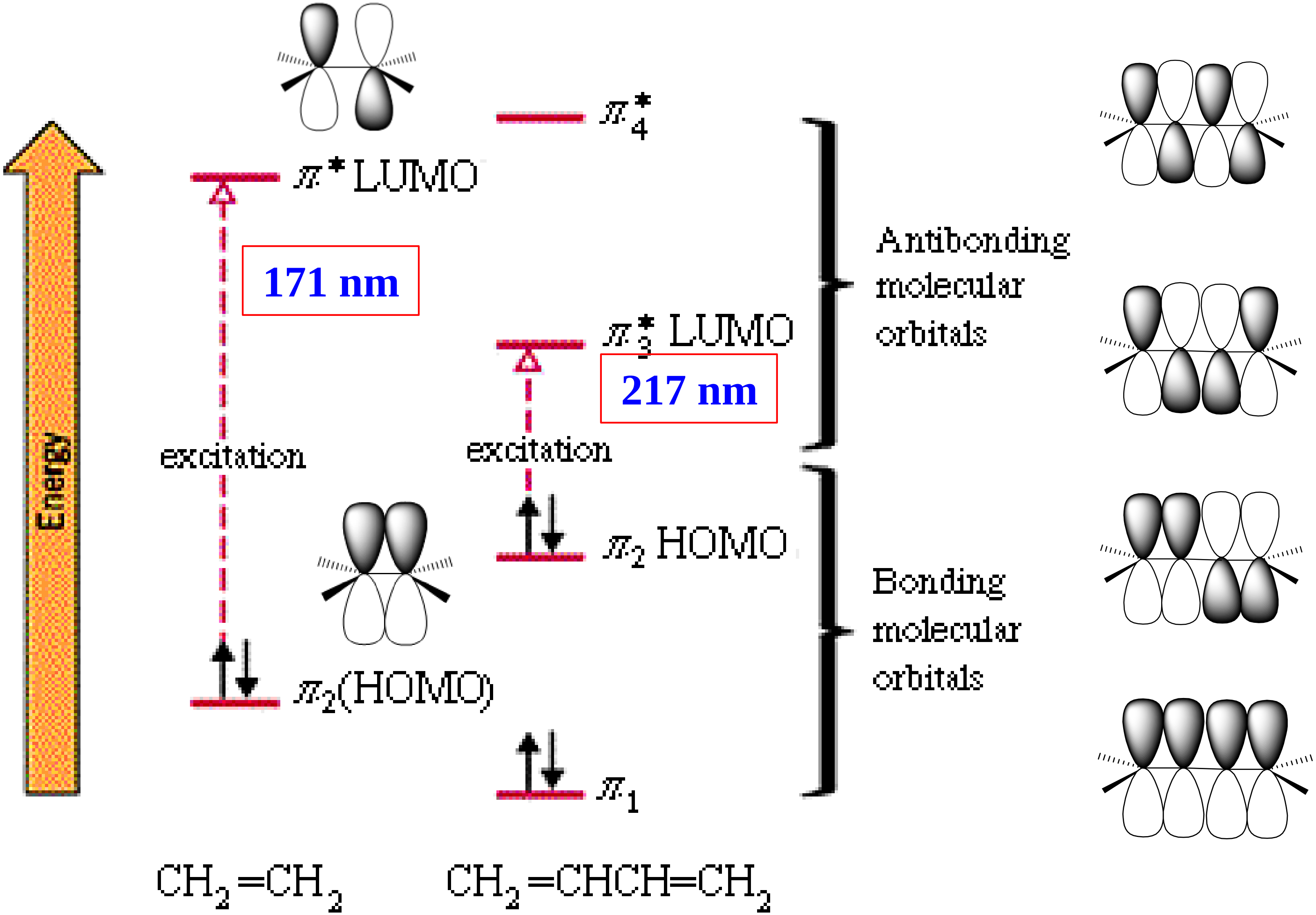
π no node

bonding MO´s

MO is bonding when the number of bonding interactions > number of nodes

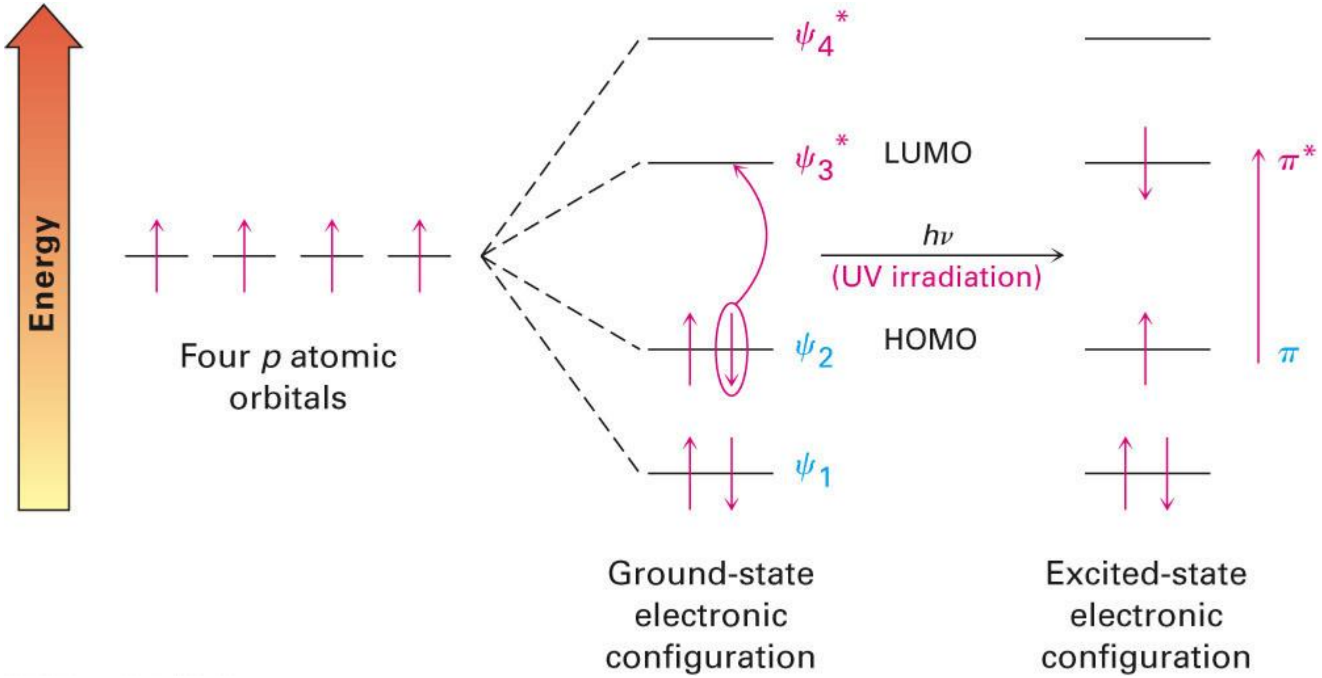
MO is antibonding when the number of bonding interactions < number of nodes

UV spectrum of ethylene versus 1,3-butadiene

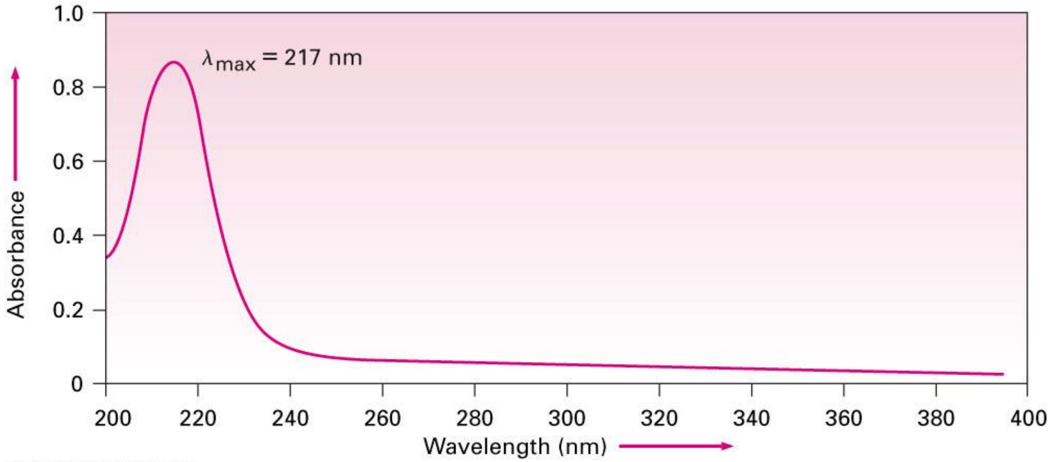


ΔE for the HOMO → LUMO transition is reduced

The UV absorption phenomena of 1,3-butadiene

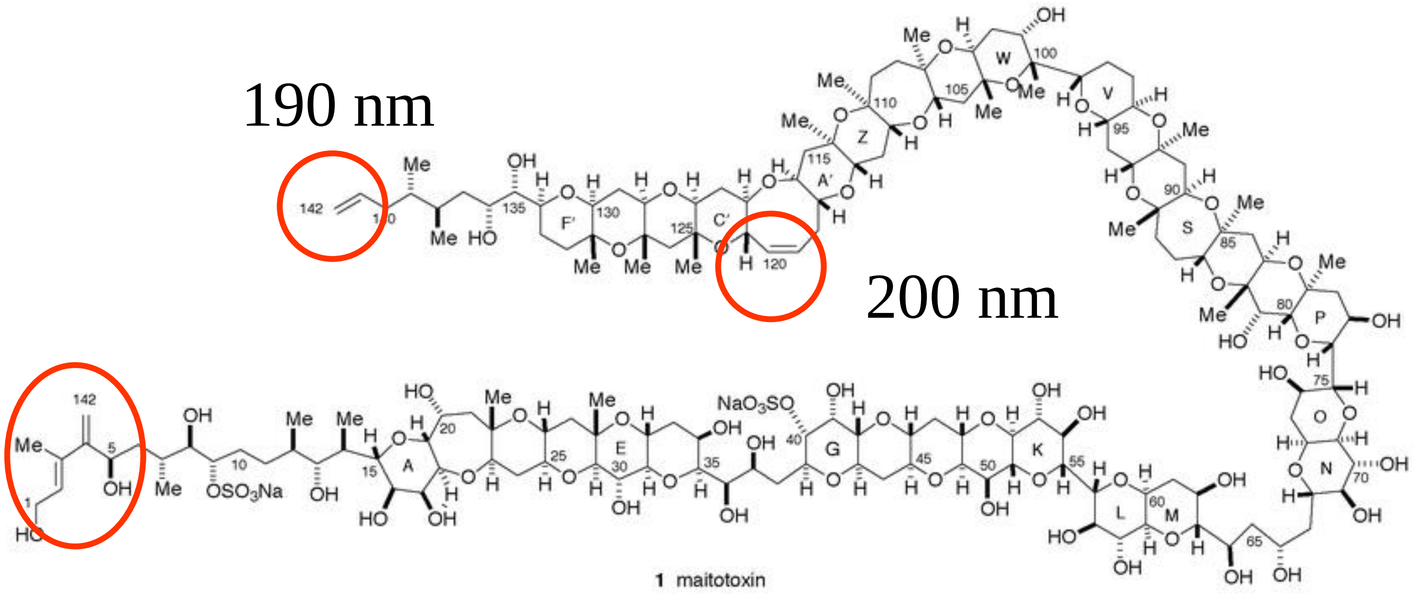


217 nm



Complex molecule: simple UV absorption curves

case of maitotoxin



190 nm

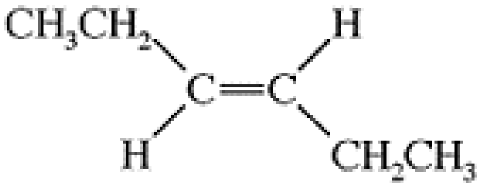
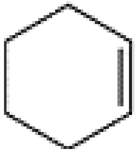
200 nm

230 nm

1 maitotoxin

Selected physicochemical properties of **1** are as follows;
a white amorphous solid, $[\alpha]_D^{25}$ +16.8 (*c* 0.36, MeOH-H_2O, 1:1);
UV (MeOH-H_2O, 1:1): 230 nm (9600).

Long-wavelength absorption maxima of unsaturated hydrocarbons

COMPOUND	STRUCTURE	λmax (nm)	εmax
Ethene	$CH_2{=}CH_2$	171	15,530
trans-3-Hexene		184	10,00
Cyclohexene		182	7,600
1-Octene	$CH_3(CH_2)_5CH{=}CH_2$	177	12,600
1-Octyne	$CH_3(CH_2)_5C{\equiv}CH$	185	2,000
1,3-Butadiene	$CH_2{=}CHCH{=}CH_2$	217	21,000

Why do we have such differences in the λ max?

Fatores que afetam os máximos de absorção

1) Tipos de cromóforos (olefínicos, heteroátomo, aromático e etc)
2) Substituíntes (ou grupos auxocromos como grupos alquílicos, heteroátomos, arílicos e outros)
3) Ligações duplas (ou triplas) conjugadas
4) Solvente (exceto dienos), pH

Stability of Conjugated Dienes

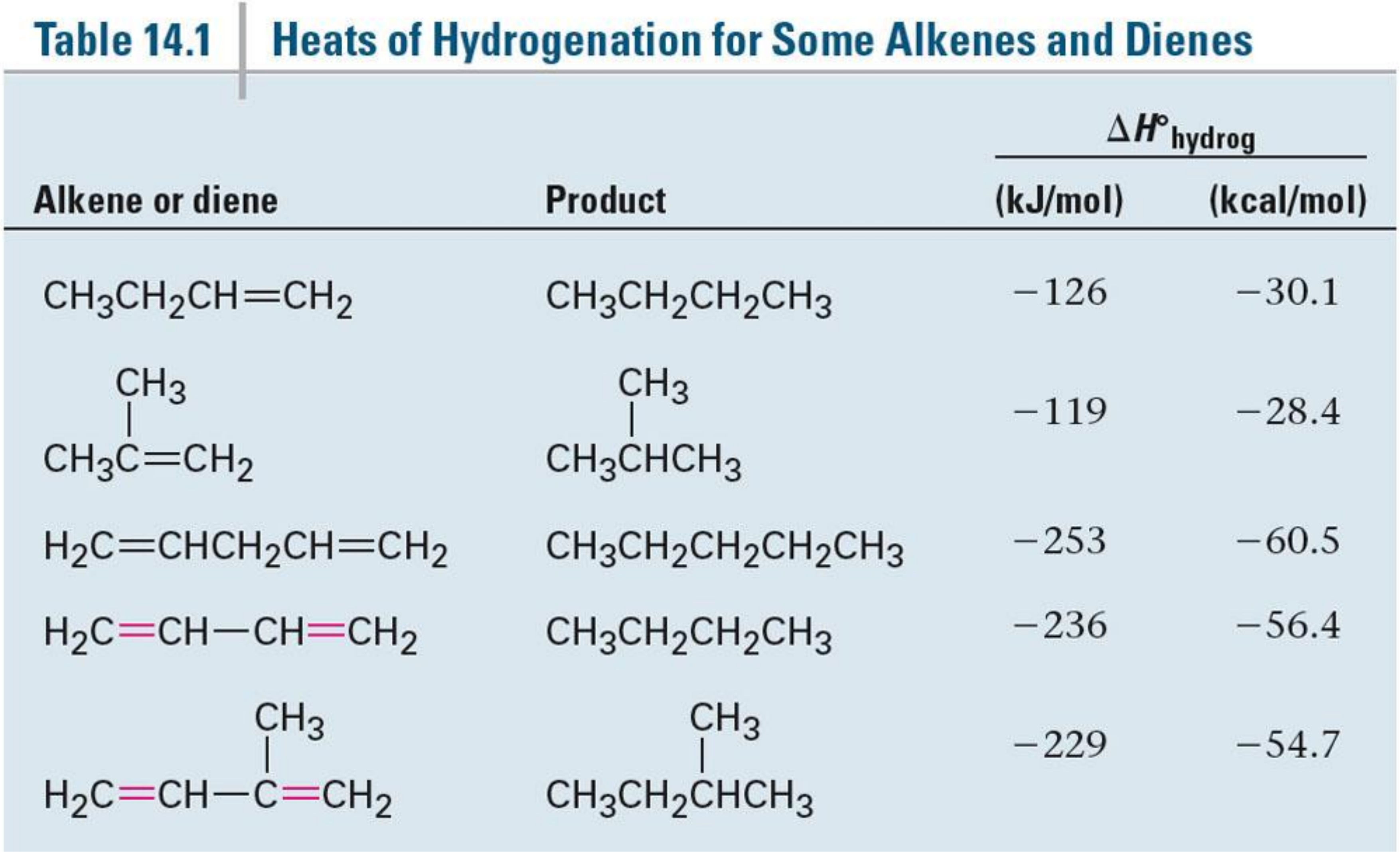
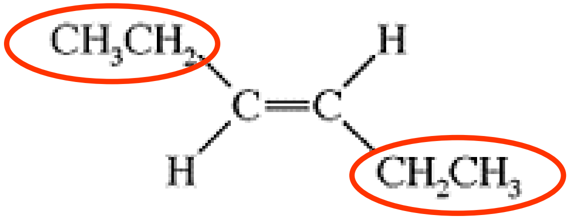
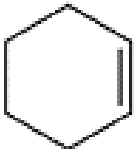


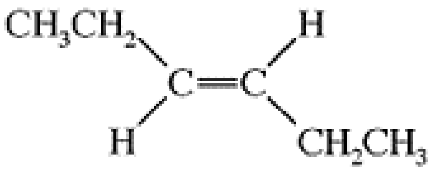
Table 14.1 **Heats of Hydrogenation for Some Alkenes and Dienes**

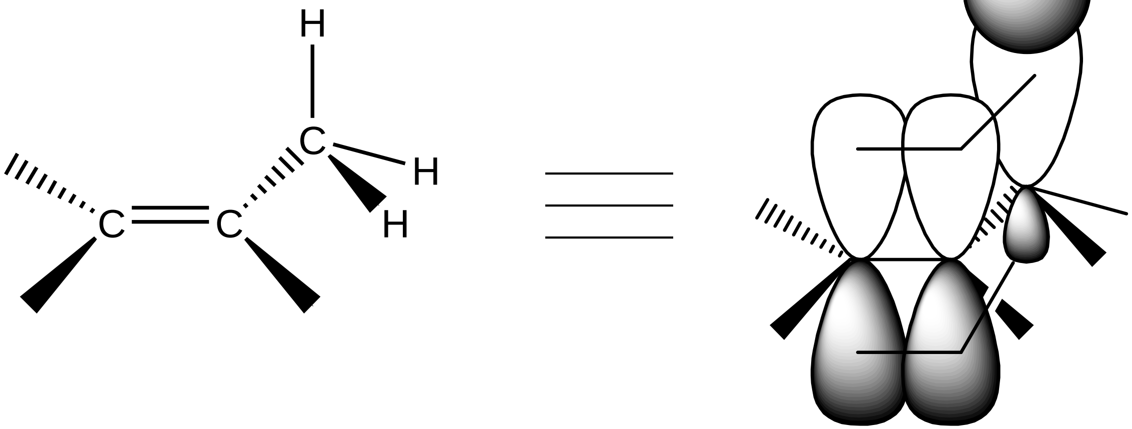
Alkene or diene	Product	$\Delta H°_{\text{hydrog}}$ (kJ/mol)	$\Delta H°_{\text{hydrog}}$ (kcal/mol)
$CH_3CH_2CH{=}CH_2$	$CH_3CH_2CH_2CH_3$	−126	−30.1
$CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$	$CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_3$	−119	−28.4
$H_2C{=}CHCH_2CH{=}CH_2$	$CH_3CH_2CH_2CH_2CH_3$	−253	−60.5
$H_2C{=}CH{-}CH{=}CH_2$	$CH_3CH_2CH_2CH_3$	−236	−56.4
$H_2C{=}CH{-}\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$	$CH_3CH_2\overset{\overset{CH_3}{\vert}}{C}HCH_3$	−229	−54.7

Long-wavelength absorption maxima of unsaturated hydrocarbons

COMPOUND	STRUCTURE	λmax (nm)	εmax
Ethene	$CH_2=CH_2$	171	15,530
trans-3-Hexene		184	10,00
Cyclohexene		182	7,600
1-Octene	$CH_3(CH_2)_5CH=CH_2$	177	12,600
1-Octyne	$CH_3(CH_2)_5C\equiv CH$	185	2,000
1,3-Butadiene	$CH_2=CHCH=CH_2$	217	21,000

Effect of alkylsubstituents

COMPOUND	STRUCTURE	λmax (nm)	εmax
Ethene	$CH_2=CH_2$	171	15,530
trans-3-Hexene		184	10,00



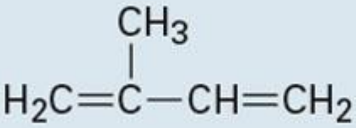
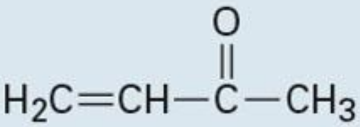
The simplest alkyl group that cause a bathochromic shift is the methyl group even though they are devoid of π- or *n*-electrons

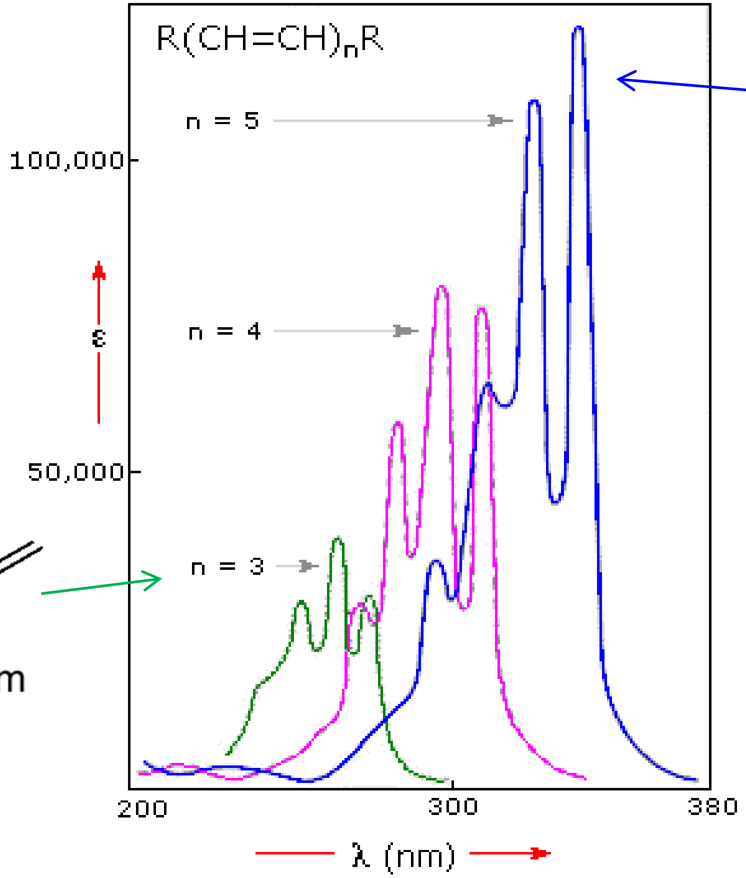
The effect of alkyl group is thought to be through what is termed "**hyperconjugation**" **or sigma bond resonance**

Additional conjugation on π system increase λ_{max}

1,3-butadiene: $H_2C{=}CH{-}CH{=}CH_2$ **217 nm**

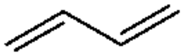
Table 14.2 Ultraviolet Absorptions of Some Conjugated Molecules

Name	Structure	λ_{max} (nm)
2-Methyl-1,3-butadiene	 $H_2C{=}\overset{\overset{CH_3}{\mid}}{C}{-}CH{=}CH_2$	220
1,3-Cyclohexadiene		256
1,3,5-Hexatriene	$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$	258
1,3,5,7-Octatetraene	$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$	290
3-Buten-2-one	 $H_2C{=}CH{-}\overset{\overset{O}{\parallel}}{C}{-}CH_3$	219
Benzene		203

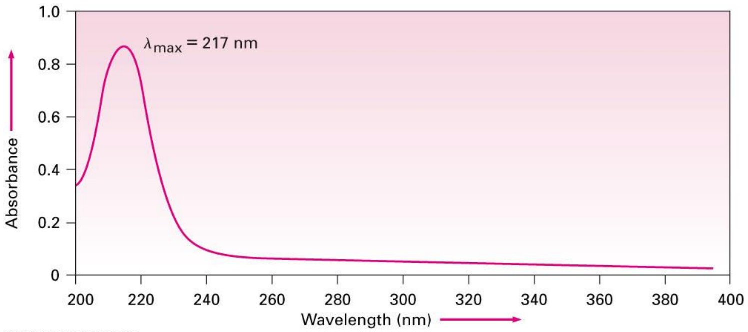


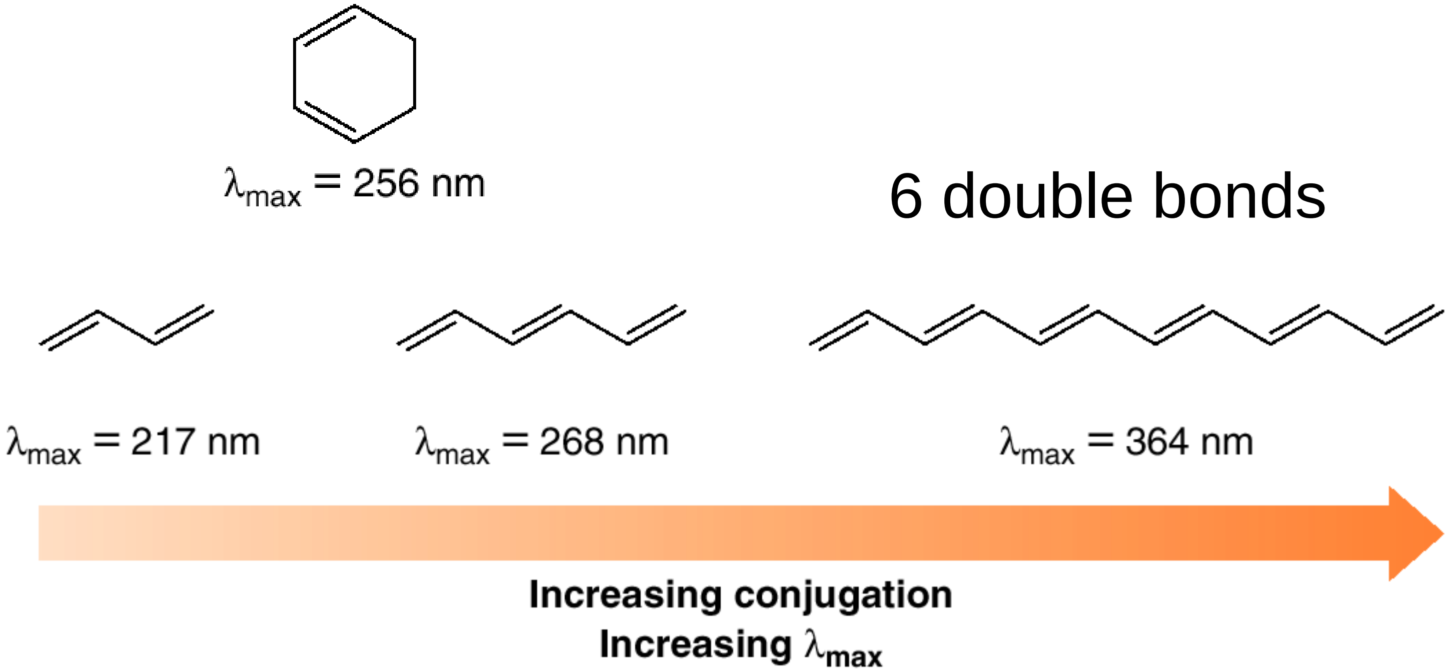
λ_{max} = 364 nm

λ_{max} = 268 nm



λ_{max} = 217 nm





λ_{max} = 256 nm

6 double bonds

λ_{max} = 217 nm

λ_{max} = 268 nm

λ_{max} = 364 nm

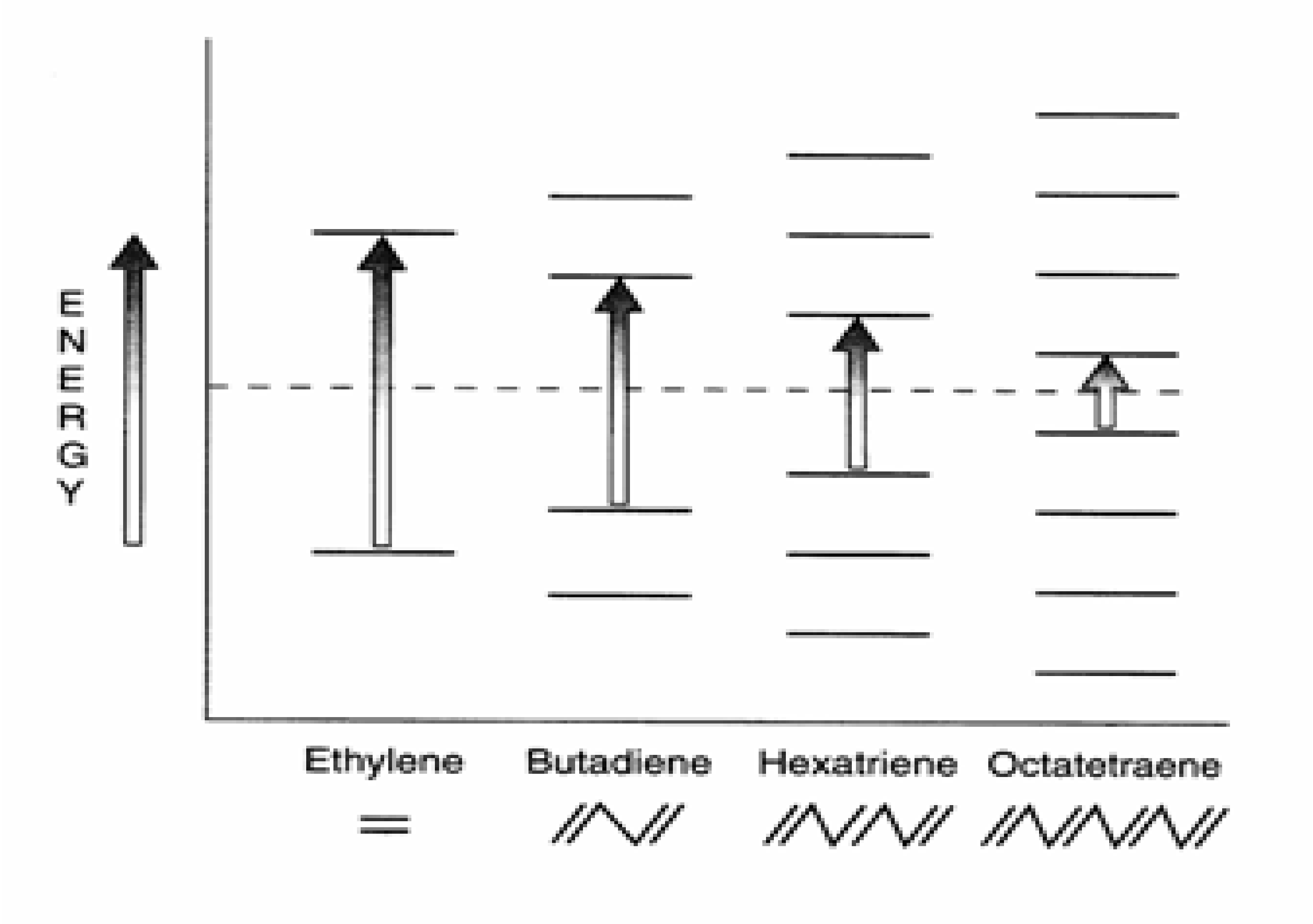
Increasing conjugation

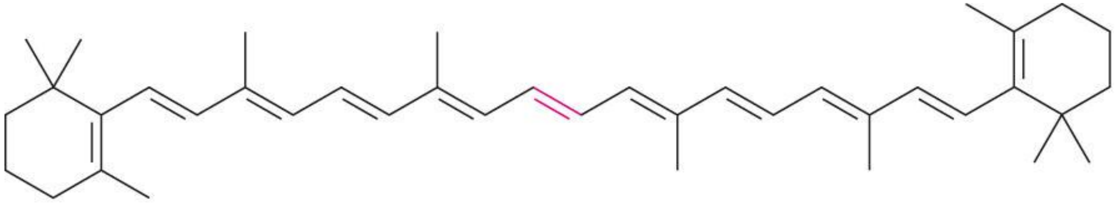
Increasing λ_{max}

- eight or more conjugated π bonds, the absorption shifts from the UV to the visible region, and the compound takes on the color of the light it does not absorb.

The HOMO and LUMO involved in the transition get closer shifting the maxima absorption to visible light wavelenght

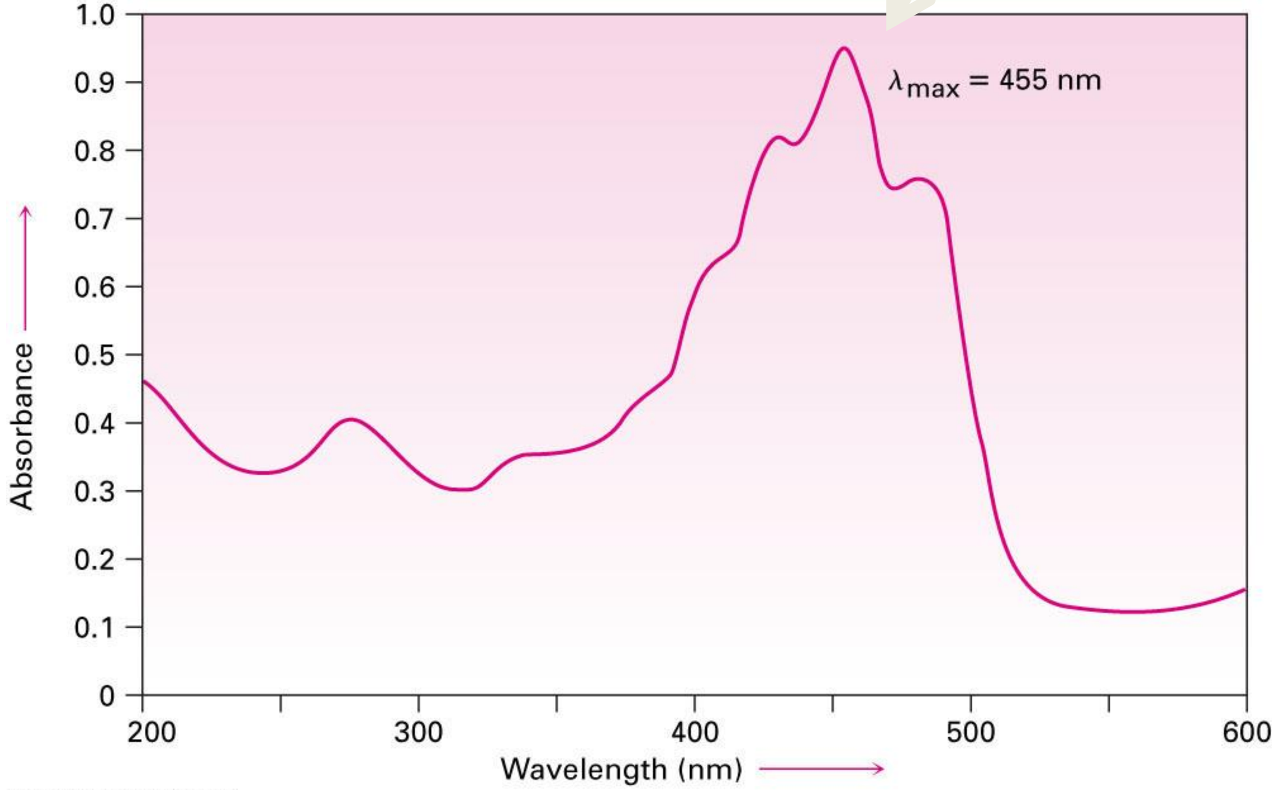
(higher wavelength and lower energy)



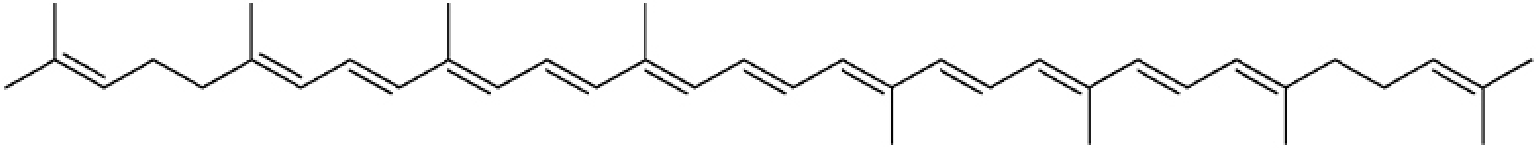


β-Carotene

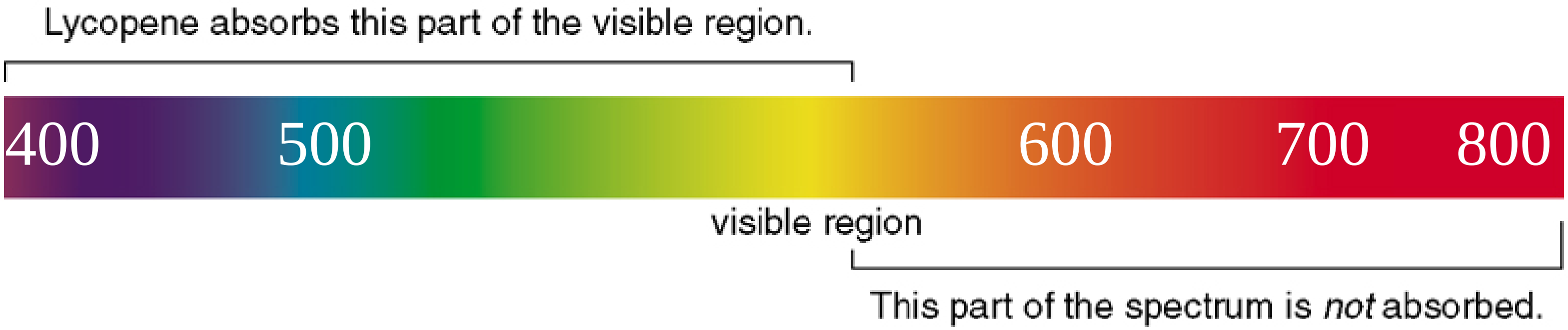
β-Carotene,
11 double
bonds in
conjugation,
λmax = **455** nm



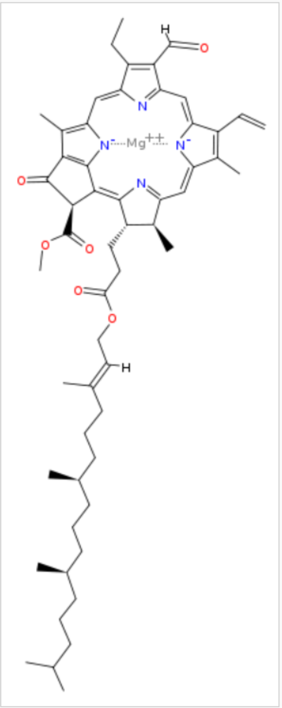
- **Lycopene** absorbs visible light at λ_{max} = **470 nm**, in the blue-green region of the visible spectrum. Because it does not absorb light in the red region, lycopene appears bright red.



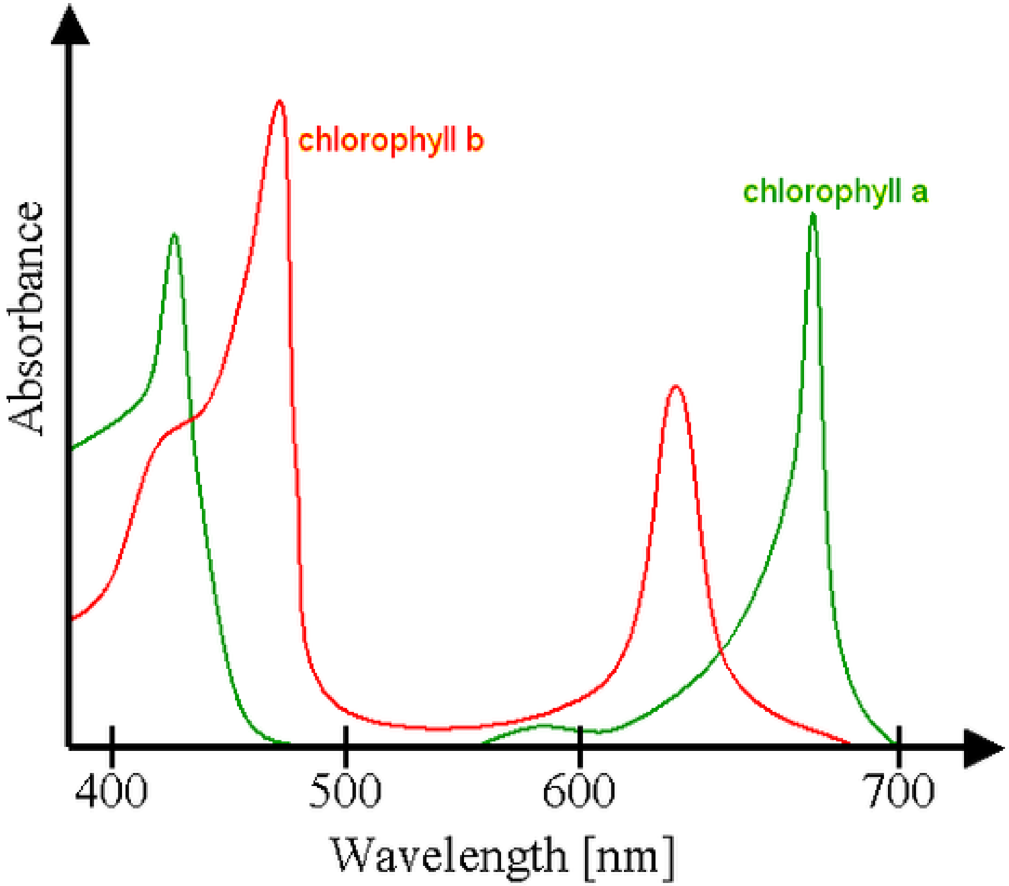
Lycopene—11 conjugated π bonds

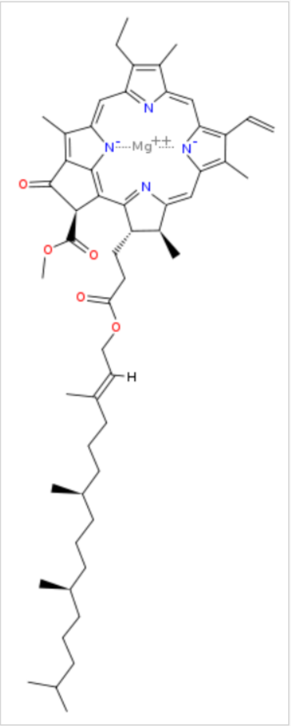


Lycopene appears red.

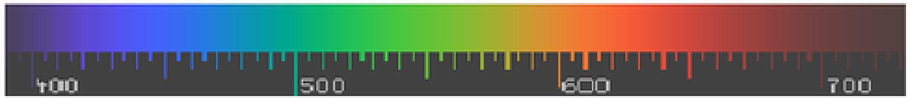


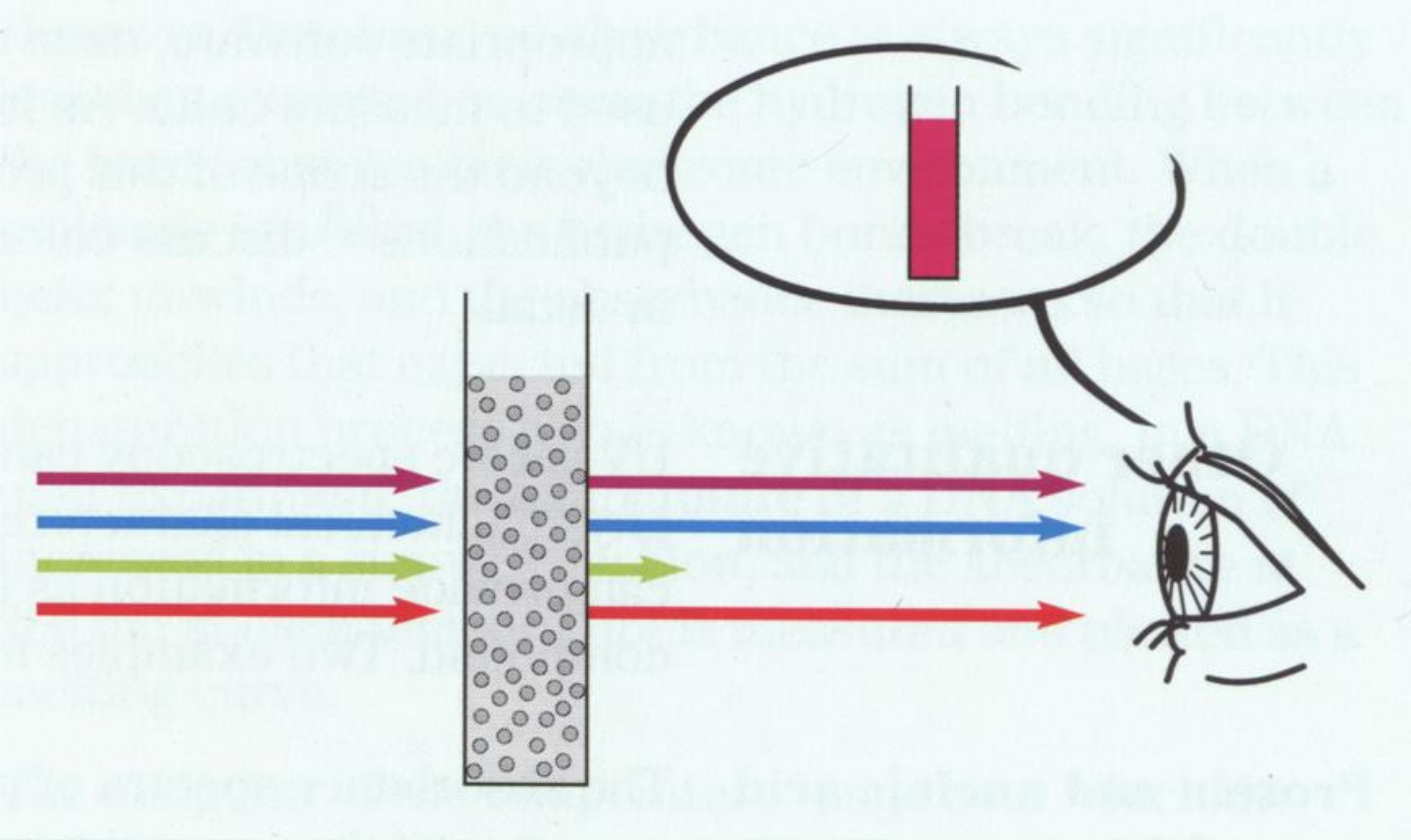
Structure of chlorophyll *b*





Structure of chlorophyll *a*





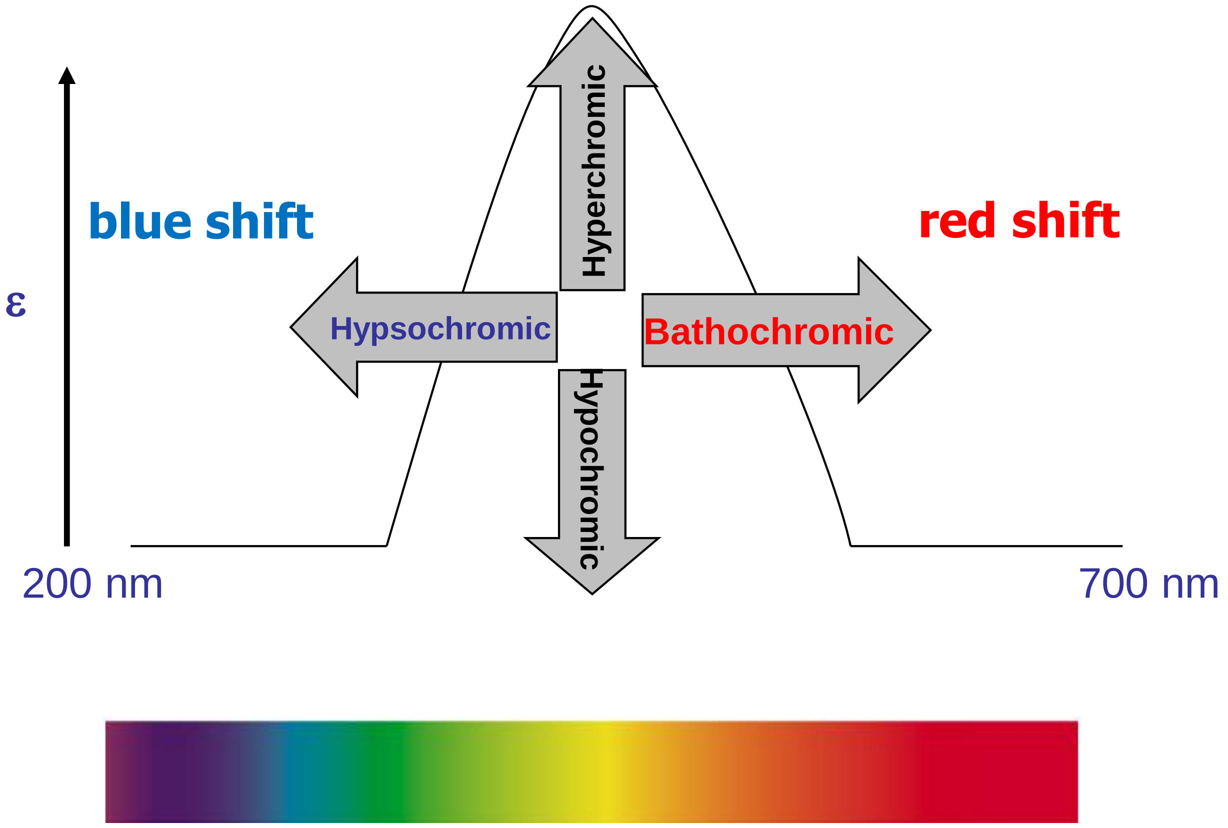
Four possible effects on a chromophore:

Bathochromic shift (red shift) – a shift to longer λ; lower energy

i. **Hypsochromic shift** (blue shift) – shift to shorter λ; higher energy

ii. Hyperchromic effect – an increase in intensity

iii. Hypochromic effect – a decrease in intensity



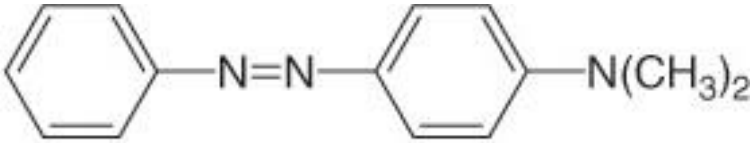
In summary

Only:
conjugates dienes (and higher homologous), **aromatic** and ***n* → π* transitions** can be routinely observed under UV region.

Substituents (other than H) affect the transition energy.

Substituents that increase the intensity and often wavelength of an absorption are called *auxochromes* (*e.g*: R-, HO-, RO-, NHR and X-).

Azo compounds (dyes)

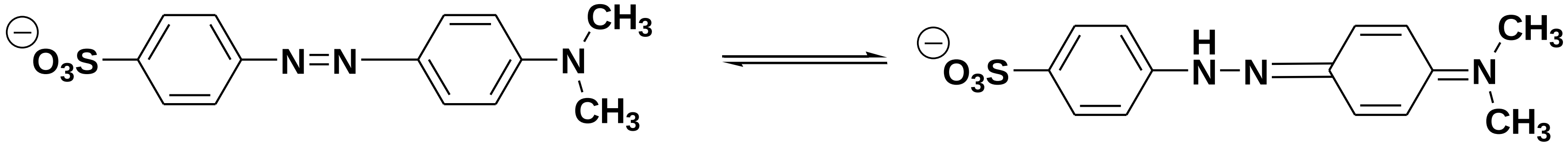


a yellow azo dye
“butter yellow”

Acid-base indicators used for the various pH ranges:

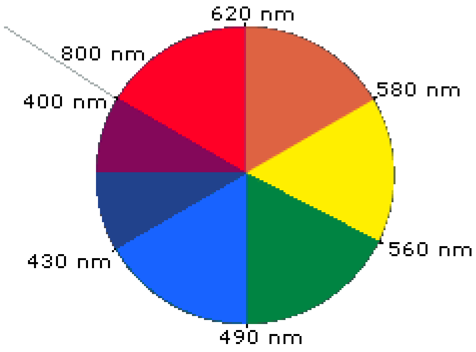
- See the effects of pH on aromatic substituents

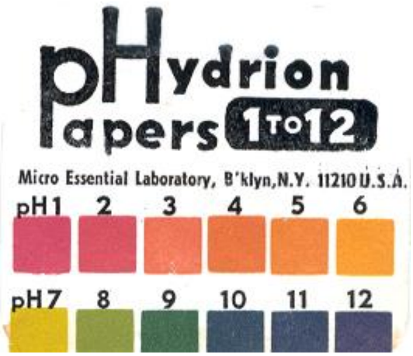
Methyl Orange



Yellow, pH > 4.4

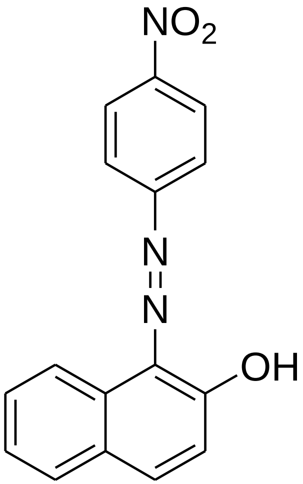
Red, pH < 3.2



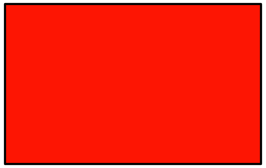


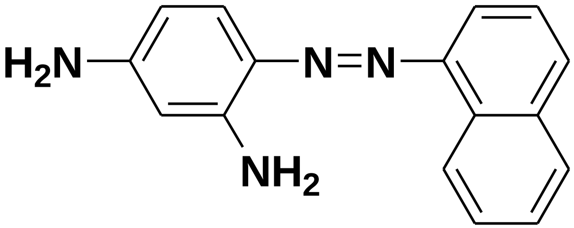
Visible Spectroscopy

These materials are amongst the more familiar colors of our “environment”.

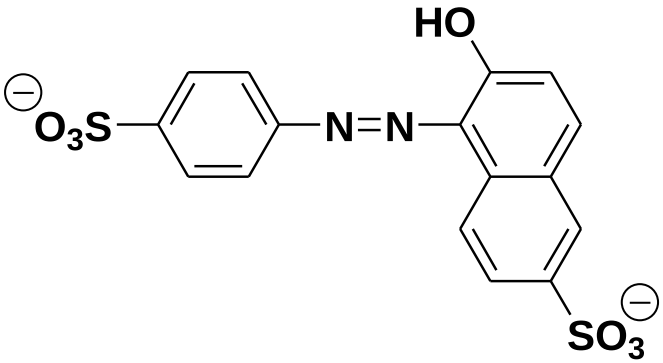


Para Red





Fast Brown



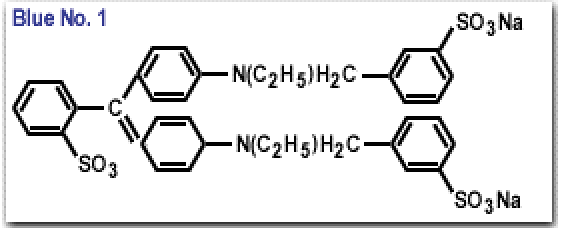
Sunset Yellow (Food Yellow 3)

The colors of M&M's: colorfull

Bright Blue

Common Food Uses

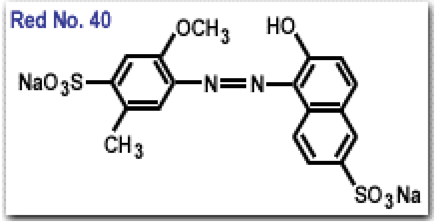
Beverages, dairy products, powders, jellies, confections, condiments, icing.


Blue No. 1

Orange-red

Common Food Uses

Gelatins, puddings, dairy products, confections, beverages, condiments.


Red No. 40

Orange

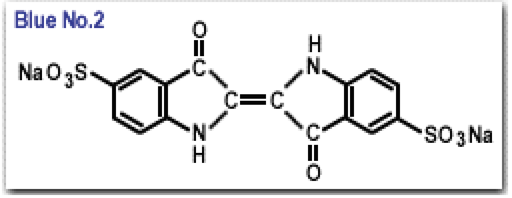
Common Food Uses

Cereals, baked goods, snack foods, ice-cream, beverages, dessert powders, confections

Royal Blue

Common Food Uses

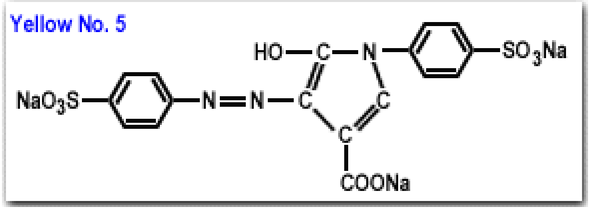
Baked goods, cereals, snack foods, ice-cream, confections, cherries.

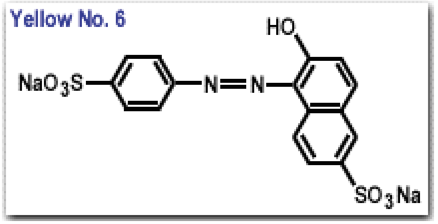

Blue No.2

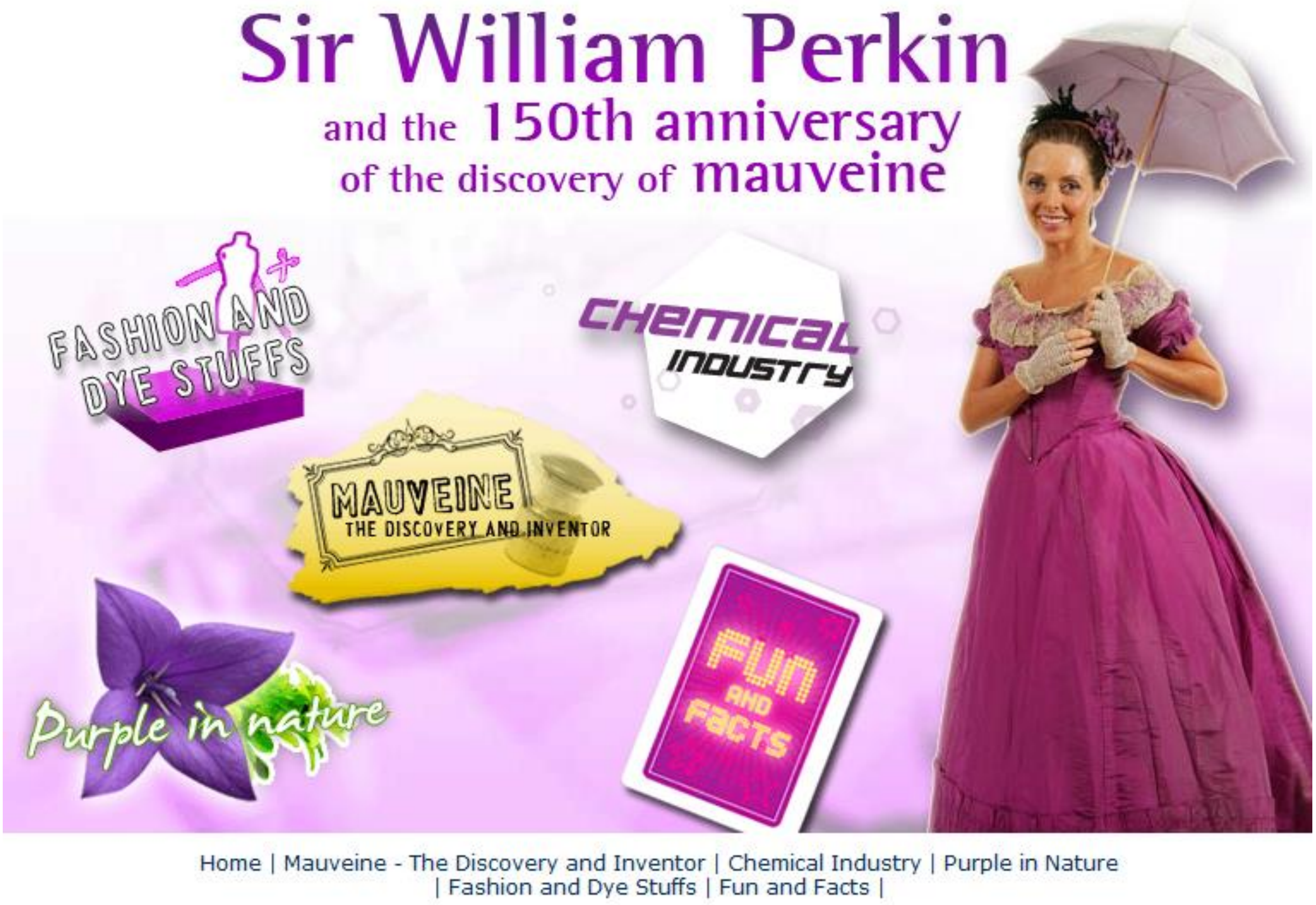
Lemon-yellow

Common Food Uses

Custards, beverages, ice-cream, confections, preserves, cereals.


Yellow No. 5


Yellow No. 6

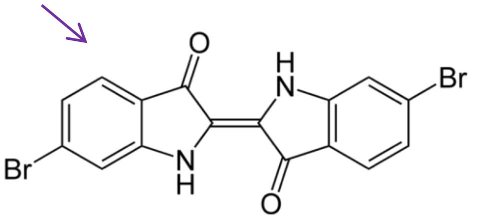


Sir William Perkin and the 150th anniversary of the discovery of mauveine

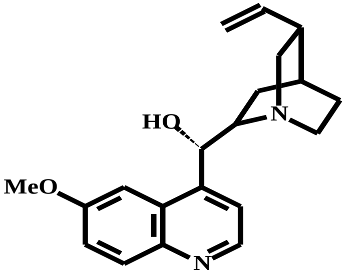
2,000 thousands of analogous compounds

http://www.rsc.org/Chemsoc/Activities/Perkin/2006/minisite_perkin_mauveine.html

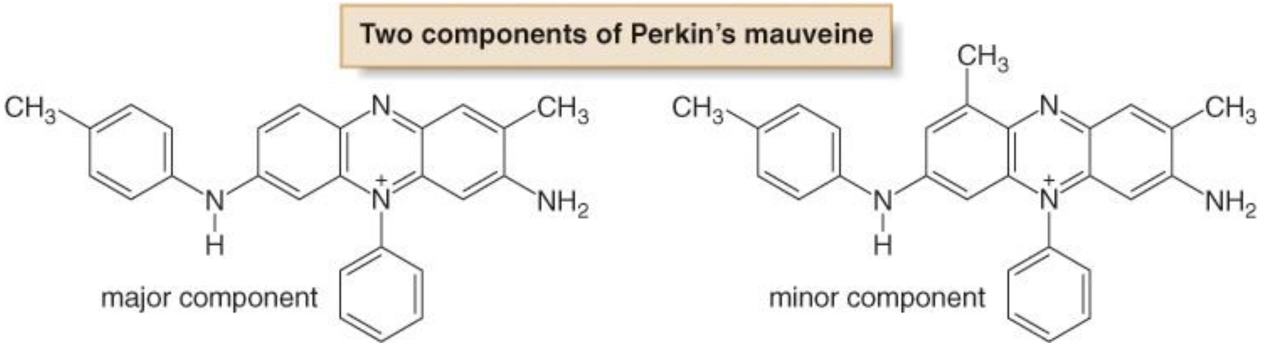
1856: Synthesis of mauveine (aniline purple and Perkin's mauve), was **the first synthetic dye** produced (to replace Tyrian Purple from mollusks).



Perkin oxidized aniline using potassium dichromate (trying to obtain quinine!). At 18 years old!
Under these conditions, the aniline reacted with toluidine impurities in it to produce a black solid (intense purple color)



quinine



major component

minor component

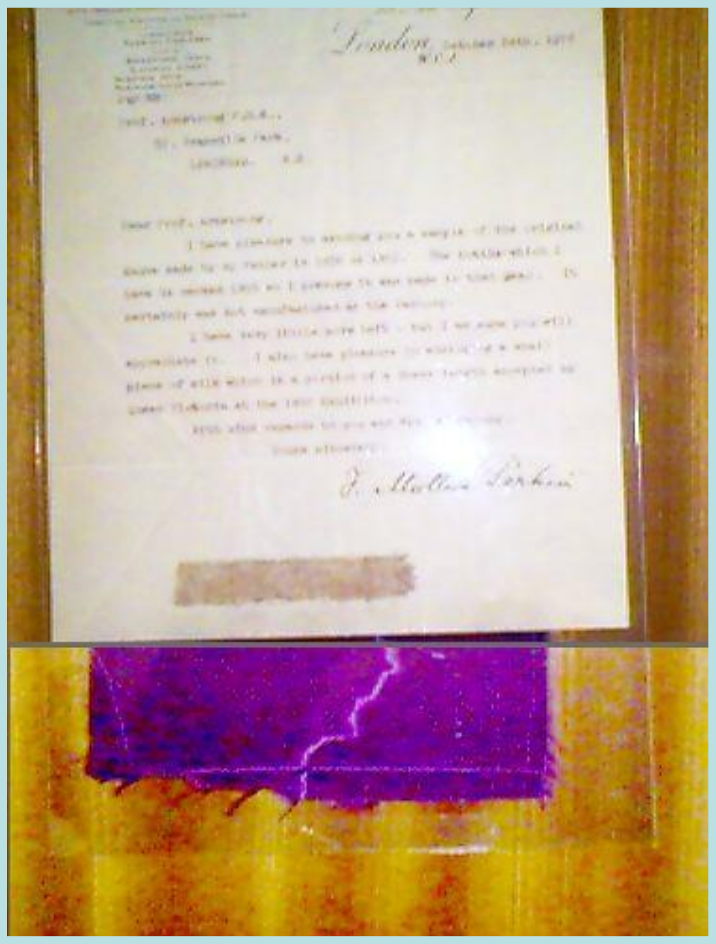
William H. Perkin

(12 March 1838 – 14 July 1907)

Malva sylvestris* *(Malvaceae)

Learn more: http://en.wikipedia.org/wiki/William_Henry_Perkin

- Then, thousants of synthetic new dyes started to appear in the market.
- Nowadays, almost all dyes in the market are synthetic.



Perkin’s letter with an example of Tyrian Purple dye on silk.

Not that nice !!!

Woodward-Fieser Rules: empirical observation of known conjugated structures which are applied to three specific chromophores.

1. Conjugated dienes
2. Conjugated dienones
3. Aromatic systems

Woodward-Fieser Rules

Origin:

Studies of terpene and steroidal alkenes: empirical prediction of the wavelength for the lowest energy p → p* electronic transition

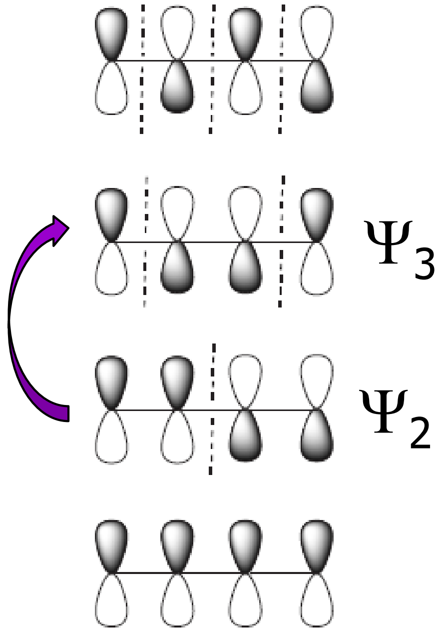
Literatura:

Donald L. Pavia e George S. Kriz, Introdução à espectroscopia. 4ª ed.

A.I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon, NY, 1964.

Rao in 1975 – (C.N.R. Rao, *Ultraviolet and Visible Spectroscopy*, 3rd Ed., Butterworths, London, 1975)

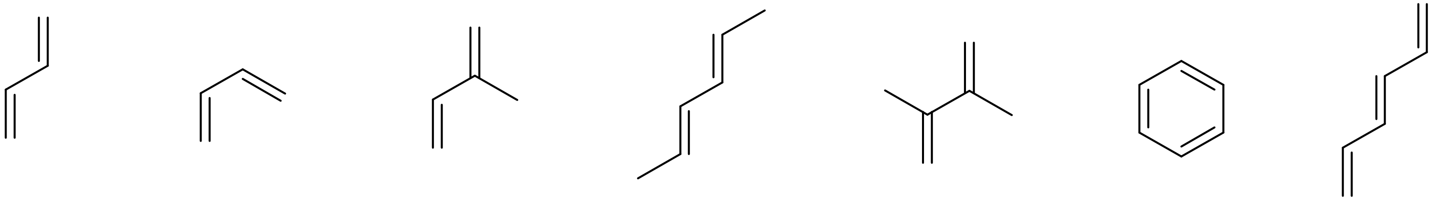
Woodward-Fieser Rules for dienes



The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption (e = 20,000+) based at 217 nm within the observed region of the UV

This band is insensitive to solvents but it is **subject to the effects of alkyl substituents as well as further conjugation**!!!

Consider:



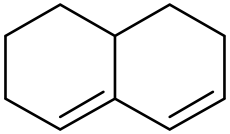
λ_{max} = 217 253 220 227 227 256 263 nm

Woodward-Fieser Rules – Dienes

Define a base value for λ_{max} of the chromophore under consideration:

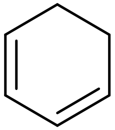
acyclic butadiene = 217 nm

Heteroannular (transoid):



base λ_{max} = 214
ε = 5,000 – 15,000

Homoannular (cisoid):

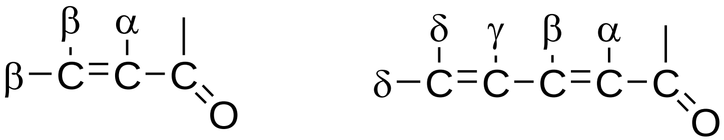


base λ_{max} = 253
ε = 12,000-28,000

The incremental contribution of substituents:

Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
$-OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
$-NR_2$	+60

Woodward-Fieser Rules - Enones



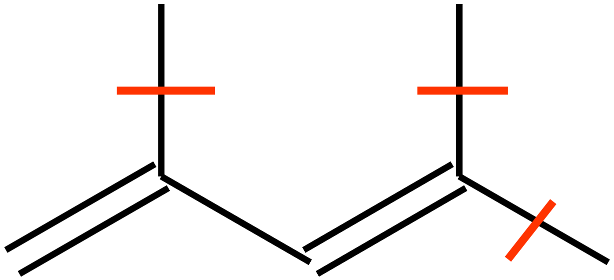
$\beta-\overset{\beta}{C}=\overset{\alpha}{C}-\overset{|}{C}=O$

$\delta-\overset{\delta}{C}=\overset{\gamma}{C}-\overset{\beta}{C}=\overset{\alpha}{C}-\overset{|}{C}=O$

Group		Increment
6-membered ring or acyclic enone		Base 215 nm
5-membered ring parent enone		Base 202 nm
Acyclic dienone		Base 245 nm
Double bond extending conjugation		30
Alkyl group or ring residue	α, β, γ and higher	10, 12, 18
-OH	α, β, γ and higher	35, 30, 18
-OR	α, β, γ, δ	35, 30, 17, 31
-O(C=O)R	α, β, δ	6
-Cl	α, β	15, 12
-Br	α, β	25, 30
$-NR_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39

Example:

- Calculate expected λ_{max} for following:

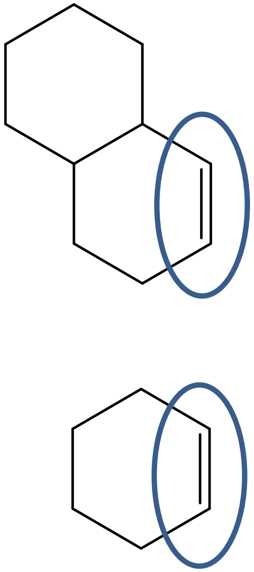


Base = 217

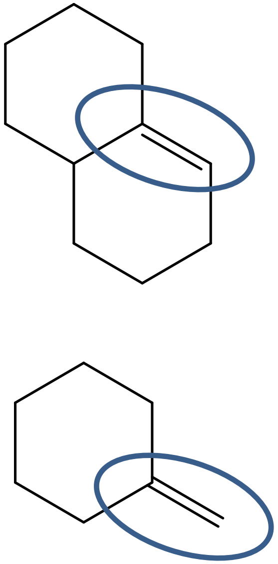
3 alkyl substituents + 5 each = 15

Calculated = 232

Observed = 232

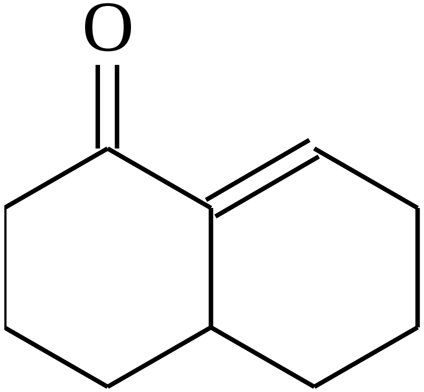


Endocyclic double bond

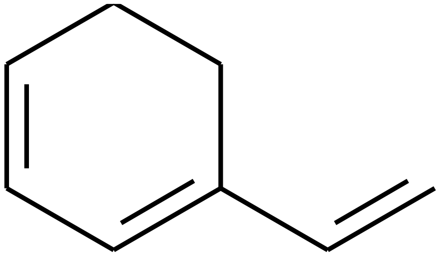


exocyclic double bond

- Calculate expected λ_{max} for following:



Base: 215 nm

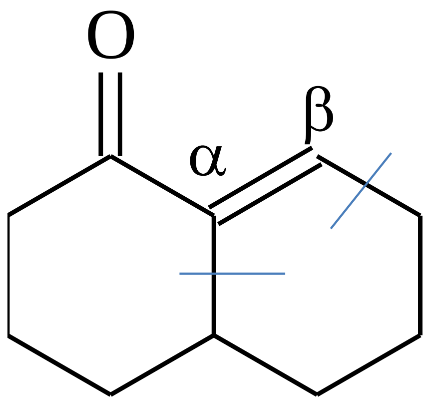


217 nm

To the base add:

1. 30 for each extra conjugated double bond;
2. 5 each time a conjugated double bond is an exocyclic double bond;
3. 36 for each conjugated double bond frozen *s*-cis;
4. 5 for each alkyl R or X bonded to conjugated system;
5. 10 for an α-substituent of a conjugated alkehyde or ketone
6. 12 for a β-substituent of a conjugated aldehyde or ketone

- Calculate expected λ_{max} for following:



Base = 215

α substituent = 10

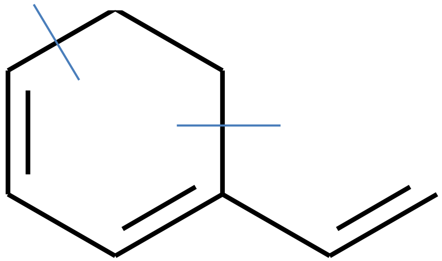
β substituent = 12

Exocyclic db = 5

Calculated = 242

Observed = 241

Db= double bond



Base = 253

Additional db bd = 30

2 alkyl substituents = 10

Calculated = 293

Observed = 293