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Spectroscopic Techniques

are non-destructive and generally require small amounts of sample.

Four common spectroscopic techniques used to determine structure:

Ultraviolet Spectroscopy

Observes electronic transitions

Provides information on the electronic bonding in a molecule.

electronic UV-Vis

Infrared spectroscopy:

– Used to determine the functional groups present in a molecule

vibrational infrared

Mass spectrometry

Breaks molecule into fragments

Analysis of the masses of the fragments gives MW and clues to the structure of the molecule

Nuclear Magnetic Resonance Spectroscopy

– Observes the chemical environment of the hydrogen (or carbon) atoms in the molecule

• Helps provide evidence for the structure of the carbon skeleton and/or the alkyl groups present

nuclear spin radiofrequency

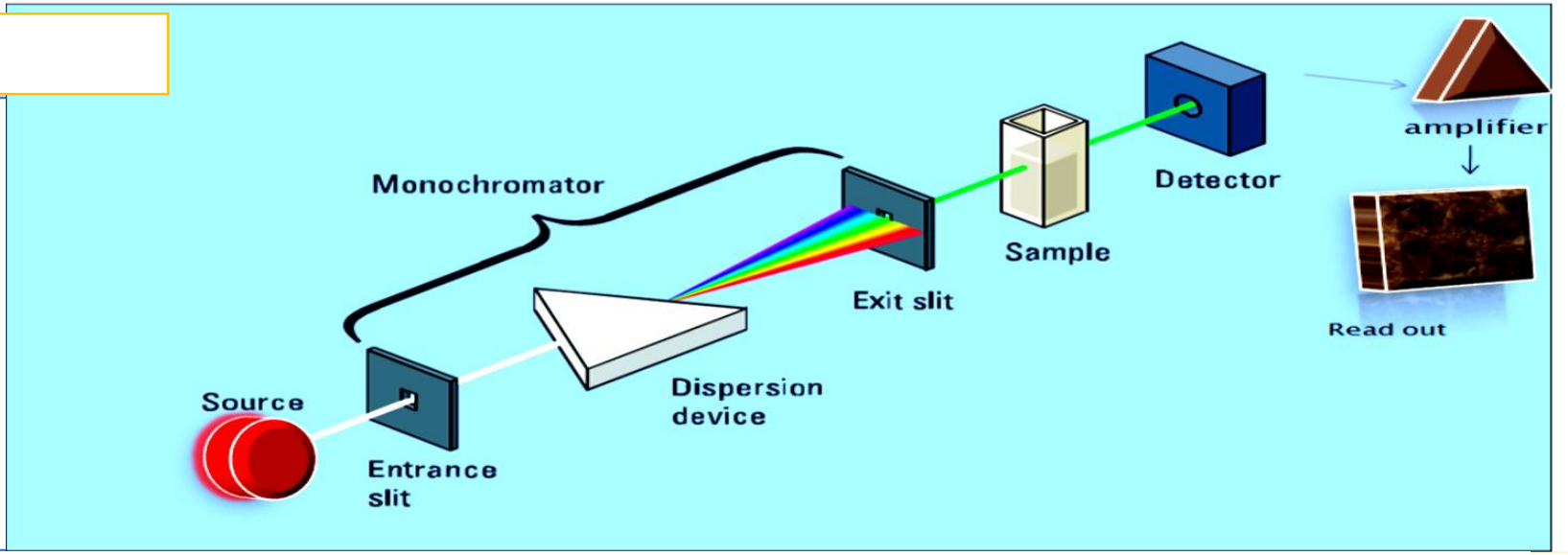
Ultra-violate spectroscopy

Ultraviolet and visible (UV-Vis)absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range.

INSTRUMENTATION

Components of spectrophotometer

- ❑Source
- ❑Monochromator
- ❑Sample compartment
- ❑Detector
- ❑Recorder

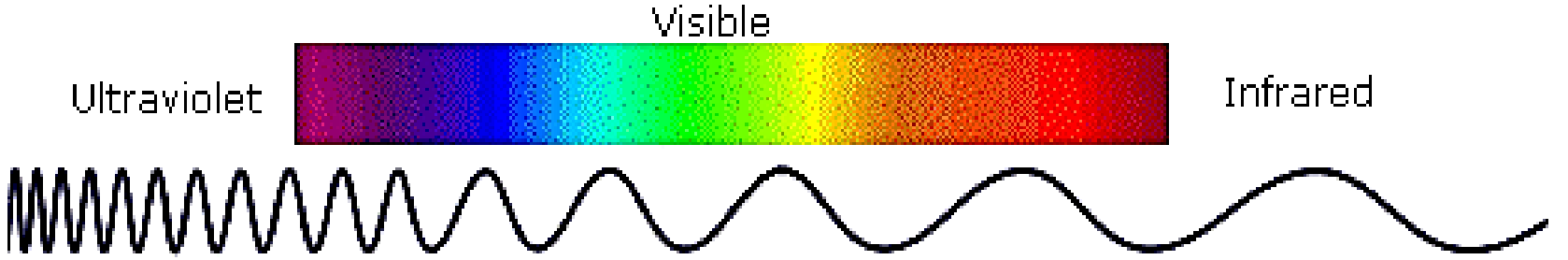


Why we use UV spectroscopy ?

- Detection of functional groups.
- Detection of impurities.
- Qualitative analysis.
- Quantitative analysis.
- Single compound without chromophore .
- Drugs with chromophoric reagent
- It is helps to show the relationship between different groups, it is useful to detect the conjugation of the compounds

UV RADIATION

The region beyond red is called infra-red while that beyond violet is called as ultra –violet. The wavelength range of uv radiation starts at blue end of visible light(4000Å) & ends at 2000A.



PRINCIPLE OF UV-VIS SPECTROMETRY

- A UV-Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum.
- A UV or visible spectrophotometer has the same basic design as an infrared spectrophotometer.
- In a standard UV-Vis spectrophotometer, a beam of light is split; one half of the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analyzed, and one half (the reference beam) is directed through an identical cell that does not contain the compound but contains the solvent.

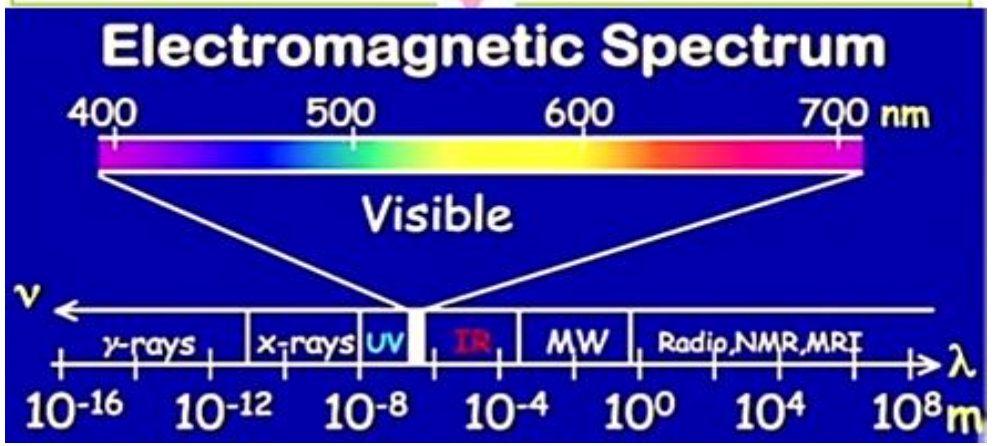
Solvents are chosen to be transparent in the region of the spectrum being used for analysis.

- The instrument is designed so that it can make a comparison of the intensities of the two beams as it scans over the desired region of the wavelengths.
- Absorption of radiation by a sample is measured at various wavelengths and plotted by a recorder to give the spectrum which is a plot of the wavelength of the entire region versus the absorption (A) of light at each wavelength.

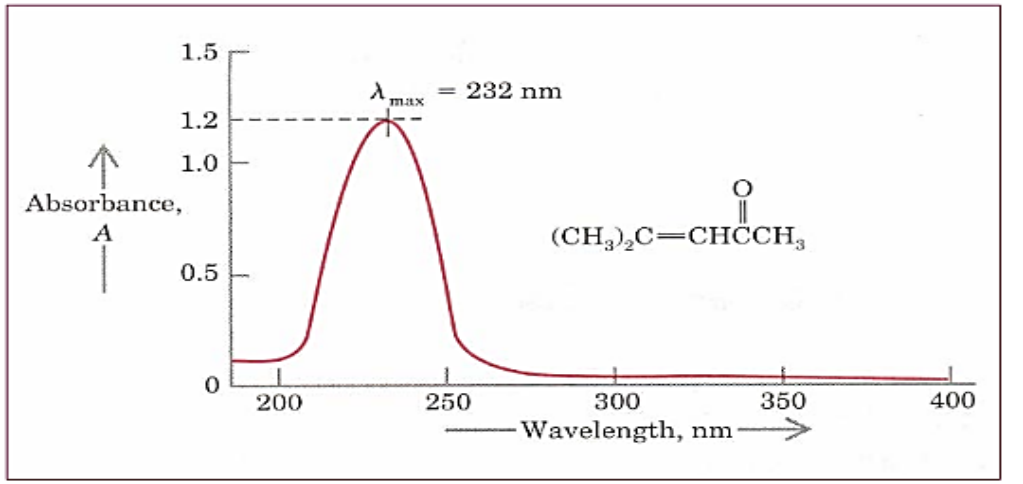
- λ max (wavelength at which there is a maximum absorption)
- ϵ max (The intensity of maximum absorption)constant(defined, no units)

UV radiation and Electronic Excitations

- This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum
- For comparison, recall the EM spectrum:



Expressions Used in Ultraviolet Spectrometry



- The spectrum shows that the scan is from 200-400 nm.
- ✓ Because absorption by atmospheric carbon dioxide becomes significant below 200 nm, the 100-200 nm region is usually not scanned unless special air-free techniques are employed.

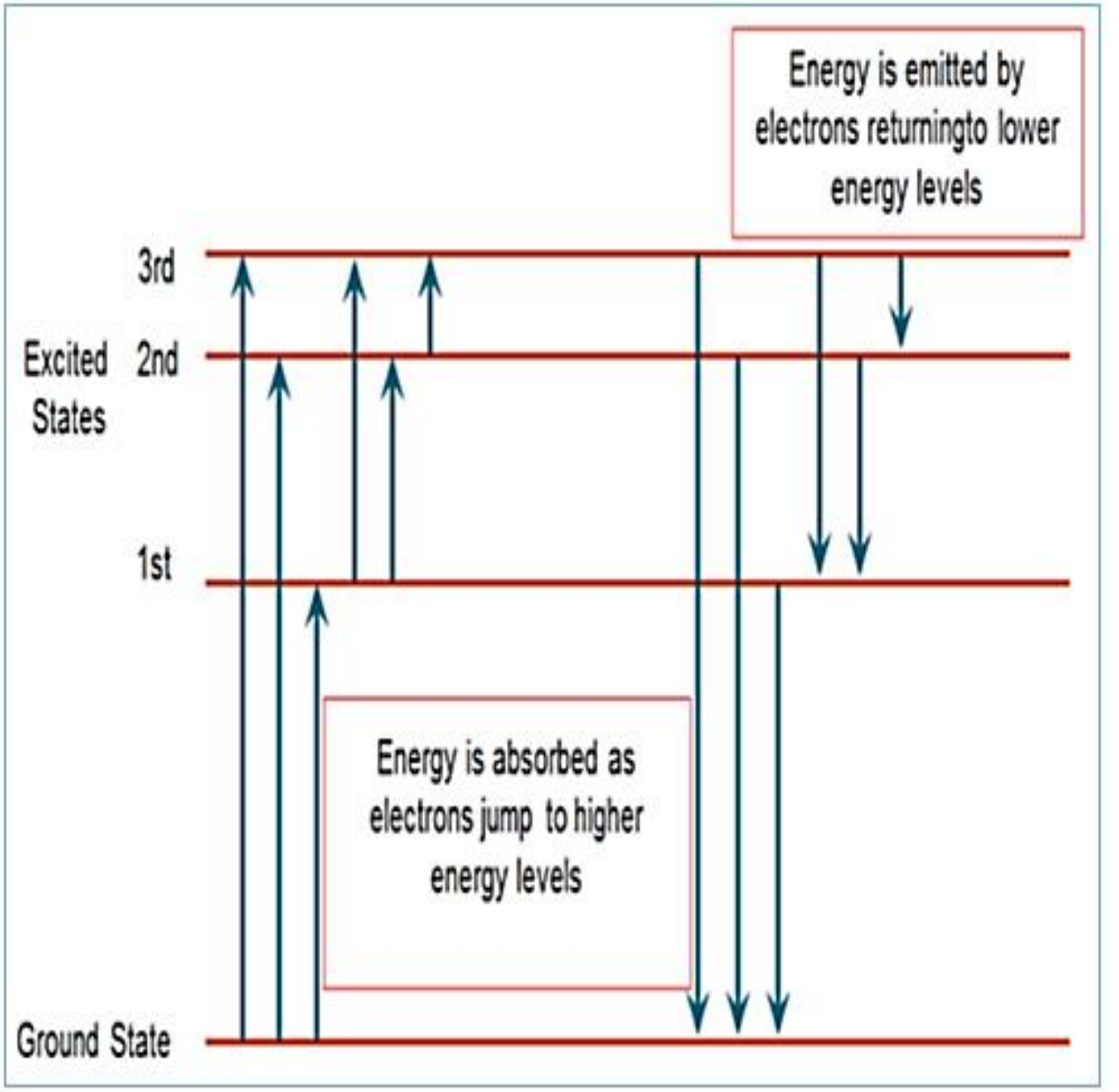
- The wavelength of absorption is usually reported as λ_{max} which represents the wavelength at the highest point of the curve.
- The absorption of energy is reported as absorbance (not transmittance as in infrared spectra).

What is Spectroscopy Techniques?

- The Spectroscopic Techniques are based on the fact that (Absorption) is directly proportional to the Concentration of the absorbing component .
- Utilises the **Absorption** and **Emission** of electromagnetic radiation by atoms.

Absorption: Low energy electrons absorb energy to move to higher energy level

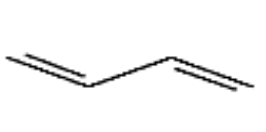
Emission: Excited electrons return to lower energy states.



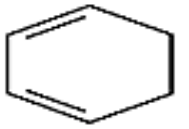
Partial structures :

❖ Strong UV (ε > 1000):-

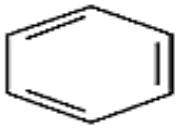
Conjugated π systems give ε > 1000.



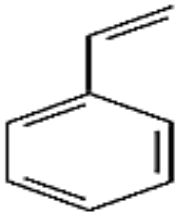
ε = 20, 900



ε = 4,580



ε = 8,000



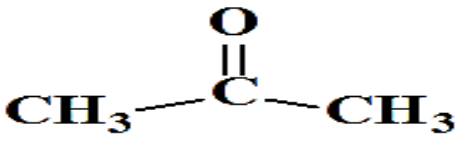
ε = 12,000

Q // If ε > 1000 , what kind of partial structure is indicated ?

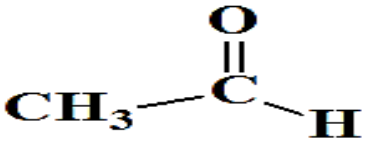
- ✓ The compound MUST CONTAIN a conjugated π system.
- ✓ It might be aromatic (like benzene).
- ✓ It might be a conjugated polyene (like 1,3-butadiene).

❖ Weak UV (ε < 100):

-Aldehydes or Ketones give e < 100



acetone ε = 19



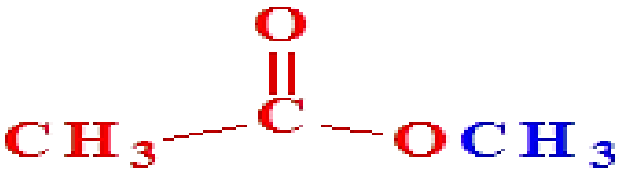
acetaldehyde ε = 12

Q// If ε < 100 , what kind of partial structure is indicated ?

- ✓ The compound must have an aldehyde or ketone carbonyl.
- ✓ There is no heteroatom next to the carbonyl carbon (only C or H).

❖ UV End Absorption (No ε) **Esters give end absorption**

methyl acetate



Q// If UV = end absorption, what partial structure is indicated?

- ✓ A carbonyl group with an Oxygen atom next to the carbonyl carbon is indicated.

- The wavelength of UV or visible light absorbed depends on the ease of electron promotion.
- Molecules that require more energy for electron promotion absorb at shorter wavelengths.

absorption at 100 nm (UV) ⟶ 750 nm (visible)

increasing ease of electronic transition

- The absorbance at a particular wavelength is defined by the equation:

$$A = \log \frac{I_0}{I}$$

where A = absorbance

I_0 = intensity of the reference beam

I = intensity of the sample beam

- The absorbance by a compound at a particular wavelength increases with an increasing number of molecules undergoing transitions.

Therefore, the absorbance depends on:

- the electronic structure of the compound.
- the concentration of the sample.
- the length of the sample cell.

- a longer path length, I through the sample will cause more UV light to be absorbed – linear effect
- the greater the concentration, C of the sample, the more UV light will be absorbed – linear effect

These effects are combined into the Beer-Lambert Law: $A = \varepsilon c l$

for most UV spectrometers , (|) would remain constant (standard cells are typically 1 cm in path length)

concentration is typically varied depending on the strength of absorption observed or expected – typically dilute – sub .001 M

molar absorptivities vary by orders as:

values of (104-106) → are termed high intensity absorptions.
values of (103-104) → are termed low intensity absorptions.
values of (0 to 103) → are the absorptions of forbidden transitions.

A is unitless , so the units for ε are $cm^{-1} \cdot M^{-1}$ and are rarely expressed

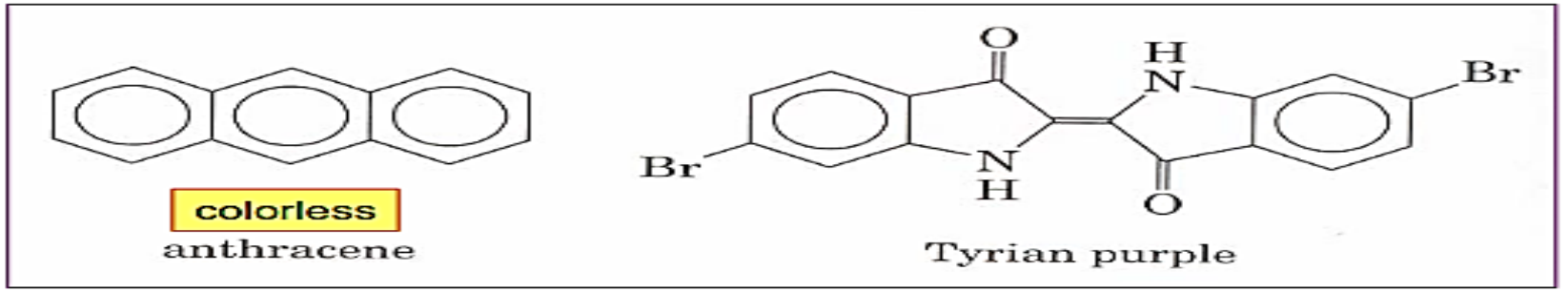
Since path length and concentration effects can be easily factored out, absorbance simply becomes proportional to ε, and the y-axis is expressed as ε directly or as the logarithm of ε

- Ultraviolet absorption spectra arise from transition of electron with in a molecule from a lower level to a higher level.

E total = E electronic + E vibrational + E rotational

The energies decreases in the following order: Electronic ⩾Vibrational ⩾ Rotational

- Compounds that absorb light in the visible region (that is colored compounds) have more-easily promoted electrons than compounds that absorb at shorter UV wavelengths.



- Although the energy absorption by a molecule is quantized, a UV or visible spectrum consists of not a spectrum of lines or sharp peaks but rather of broad absorption bands over a wide range of wavelength.
- The reason for the broad absorption is that the energy levels of both the ground state and the excited state of a molecule are subdivided into rotational and vibrational sublevels.

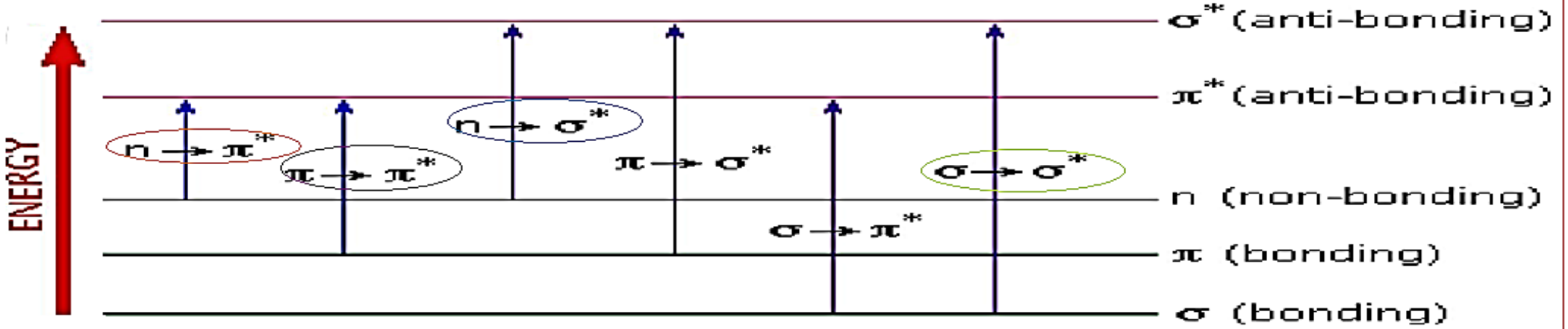
Types of Electron Transitions

- The ground state of an organic molecule contains valence electrons in three principal types of molecular orbitals: sigma (σ) orbitals; pi (π) orbitals; and filled but nonbonded orbitals (n).

- Both σ and π orbitals are formed from the overlap of two atomic or hybrid orbitals. Each of these molecular orbitals therefore has an antibonding σ^* or π^* orbital associated with it.
- An orbital containing *n* electrons does not have an antibonding orbital (because it was not formed from two orbitals).

- Electron transitions involve the promotion of an electron from one of the three ground states (σ, π, or n) to one of the two excited states ($\sigma*$, or $\pi*$).
- There are six possible transitions; the four important transitions and their relative energies are:

The possible electronic transitions can graphically shown as:



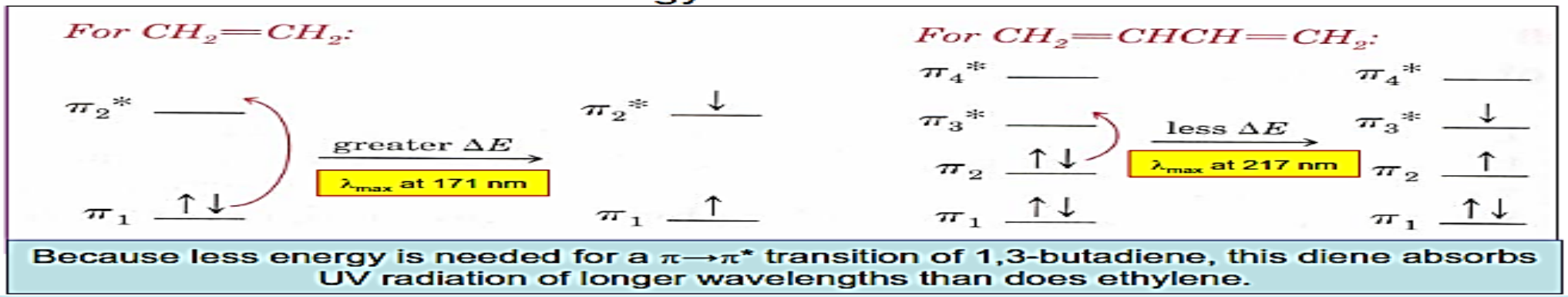
- The most useful region of the UV spectrum is at wavelengths longer than 200 nm.
- The following transitions give rise to absorption in the nonuseful 100–200 nm range:
  - $\pi \longrightarrow \pi^*$ for an isolated double bond, and
  - $\sigma \longrightarrow \sigma^*$ for an ordinary carbon-carbon bond.
- The useful transitions (200 nm–400 nm) are $\pi \longrightarrow \pi^*$ for compounds with conjugated double bonds, and some $n \longrightarrow \sigma^*$ and some $n \longrightarrow \pi^*$ transitions.
- Alkenes and nonconjugated dienes usually have absorption maxima below 200 nm.

➢ ***Example:***
- Ethene gives an absorption maximum at 171 nm,
- 1,4-pentadiene gives an absorption maximum at 178 nm.

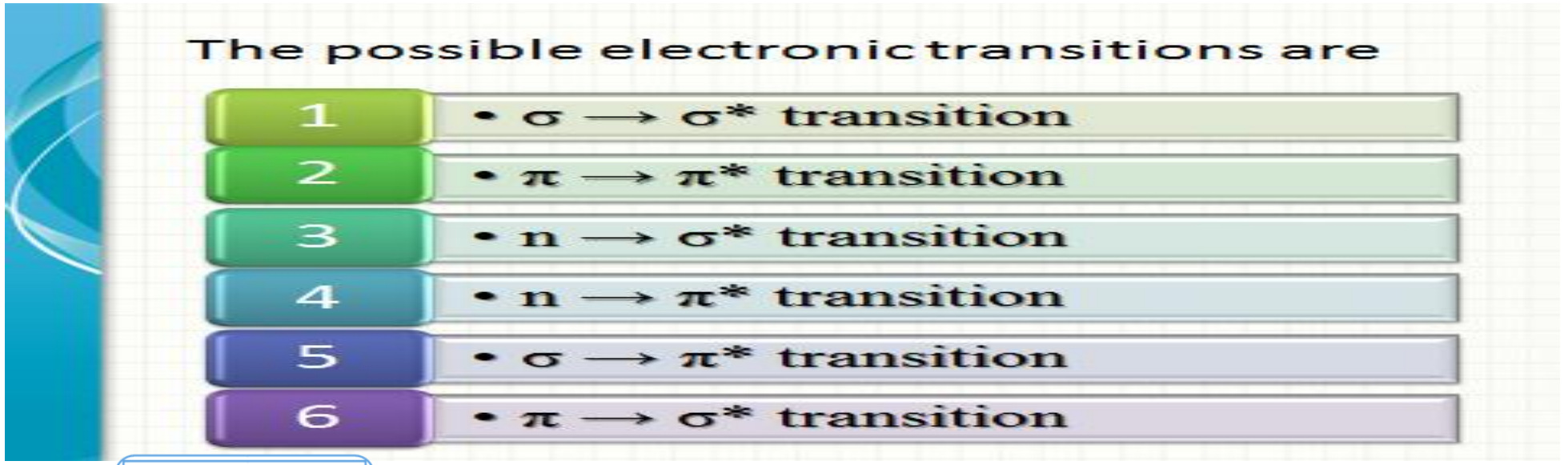
highest occupied molecular orbital (HOMO)
lowest unoccupied molecular orbital (LUMO)

➢ Absorption by Polyenes

- Compounds whose molecules contain conjugated multiple bonds have absorption maxima at wavelengths longer than 200 nm.
- For example, less energy is required to promote a π electron of 1,3-butadiene than is needed to promote a π electron of ethylene.
- The reason is that the energy gap between the HOMO and the LUMO for conjugated double bonds is less than the energy difference for an isolated double bond.
- Resonance-stabilization of the excited state of a conjugated diene is one factor that decreases the energy of the excited state.



Because less energy is needed for a $\pi \longrightarrow \pi^*$ transition of 1,3-butadiene, this diene absorbs UV radiation of longer wavelengths than does ethylene.



1 • σ → σ* transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.
- The energy required is large for this transition.
- e.g. Methane (CH_4) has C-H bond only and can undergo σ → σ* transition and shows absorbance maxima at 125 nm.

Q. The energy required is the highest one forσ → σ* transition ?

ANS. All saturated alkane need highest energy, so they show shortest wave length, with an exception Cyclopropane because of ring strength which give normal UV region above 200 nm.

2 • $\pi \rightarrow \pi^*$ transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.

3 • $n \rightarrow \sigma^*$ transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of $n \rightarrow \sigma^*$ transition.
- These transitions usually requires less energy than $\sigma \rightarrow \sigma^*$ transitions.
- The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in UV region is small (150 – 250 nm).

4 • $n \rightarrow \pi^*$ transition

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.
- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.
- $n \rightarrow \pi^*$ transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5 • $\sigma \rightarrow \pi^*$ transition

& • $\pi \rightarrow \sigma^*$ transition 6

- These electronic transitions are forbidden transitions & are only theoretically possible.
- Thus, n → π* & π → π* electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.
- The UV spectrum is of only a few broad of absorption.

Note:

Energy ↑

δ to δ*
n to δ*
π to π*
n to π*

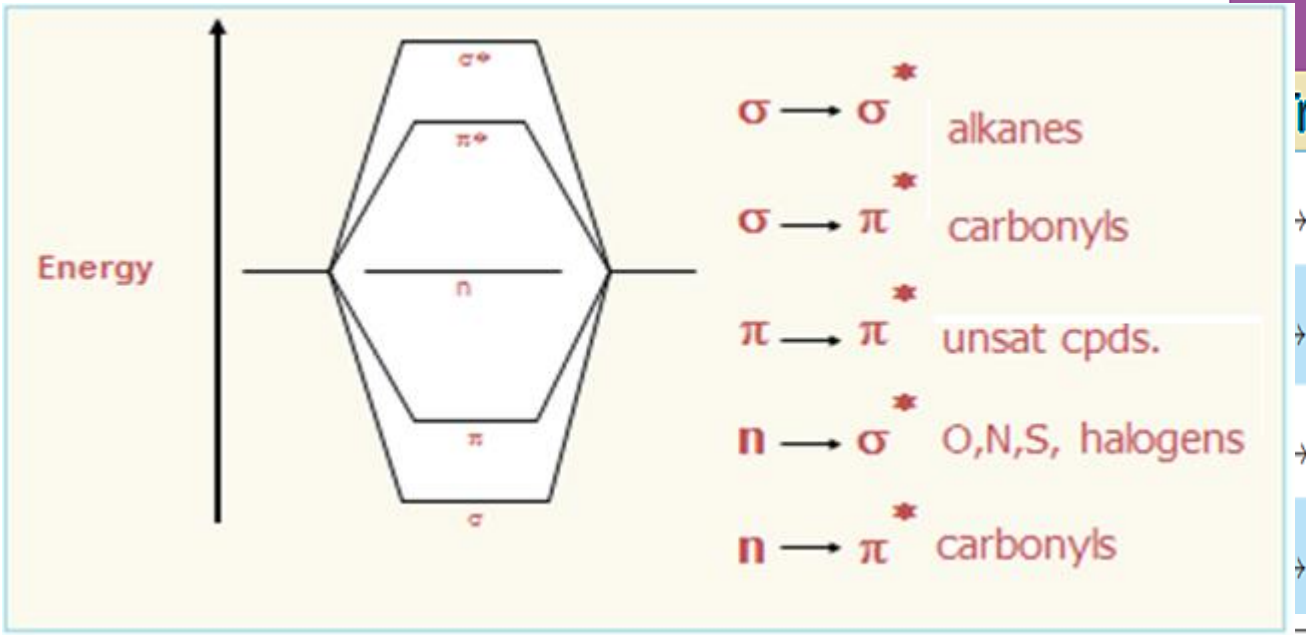
↓ λ max
Wave Strength

Band Structure

In molecules, when a bulk sample of molecules is observed, not all bonds (read – pairs of electrons) are in the same vibrational or rotational energy states

This effect will impact the wavelength at which a transition is observed – very similar to the effect of H-bonding on the O-H vibrational energy levels .

Observed electronic transitions



Electronic Transitions Involving *n*, σ, and π Molecular Orbitals

Transition	Wavelength Range	Examples
→ σ*	<200 nm	C–C, C–H
→ σ*	160–260 nm	H_2O, CH_3OH, CH_3Cl
→ π*	200–500 nm	C=C, C=O, C=N, C≡C
→ π*	250–600 nm	C=O, C=N, N=N, N=O

CH_4 σ ⟶ σ*

$CH_2=CH_2$ σ ⟶ σ* π ⟶ π*

CH_3-(R) C=O 1-σ ⟶ σ* 2- π ⟶ π*

3- n ⟶ σ* 4- n ⟶ π*

$CH_2=CH-OH$ $CH_2=CH-CH_2-OH$

As the above example (1-4) **As the above example (1-3) no 4 x**

π−π∗ Transition is the most convenient and useful transition in UV-Vis Spectroscopy. Why?

In σ−σ* transitions :

- The high energy required can cause rupture of the s bonds and breakdown of the molecule.
- Air components absorb in vacuum UV which limits the application of the method ,working in vacuum UV requires special training
- Special sources and detectors.
- All solvents contain σ bonds

In n-σ* transitions :

- The absorption wavelength for a n-σ * transition occurs at about 185 nm where, unfortunately, most solvents absorb. For example, water which has two pairs of nonbonding electrons that will strongly absorb as a result of the n-σ * .(H2O and other solvents with nonbonding electrons).
- in polar solvents the energy required for the n-σ* increases and thus the probability for the transition decreases.

In n-π* transitions :

- requires very little energy , However, unfortunately, the absorptivity of this transition is very small which precludes its use for sensitive quantitative analysis.
- using polar solvents increases the energy required for this transition, thus decreasing its probability.

In π−π* transitions : The most frequently used transition is the π−π* transition for the following reasons:

- The molar absorptivity for the π−π* transition is high allowing sensitive determinations.
- The energy required is moderate, far less than dissociation energy.
- In presence of the most convenient solvent (water), the energy required for a π−π* transition is usually smaller.

ABSORBANCE LAWS

BEER'S LAW

" The intensity of a beam of monochromatic light decrease exponentially with the increase in concentration of the absorbing substance" .

Lambert's law:

the intensity of the transmitted light decreases as the thickness of the layer increases

Beer's law: the absorption is proportion to the numbers of the absorbing molecules.

- Beer's law doesn't hold over the entire concentration range, it's operate in very dilute solution only.
- At concentrated solution we have +ve or _ve deviation which may be due to:

1. Association of the molecules.
2. The formation of the complex.
3. Change in the refracting index of the solution.

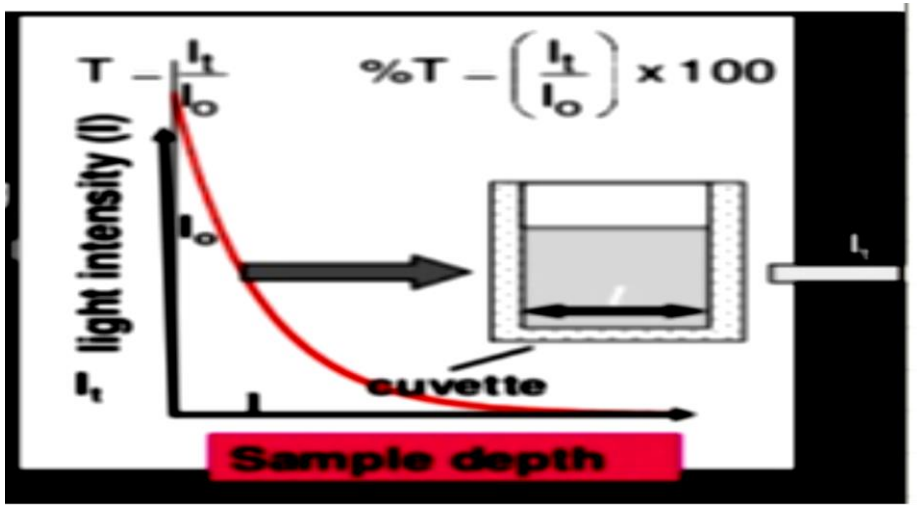
These laws can be represented by this relationship:

The measurement of light absorption by a solution of molecules is governed by the Beer-Lambert Law, which is written as follows:

$$\log I_o/I_t = A = \varepsilon\, b\, c$$

where I_o is the intensity of incident radiation, I_t is the intensity of transmitted radiation; A is known as the absorbance and is a measure of the amount of light absorbed by the sample; ε is a constant known as the molar extinction coefficient and is the absorbance of a 1M solution of the analyte, b is the pathlength of the cell in cm, usually 1 cm and c is the concentration of the analyte in moles liter^{-1}.

$E_{1cm}^{1\%}$?



Q. A 5.00 × 10–4 M solution of an analyte is placed in a sample cell with a pathlength of 1.00 cm. When measured at a wavelength of 490 nm, the solution's absorbance is 0.338. What is the analyte's molar absorptivity at this wavelength?

SOLUTION

$$\varepsilon = \frac{A}{bC} = \frac{0.338}{(1.00\ \text{cm})(5.00\times10^{-4}\ \text{M})} = 676\ \text{cm}^{-1}\ \text{M}^{-1}$$

In pharmaceutical products, concentrations and amounts are usually expressed in grams or milligrams rather than in moles and, thus, for the purposes of the analysis of these products, the Beer-Lambert equation is written in the following form:

$$A = A\ (1\%,\ 1\ \text{cm})\ bc$$

where A is the measured absorbance; A (1%, 1 cm) is the absorbance of a 1% w/v (1 g/100 ml) solution in a 1 cm cell; b is the pathlength in cm (usually 1 cm); and c is the concentration of the sample in g/100 ml. Since measurements are usually made in a 1 cm cell, the equation can be written:

$$\left[c = \frac{A}{A(1\%, 1\ \text{cm})}\right]$$

which gives the concentration of the analyte in g/100 ml.

Applications in pharmaceutical analysis

- A robust, workhorse method for the quantification of drugs in formulations where there is no interference from excipients.
- Determination of the p*K*a values of some drugs.
- Determination of partition coefficients and solubilities of drugs.
- Used to determine the release of drugs from formulations with time, e.g. in dissolution testing.
- Can be used to monitor the reaction kinetics of drug degradation.
- The UV spectrum of a drug is often used as one of a number of pharmacopoeial identity checks.

Strengths

- An easy-to-use, cheap and robust method offering good precision for making quantitative measurements of drugs in formulations
- Routine method for determining some of the physico-chemical properties of drugs which need to be known for the purposes of formulation
- Some of the problems of the basic method can be solved by the use of derivative spectra.

LIMITATION OF LAWS

- The real limitation of the beer's law is successfully in describing the absorption behavior of dilute solution only.
  - In this regarding it may be considered as a limiting law.
- As degree of interaction depends upon the contraction, the occurrence of this phenomenon causes deviations from linear relationship between absorbance and contraction.

CHROMOPHORE

The part of a molecule responsible for imparting color, are called as chromospheres.

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions. e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

To interpretate UV – visible spectrum following points should be noted:

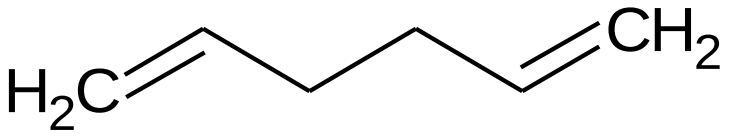
1. Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.

2. Non-conjugated carbonyl group compound give a weak absorption band in the 200 - 300 nm region.

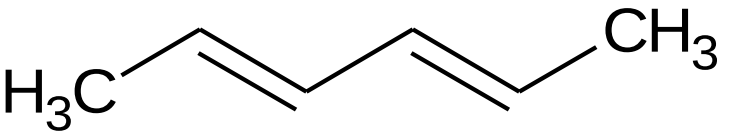
Chromophore

When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm



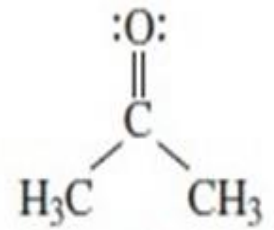
2,4 - hexadiene has λ_{max} = 227 nm



Effect of Conjugation on λ_{max}

The n→π* transition for methyl vinyl ketone is at 331 nm, and the π→π* transition is at 203 nm. Both λ_{max} values are at longer wavelengths than the corresponding λ_{max} values of acetone because methyl vinyl ketone has two conjugated double bonds.

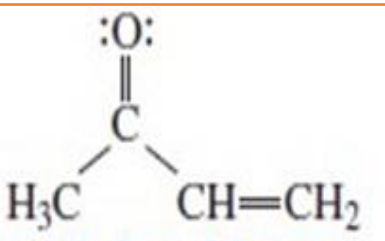
"The λ_{max} increases as the number of conjugated double bonds increases."



acetone

$n \longrightarrow \pi^*$ λ_{max} = 274 nm (ε_{max} = 13.6)

$\pi \longrightarrow \pi^*$ λ_{max} = 195 nm (ε_{max} = 9000)



methyl vinyl ketone

λ_{max} = 331 nm (ε_{max} = 25)

λ_{max} = 203 nm (ε_{max} = 9600)

The more conjugated double bonds there are in a compound, the less energy is required for the electronic transition, and therefore the longer is the wavelength at which the electronic transition occurs.

Auxochrome

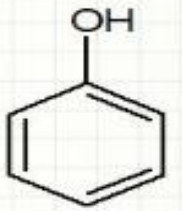
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

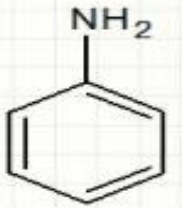
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

e.g. Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm



If the group attached to the ring bears *n* electrons, they can induce a shift in the primary and secondary absorption bands

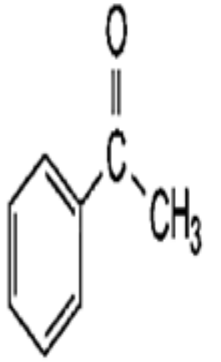
Increase λmax. Of E1 (not appear)
E2 (shorter to appear)
& B with increase E max.
Or stable and loss its fine structure

→ Bathochromic Shift (Red Shift)

Another method of classification uses the symbols:

B	(for benzenoid)	R	(for radical-like)
E	(for ethylenic)	K	(for conjugated)

A molecule may give rise to more than one band in its UV spectrum, either because it contains more than one chromophore or because more than one transition of a single chromophore is observed.



acetophenone

λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$	Assignment	
244	12,600	4.1	$\pi \rightarrow \pi^*$	K
280	1,600	3.2	$\pi \rightarrow \pi^*$	B
317	60	1.8	$n \rightarrow \pi^*$	R

B band (Benzene band, Benzenoid bands) from the π → π* transition of Benzene. Broad band with fine structure between 230 – 270 nm. This band can be used to identify aromatic compound.

E band (Ethylenic bands) also from π → π* transition of ethylenic band in benzene
E1 band and E2 band

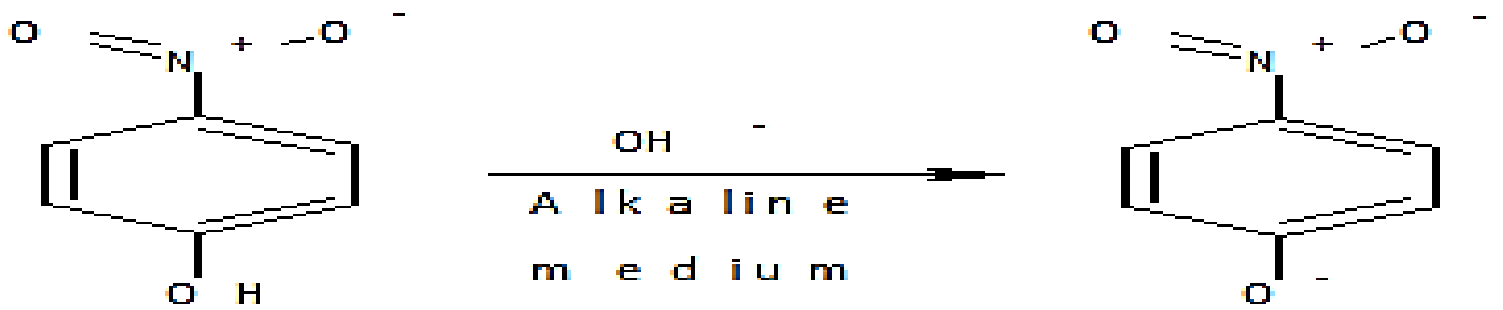
R band originated from *n* - π* transition transition.
The maximum absorption wavelength > 270 nm, $\epsilon_{max} < 100$
Example: Acetone λ_{max} 279 nm, $\epsilon_{max} = 15$

K band (conjugation band, form π → π* transition.
High ϵ_{max} (> 10^4)
Example: Dienes , Acetophenone

1 • Bathochromic Shift (Red Shift)

- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an auxochrome or by the change of solvent.
- e.g. An auxochrome group like –OH, -OCH_3 causes absorption of compound at longer wavelength.

- In alkaline medium, *p*-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.

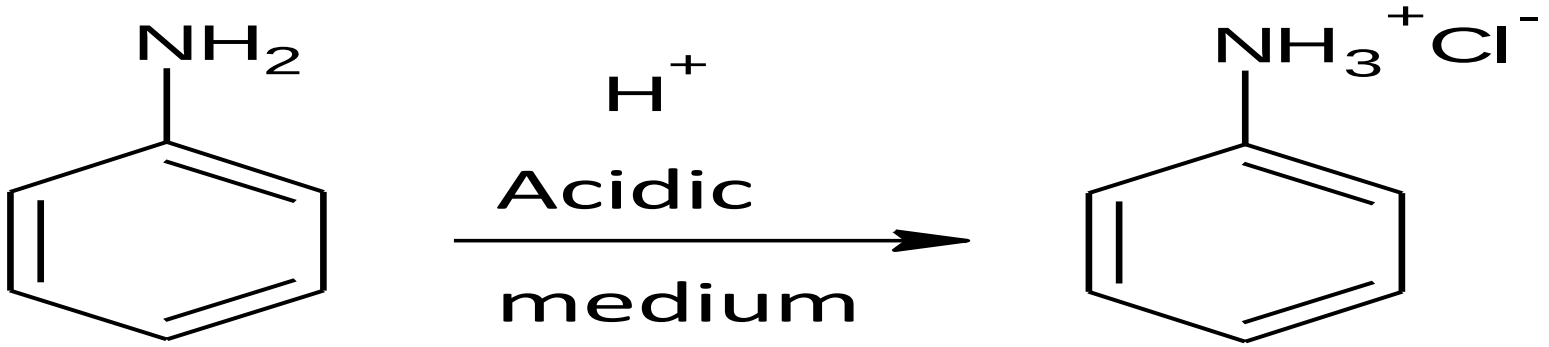


2 • Hypsochromic Shift (Blue Shift)

- When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.

- **Aniline shows blue shift in acidic medium, it loses conjugation.**



Aniline

λ_{max} = 280 nm

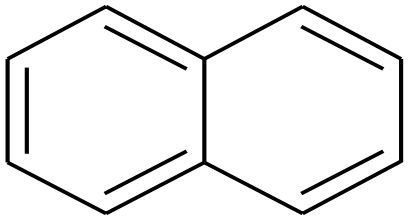
λ_{max} = 265 nm

3 • Hyperchromic Effect

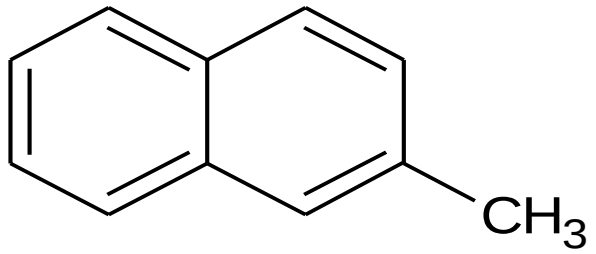
- When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.
- If **auxochrome** introduces to the compound, the **intensity** of absorption **increases.**

4 • Hypochromic Effect

- When absorption intensity (ε) of a compound is decreased, it is known as hypochromic shift.

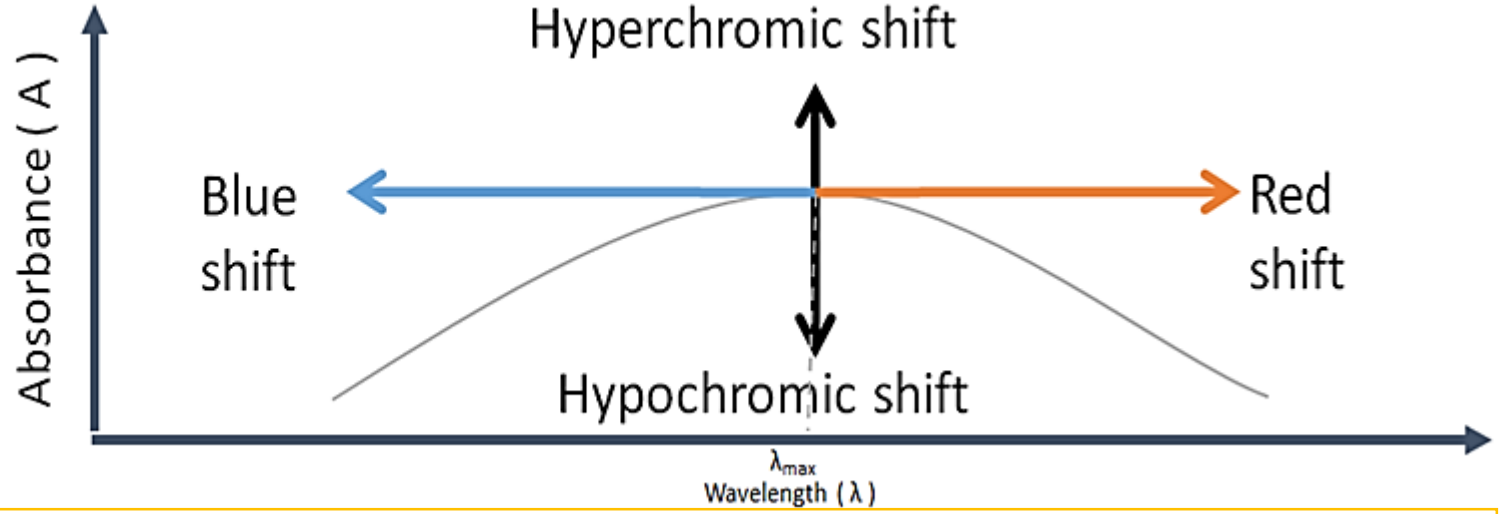


Naphthalene
ε = 19000



2-methyl naphthalene
ε = 10250

Shifts and Effects



Factors affecting UV/Vis absorption :

Biochemical samples are usually buffered aqueous solutions, which has two major advantages.

- Firstly, proteins and peptides are comfortable in water as a solvent, which is also the 'native' solvent. Secondly, in the wavelength interval of UV/Vis (700–200 nm) the water spectrum does not show any absorption bands and thus acts as a silent component of the sample.
- The absorption spectrum of a chromophore is only partly determined by its chemical structure.
- The environment also affects the observed spectrum, which mainly can be described by three parameters :
  - protonation/deprotonation (pH, RedOx).
  - solvent polarity (dielectric constant of the solvent).
  - orientation effects.

❖ Protonation/deprotonation :

- arises either from : changes in pH or oxidation/reduction reactions

which makes chromophores pH- and RedOx-sensitive reporters.

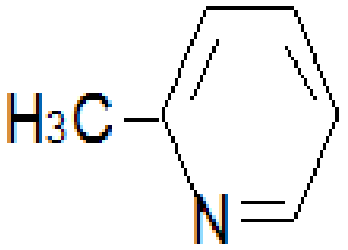
- As a rule of thumb, λ max and ε increase i.e. the sample displays a bathe- and hyperchromic shift, if a group becomes charged.

Substituent Effects

General - only the weak : $n \rightarrow \pi^*$ transition occurs in the routinely observed UV

- The attachment of substituent groups (other than H) can shift the energy of the transition.
- Substituents that increase the intensity and often wavelength of an absorption are called auxochromes.
- Common auxochromes include alkyl, hydroxyl, alkoxy and amino groups and the halogens.

- ❖ solvent polarity: Affects the difference between the ground and excited states
- ➢ when shifting to a less polar environment one observes a Bathochromic Shift (Red Shift)- and hyperchromic effect.
- ➢ a solvent with higher polarity elicits a Hypsochromic Shift (Blue Shift)
- ➢ - and hypochromic effect
- ➢ Lastly, orientation effects, such as an increase in order of nucleic acids from single stranded to double-stranded DNA, lead to different absorption behaviour.



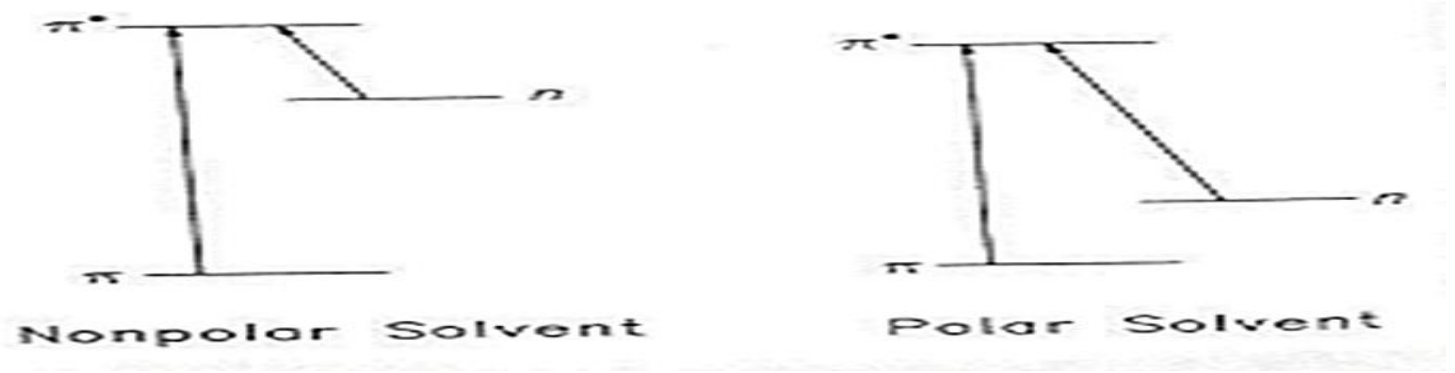
Absorption characteristics of 2-methylpyridine

Solvent	λ_{max}	ε_{max}
Hexane	260	2000
Chloroform	263	4500
Ethanol	260	4000
Water	260	4000
Ethanol - HCl (1:1)	262	5200

- ➢ **The solvent should be UV transparent at the measuring wavelength so as not to cause interference which could affect quantitative results.**

π ➡ π* transitions leads to more polar excited state that is more easily stabilized by polar solvent associations (H-bonds). The **π* state** is more polar and stabilized more in polar solvent relative to nonpolar one, thus in going from nonpolar to polar solvent there is a **red shift** or bathochromic shift (increase in λ_{max}, decrease in ΔE).

For n ➡ π* transition, the **n state** is much more easily stabilized by polar solvent effects (H-bonds and association-solvation of the lone pair), so in going from nonpolar to polar solvent there is a **blue shift** or hypsochromic shift (decrease in λ_{max}, increase in ΔE). (same with n → σ* transition)



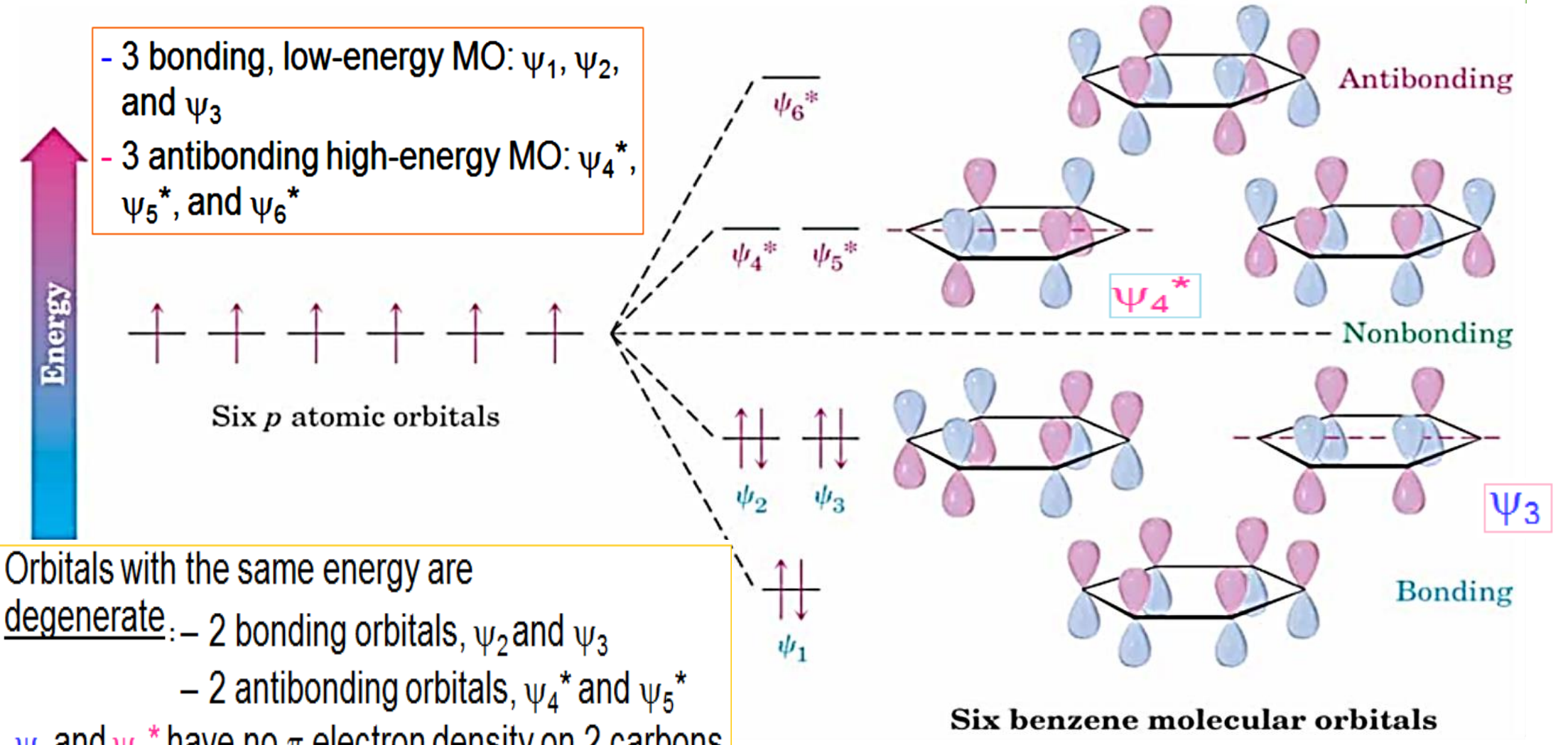
- Ground state polar > Excited state λ max decrease with increase solvent polarity.
- Ground state < Excited state λ max increase with increase solvent polarity.

Aromatic Compounds

1.General Features

benzene has six π-MOs, 3 filled π, 3 unfilled π^*

- 3 bonding, low-energy MO: ψ_1, ψ_2, and ψ_3
- 3 antibonding high-energy MO: ψ_4^*, ψ_5^*, and ψ_6^*



Orbitals with the same energy are degenerate:
- 2 bonding orbitals, ψ_2 and ψ_3
- 2 antibonding orbitals, ψ_4^* and ψ_5^*

ψ_3 and ψ_4^* have no π electron density on 2 carbons because of a node passing through these atoms

Benzene chromophore

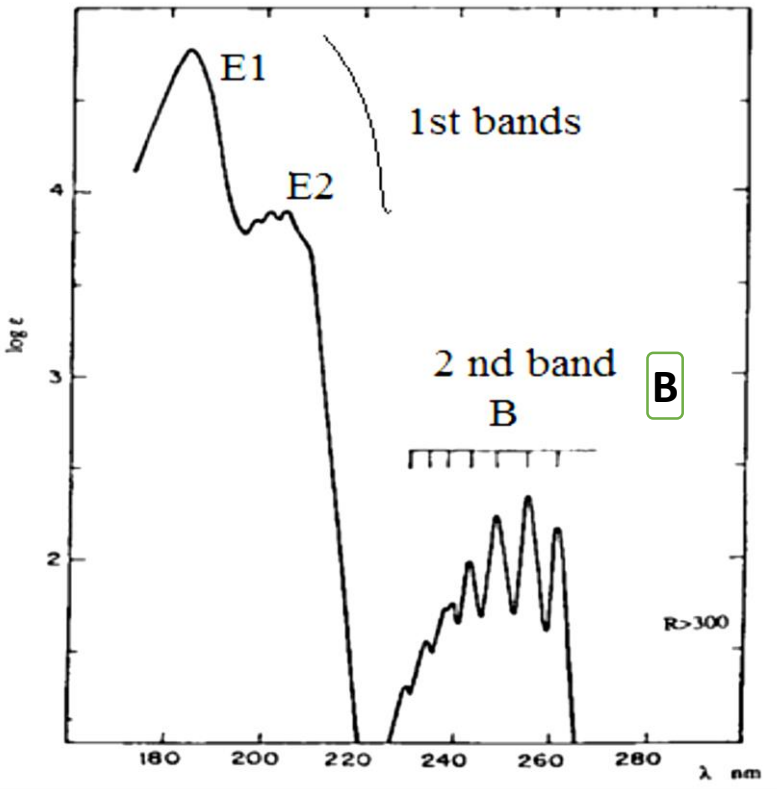
Benzene displays three absorption

Bands	λ max. nm	Emax.	Type of bands
E1(allowed)	180-184	60000	Primary band
E2(forbidden)	200-204	7900	Primary band
B(forbidden)	254-257	200	Secondary band(benzoid band) fine str.

These bands arise from transition π → π *

- ✓ **Allowed transition == intense band near 180nm**
- ✓ **Forbidden transition === weaker bands near 200&260nm (230-260) ,In highly symmetrical benzene molecule**

Increase λmax ➡ E1 (not appear)E2 (shorter to appear)
& B with increase E max. Or stable and loss its fine structure

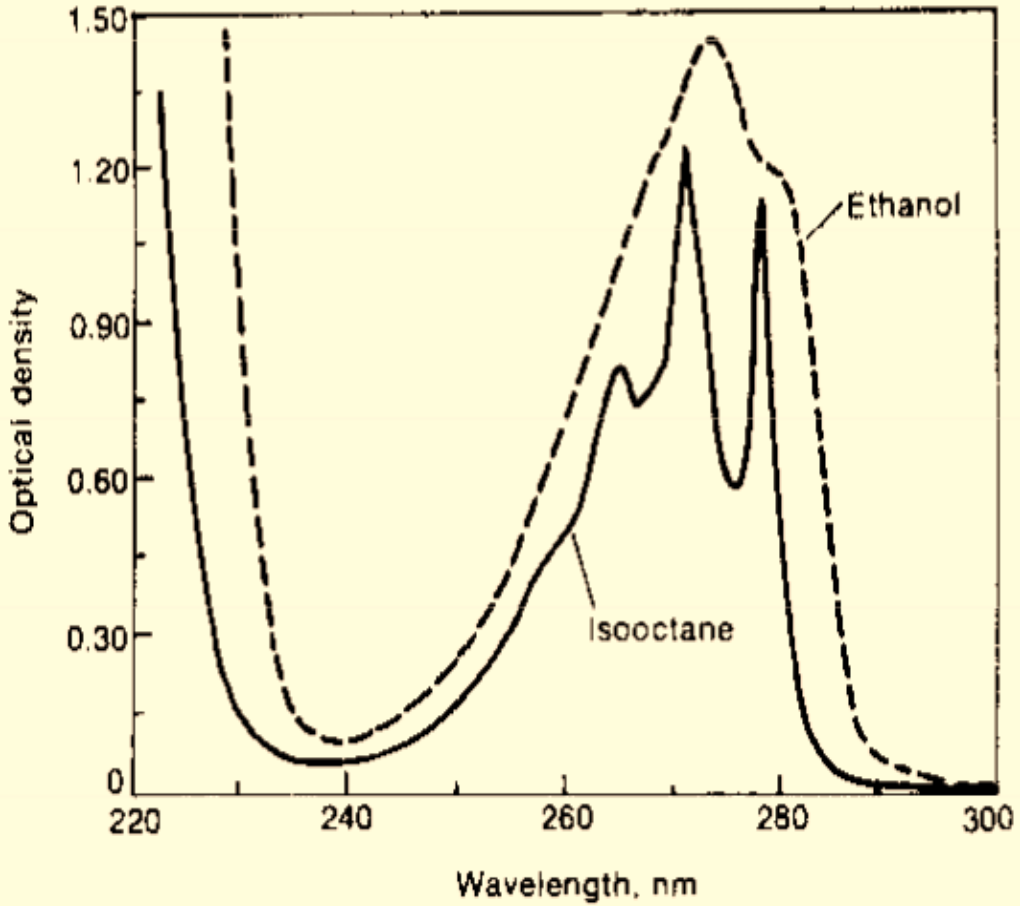


❖ The B-band of benzene & many of its homologs is characterize by considerable fine structure (in case of vapor phase or in nonpolar solvent

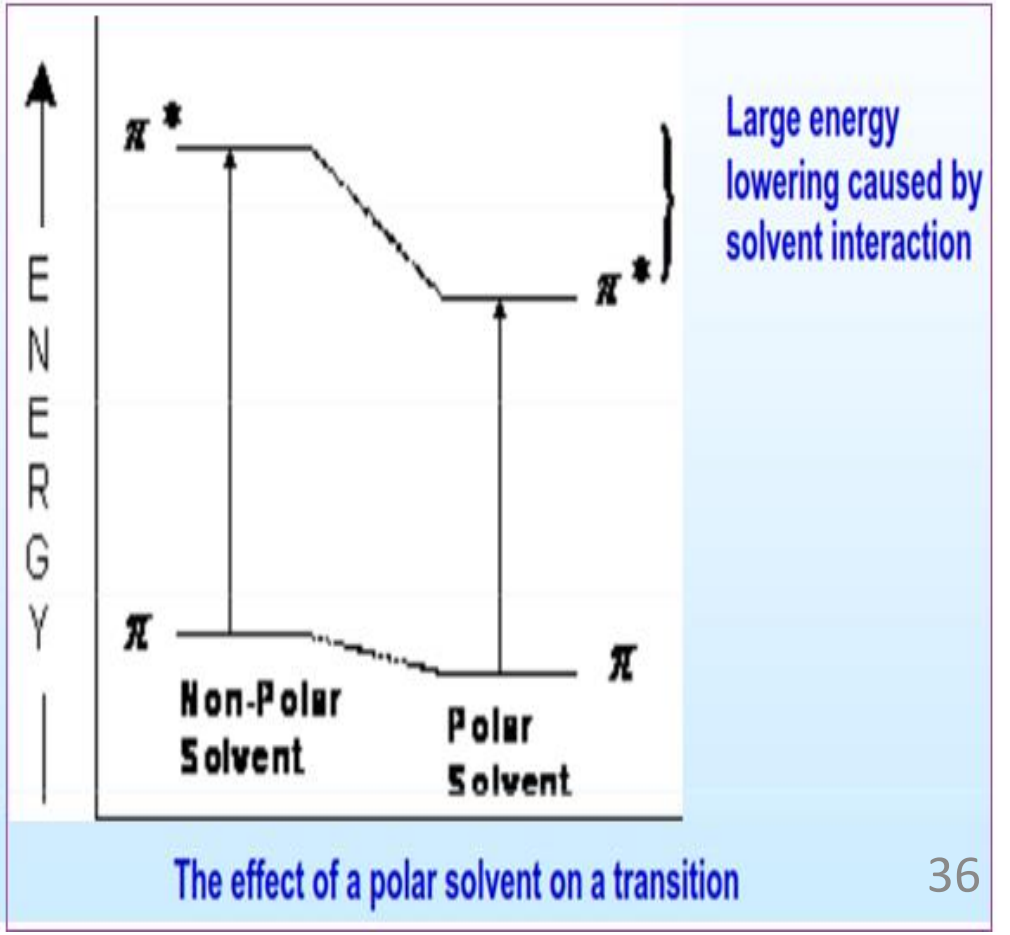
In polar solvent → large energy lowering caused by solvent interaction

solvent interaction → decrease fine structure

- Non-polar solvents do not form H-bond with solute, so "fine structure" is often observed.
- Polar solvents form solute- solvent complexes through H- bonding, hence, "fine structure" may disappear.



Ultraviolet Spectra of Phenol in Ethanol and in Isooctane



The effect of a polar solvent on a transition

Substation of alkyl group on the benzene ring

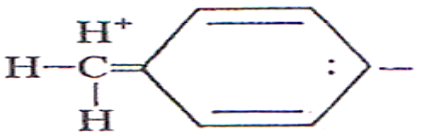
B-band → Bathochromic shift (red shift)

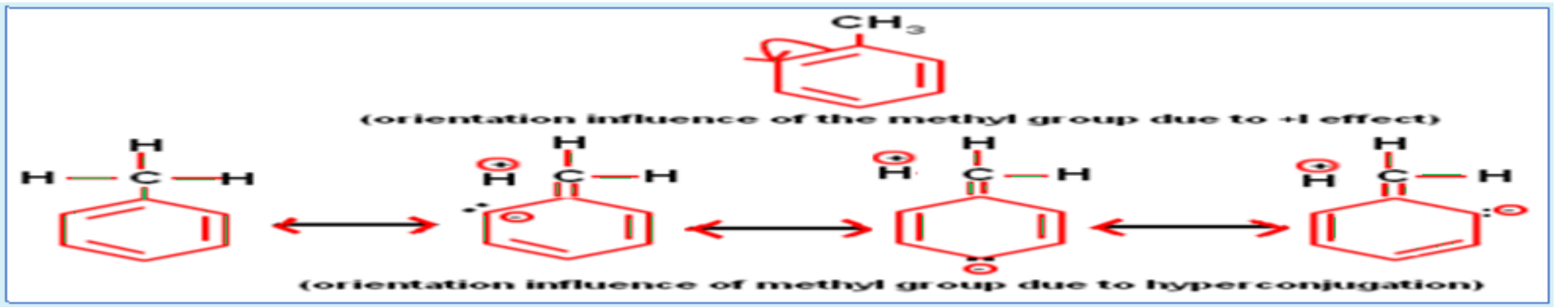
- But the effect of alkyl substation upon the E-band is not clear defend

Q) Why this substation → Bathochromic shift (red shift)

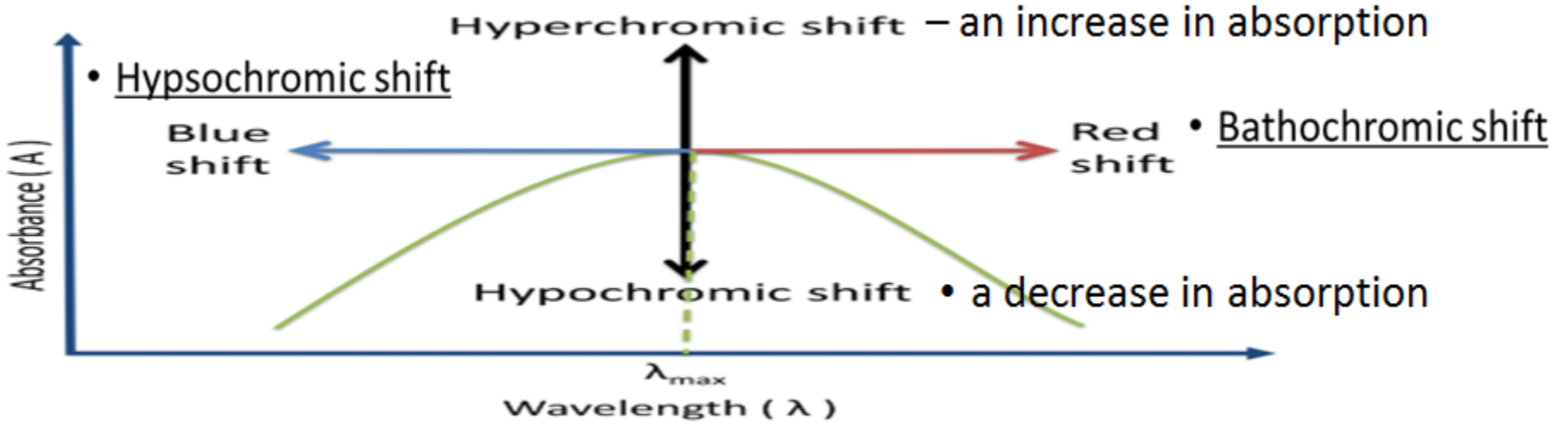
Ans.) that due to hyperconjugat in which the σ electrons of alkyl C-H bond participate in resonance with the ring .

Note :- the CH3 group is more effective in hyperconjugat than other alkyl group





Shifts and Effects



Q) The ortho isomer generally absorbs at the shortest wavelength with reduce E max. Why?

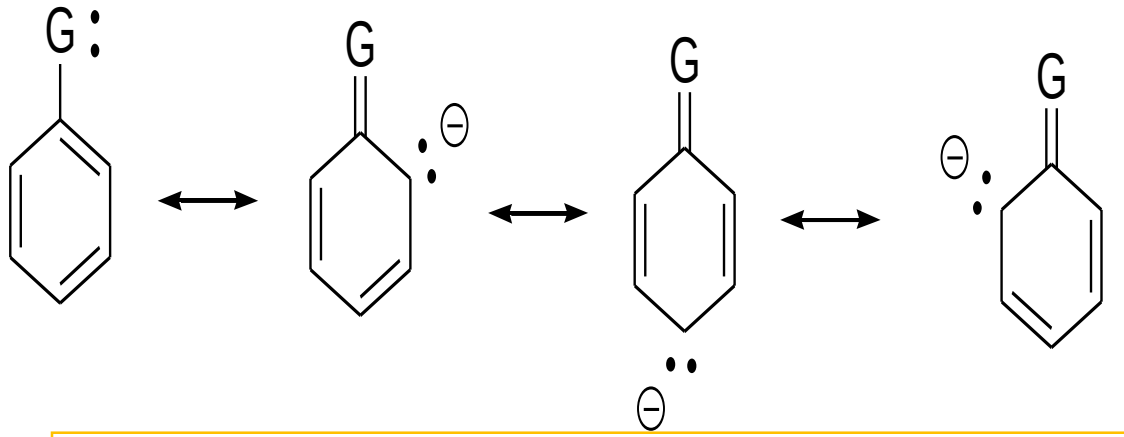
Ans.) because of steric interact is between the ortho substituents decrease the hyperconjugation and decrease the E max. & λmax.

Compounds	λmax.	E max.
Benzene	256	200
Toluene	261	300
M-xylene	262.5	300
3.5-tri methyl benzene	266	305
Hexamethyl benzene	272	300

$P > m > O$

Absorption data for alkyl benzene (B-band)
λmax. Of the most intense peak in band with fine structure

Compound	E2-band		B-band	
	λmax.	E max.	λmax.	E max.
Benzene	204	7,900	256	200
Phenol	210.5	6200	270	1450
Phenolode anion	235	9400	287	2600
Aniline	230	8600	280	1430
Anilinium cation	203	7500	254	160



Q) The nonbonding electrons resonance with π bonds of the ring to increase E max. & λmax. Why?

Ans.) as The nonbonding electrons are more available for interaction with the π system to greater the shift will be

- Non-bonding electrons extend the π-system through resonance – lowering the energy of transition π → π*
- More available *n*-pairs of electrons give greater shifts
- The presence of n-electrons gives the possibility of *n* → π* transitions

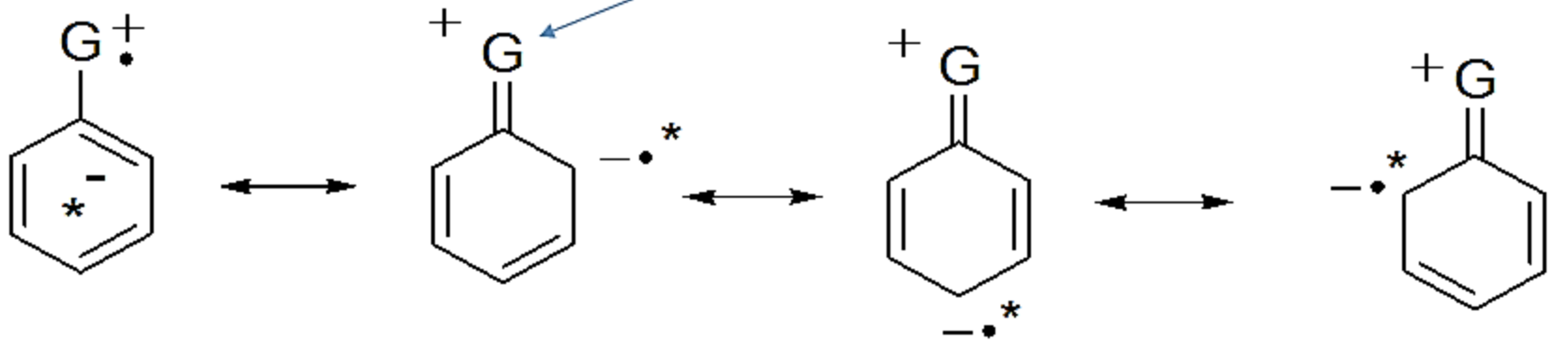
o EWG has little effect on B band o EDG shifts B band to longer λ

Because the unshared of electrons activating the ring by the resonance
Decrease of excited state to decreases required energy for transition (red shift)

By resonance

- If this occurs, the electron now removed from G, becomes an extra electron in the anti-bonding π^* orbital of the ring

  This state is referred to as a *charge-transfer excited state*



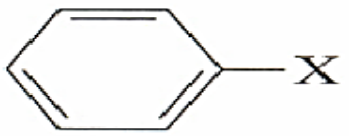
In the case the effect of the ***n→π**** ***on the compound is , if an n-electron is excited to the extended π**** chromophore , the atom from which it was removed become electron deficient while the ***π system of the aromatic ring acquire an extra electron this cause a separation of charge in the molecules***

Note :-

- ✓ *extra electron in the ring acutally in a π* orbital*
- ✓ *Charge transfer or electron transfer excited state*

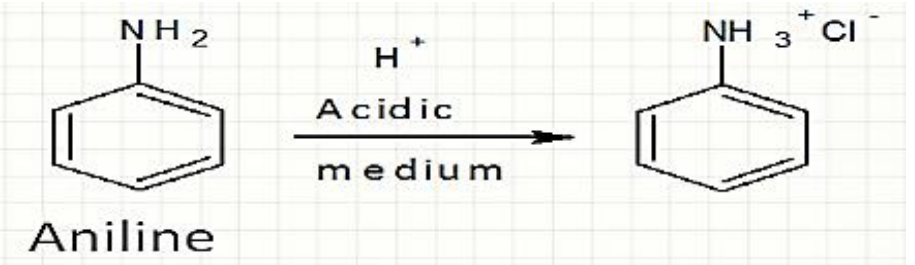
The effect of PH :- i,.e. 1) Aniline 2) phenol

- In arylamines the interaction of the nitrogen lone pair with the π-electron system of the ring shifts the ring's absorptions to longer wavelengths.
- Tying up the lone pair by protonation causes the UV-Vis spectrum of anilinium to resemble benzene.



	X	λ_{max} (nm) E≥ , B	ε max E≥ , B
Benzene	H	204, 256	7,900 , 200
Aniline	NH_2	230, 280	8,600 , 1,430
Anilinium ion (resemble benzene)	NH_3^+	203, 254	7,500 , 160

protonation of nitrogen eliminates the *n*-pair, *raising* transition energy

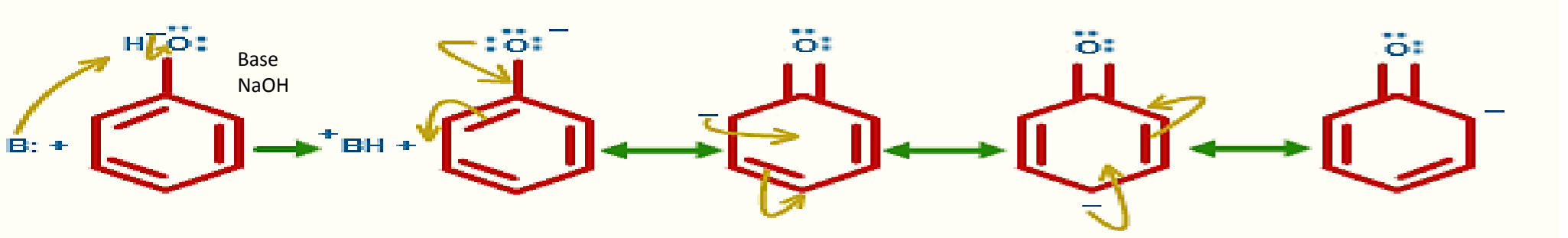


Aniline shows blue shift in acidic medium, it loses conjugation.

the pair of nonbonding electron of aniline is no longer available for interaction with π-electron system of the ring . Its spectrum almost identical to that of benzene result .

Q/ it was found that trimethyl amine in acidic media don't show absorption due to n → σ*?

- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an auxochrome or by the change of solvent.
- e.g. An auxochrome group like –OH, -OCH_3 causes absorption of compound at longer wavelength.



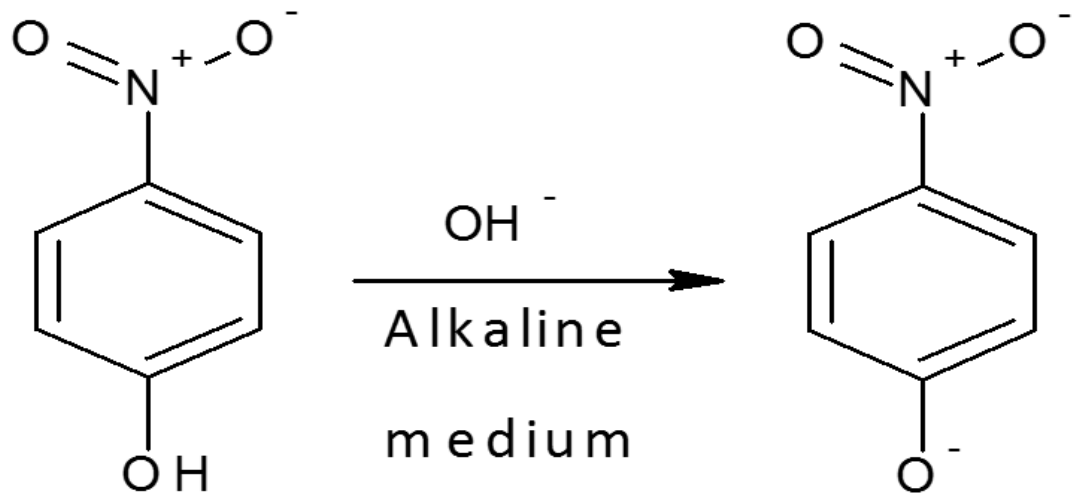
bathochromic shift of the E2 and B-bands and increase in ε max.

Compound	E2-band		B-band	
	λmax.	E max.	λmax.	E max.
Benzene	204	7,900	256	200
Phenol	210.5	6200	270	1450
Phenolode anion	235	9400	287	2600

The negative charge of oxygen delocalizes more effectively than the unshared pair of electron

deprotonation of oxygen gives more available *n*-pairs, *lowering* transition energy

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



p-nitrophenol

λ_{max} = 255 nm λ_{max} = 265 nm

If an unk. sample of benzene derv.(aniline or phenol) ,how to diff. between them by uv only ?

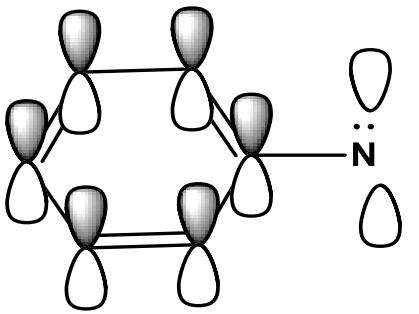
To one of them :(you can do it to each one):

1 - take the uv at neutral pH ---------- uv spectra I .

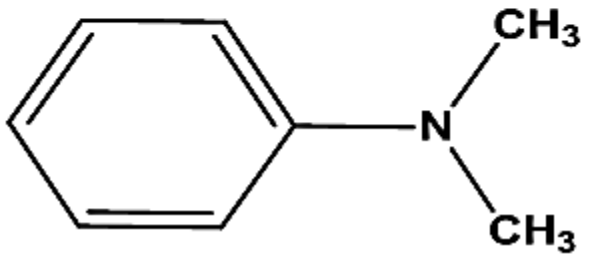
2 - take the uv at acidic pH(i.e.=1) ---------- uv spectra II .

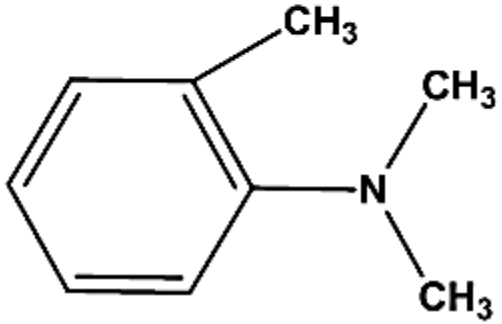
3 - take the uv at basic pH (i.e.-13) ---------- uv spectra III .

Interaction between the nonbonding electron pair of heteroatom attached to the ring & and the π electrons of the ring is most effective when the p orbital of the nonbonding electron is parallel to the π orbital of the ring



Thus, bulky substitution in the ortho position of molecules such as N,N-dimethyl aniline cause a hypsochromic (Blue shift) shift in the E2 band & accompanied by a marked reduction E max





ortho

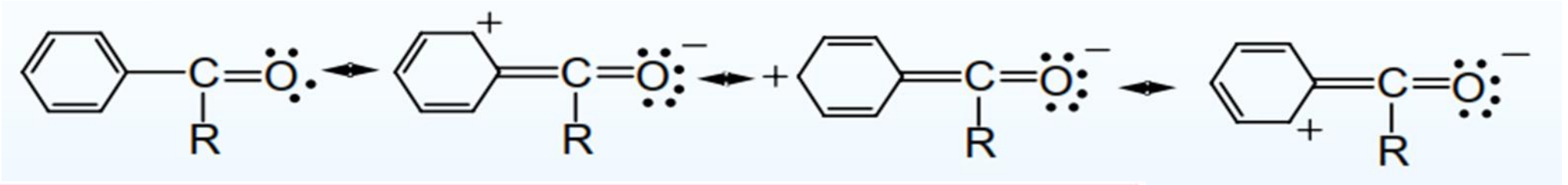
N,N-dimethyl aniline
λmax 251
ε max 15.500

2-methyl-N,N-dimethyl aniline
2.48 ⇒ λ
6360 ⇒ ε max

b ^ (the)nonbonding e pair of N not effectively interaction w(with) the π.es of ^ ring . (not completely parallel)

*** This effect in case of O > m >>> P ⇐ very very ↓**

Substituents capable of π-conjugation



Interaction of the benzene ring electrons and the π electrons of the substituent can also produce a new electron transfer band. This new band may be so intense as to obscure the secondary band of the benzene system.

Notice that the opposite polarity is induced; the ring becomes electron deficient.

Interaction of ∧ benzene ring e-s & the π e-s of the substituent can also produce a new e: transfer band (k-band)

- 1- strong bathochronic shift (Red shift) of the B-band.
- 2- The appearance of a K-band (conj.) a (Emax , 10.000) in the 200-250 nm roa
- 3- Generally E-bands are less intense
- 4- B-bands are sometimes **buried** under the K-bands (K-bands cover ∧ B-band)

Disubstituted benzene Derivatives (2 nd. law)

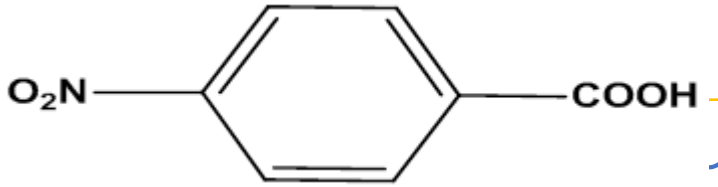
- When auxochromic gr.s appear on the same ring as the chromophore, both groups (gr.s) influence the absorption.
- For predicting λmax of the primary band of substituted benzene the following rules are used. (in case of disubtituted benzene)
- Table XXV:

substituent	shift	substiotuent	shift
- CH3	3	-NH2	26.5
- CHO	46	- OH	7.0
- COCH3	42	- OCH3	13.5
- CO2H	25.5	- NO2	65.0

Base value is (203.5 nm) for 1° band ($\pi \rightarrow \pi^*$ interact)

A- For Para substitution

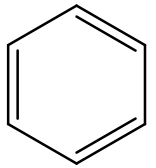
1- Both groups are e. donating EDG or e with drawing EWG: only the effect of the group causing the larger shift is used (so it is similar to monosubstituted benzene)

i.e P- nitrobenzenic acid 

its λmax

Would be expected to be the same as that of nitro-benzene

Why ? because λmax parent cpd. = 203.5 nm



+ 65

268.5 nm ← 65 25.5

NO2 > CO2H

So if both the groups are electron-donating then the observed spectrum is closer to monosubstituted benzene. The group with stronger effect determines the extent of shifting of primary band.

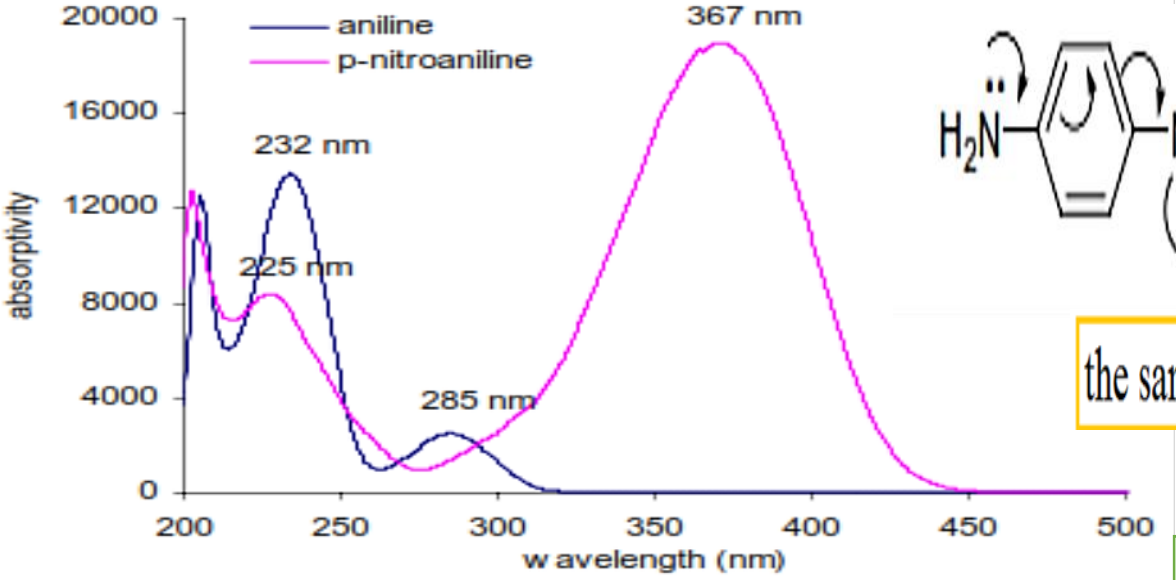
2. One gr. Is EDG and other one is EWG : The calculated λmax is usually much lower then the observed λmax (the same reasons) given for p-nitrophenal (resonance)

Calc.≠ obs

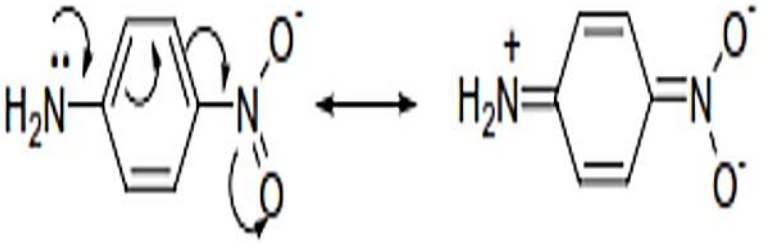
Resonance effect { With π ring }

(greater extension of conjugat) → λmax

So if one group is electron-releasing and other is electron-withdrawing, the magnitude of red shift is grater compared to the effect of single substituent individually. This is attributed to the increased electron drift from electron-donating group to the electron-withdrawing group through π-bond of benzene ring. For example, aniline shows secondary band at 285 nm which due to presence of electron-withdrawing p-nitro substituent is shifted to 367 nm with a significant increase in absorptivit .



UV-spectra of aniline and p-nitroaniline in methanol



the same in case *p*-nitrophenol

Aniline secondary band at 285 nm

p-nitro aniline secondary band at 367 nm

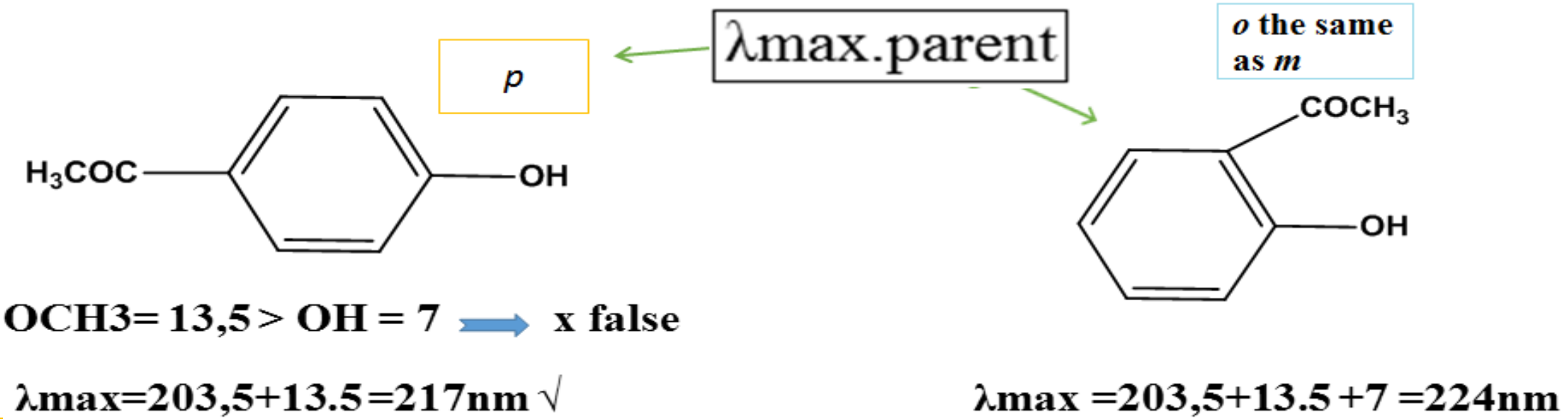
* The red shift & ↑ in intensity of the k-band

* The influence is most pronounced when an electron donating gr EDG & e attracting gr. are para to the another (complementary substitut)

B/Meta and ortho: if the two gr.s are *o*- or *m*- to one another the effect is usually the sum of the two individual effects (the shift effect are additive (meta : no resonance ….ortho steric effect)

So: by Uv: we can diff . between p & (-o,-m) derivetave…… no resonance

Note: -o,-m can not diff . between them by Uv

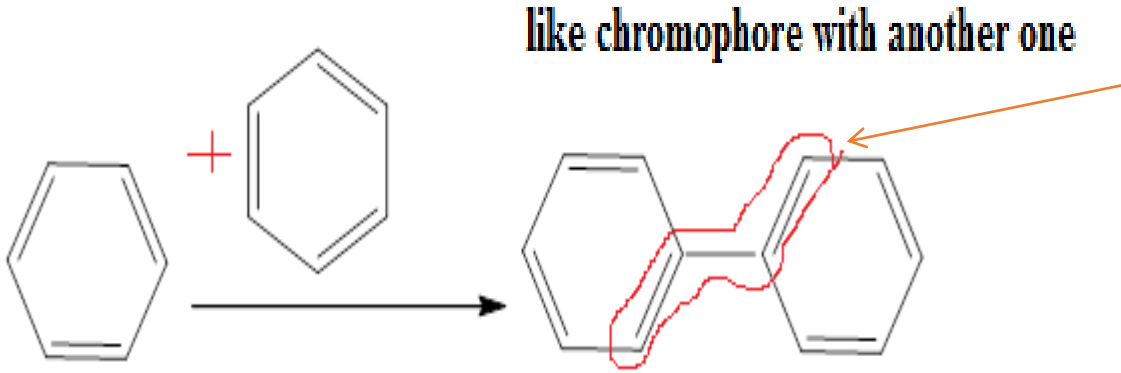


Biphenyl is the parent molecule of a series of cpd.s in which two aromatic rings are in conjugation.

- Resonance energy is at maximum when the rings are coplanar and zero when the rings are at 90° to one another

One benzene ring

(E1,E2& B)



conj.

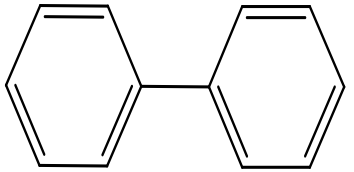
K-band

Appearance

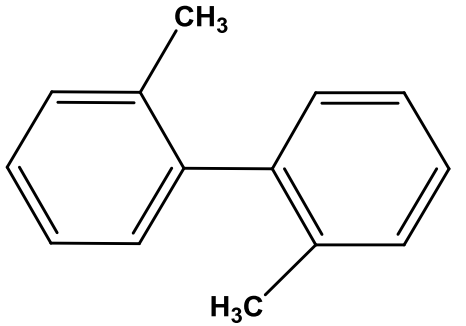
No conjugation.

The effect of forcing the rings out of coplanarity is readily seen from a comparison of the absorption characteristics of biphenyl and its 2,2'-dimethyl homolog whose absorption characteristics are similar to those of *o*-xylene.

Only ortho



Both of them are on o-position



↓ Decrease Co-planarity

↓ Effect of one ring on the other one

↓ Conj. (no resonance

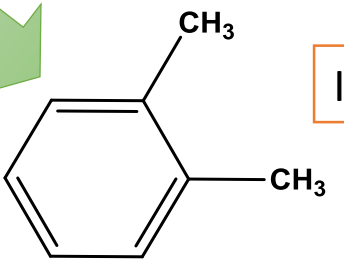
NO **K** band

(E1,E2,B& **K**) bands
K-band λmax.252 E max =19,000
Coplanar → interact (conj.)between them

As the size of sub. gr. ↑

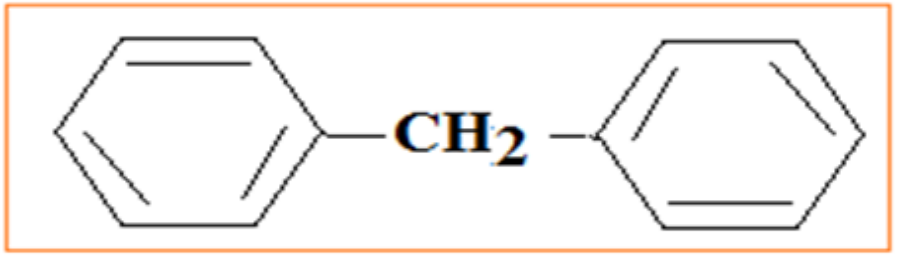
coplanar prop. ↓

2nd ring is considered as CH3group Sub. On the st. ring



It like o-xylene

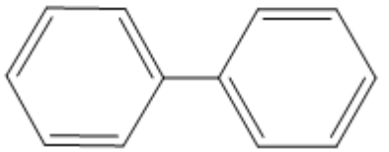
Introduction of a methylene group between two chromophores is generally considered capable of destroying conjugation. Compare the data of diphenylmethane.



λ max 262 nm
E max 5000

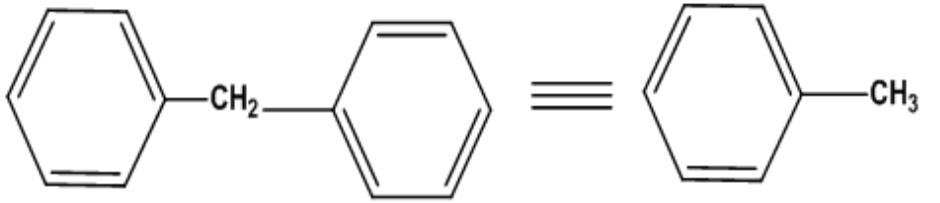
It is similar to that of toluene

Conj. √



Biphenyl

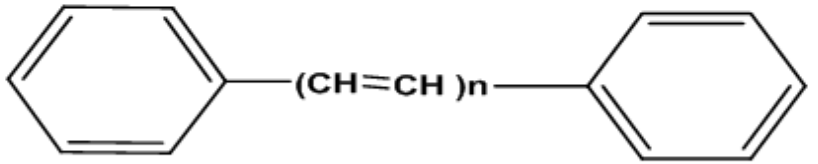
no conj.



Diphenyl

Diphenyl polyene series $(\text{Ø-}(\text{C}_\text{I} = \text{C}_\text{I})_\text{n} \text{–Ø})$

The 1 st homolog in this



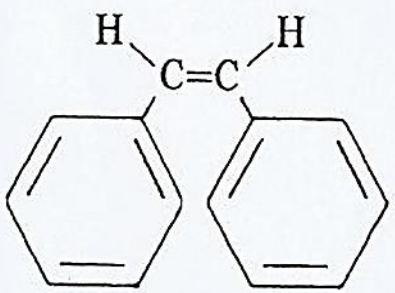
system is Stilbene (n=1)

which offers an interesting example of steric effects in electronic spectra .

UV/vis spectroscopy can also be used to study geometric isomerism of molecules. The trans isomer absorbs at longer wavelength with a larger molar extinction constant than cis isomer. This can be explained by the steric strain introduced in the cis isomer resulting in lesser π orbital overlap.

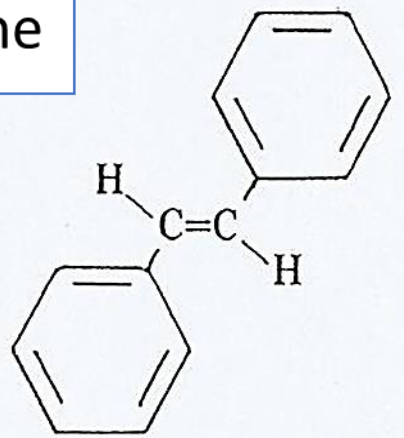
The destruction of coplanarity by steric interference, in the cis-structure, is reflected by the lower intensity of the 283 nm band compared with the corresponding band (295 nm) in the *tram* isomer. The *B-band* appears to be swamped by this intense absorption.

Stilbene



cis-Stilbene

λ_{max}^{EtOH}	ϵ_{max}
222	25,000
283	12,300

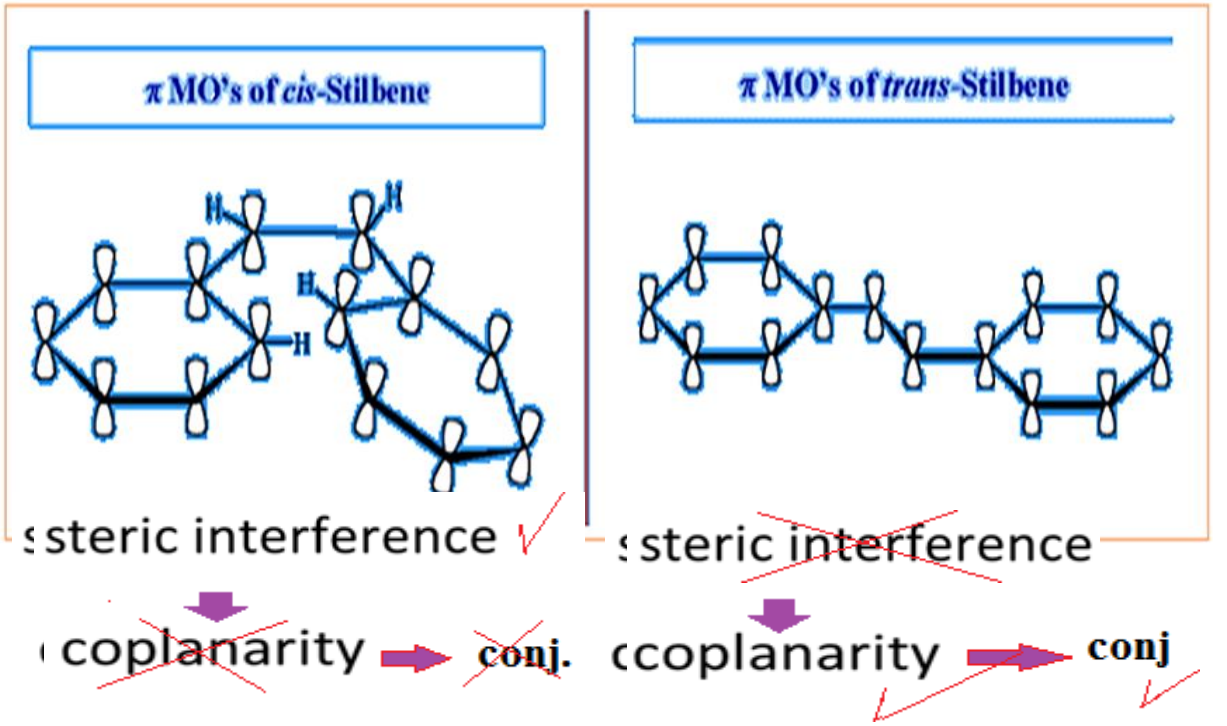


trans-Stilbene

E 2

K

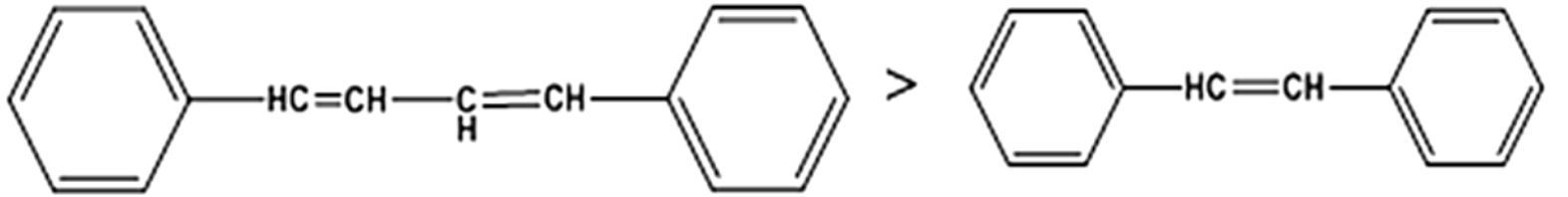
λ_{max}^{EtOH}	ϵ_{max}
229	15,800
295	25,000
308	25,000
320 (shoulder)	15,800



When n=7 ⇨ the molecule absorbs in the region = 400-465 with Emax 135.000 (visible region)

The absorption band of the parent stilbene molecule move to longer wave lengths and increase in intensity as n in Ø (CH=CH)-Ø **Diphenyl polyene** increase

=(As the no of -CH=CH- ↑ ➡ ↑ λmax & ↑ E max) ➡ red shift



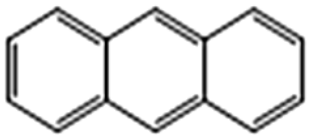
When n = 7 it absorbs in the visible region { 400-465)nm E max = 135.000

10 **Far** 200 **near** 400 **visible** 780(800)

Condense Aromatic System (fused aromatic rings)

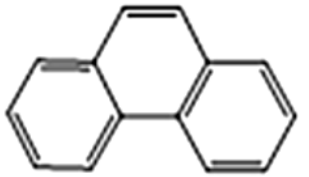
Two common series of aromatic compounds are:

1) The linear series such as anthracence
2) The angular series such as phenathrene



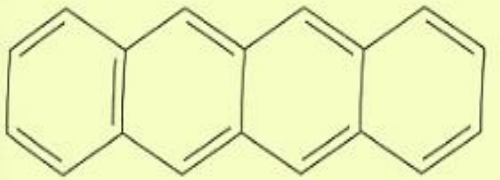
one benzoid ring
λmax = 345.360

A correlation between the bands of benzene & the acenes as well as naphthalene can be mode.

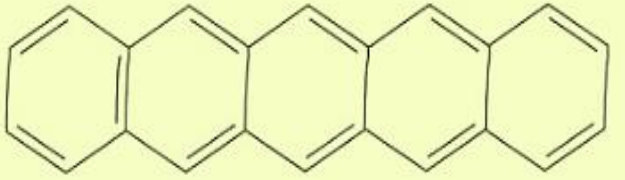


Two benzoid ring
λmax = 250nm

As the number of condensed rings increases in the acene series, the absorption moves to progressively longer wavelengths until it occurs in the visible region.



naphthacene
λ_{max} = 375 nm
(yellow)



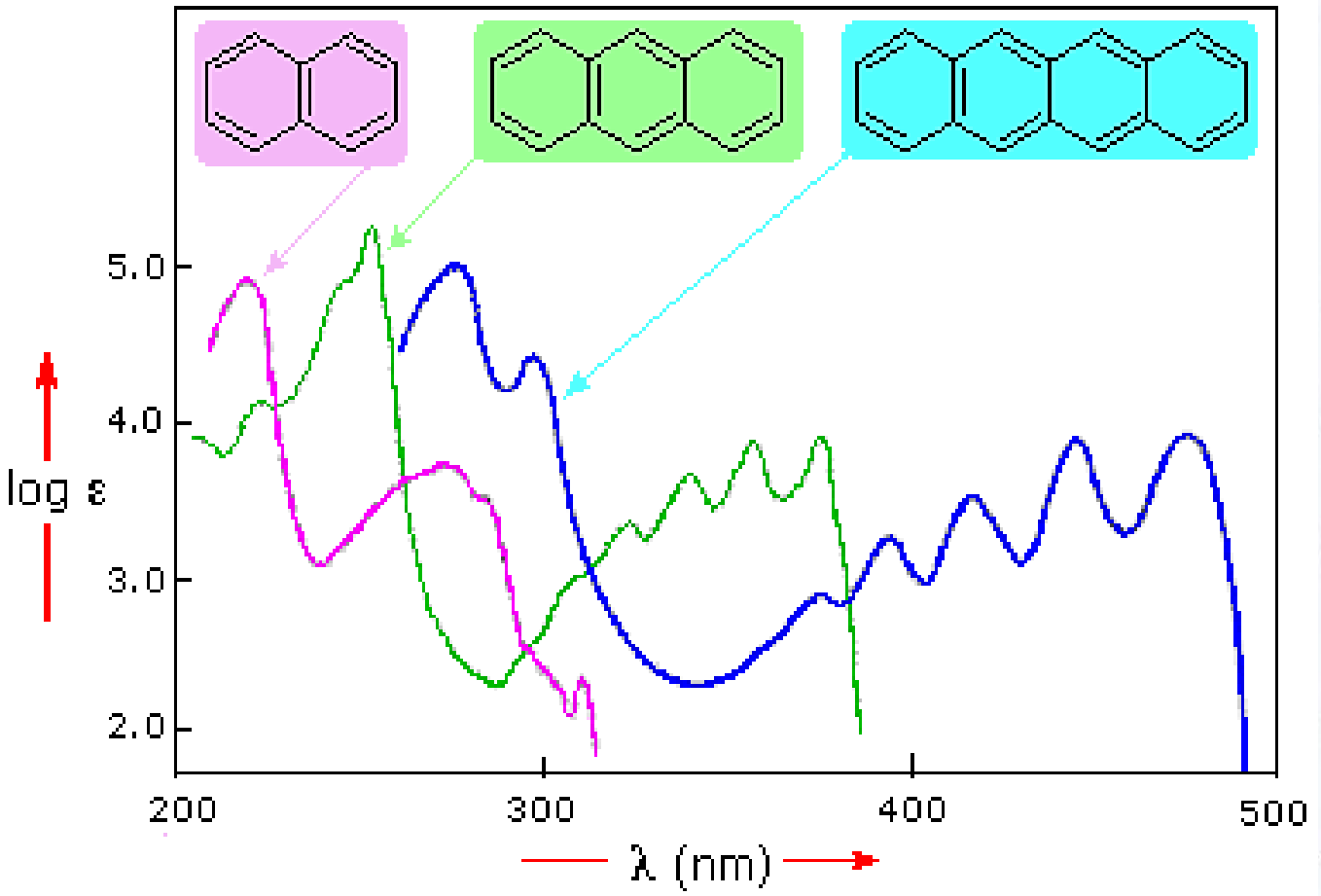
pentacene
λ_{max} = 575 nm
(blue)

Table XXVII. Correlation of Aromatic Absorption

Compound	E_1 band λ_{max} (ϵ_{max})	E_2-band λ_{max} (ϵ_{max})	B-band λ_{max} (ϵ_{max})	λ_{max} (ϵ_{max})
Benzene	184 (60,000)	204 (7900)	256 (200)	
Naphthalene	221 (133,000)	286 (9300)	312 (289)	
Anthracene	256 (180,000)	375 (9000)	Submerged	221 (14,500)

The angular polycyclic compounds, the aphenes, also show a bathochromic shift of the 3-band system with an increase in the number of rings. However, the increase in λ_{max}, per ring added, is less than for the acenes. The 3-band system is still distinct for phenanthrene but in the spectrum of anthracene the E_2-band has already swamped the B-band.

The spectra of polynuclear aromatics are characterized by vibrational fine-structure as observed in the spectrum of benzene.



Compound	E_1 band λ_{max} (ϵ_{max})	E_2-band λ_{max} (ϵ_{max})	B-band λ_{max} (ϵ_{max})	λ_{max} (ϵ_{max})
Benzene	184 (60,000)	204 (7900)	256 (200)	
Naphthalene	221 (133,000)	286 (9300)	312 (289)	
Anthracene	256 (180,000)	375 (9000)	Submerged	221 (14,500)

Q) Explain the effects of EDG & EWG substituents on benzene ring.

Ans) 1) these substituents shift the 1° absorption band to longer wave length.

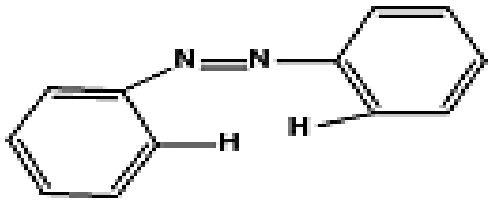
2) EWGA cause no effect on posit of 2nd absorption band

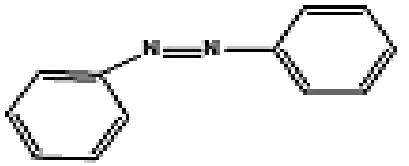
EDG ⟹ ↑ λ max & ℰmax of 2nd absorption band

Q) Why does a methyl gr. Produce a red shift even though it does not possess unshared e.s..as in the diagram (slide 13)

Ans) because it interacts with the double band (π band of benzene ring) by hyperconjugat given the overall effect of an extension of π system.

Q) Explain the reason for the differences in the uv spectra of cis and trans azobenzenes





π ⟶ π * 281nm(5260)

n ⟶ π * 433nm(4520)

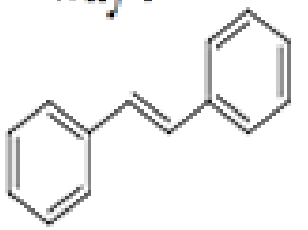
π ⟶ π * 320 nm (21300)

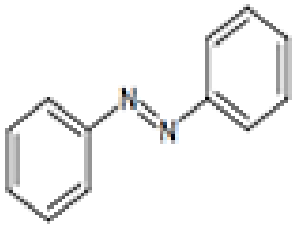
n ⟶ π * 443 nm(5100)

Ans) steric factor force the rings out of coplanarity

& ⬇ conjugat

Why ?





Ans:

λ-max = 295

λ-max = 325 π ⟶ π*

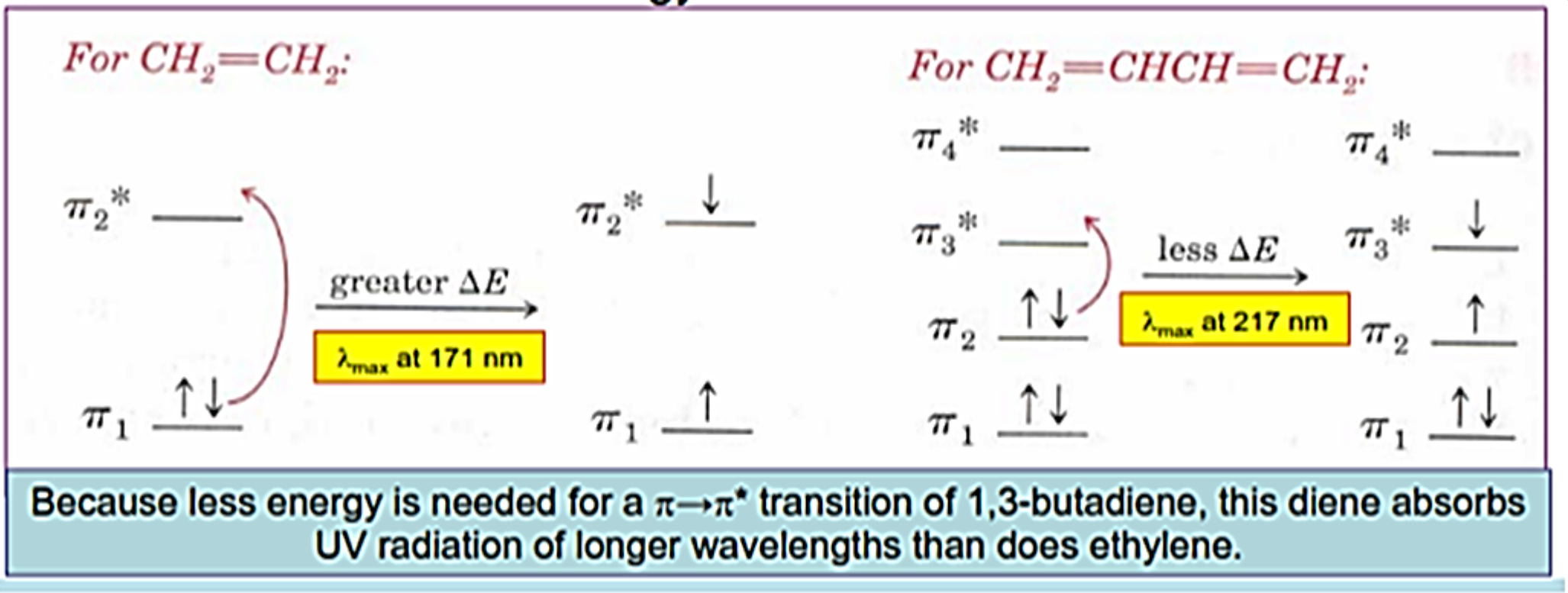
λ-max = 440 n ⟶ π*

White in color

Yellow in color

The λ max in ethylene molecules appear at 171 nm ,while the λ max of 1,3-butidene is 217 nm .that because of :

the double bond of 1,3- butidene is conjugated & less energy is needed for $\pi \longrightarrow \pi^*$ transition ,this diene absorbs UV. Radiation of wavelength than dose ethylene .

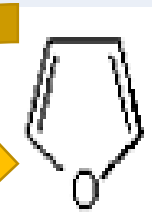


Because less energy is needed for a $\pi \rightarrow \pi^*$ transition of 1,3-butadiene, this diene absorbs UV radiation of longer wavelengths than does ethylene.

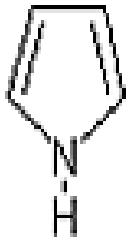
Heteroaromatic Compounds

- Saturated five (5)& (6) membered heterocyclic compounds are transparent at λ longer than 200 nm.
- Only the unsaturated heterocyclic compounds show absorption in the near UV region.

5 membered heterocyclic



furan

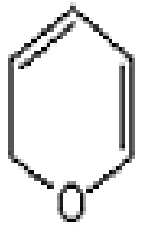


pyrrole

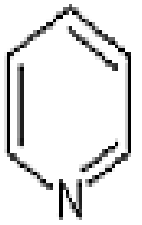
thiophene

imidazole

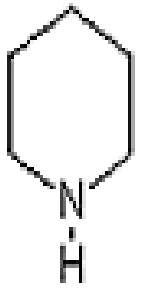
6- membered heterocyclic



pyran



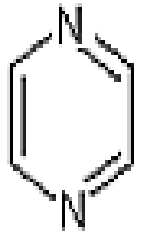
pyridine



piperidine

pyrimidine

pyridazine



pyrazine

The spectrum of pyridine similar to that of benzene but there are differences :

- ❖ B – band of pyridine is more intense & has less distinct fine structure.
- ❖ 2- pyridine show weak R band $n \longrightarrow \pi^*$ this band swamped by the more intense B-band.
- ❖ Benzene have no R band unless if there is a chromophore i.e NO2,C=O

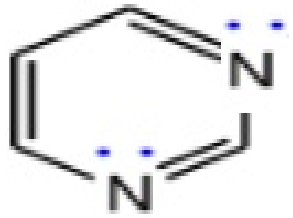
According to UV measurement; what effects has polar solvent on both of benzene and pyridine. Explain your answer.

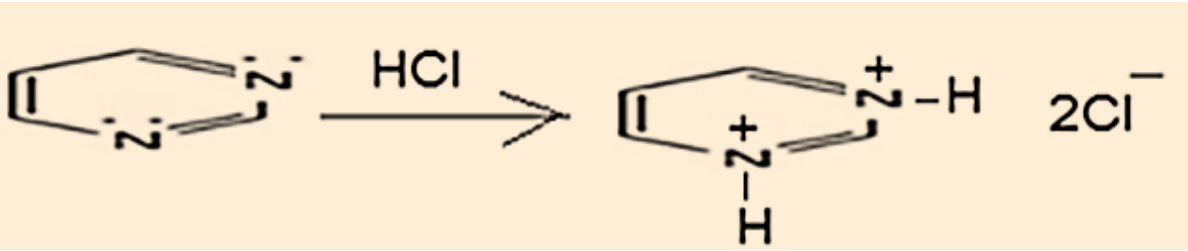
benzene

pyridine

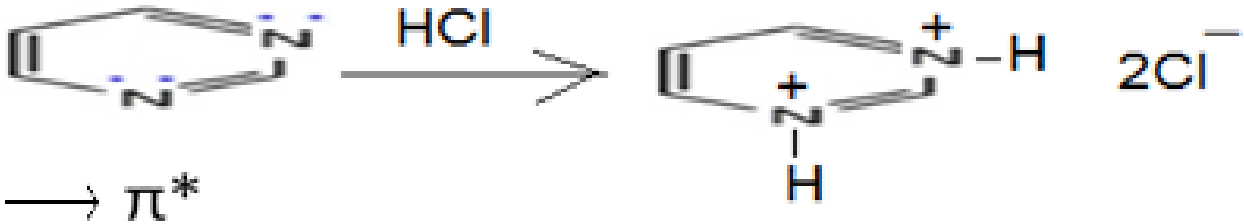
An increase in solvent polarity has little or no effect on the position or intensity of benzene, but produces a marked hyperchromic effect on the B-band of pyridine and its homologs. The hyperchromic effect results from hydrogen bonding through the ion pair of electrons of the nitrogen atom.

❑ the spectra of diazene are affected by acidic solution. As shown with that equation.





solution



$n \longrightarrow \pi^*$

R- band
due to the lone
pair of e- on N atom

lone pair of e- on N
atom not available
(it is a salt)

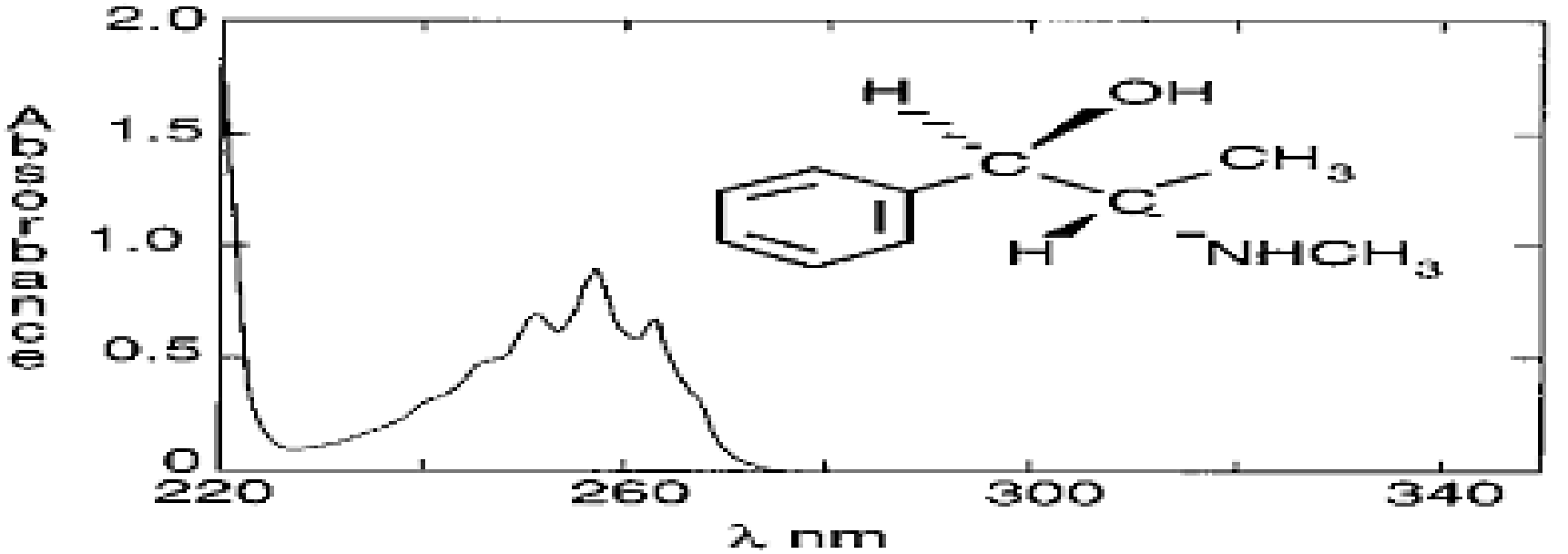
NO: 1. $n \longrightarrow \pi^*$

2. R- band

Ephedrine: the benzoid chromophore

- Ephedrine has the simplest type of benzene ring chromophore, which has a spectrum similar to that of benzene with a weak symmetry *forbidden band 260 nm* .Like benzene its most intense absorption maximum is *below 200 nm.*

- There are no polar groups attached to or involved in the chromophore so that *its vibrational fine structure is preserved* .

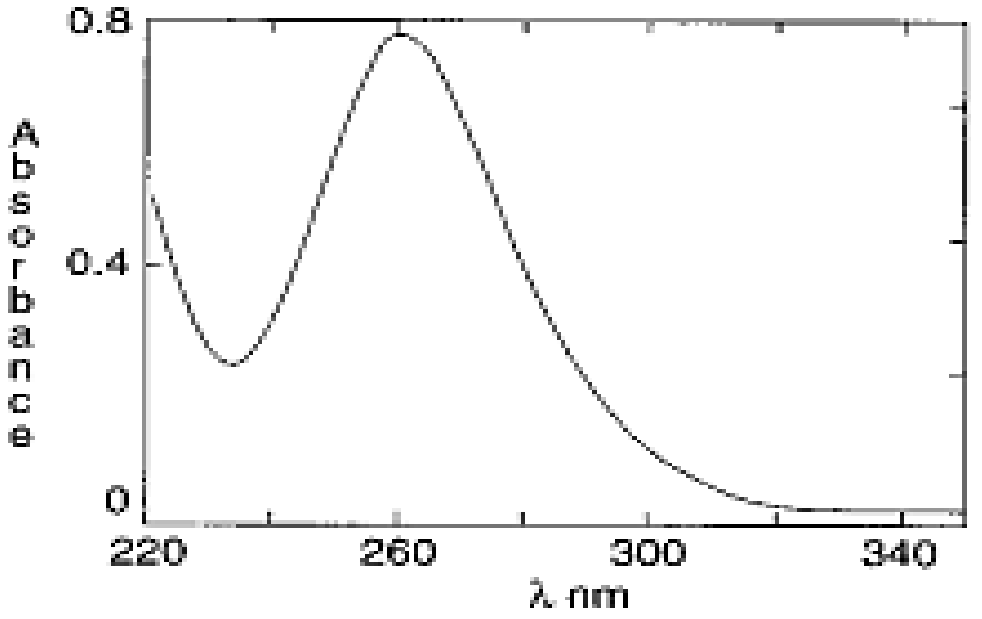


The UV spectrum of ephedrine, a simple benzoid spectrum

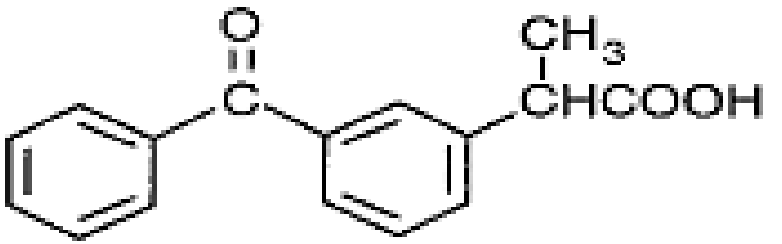
Ketoprofen: extended benzene chromophore

- In this case the *simple benzoid chromophore has been extended by four double bonds and thus the symmetry of the benzene ring has been altered.*

- In addition, the strong absorbance band present in benzene at 204 nm has undergone a bathochromic shift giving a λ max for ketoprofen *at 262 nm* having a value of 647 nm.



UV absorption spectrum of ketoprofen



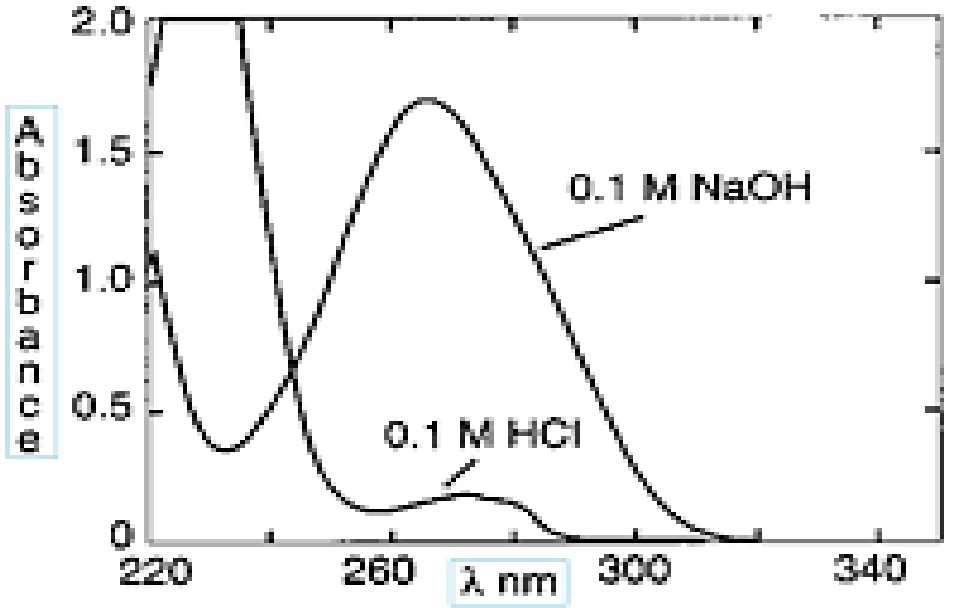
Ketoprofen

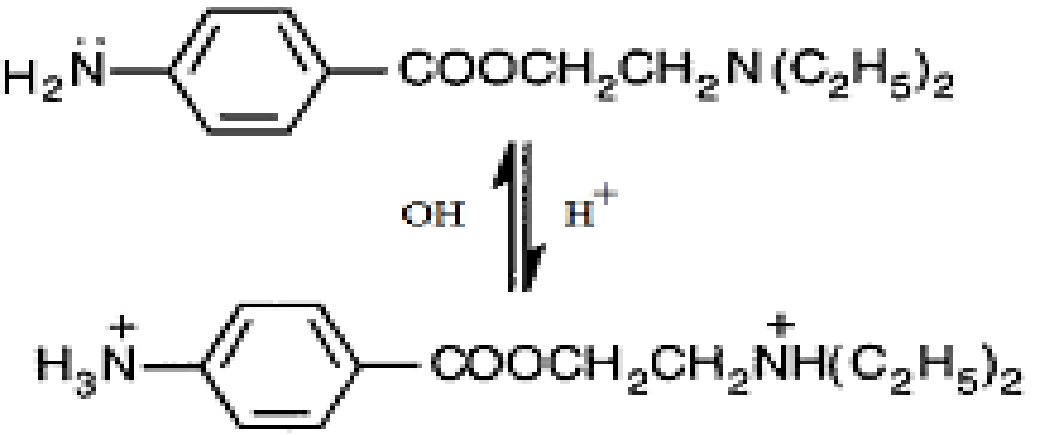
Procaine: amino group auxochrom

UV absorption spectra of a solution of procaine in 0.1 M HCl and 0.1M NaOH. In procaine, the benzene chromophore has been extended by addition of a C = O group and under acidic conditions, the molecule has an absorption *at 279 nm* .

- In addition to the extended chromophore, the molecule also contains an auxochrome in the form of an amino group, which under basic conditions has *alone pair of electrons* that can interact with the chromophore *producing a bathochromic shift.*

•Under acidic conditions the amine group is protonated and does not function as an auxochrome but when the proton is removed from this group *under basic conditions a bathochromic shift is produced* and an absorption *with λ max at 270 nm* .





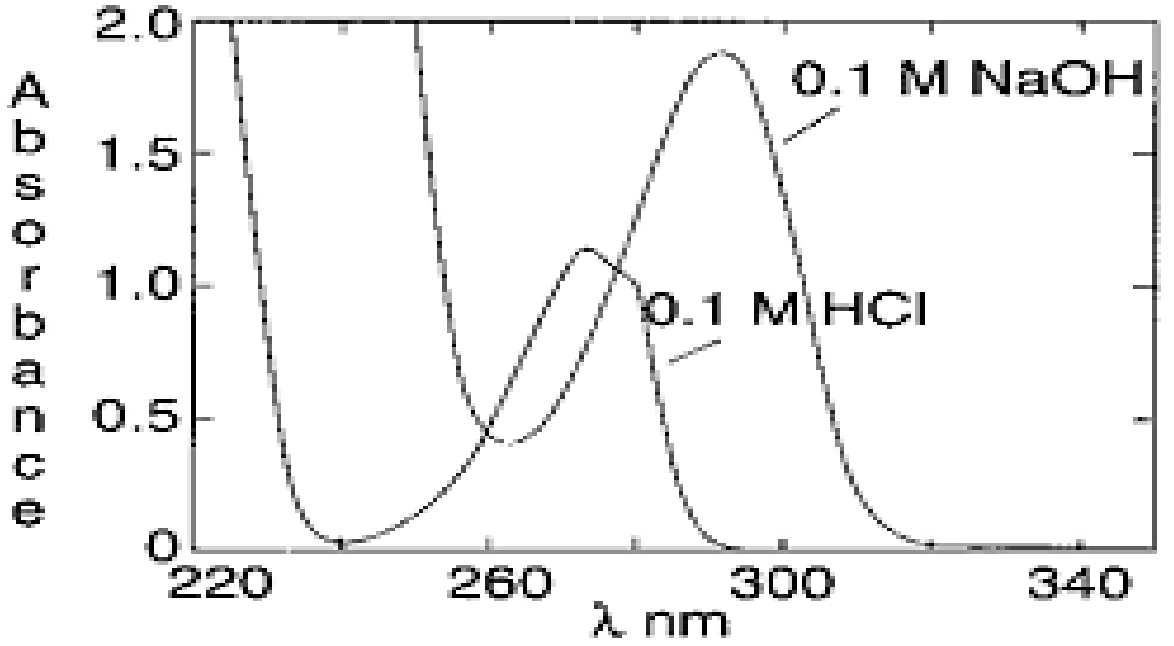
Phenylephrine: hydroxyl group auxochrome

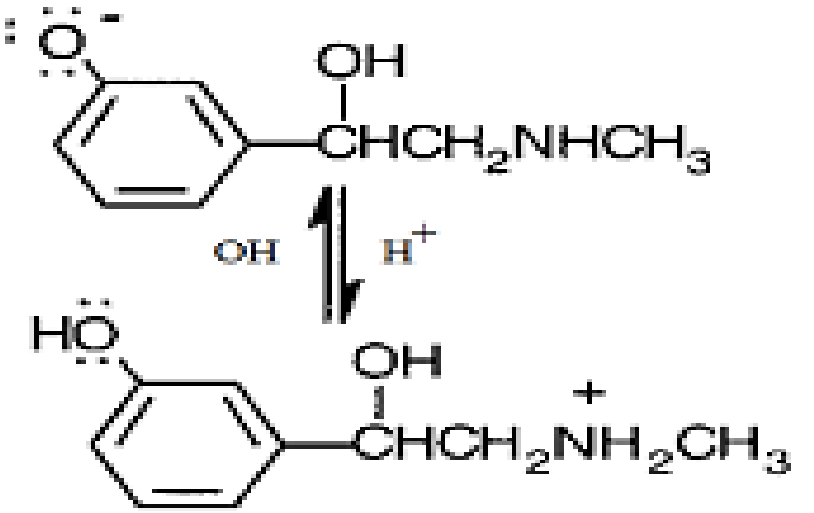
The chromophore of phenylephrine is not extended *but its structure includes a phenolic hydroxyl group*.

The phenolic group functions as an auxochrome under both acidic and alkaline conditions. Under acidic conditions it *has two lone pairs of electrons*, which can interact with the benzene ring and *under basic conditions it has three*.

Bathochromic shift and hyperchromic shift

Under acidic conditions the λ max is at *273* and under alkaline conditions the λ max is a *292 nm* .





APPLICATION OF WOODWARD FIESER RULES

ADVANTGE:

- It is used to calculate the position and maximum wave length for a given structure.
- By relating the position and degree of substitution of chromophore

- Conjugated diene :-organic compound containing two or more double bonds each separated from other by a single bond
- Dienes :-it is also known as a alkadiene, diolefin. It is one class of organic compound containing two ethyelnic linkages(carbon to carbon double bond)

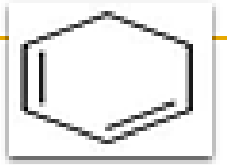
WOODWARD FIESER RULE

- It mean each type of diene or triene system is having a certain fixed values at which absorption takes place; this constitutes the base value or parent value.
- The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as -Cl,-Br etc ... are added to the base value to obtain for a particular compound

BASIC INTRODUCTION:-

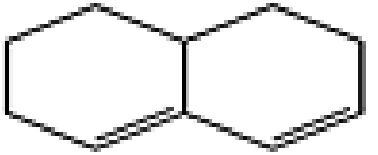
The central bond is a part of the ring system, the diene chromophore is usually held rigidly in either the *s-trans* or the *s-cis* conformation

- HOMOANNULAR:- cyclic diene having conjugated double bonds in same ring.



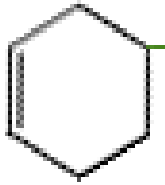
(s-cis) cyclic dienes having conjugated double bonds in the same ring. e.g.

- HETEROANNULAR:-cyclic diene having conjugated double bonds in different rings



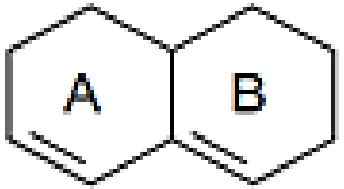
(s-trans) cyclic dienes having Conjugated double bonds not in the same ring. e.g

ENDOCYCLIC DOUBLE BOND:-double bond present in a ring.

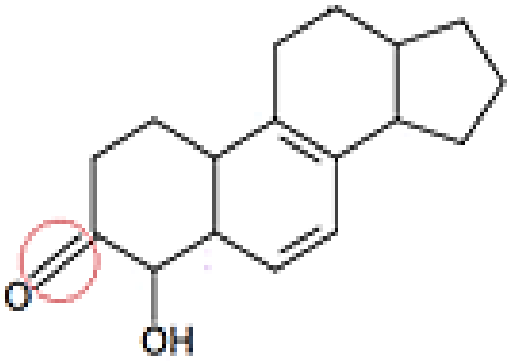


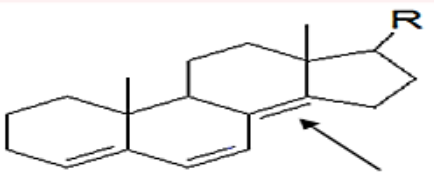
EXOCYCLIC DOUBLE BOND:-double bond in which one of the doubly atoms is a part of ring system.ring A has only one endocyclic double bond

ring B has one exocyclic and endocyclic double bond .

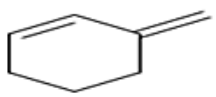


Double bond extending :- When more double bonds are present other than conjugations.

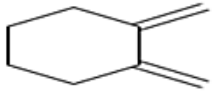




This compound has three exocyclic double bonds, the indicated bond is exocyclic to two rings



This is not a heteroannular diene; you would use the base value for an acyclic diene



Likewise, this is not a homooannular diene; you would use the base value for an acyclic diene

Parent values and increments for different Substituents or Groups

Conjugated Dienes and Polyenes

Parent Value	
Acyclic conjugated dienes and Heteroannular conjugated dienes	215 nm
Homoannular conjugated dienes	253 nm
Acyclic trienes	245 nm
Increments	
Each alkyl substitute or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Auxochromes	
-OR	6 nm
-SR	30 nm
-Cl,-Br	5 nm
-NR2	60 nm
-OCOCH3	0 nm

α,β-unsaturated carbonyl compounds

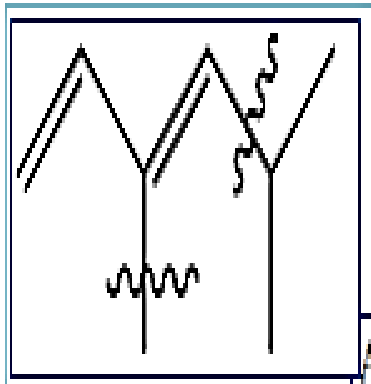
Parent Value	
α,β -unsaturated acyclic or six membered ring ketone	215 nm
α,β -unsaturated five membered ring ketone	202 nm
α,β -unsaturated aldehyde	207 nm

Increments	
Each alkyl substitute or ring residue	
At position **α**	10 nm
At position **β**	12 nm
At **γ** position and higher position	18 nm
Each Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Homoannular conjugated diene	39 nm

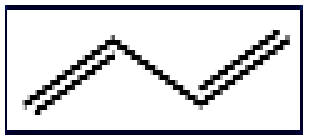
Auxochromes	α	β	γ
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
-OCOCH3	6	6	6

Aromatic compounds or Benzoyl derivatives.

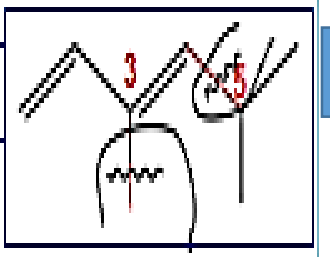
Parent Value	
X = alkyl / ring residue, ArCOR	246 nm
X = H, ArCHO	250 nm
X = OH / O-alkyl, $ArCO_2H$, $ArCO_2R$	230 nm
Increments	
R = alkyl / ring residue	o, m = 3 nm
	p = 10 nm
R = OH / O-alkyl	o, m =7 nm
	p = 25 nm
R = NH_2	o, m = 23 nm
	p = 58 nm



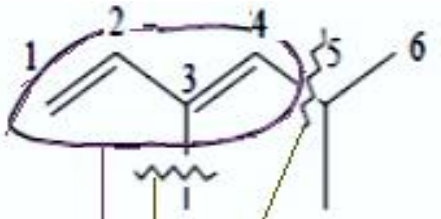
Parent value for Acyclic conjugated diene = 215 nm



Alkyl Substitute or Ring residue at C-3 and C-5 = 5+5= 10 nm

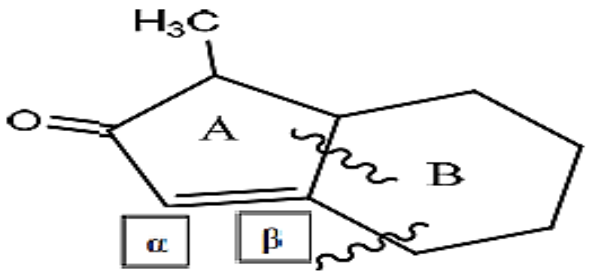


So, λ_{max} would be = (215+10) nm = 225 nm Observed value = 225 + - 5 nm



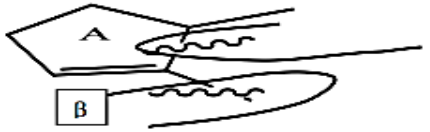
One way to identify an auxochrome is :

- draw a loop around the entire conjugated system (including extending olefins)
- then add hash marks across all bonds attached to the loop. The hash marks define auxochrome attachments.



Parent value for **α, β** unsaturated 5 membered enone = 202 nm

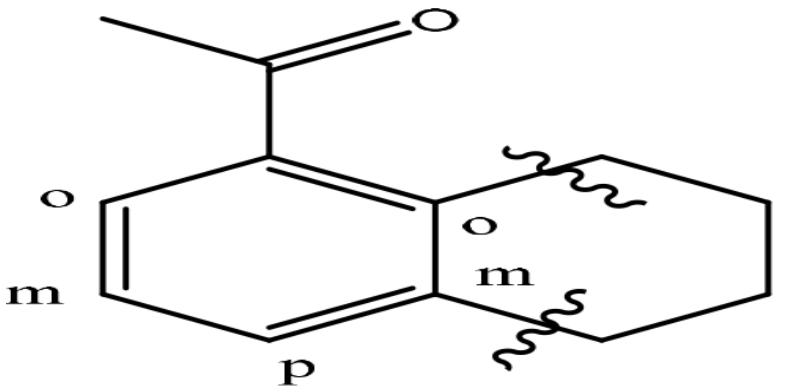
β ring residue = (12 x 2) nm = 24 nm

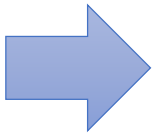


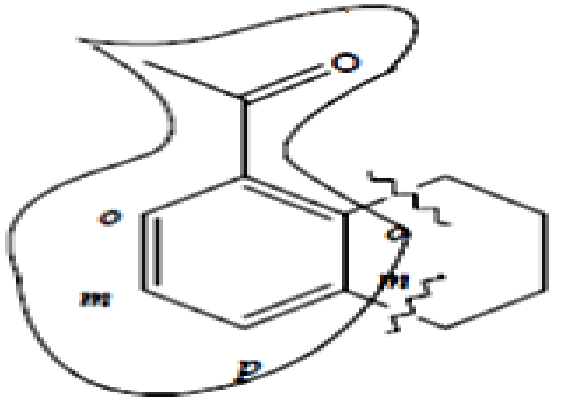
Exocyclic double bond (in respect of ring B) = 5 nm

So, λ_{max} would be = (202+24+5) nm = 231 nm

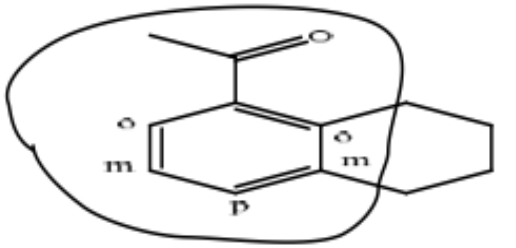
Observed value would be = 231 + - 5 nm



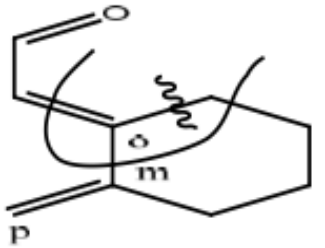




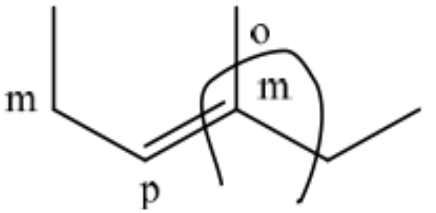
Parent value for Benzoyl group (aliphatic methyl group) = 246 nm



Auxochrome at Ortho Position = 3 nm

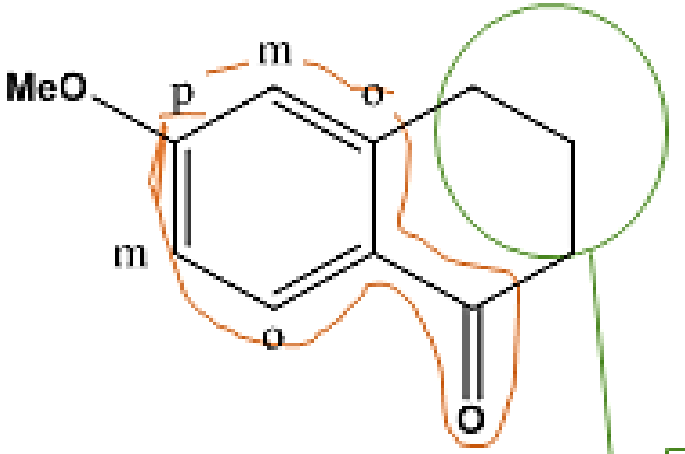


Auxochrome at Meta position = 3 nm



So, λ_{max} would be = (246+3+3) nm = 252 nm

Observed value would be = 252 + - 5 nm



Ketone

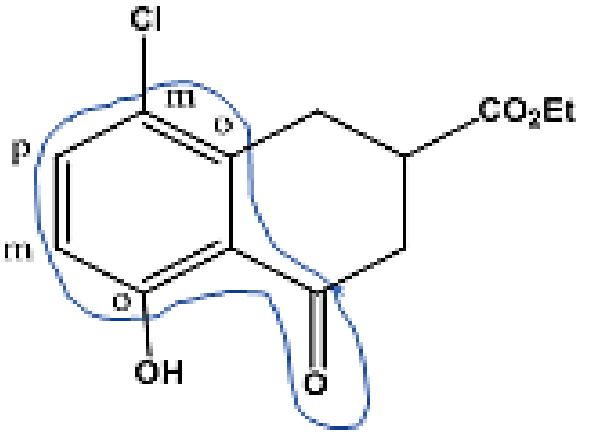
λmax.

Parent comp.	**246**
Ring residue	**+3**
***P*-OCH3**	**+25**

λmax. EtOH

calc. 274 nm

Obs. 276nm



Ketone

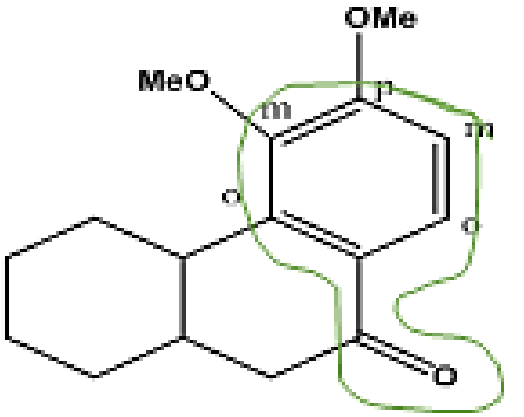
λmax.

Parent comp.	**246**
Ring residue	**+3**
***O*-OH**	**+7**
m- Cl	**+0**

λmax. EtOH

calc. 256 nm

Obs. 257nm



Ketone

λmax.

Parent comp.	**246**
Ring residue	**+3**
***P*-OCH3**	**+25**
***m*- OCH3**	**+7**

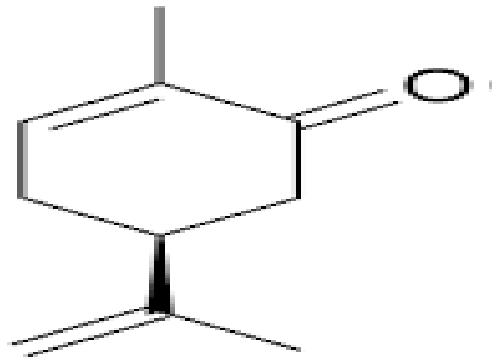
λmax. EtOH

calc. 281 nm

Obs. 278nm

Calculate the λmax for the following compounds :

1



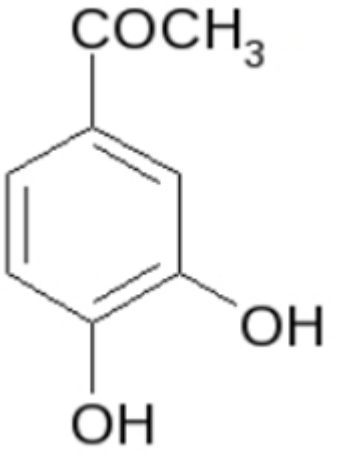
Parent conjugated enone in six membered ring = 215 nm

Substitution of alkyl groups at α position = 10 nm

Substitution of alkyl residue at β position = 12 nm

λ_{max} = **237 nm**

2



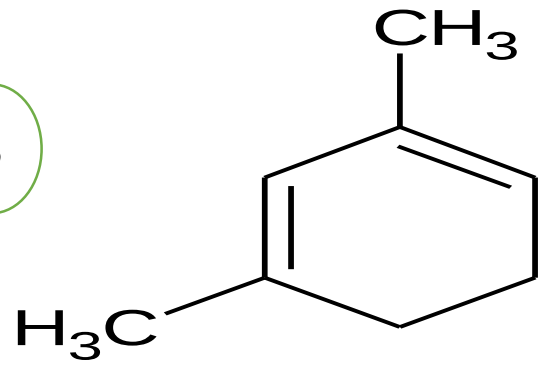
base value = 246 nm

Hydroxy group at meta position = 07 nm

Hydroxy group at para position = 25 nm

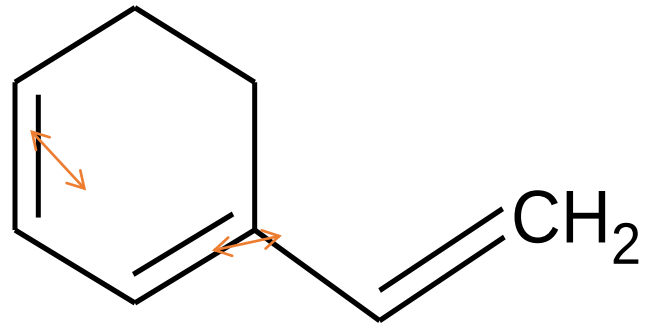
λ_{max} = 278 nm

3



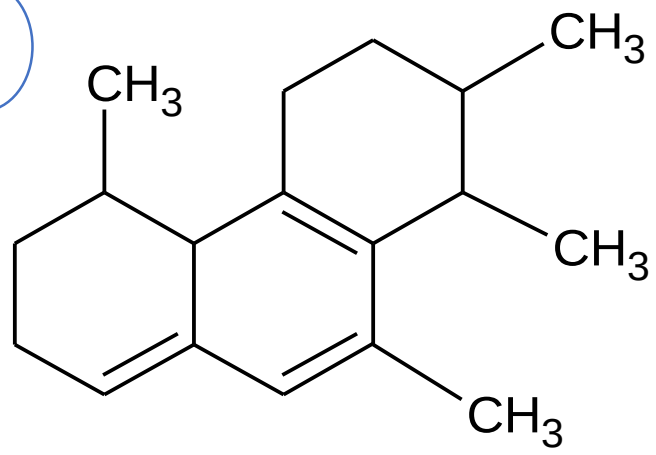
- Parent value for homoannular ring := 253 nm
- Two alkyl substituents : 2 x 5 = 10 nm
- Two ring residue : 2 x 5 = 10 nm
- calculated value : = 273 nm
- observed value : = 263 nm

4

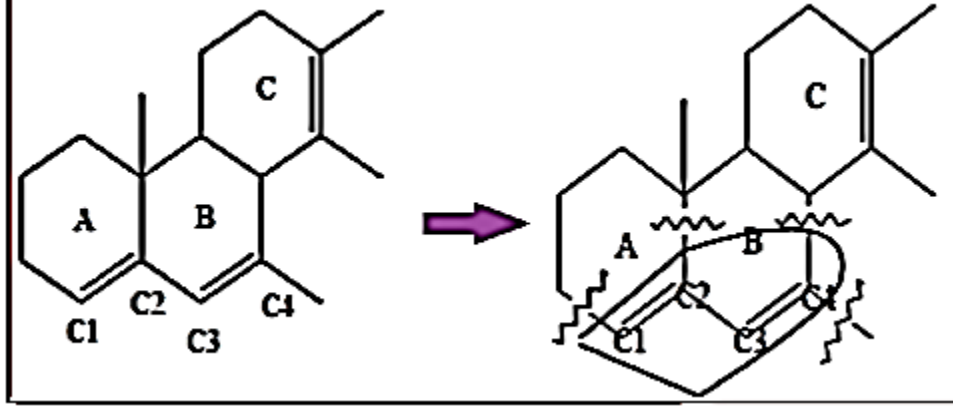


Parent value for homoannular :		= 253 nm
Extended conjugation	1 X30	= 30 nm
Alkyl substitution	2x5	=10 nm
Calculated value :		= 293 nm

5



Parent value for homoannular (the highest value)		= 253 nm
Extended conjugation	1 X30	= 30 nm
Exocyclic double bond		=5 nm
Alkyl substitution or ring residue	6x5	=30 nm
Calculated value :		= 318 nm



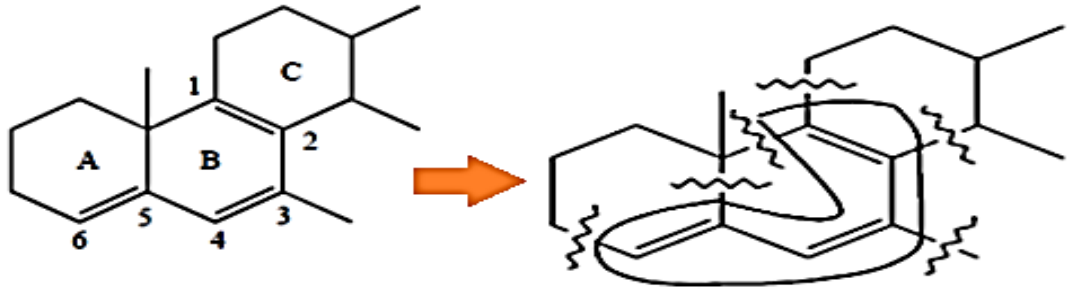
Calc. λ_{max} =

215 (heteroannular since two pi bonds are not in the same ring)

+20 (5 + 5 + 5 + 5 = 20, for each of the alkyl or ring auxochromes attached to C_1, C_2, C_4, and C_4)

+5 (pi bond of C_1-C_2 is exocyclic to ring B)

=240 nm



Calc. λ_{max} =

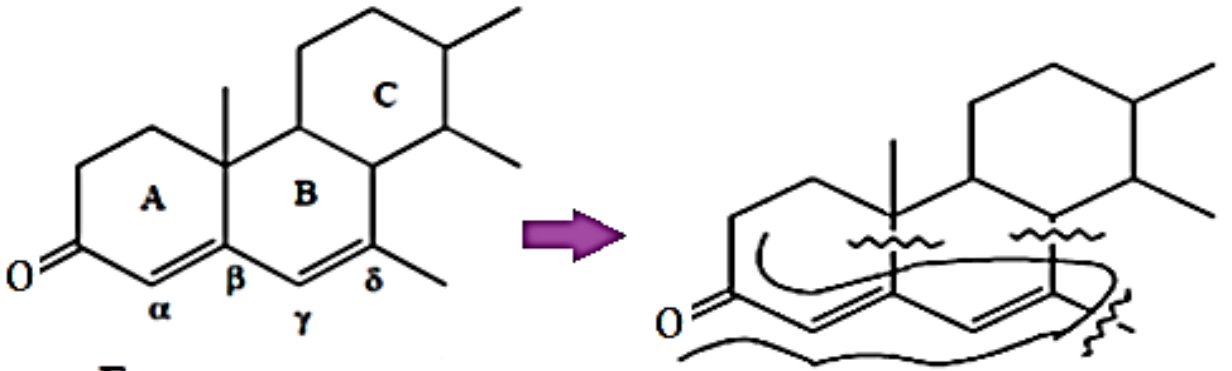
253 (choose diene with highest base value, pi bonds C_{1-2} and C_{3-4} are within same ring, so homoannular base should be selected)

+ 30 (C_{5-6} pi bond is conjugated to diene and is therefore an extending diene)

+ 5 (C_{5-6} is exocyclic to ring B)

+ 30 (5 + 5 + 5 + 5 + 5 + 5 = 30, for the alkyl or ring auxochromes at C_1, C_1, C_2, C_3, C_5, and C_6)

= 318 nm



Enone

Calc. λ_{max} :

215 (cyclohexenone base)

+ 30 (extending conjugation)

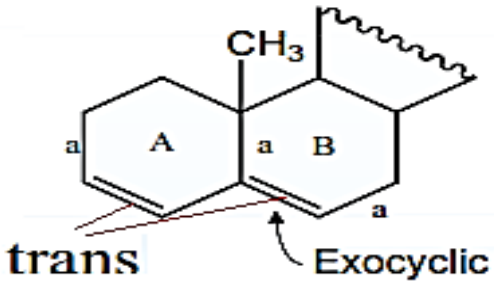
+ 5 (α,β olefin is exocyclic to ring B)

+ 12 (β auxochrome)

+ 36 (2 δ auxochromes)

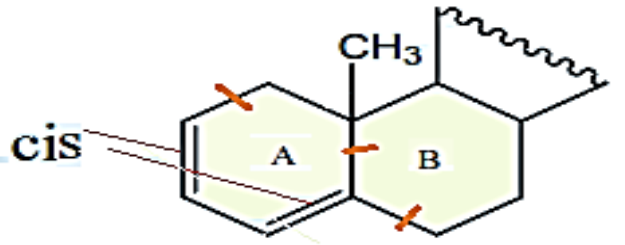
= 298 nm

Distinguish Isomers



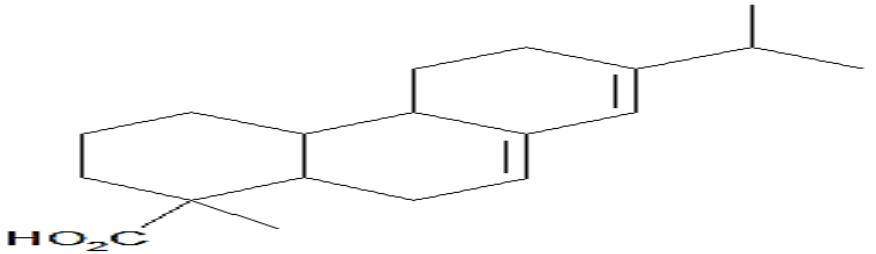
heteroannular or open diene 214 nm

ring residues:	3 × 5 =	15
exocyclic double bond:		5
		234 nm
observed:		235 nm

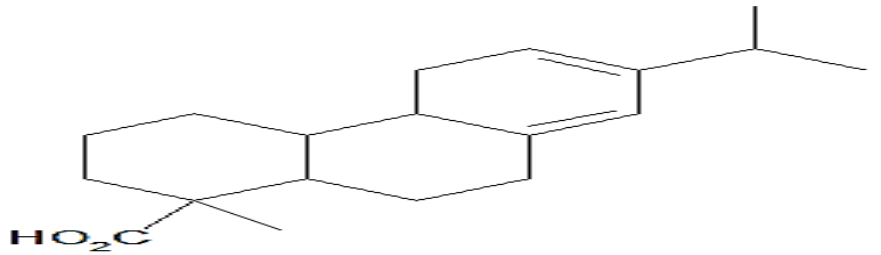


homoannular diene 253 nm

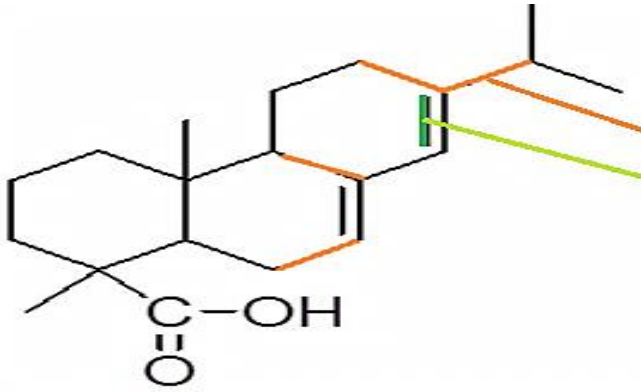
ring residues:	3 × 5 =	15
exocyclic double bond:		5
		273 nm
observed:		275 nm



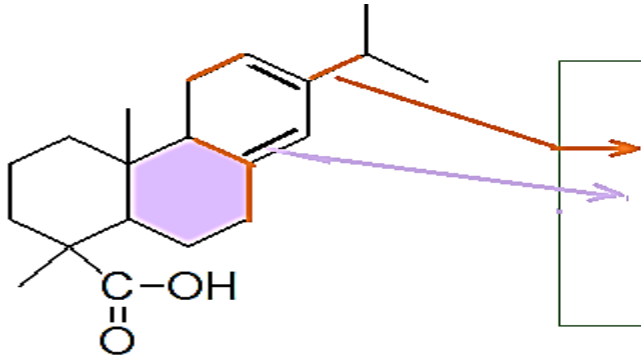
Base value	214
4 x alkyl subst.	20
exo DB	5
total	239
Obs.	238



Base value	253
4 x alkyl subst.	20
total	273
Obs.	273

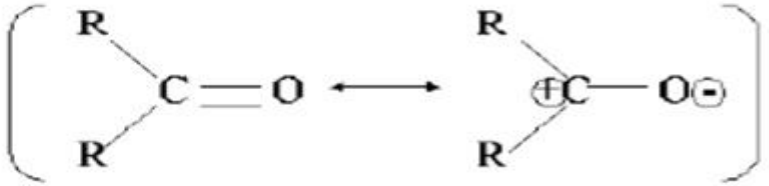


heteroannular diene = 214 nm
4 alkyl subs. (4 x 5) +20 nm
1 exo C=C + 5 nm
239 nm



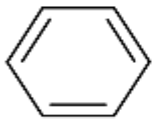
homoannular diene = 253 nm
4 alkyl subs. (4 x 5) +20 nm
1 exo C=C + 5 nm
278 nm

The structure of aldehydes and ketones has been studied and they were shown:



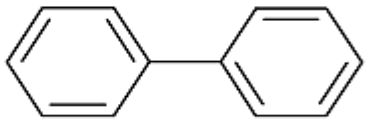
The position of absorption that involves nonbonding electrons n to δ and n to π is particularly sensitive to polarity of the solvent used.

How do you explain the fact that λ_{max} for compounds **I** and **II** are vastly different whereas those of **III** and **IV** are very similar?



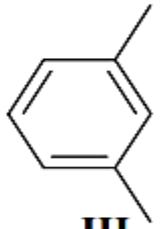
I

204 nm



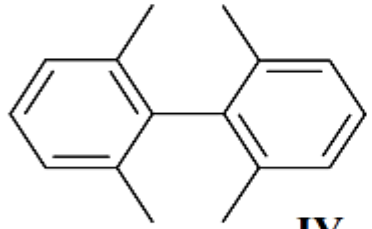
II

246 nm



III

211 nm



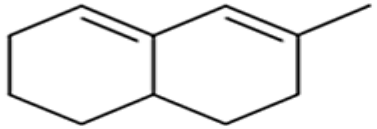
IV

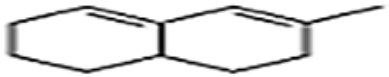
218 nm

I and II: II more or less planar, extended conjugation over both rings

III and IV: IV considerably twisted, conjugation only over one ring as in III; IV is just twice III

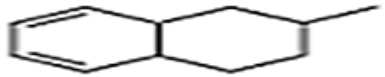
A diene $C_{11}H_{16}$ was thought to have the structure below. Its UV spectrum showed a λ_{max} of 263 nm. Can the structure below be correct? If not, draw a structure with the same skeleton that satisfies the spectral data.





I

Heteroannuler dienes



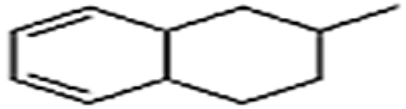
II

Homoannular dienes

Answer: I not correct one because

215 + 4×5 + 5 = 240 nm, too far off. Probably due to wrong base system:

II is the correct one because :263 − 253 = 10 nm > 2×5, 2 alkyl substituents:



A)) What are the concentrations of the following solutions of drugs in g/100ml and mg/100ml?

1. hydrocortisone sodium phosphate , A(1% ,1cm)value 333 at 248 nm ,measured absorbance 0.666 at 248 nm

2. isoprenaline , A(1% , 1cm) value =100 at 280nm , measured absorbance 0.500 at 280 nm.

$$c = \frac{A}{A\,(1\%,\ 1\ cm)}$$

hydrocortisone sodiumphosphate

$$\text{conc.} = \frac{A}{A(1\%,\ 1\ cm)}$$

$$\text{Conc.} = \frac{0.666}{333} = 0.002\ g/100ml$$

$$\text{Conc} = 0.002\ g/100ml * 1000$$

$$= 2mg/100ml$$

isoprenaline

$$\text{conc.} = \frac{A}{A(1\%,\ 1\ cm)}$$

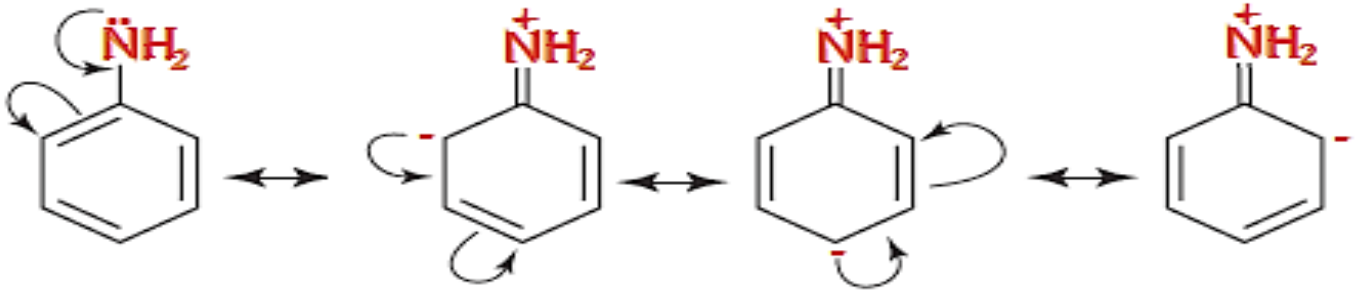
$$\text{Conc.} = \frac{0.4}{100} = 0.005\ g/100ml$$

$$\text{Conc} = 0.005\ g/100ml * 1000$$

$$= 5mg/100ml$$

The λ_{max} of benzene is 204 nm, whereas the λ_{max} of aniline is 230 nm?

The lone pair of electrons on the NH_2 interacting with the ring electrons to increase the electron density throughout the ring, particularly at the *ortho* and *para* positions of the ring.



This effect is seen when the basic aniline is unionised. pH 8–14.

When aniline is placed in a solution of pH < 7, the λ_{max} returns to virtually the value obtained for benzene (203 nm) What is happening is that aniline in acidic solution reacts to form the anilinium salt.The lone pair of electrons on the nitrogen is now involved in bond formation to an H^+ ion and can no longer function as an auxochrome.

λ_{max} = 203 nm

- Q: the anilinium ion shows λmax = 265nm. Explain.
- End absorption:
- Is an absorption that are increased in intensity towards shorter wave length due to n → δ* transition, occur near 200 nm with the molecule contain O, N, S or halogen atoms