DEPARTMENT OF CHEMISTRY

Udai Pratap Autonomous College

Varanasi -221002

E-content

Subject	:	Organic Chemistry
Class	:	B. Sc. IV Semester
Year	:	2025-26

Unit	:	IV
Topic	:	Spectroscopy
Sub-topic	:	Ultra Violet-Visible Spectroscopy
Key words	:	Beer's-Lambert's Law, Chromophore, Types of Transition, Bathochromic and Hypsochromic shift, Effect of conjugation

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Ultra Violet-Visible Spectroscopy

Spectroscopy is defined as the interaction of matter with electromagnetic radiation. The most important consequence of electromagnetic interaction is that energy is absorbed or emitted by the matter.

The field of spectroscopy can be divided into two categories:

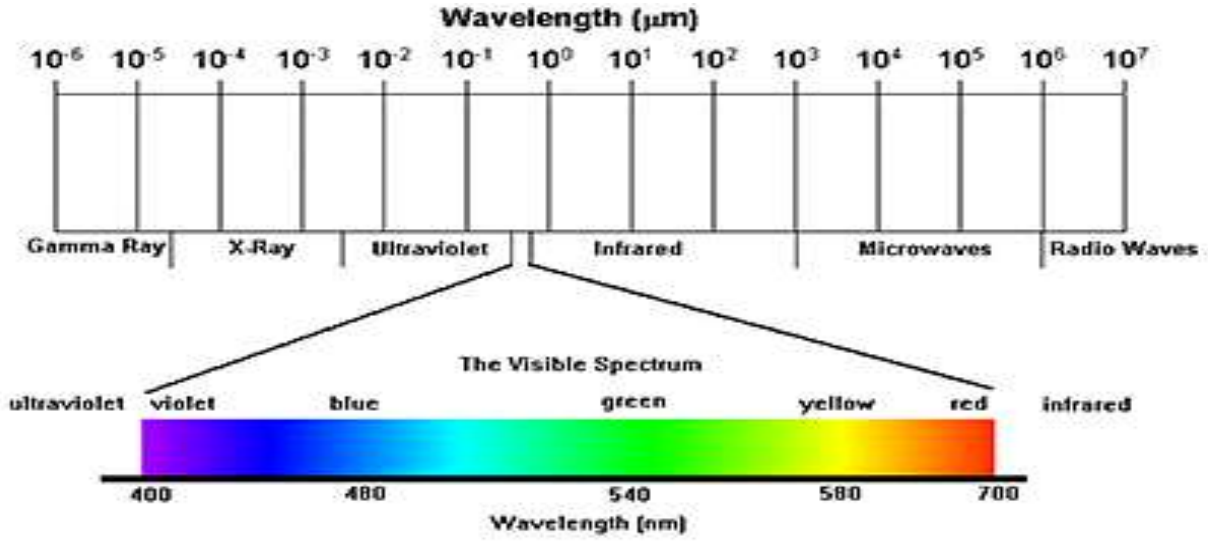
(i) Emission spectroscopy:

Example: Atomic spectra etc.

(ii) Absorption spectroscopy:

Example: UV-Visible, IR, NMR, NQR and ESR spectroscopy etc.

Electromagnetic Spectrum:



Energy is proportional to frequency, Frequency is inversely proportional wavelength

The ultraviolet spectroscopy is comparatively less informative than the infrared or NMR spectroscopy. However, it is a valuable tool for the identification of organic compounds. The main feature of ultraviolet spectroscopy is to get information about the extent of multiple bond and conjugation, aromatic and heteroaromatic systems.

UV light can be absorbed by molecules to excite higher energy (most loosely bound) electrons from lower energy states to higher states. Such transitions can be studied extensively to understand the binding energy of the corresponding electrons undergoing transition. Since π-electrons are most loosely bound in an organic molecule, UV spectroscopy yields a lot of

information about the degree of unsaturation in a molecule. When the wavelength of the transition exceeds the UV range, based on the same principle, even the colours of molecules can be explained on the basis of absorption of visible light.

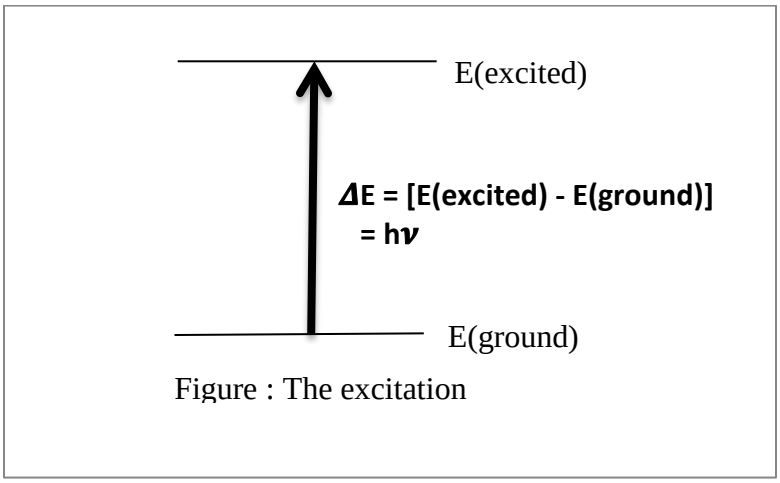
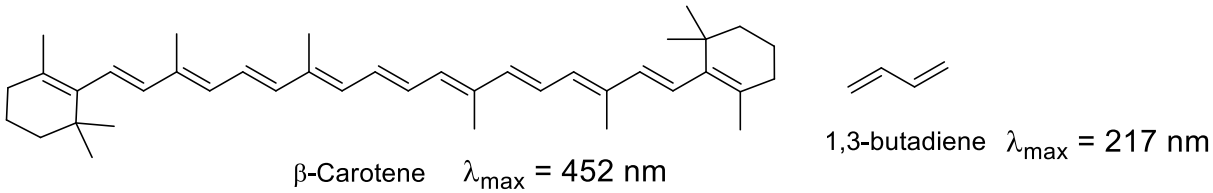


Figure : The excitation



Beer's-Lambert Law:

"When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution".

$$\log \frac{I_o}{I} = \epsilon c l = A$$

where, I_o =Intensity of the incident light.

I = Intensity of the transmitted light.

c= Concentration of the solution in moles/litre.

l = Path length of the sample usually 1 cm.

ϵ= Molar absorptivity or molar extinction coefficient.

A = Absorbance

Molar absorptivity = Absorbance of 1 mol dm^{-3} solution if cell length = 1 cm.

$$\log \frac{I_o}{I} = \epsilon c l = A$$

Electronic Transitions: According to molecular orbital theory, the excitation of a molecule by the absorption of radiation in the UV-visible regions involves promotion of its electron from a bonding, or non-bonding (n) orbital to an antibonding orbital.

I. $\boldsymbol{\sigma \rightarrow \sigma^*}$ **Transition:** The promotion of an electron from a bonding sigma orbital to the associated antibonding sigma orbital is $\sigma \rightarrow \sigma^*$ transition. It is a high energy process because σ bonds are generally very strong. Example: In alkane

II. $\boldsymbol{n \rightarrow \sigma^*}$ **Transition:** The promotion of an electron from a non-bonding orbital to the associated antibonding sigma orbital is $n \rightarrow \sigma^*$ Transition. Compounds containing non-bonding electrons on a heteroatom are capable of showing absorption due to $n \rightarrow \sigma^*$ transitions. These transitions require lower energy than $\sigma \rightarrow \sigma^*$ transition. Example: In oxygen, nitrogen, sulphur and halogen compounds

III. $\boldsymbol{\pi \rightarrow \pi^*}$ **Transition:** The promotion of an electron from a bonding π orbital to the associated antibonding π^* orbital is $\pi \rightarrow \pi^*$ transitions. These transitions require lower energy than $n \rightarrow \sigma^*$ transition. Example: In alkenes, carbonyl compounds, alkynes, azo compounds, nitro-compounds and so on.

IV. $\boldsymbol{n \rightarrow \pi^*}$ **Transition:** The promotion of an electron from a non-bonding orbital to the associated antibonding π^* orbital is $n \rightarrow \pi^*$ Transition. This transition requires lowest energy. Example: In carbonyl compounds.

The usual order of energy required for various electronic transitions is

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

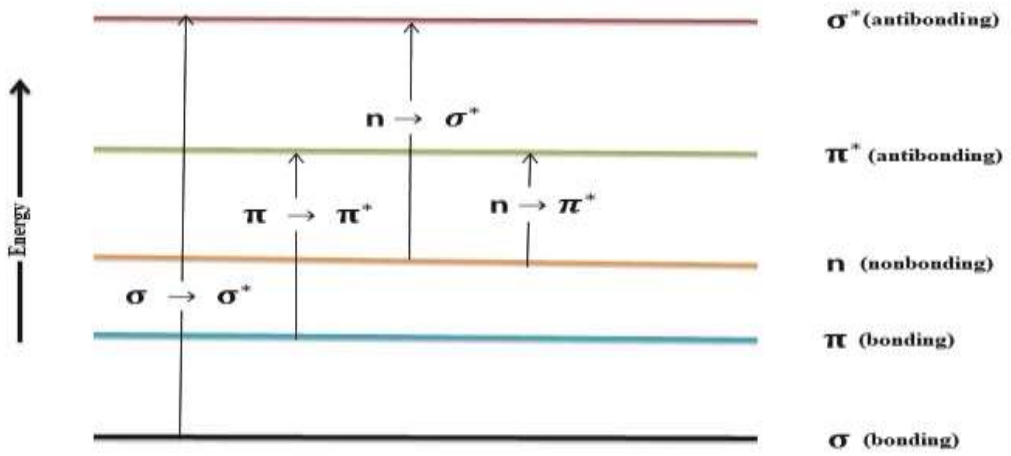


Fig. Relative energies of electronic transitions

Chromophore:

A covalently unsaturated group responsible for electronic absorption in the UV-visible region is known as a chromophore. (e.g., C=C, C=O, esters, amides, -NO_2 etc.).

Auxochrome:

A covalently saturated group with non-bonded electrons which, when attached to a chromohore, alters both the wavelength and the intensity of the absorption is known as auxochrome (e.g., -OH, -NH_2, -NR_2 -SH etc.)

Bathochromic Shift:

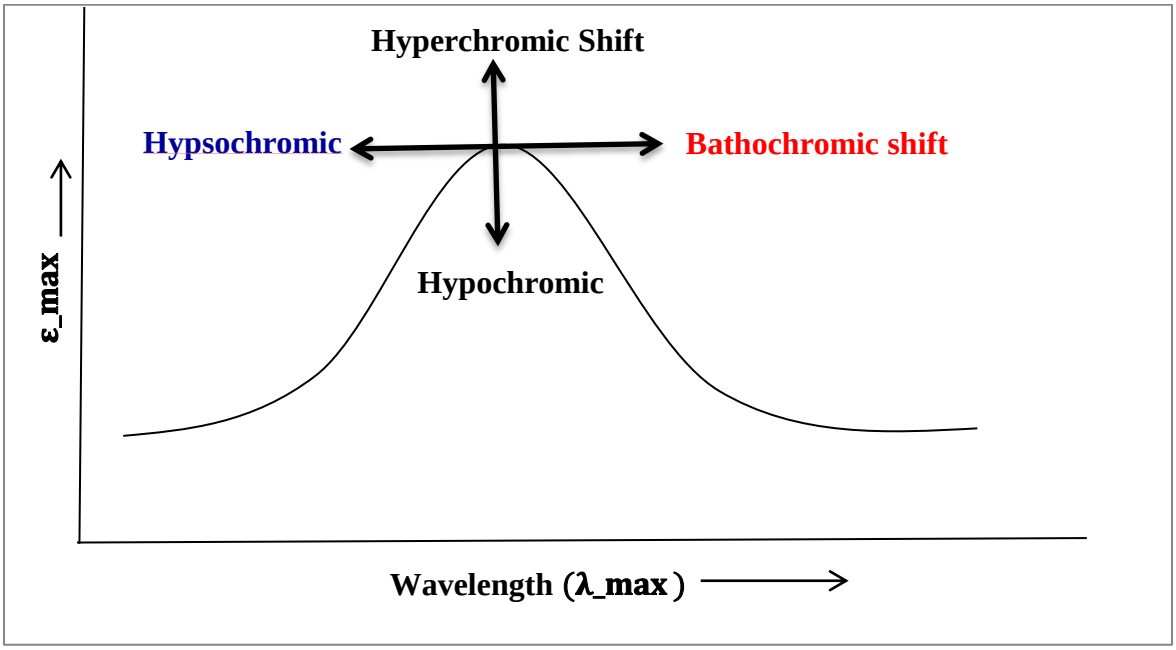
A shift to a longer wavelength or lower energy (also known as red shift), for example: benzene shows λ_{max} 256 nm and aniline shows λ_{max} 280 nm due to presence of the auxochrome NH_2.

Hypsochromic Shift:

The shift to a shorter wavelength or higher energy is known as blue shift. This is caused by the removal of conjugation or change in solvent polarity. For example: aniline shows λ_{max} 280 nm, whereas anilinium ion (acidic solution of aniline) shows λ_{max} 256 nm.

Hyperchromic Effect: An increase in absorption intensity.

Hypochromic Effect: A decrease in absorption intensity.

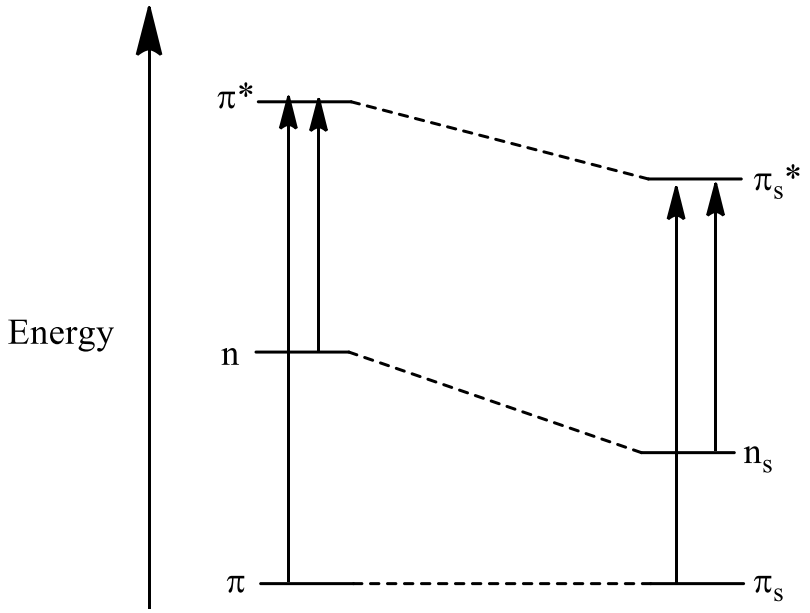


Solvent Effects:

The position and intensity of an absorption band may shift if the spectrum was recorded in different solvents. Conjugated dienes and aromatic hydrocarbons experience very less "solvent effect". α, β-unsaturated carbonyls show two different shifts in bands for changing solvents from non-polar to a polar.

$\boldsymbol{\pi \rightarrow \pi^*}$ **Transition:** The $\pi \rightarrow \pi^*$ transitions of non-polar compounds e.g. alkenes, dienes and polyenes are not appreciably affected by changing solvent polarity. The $\pi \rightarrow \pi^*$ transitions of polar compounds e.g. saturated as well as α,β-unsaturated carbonyls compounds are shifted to longer wavelength (higher intensity with increasing solvent polarity).

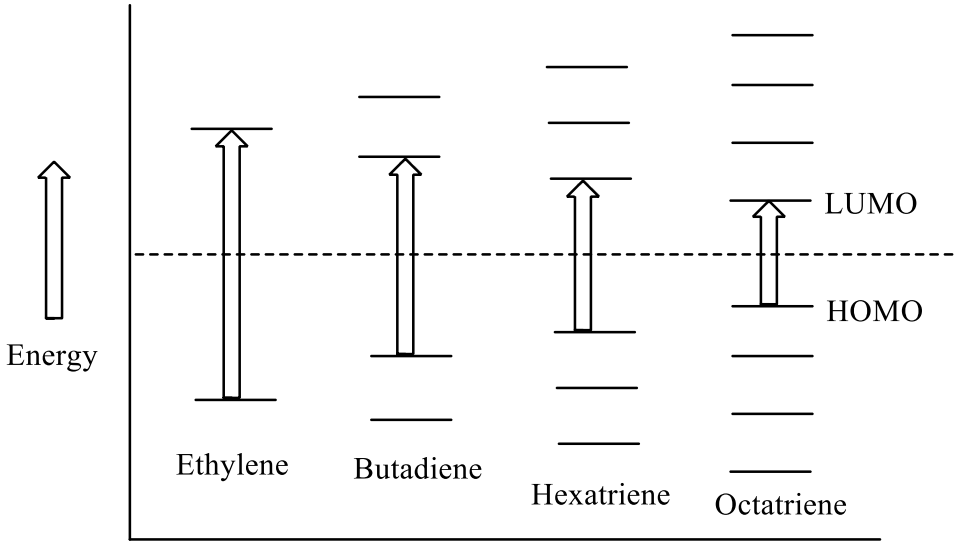
$\boldsymbol{n \rightarrow \pi^*}$ **Transition:** It has been found that an increase in solvent polarity usually shifts transitions to shorter wavelength (higher energy). π^* Orbitals get stabilized (due to more polarity) by solvation than π orbitals. n orbitals get stabilized mainly by H-bonding.



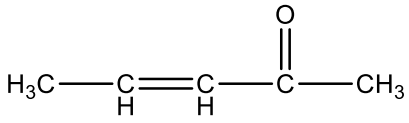
$\pi \rightarrow \pi^* > \pi_s \rightarrow \pi_s^*$ and $n \rightarrow \pi^* < n_s \rightarrow \pi_s^*$

Factors affecting λ_{max}:

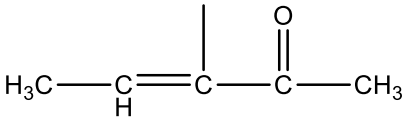
1. **Conjugation:** When two or more chromophoric groups are conjugated, the absorption maximum is shifted to a longer wavelength (greater intensity). As we increase the number of p orbitals making up the conjugated system, the transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) has progressively lower energy. The energy gap between bonding and antibonding orbital gradually decreases which corresponds to increase in absorption maximum.



2. **Hyperconjugation:** Hyperconjugation stabilizes the excited state as well as ground state, it shows similar effect as resonance effect i.e. λ_{max} increases with hyperconjugation.



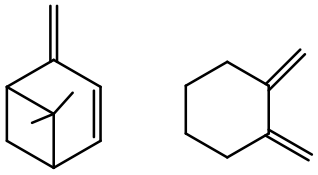
λmax = 224 nm



λmax = 236 nm

3. **Hydrogen bonding:** Intramolecular hydrogen bonding increases in the excited state relative to the ground state. Therefore intramolecular hydrogen bonding stabilizes the excited state than its ground state and thus decreases the energy content of the excited state.
4. **Steric effect:** Distortion of the chromophore may lead to red or blue shifts depending upon the nature of distortion. The strained molecule verbena (I) exhibits at 245.5 nm whereas the usual calculation shows a value of 229 nm. The diene (II) might be expected to have a maximum at 273 nm but distortion of the chromophore presumably out of

planarity with consequent loss of conjugation, causes the maximum to be as low as 220 nm.



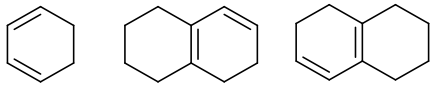
(I) (II)

Woodward-Fiesser Rules for calculating λ_{max} in Conjugated Dienes and Trienes:

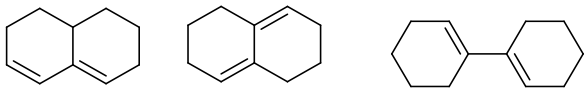
Woodward (1941) formulated a set of empirical rules for calculating or predicting λ_{max} in conjugated acyclic and six-membered rings dienes.

Woodward-Fiesser Rules for calculating λ_{max} in Conjugated Dienes and Trienes	
Base value for acyclic or heteroannular diene	215 nm
Base value for homoannular diene	253 nm
Increment for each:	
Alkyl substituent or ring residue	5 nm
Exocyclic conjugated double bond	5 nm
Double bond extending conjugation	30 nm
-OR	6 nm
-Cl, -Br, -I	5 nm
-OCOR	0 nm
-SR (alkylthio)	30 nm
$-NR_2$ (dialkylamino)	60 nm
In the same double bond exocyclic to two rings simultaneously	10 nm
Calculated λ_{max} of the compound	Total nm

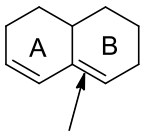
i. **Homoannular Dienes:** In homoannular dienes double bonds are present in the same ring and having *s-cis* (cisoid). Example:



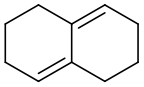
ii. **Heteroannular dienes:** In heteroannular dienes double bonds are not present in the same ring and having *s-trans* (transoid). Example:



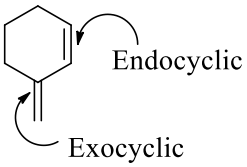
iii. **Exocyclic double bond:** The carbon–carbon double bonds projecting outside a ring are called exocyclic double bonds. Example:



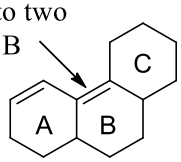
Exocyclic to ring A
Endocyclic to ring B



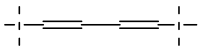
Two exocyclic double bond



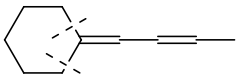
Exocyclic to two
ring A and B



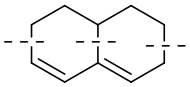
iv. **Alkyl substituents and Ring residue:** Only the alkyl substituents and ring residue attached to the carbon atoms constituting the conjugated system of the compound are taken into account. Example:



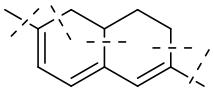
Two alkyl substituents



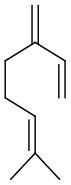
Two ring residue



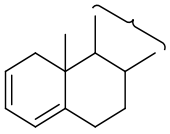
Three ring residue



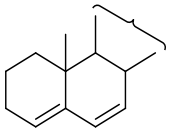
Three ring residue
Two alkyl substituents



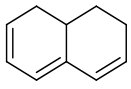
Base value		= 215 nm
Alkyl substituent	1 x 5 =	5 nm
Calculated λ_{max}		= 220 nm



Base value		= 253 nm
Alkyl substituent	3 x 5 =	15 nm
One exocyclic	1 x 5 =	5 nm
Calculated λ_{max}		= 273 nm



Base value		= 215 nm
Alkyl substituent	3 x 5 =	15 nm
One exocyclic	1 x 5 =	5 nm
Calculated λ_{max}		= 235 nm

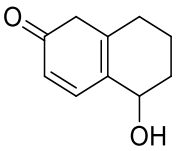


Base value	= 253 nm
Alkyl substituent	3 x 5 = 15 nm
One exocyclic	1 x 5 = 5 nm
Double bond extending conjugation	= 30 nm
Calculated λ_{max}	= 303 nm

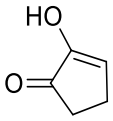
Woodward-Fiesser Rules for calculating λ_{max} in α,β-unsaturated Carbonyl compounds:

Woodward-Fiesser Rules for calculating λ_{max} in α,β-unsaturated Carbonyl compounds:

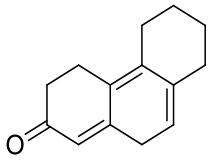
Base value for		
Acyclic α,β-unsaturated ketones		215 nm
Six-membered cyclic α,β-unsaturated ketones		215 nm
Five-membered cyclic α,β-unsaturated ketones		202 nm
α,β-unsaturated aldehydes		207 nm
Increment for each:		
Double bond extending conjugation		30 nm
Alkyl group or ring residue	α	10 nm
	β	12 nm
	γ and higher	18 nm
-OH	α	35 nm
	β	30 nm
	γ	50 nm
-OAc	α,β,δ	6 nm
-OMe	α	35 nm
	β	30 nm
	γ	17 nm
	δ	31 nm
-SR	β	85 nm
-Cl	α	15 nm
	β	12 nm
-Br	α	25 nm
	β	30 nm
NR_2	β	95 nm
Exocyclic carbon-carbon double bond		5 nm
Homoannular diene component		39 nm
Calculated λ_{max} of the compound		Total nm



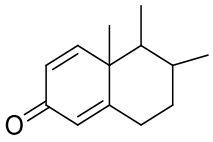
Base value	= 215 nm
γ-ring residue	= 18 nm
δ-ring residue	2 x 18 = 36 nm
One homoannular diene component	= 39 nm
Double bond extending conjugation	= 30 nm
Calculated λ_{max}	= 338 nm



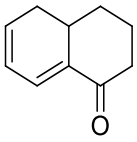
Base value	= 202 nm
β-ring residue	= 12 nm
α-hydroxy group	= 35 nm
Calculated λ_{max}	= 249 nm



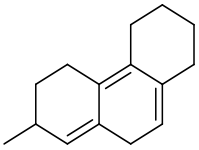
Base value	= 215 nm
β-ring residue	= 12 nm
γ-ring residue	= 18 nm
δ-ring residue	= 36 nm
Exocyclic double bond	= 20 nm
One homoannular diene component	= 39 nm
Double bond extending conjugation	= 60 nm
Calculated λ_{max}	= 418 nm



Base value	= 215 nm
β-ring residue	2 x 12 = 24 nm
One exocyclic double bond	= 5 nm
Calculated λ_{max}	= 244 nm



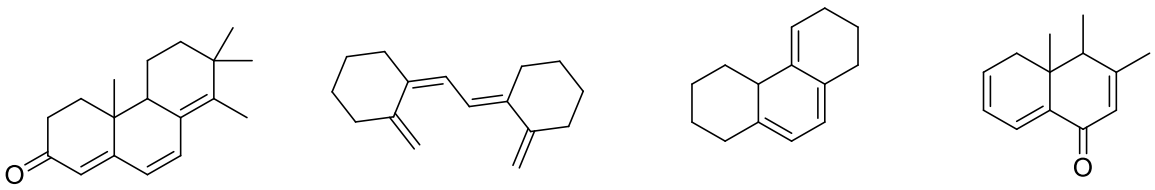
Base value	= 215 nm
α-ring residue	= 10 nm
δ-ring residue	= 18 nm
Exocyclic double bond	= 5 nm
One homoannular diene component	= 39 nm
Double bond extending conjugation	= 30 nm
Calculated λ_{max}	= 317 nm



Base value	= 253 nm
Alkyl ring residue	6 x 5 = 30 nm
Exocyclic double bond	= 20 nm
Double bond extending conjugation	= 30 nm
Calculated λ_{max}	= 333 nm

Question:

1. Explain briefly conjugation and Hydrogen bonding effect on wavelength of absorption maximum.
2. Explain different types of electronic transition with suitable examples.
3. Give the difference between chromophore and auxochromophore.
4. Calculate the λ_{max} value of following compounds.



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1. Modern organic chemistry by M. K. Jain and S. C. Sharma.
2. organic spectroscopy by LDS Yadav
3. Organic spectroscopy by Donald L. Pavia, Gary M. Lampman, George A. Kriz and James R. Vyvyan
4. Organic spectroscopy by Jag Mohan
5. Organic spectroscopy by William Kemp

Declaration: