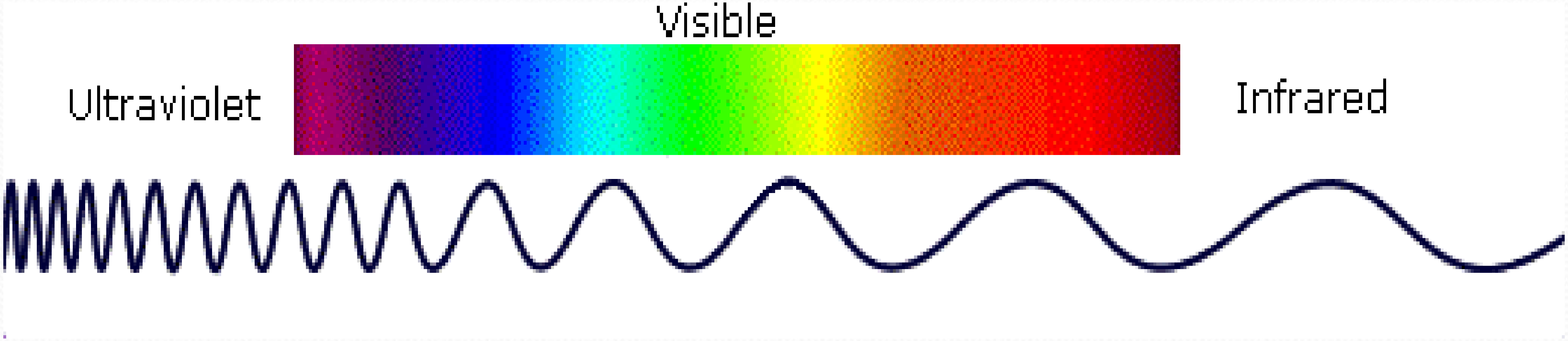
CHAPTER 2:
ULTRA VIOLET SPECTROMETRY
UV

Spectrum of Radiation



Energy Absorption

The mechanism of absorption energy is different in the Ultraviolet, Infrared, and Nuclear Magnetic Resonance regions.

However, the fundamental process is the absorption of certain amount of energy.

The energy required for the transition from a state of lower energy to a state of higher energy is directly related to the frequency of electromagnetic radiation that causes the transition.

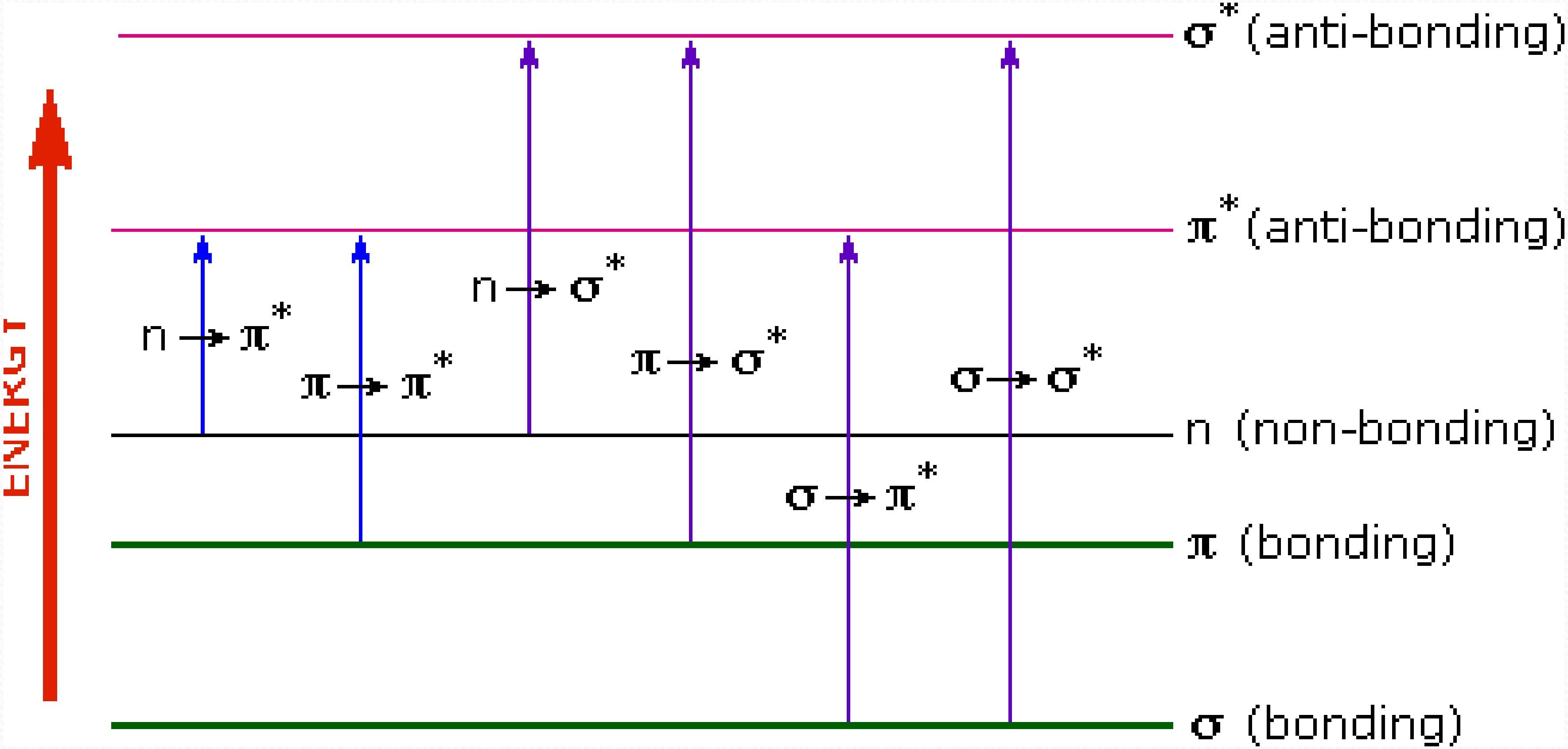
II. Ultra Violet Spectrometry

The absorption of ultraviolet radiation by molecules is dependent upon the electronic structure of the molecule. So the ultraviolet spectrum is called electronic spectrum.

Electronic Excitation

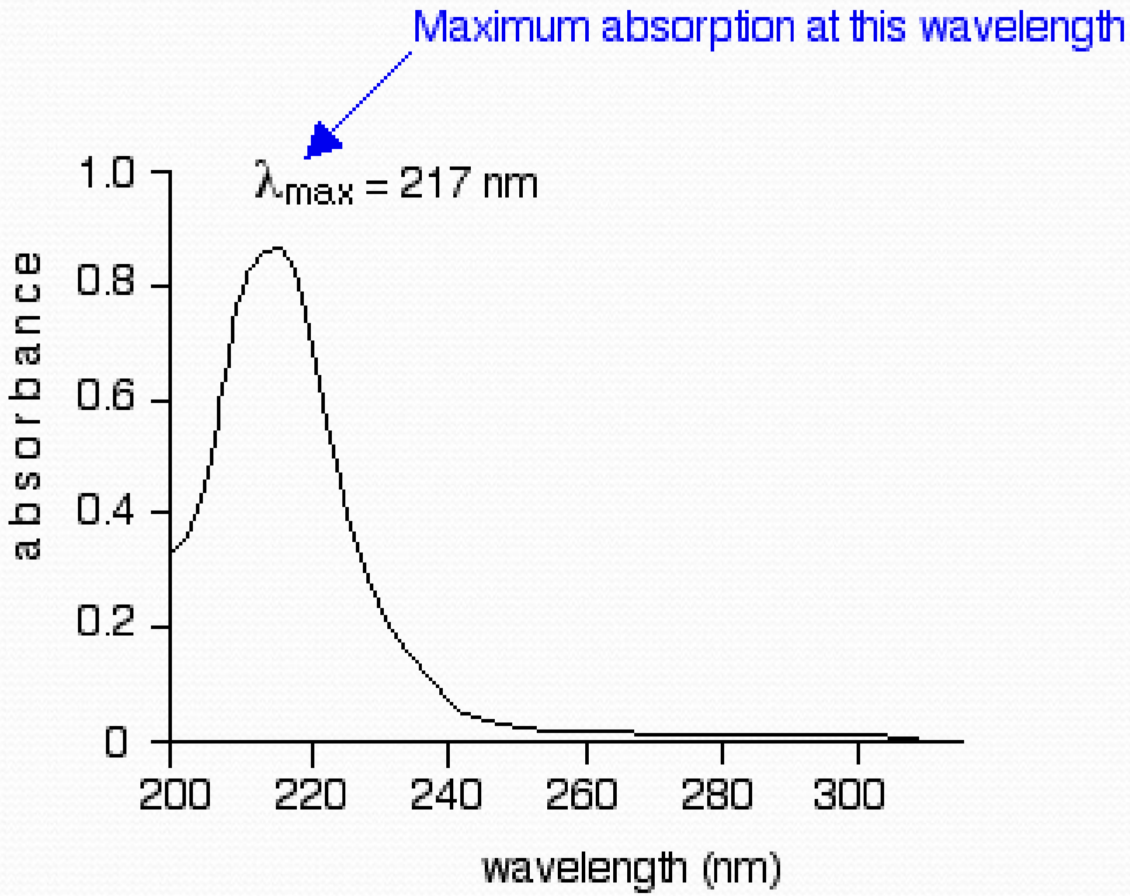
The absorption of light energy by organic compounds in the visible and ultraviolet region involves the promotion of electrons in σ, π, and n-orbitals from the ground state to higher energy states . This is also called Energy Transition. These higher energy states are molecular orbitals called antibonding.

Electronic Ground and Excitation States



The origin of UV Band structure

Because there are so many possible transitions in a molecule, each differing from the others by only a slight amounts, what is observed from these combined transitions is that the UV spectrum of a molecule consists of a broad band of absorption centered near the wavelenght of the major transition.



Maximum absorption at this wavelength

UV-spectra of butadienne

$A = \log(I_o/I) = \varepsilon c l$ for given wavelenght

A: Absorbance

Io: Intensity of light incident upon sample cell

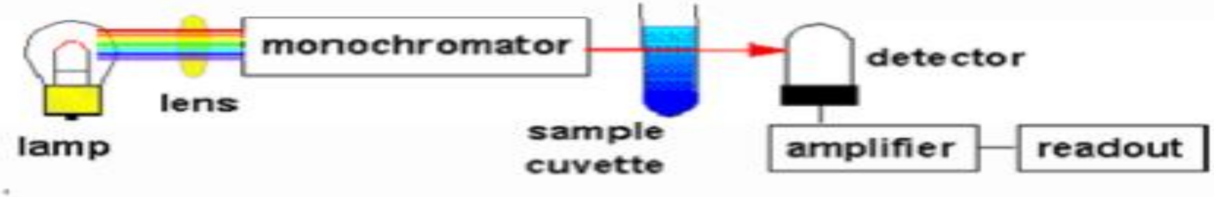
I: Intensity of light incident leaving sample cell

c: molar concentration of solute

l: length of a sample cell (cm)

ε: molar absorptivity (molar extinction coefficient)

Instrumentation



Solvents:

To choose a good solvent 3 points:

a)- it should not absorb UV radiation in the same region as the substance whose spectrum is being determined (ex: water, ethanol, hexane)

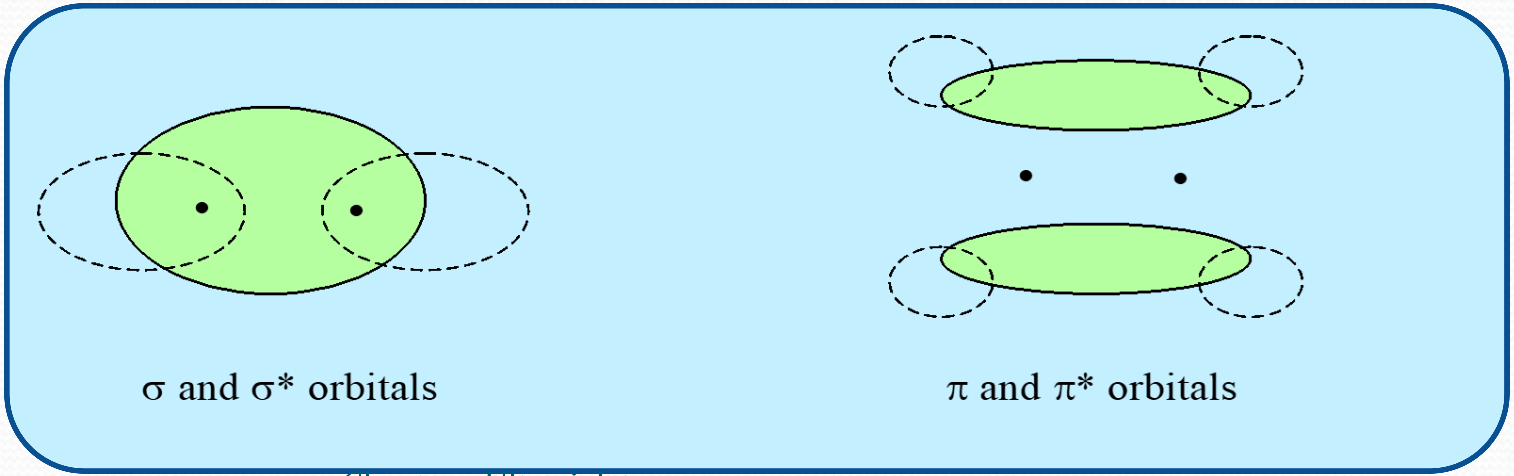
b)- It should not affect the fine structure of the band Polar solvent may form hydrogen bonding (solute-solvent complex) .

C)- Solvent may influence the wavelength. Polar solvent form hydrogen bond with the ground states of polar molecules, which increase the energy , and decrease λ of n to π* type transitions. Sometimes it form hydrogen bond with the excited state rather than the ground states, which decrease the energy, and increase λ value.

Chromophore

Chromophore is a functional group which absorbs a characteristic ultraviolet or visible region.

210 nm	Double Bonds
233 nm	Conjugated Diene
268 nm	Conjugated Triene
315 nm	Conjugated Tetraene



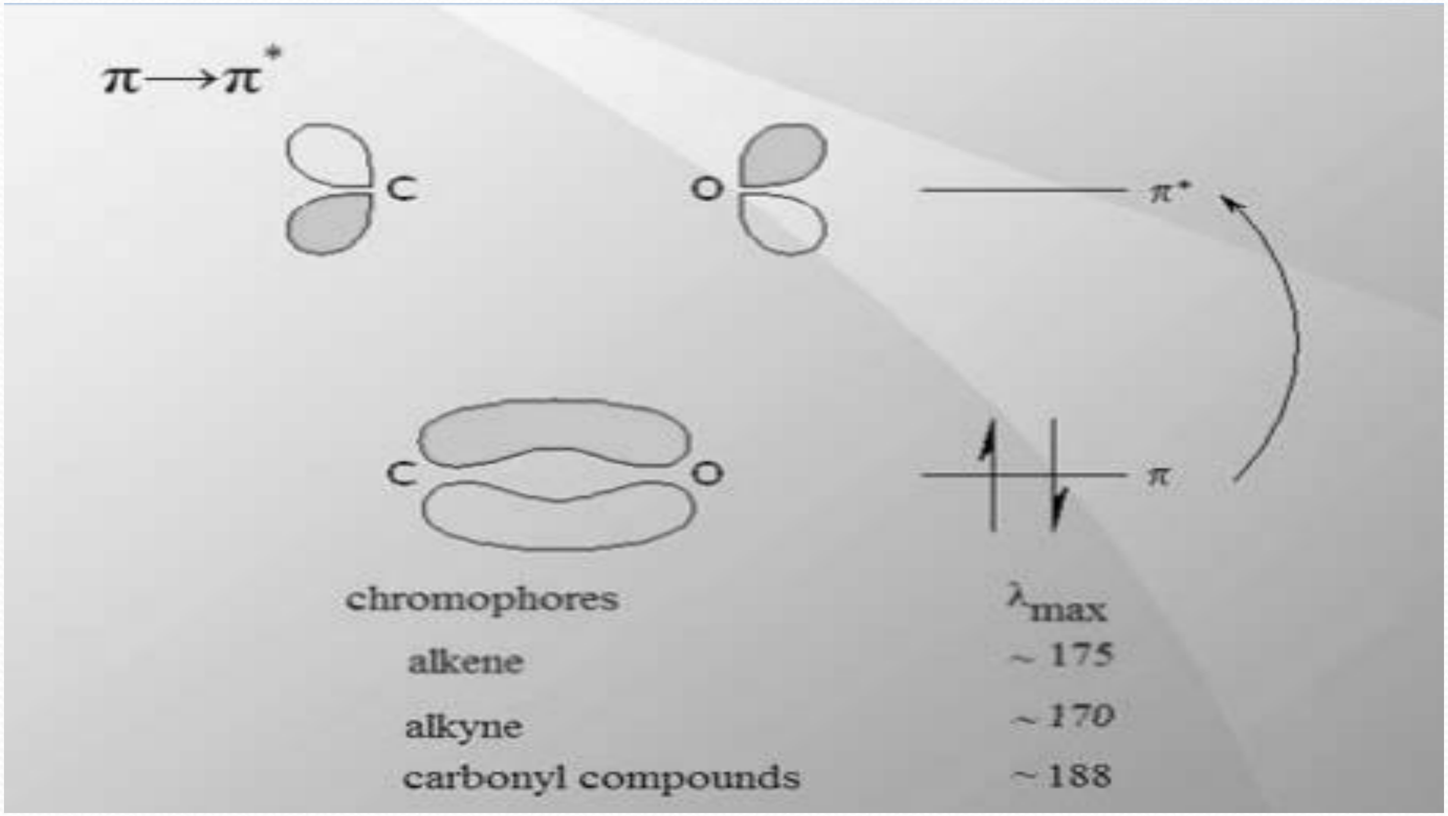
σ and σ* orbitals

π and π* orbitals

- ➢**There are several types of electronic transitions**
- ➢**available to a molecule including:**
  - ✓**σ to σ^* (alkenes)**
  - ✓**π to π^* (alkenes, carbonyl compounds, alkynes, azo**
  - ✓**compounds)**
  - ✓**n to σ^* (oxygen, nitrogen, sulfur, and halogen**
  - ✓**compounds)**
  - ✓**n to π (carbonyl compounds)**

✓**lcohols, ethers, amines and sulfur compounds, in saturated molecules that contain atoms bearing nonbonding pairs of electrons, transitions of n ð →**

lkenes π π^* transitions become possible.



chromophores	λ_{max}
alkene	~ 175
alkyne	~ 170
carbonyl compounds	~ 188

Auxochromes:

The attachment of substituent groups in place of hydrogen on the basic chromophore change the position and intensity of an absorption band. These substituents which increase the intensity and wavelength are called auxochromes.

Ex: Methyl, hydroxyl, alkoxy halogen, amino groups….

- **Other substituents may have any of four kinds of effects on the absorption :**

  1- Bathochromic shift (red shift): lower energy, longer λ.

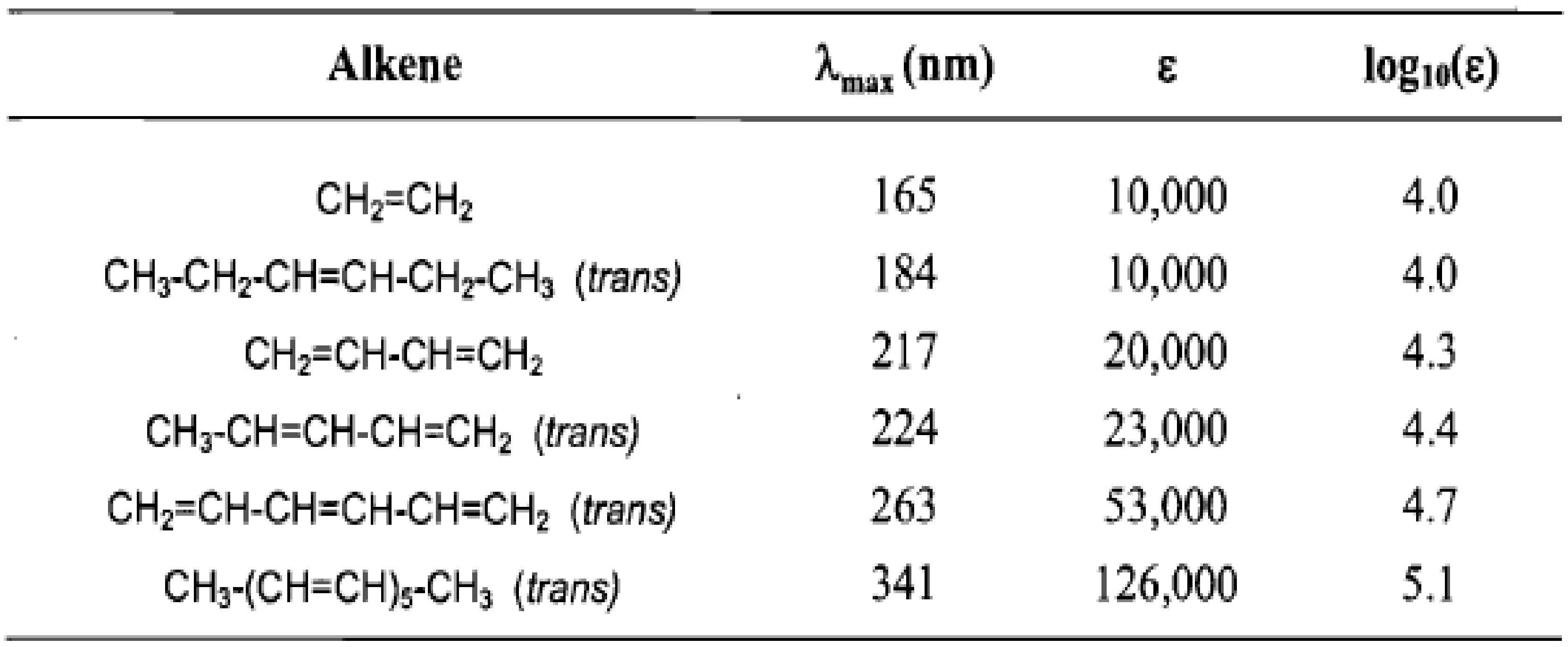
  2- hypsochromic shift (blue): higher energy, shorter λ.

  3- Hyperchromic effect: an increase in intensity.

  4- Hypochromic effect: a decrease in intensity.

the Woodward-Fieser Rules for Dienes

The effect of extended conjugation on Uv absorption



Alkene	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
$CH_2{=}CH_2$	165	10,000	4.0
$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$ (*trans*)	184	10,000	4.0
$CH_2{=}CH\text{-}CH{=}CH_2$	217	20,000	4.3
$CH_3\text{-}CH{=}CH\text{-}CH{=}CH_2$ (*trans*)	224	23,000	4.4
$CH_2{=}CH\text{-}CH{=}CH\text{-}CH{=}CH_2$ (*trans*)	263	53,000	4.7
$CH_3\text{-}(CH{=}CH)_5\text{-}CH_3$ (*trans*)	341	126,000	5.1

the Woodward-Fieser Rules for Dienes

conjugated dienes :

π→π* transition ε=20,000 to 26,000 λ =217 to 245nm

Butadiene and many simple conjugated dienes exist in a planar s-*trans* conformation.

Generally, alkyl substitution produces bathochromic shifts and hyperchromic effects .

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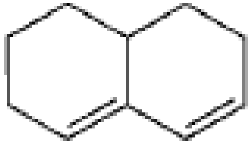
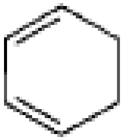


$\lambda_{max} = 214$ nm

$\varepsilon = 16{,}000$

$\log_{10}(\varepsilon) = 4.2$



$\lambda_{max} = 253$ nm

$\varepsilon = 8{,}000$

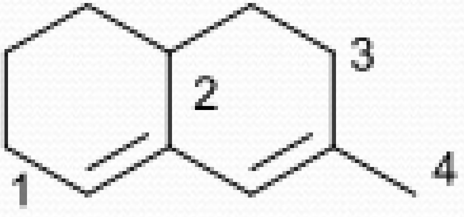
$\log_{10}(\varepsilon) = 3.9$

Cyclic dienes

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	λ=253 nm	λ =214 nm =217 (acyclic)
Increments for:		
Double bond extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
$-OC(O)CH_3$	0	0
-OR	6	6
-Cl, -Br	5	5
$-NR_2$	60	60
-SR	30	30

Examples

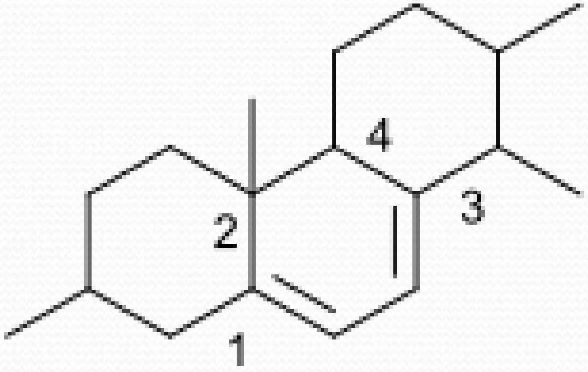
Absorption maximum : 214 + 20 + 5 = 239 nm



heteroannular diene : 214

alkyl substitutents 4 x 5 = 20

exocyclic double bond : 5



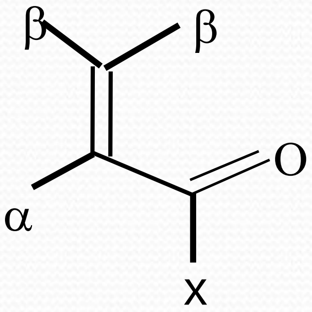
homoannular diene : 253

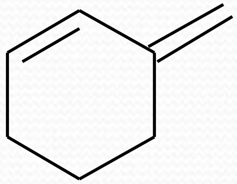
alkyl substituents : 4 x 5

exocyclic double bond : 2 x 5

Absorption maximum : 253 + 20 + 10 = 283 nm

Similar for Enones

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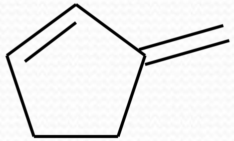
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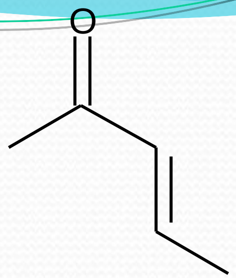
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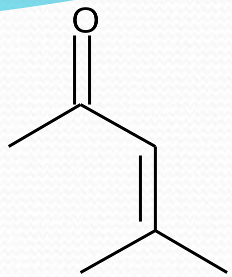
239

X=H 207

X=R 215

X=OH 193

X=OR 193

Base Values, add these increments…

	α	β	γ	δ,+
Extnd C=C	+30			
Add exocyclic C=C	+5			
Homoannular diene	+39			
alkyl	+10	+12	+18	+18
OH	+35	+30		+50
OAcyl	+6	+6	+6	+6
O-alkyl	+35	+30	+17	+31
NR_2				
S-alkyl				
Cl/Br	+15/+25	+12/+30		

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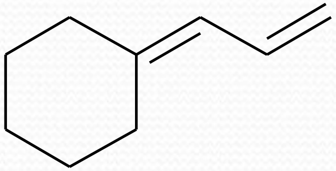
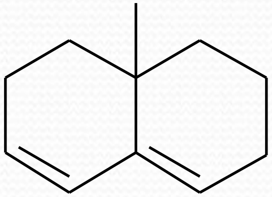
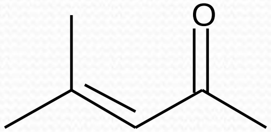


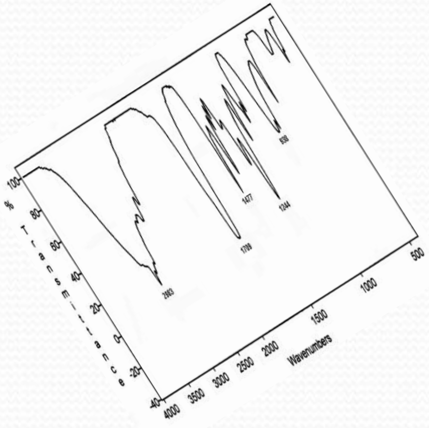
217 Base value
2 x alkyl subst.
10 exo DB
5 total
232 Obs.
237

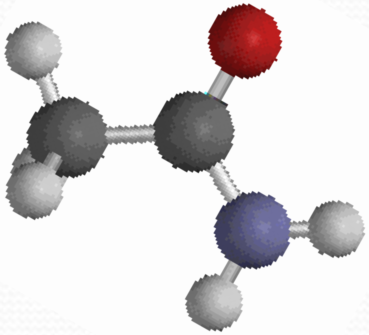


214 Base value
3 x alkyl subst.
30 exo DB
5 total
234 Obs.
235



215 Base value
2 ß alkyl subst.
24 total
239 Obs.
237





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