

ULTRAVIOLET (UV) & VISIBLE SPECTROSCOPY

- Ultraviolet and visible spectroscopy also known as electronic spectroscopy is used to measure the number of conjugation of double bond and aromatic conjugation within the molecule.
- It involves the promotion of electrons from HOMO to LUMO (HOMO means Highest Occupied Molecular Orbital whereas LUMO means Lowest Unoccupied Molecular Orbital).
- The HOMO-LUMO gap decrease as the conjugation increase.



- The ultraviolet region corresponds to 400-200 nm and visible region to 800-400 nm.
- UV-visible spectroscopy based on **Beer-Lambert law**.

$$\log \frac{I_0}{I} = \epsilon \cdot l \cdot c \text{ or } \epsilon = A/c l$$

Where,

I_0 = intensity of incident light

I = intensity of transmitted light

ϵ = molar absorptivity

l = path length of sample

c = concentration of sample

A = Absorbance

- Absorbance (A): It is reciprocal of Transmittance

$$\text{Absorbance (A)} = \text{Optical density (D)} = \log \frac{1}{T} \text{ or } \log \frac{I_0}{I}$$

- Transmittance (T): The fraction of incident light transmitted is known as Transmittance.

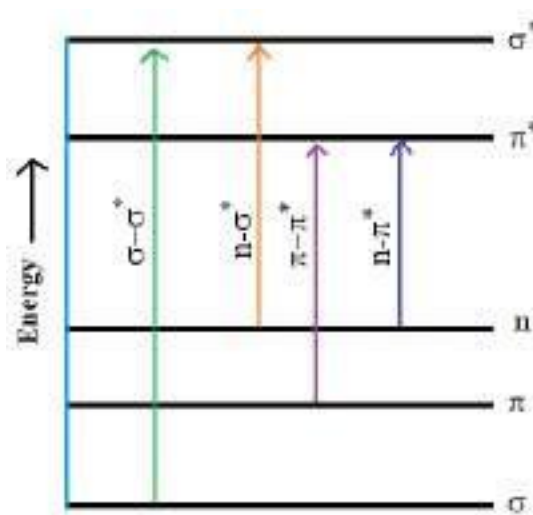
$$\text{Transmittance (T)} = \frac{I}{I_0}$$

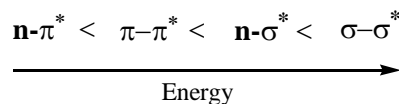
Electronic transitions

When molecule is getting excited by the absorption of electromagnetic radiation in UV-visible region then its electrons are promoted from ground state to excited state or from bonding orbital to anti-bonding orbital.

Types of electronic transitions

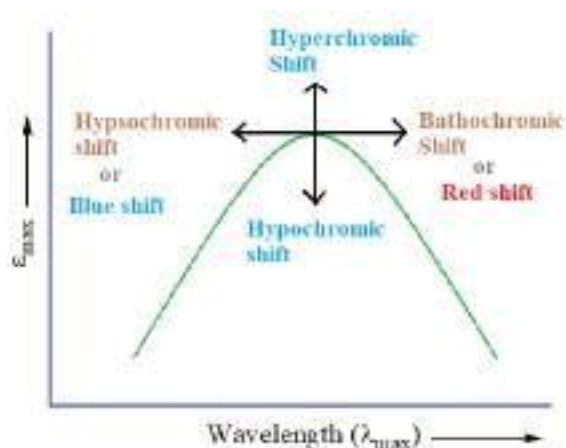
- $\sigma - \sigma^*$ Transition: transition of an electron from bonding sigma orbital (σ) to anti-bonding sigma orbital (σ^*), is represented by $\sigma - \sigma^*$ transition. For example, alkanes because in alkane all the atoms are held together with sigma bond.
- $n - \sigma^*$ & $n - \pi^*$ Transition: Transitions from non-bonding molecular (n) orbital to anti-bonding sigma orbital or anti-bonding pi orbital (π^*), are represented by $n - \sigma^*$ or $n - \pi^*$ transition respectively. These transition required less energy than $\sigma - \sigma^*$ transition. For example, alkyl halide, aldehydes, ketones etc.
- $\pi - \pi^*$ Transition: This type of transition generally show in unsaturated molecules like alkenes, alkynes, aromatics, carbonyl compounds etc. This transition required less energy as compare to $n - \sigma^*$ transition.



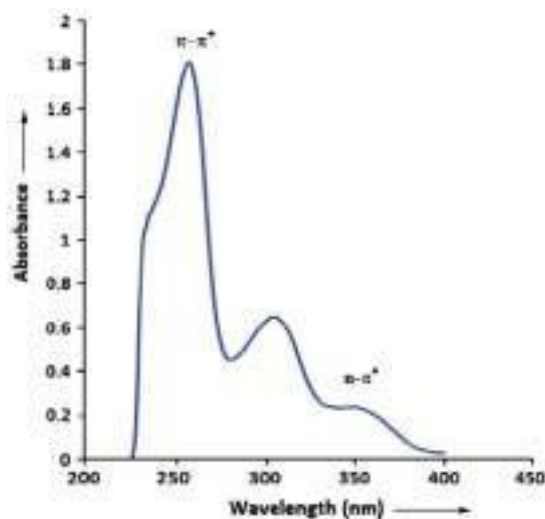


Absorption, intensity shift & UV spectrum

- Bathochromic shift: It is also known as Red shift, in this case absorption shift towards longer wavelength (λ_{\max}).
- Hypsochromic shift: It is also known as Blue shift, in this case absorption shift towards shorter wavelength (λ_{\max}).
- Hyperchromic shift: Intensity of absorption maximum (ϵ_{\max}) increases.
- Hypochromic shift: Intensity of absorption maximum (ϵ_{\max}) decrease.



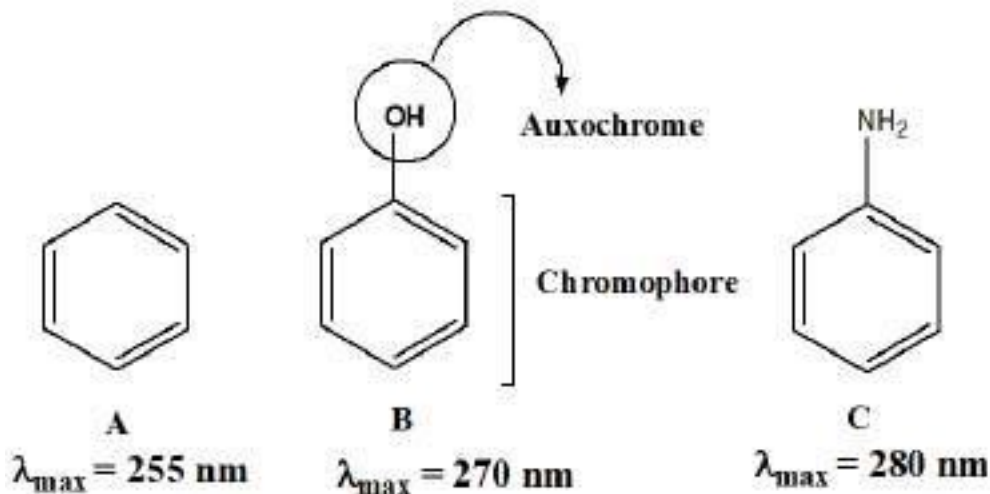
Absorption & intensity shift



UV spectrum of unknown compound

Chromophores & Auxochromes

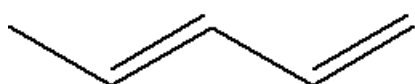
- a) **Chromophores:** Chromophore is a covalently unsaturated group absorbed electromagnetic radiation in UV-visible region and impart color to the compound. For example, C=C, C≡C, benzene, NO₂ etc.
- b) **Auxochromes:** Auxochrome is a saturated group (containing lone pair of electron), when auxochrome attach to the Chromophore absorption shift towards longer wavelength. For example, -OH, -SH, -NH etc.



Factor affecting absorbance & intensity

a) Conjugation

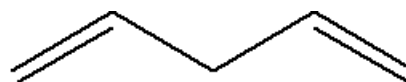
Absorption shift towards longer wavelength, if double bonds (chromophore) present in the molecule are in conjugation. For example,



$$\lambda_{\max} = 217 \text{ nm}$$

conjugated

A



$$\lambda_{\max} = 175 \text{ nm}$$

non-conjugation

B

In compound 'A', double bonds are in conjugation therefore 'A' possessing higher wavelength (λ_{\max}) as compare to compound 'B' (non-conjugated derivative).

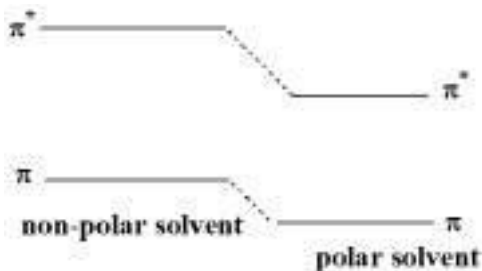
We know that,

$$E = \frac{hc}{\lambda}$$

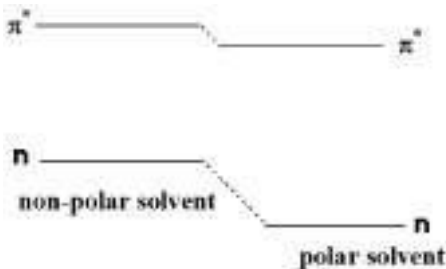
As the conjugation increase transition energy (E) between the orbitals is decrease and therefore wavelength (λ_{\max}) increase.

b) Effect of solvent:

In polar solvent, $\pi - \pi^*$ transitions shift towards longer wavelength (Red shift), because dipole interactions with polar solvent molecules lower the energy of excited state (π^*) than that of the ground state (π orbital's are stabilized by hydrogen bonding with polar solvent).



Whereas in polar solvent, $n - \pi^*$ transitions shift towards lower wavelength (Blue shift), because dipole interactions with polar solvent molecules lower the energy of ground state (n) than that of the excited state (n orbital's are stabilized by hydrogen bonding with polar solvent).

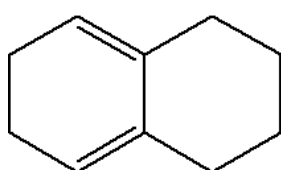


The Woodward-Fieser rules (Calculation of λ_{\max} (nm) in conjugated dienes)

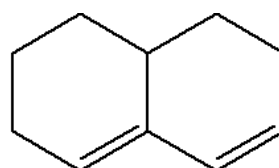
	λ_{\max} (nm)
Base value:	
Acyclic or heteroannular dienes	214
Homoannular dienes	253
Increments for:	

Double bond extending conjugation	30
R alkyl substituent or ring residue	5
Exocyclic double bond	5
Polar groupings:	
-OCOCH ₃	0
-OR	6
-Cl, -Br	5
-NR ₂	60

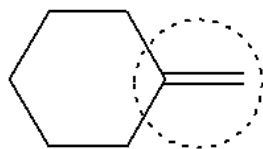
Explanation of terminology used in Woodward-Fieser rules



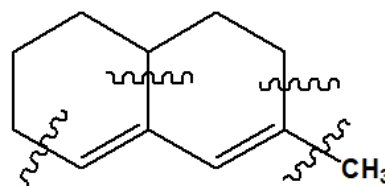
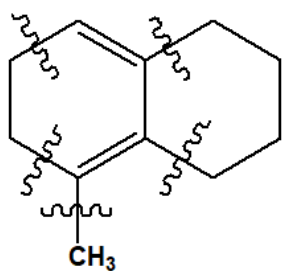
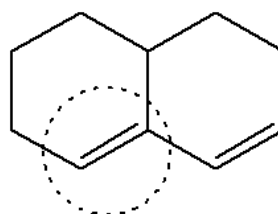
homoannular diene



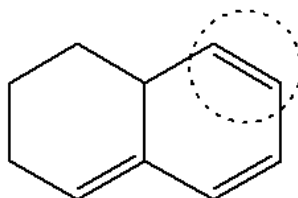
heteroannular diene



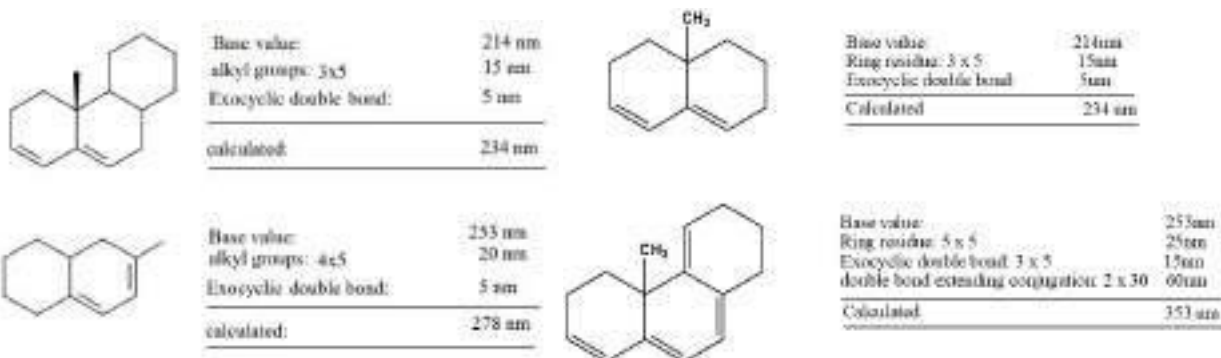
double bond exocyclic to the double bond



~~~~~ sign represent R alkyl group or ring residue

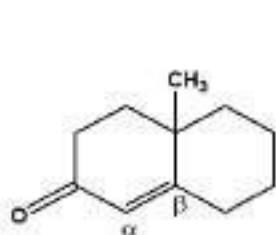


**Double bond extending conjugation**

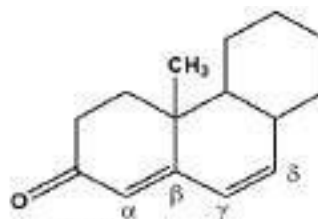


### The Woodward-Fieser rules (Calculation of $\lambda_{max}$ (nm) in $\alpha,\beta$ -unsaturated carbonyl compounds)

|                                     | $\lambda_{max}$ (nm)                                     |
|-------------------------------------|----------------------------------------------------------|
| <b>Base value:</b>                  |                                                          |
| Acyclic or 6-membered cyclic ketone | 215                                                      |
| 5-membered cyclic ketone            | 202                                                      |
| Aldehyde                            | 210                                                      |
| <b>Increments for:</b>              |                                                          |
| Homocyclic diene component          | 39                                                       |
| Double bond extending conjugation   | 30                                                       |
| R alkyl substituent or ring residue | $\alpha = 10, \beta = 12, \gamma \text{ \& higher} = 18$ |
| Exocyclic double bond               | 5                                                        |
| <b>Polar groupings:</b>             |                                                          |
| -OH                                 | $\alpha = 35, \beta = 30, \gamma = 30$                   |
| -OR                                 | $\alpha = 35, \beta = 30, \gamma = 17$                   |
| -Cl,                                | $\alpha = 15, \beta = 12, \gamma = 12$                   |
| -Br                                 | $\alpha = 25, \beta = 30, \gamma = 25$                   |
| -NR <sub>2</sub>                    | $\beta = 95$                                             |
| -OCOCH <sub>3</sub>                 | $\alpha = 6, \beta = 6, \gamma = 6$                      |



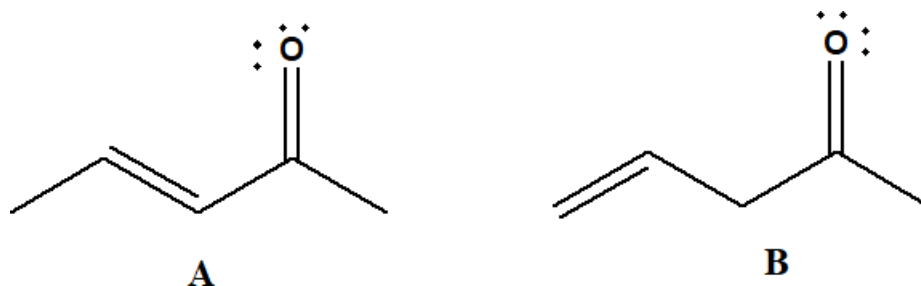
|                              |        |
|------------------------------|--------|
| Base value:                  | 215 nm |
| $\beta$ Ring residue: 2 x 12 | 24 nm  |
| Exocyclic double bond:       | 5 nm   |
| <hr/>                        |        |
| Calculated:                  | 244 nm |



|                                           |        |
|-------------------------------------------|--------|
| Base value:                               | 215 nm |
| $\beta$ Ring residue:                     | 12 nm  |
| $\delta$ Ring residue:                    | 18 nm  |
| Exocyclic double bond: 1 x 5              | 5 nm   |
| double bond extending conjugation: 1 x 30 | 30 nm  |
| <hr/>                                     |        |
| Calculated:                               | 280 nm |

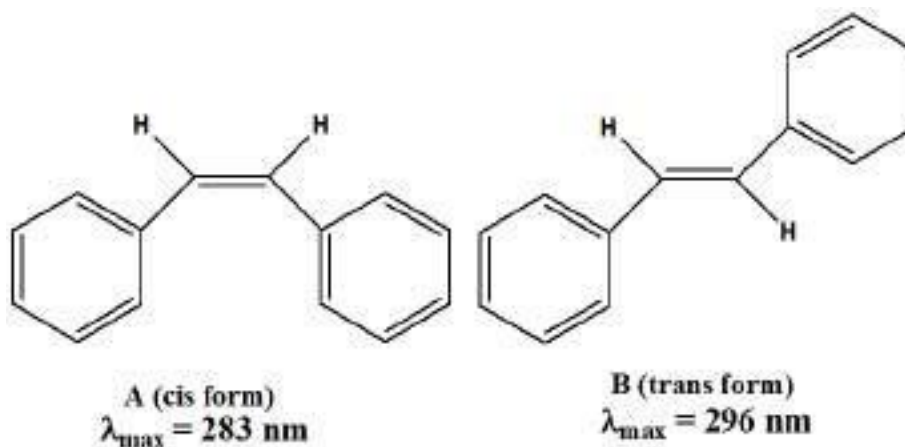
## Application of UV spectroscopy

- i) Extent of conjugation: As the double bond increase, absorption shift towards longer wavelength.
- ii) Distinction between conjugated and non conjugated compounds:



Both the above compound A & B are isomer of each other. Due to  $n - \pi^*$  transition, compound A appear at longer wavelength than compound B.

- iii) Study of geometric isomerism:



In isomer A, due to steric hindrance, absorption shift towards lower wavelength. We know that, steric hindrance destabilize the compound means energy of the molecule increase which decreases the wavelength.

- iv) Used in the detection of impurities: Due to presence of impurities in the compound, give additional peaks are observed in UV spectrum.



### Exercise

1. What is electronic spectroscopy?
2. What is Chromophore? How does it differ from auxochrome?
3. Discuss how conjugation affects the intensity of absorption band.
4. Write the short note on electronic transitions.
5. Write notes on application of UV-visible spectroscopy.
6. Explain the term Hypsochromic shift and Bathochromic shift. What structural features may lead to these shifts in organic molecules?
7. Explain the effect of polar solvent on  $\pi - \pi^*$  and  $n - \pi^*$  transition.
8. How 1,3-pentadiene and 1,4-pentadiene can be distinguished by UV spectroscopy?
9. Why aniline behaves like that of benzene in acidic medium?
10. Two isomeric dienes 'A' and 'B' having the molecular formula  $C_5H_8$  absorb at  $\lambda_{max}$  225 nm and  $\lambda_{max}$  180 nm respectively. Write the structure of the two isomers.
11. Find out the  $\lambda_{max}$  of following molecules;

