30 06 2025

1] Introduction to spectroscopy.

1. Meaning of Spectroscopy
2. Nature of electromagnetic Radiation
3. Different Regions of electromagnetic radiations
4. Interaction of Radiation with matter.
5. Types of ~~st~~ spectroscopy and advantages of spectroscopic methods.
6. Energy types and energy Levels of atoms and molecules.
7. Numerical problems.
8. Exercises.

2] Ultraviolet and visible spectroscopy

1. Introduction
2. Beer Lambert's law.
3. Terms used in ultraviolet spectroscopy.
4. Modes of electronic Transitions.
5. Effect of conjugation on the position of UV and visible Band.
6. Calculation of λmax by woodword - Fieser Rule
7. Colour and visible spectrum.
8. Applications of ultraviolet spectroscopy.

3] Infrared spectroscopy

1. Introduction.
2. Principle of I. R. Spectroscopy.
3. Instrumentation
4. Fundamental modes of vibrations.
5. Conditions for the absorption of IR - radiation
6. Regions of IR spectrum.

7. Hook's low.
8. Factors affecting IR absorption frequency
9. Characteristic I.R absorption of ~~Ultraviolet spectro~~ functional Groups.
10. Solved Illustrative exomples.

4] Nuclear magnetic Resonance (NMR) spectroscopy.
1. Introduction
2. Principles of PMR- spectroscopy.
3. NMR - Instrumentation.
4. Magnetic and Non- magnetic Nuclei.
5. chemical shift.
6. Shieldings and De-shielding.
7. Peak- area. (Integration)
8. Coupling constant
9. Types of coupling constant
10. spin - spin splitting (n+1 Rule).
11. Applications.
12. solved problems.

5] Mass spectroscopy.
1. Introduction
2. Principle of Mass spectroscopy.
3. Mass spectrometer.
4. Types of ions produced during fragmentation
5. Nitrogen Rule.
6. Fragmentation patterns of selected classes of organic compounds.
7. Carbonyl Compounds.
8. McLafferty Rearrangment.
9. Solved problems.

6| combined spectroscopic problems.

1. Introduction
2. combined spectroscopic solved problems.
3. Exercises.
4. Characterstic IR absorption of fundamental groups.

2. Ultraviolet and visible spectroscopy.

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Duterium dischorge lamp - UV = 100-400 nm → 100-200 nm.

Tungsten filament lamp - visible → 400-800 nm

The light absorbance study carried out in ultra violet and visible region are called UV visible spectroscopy.

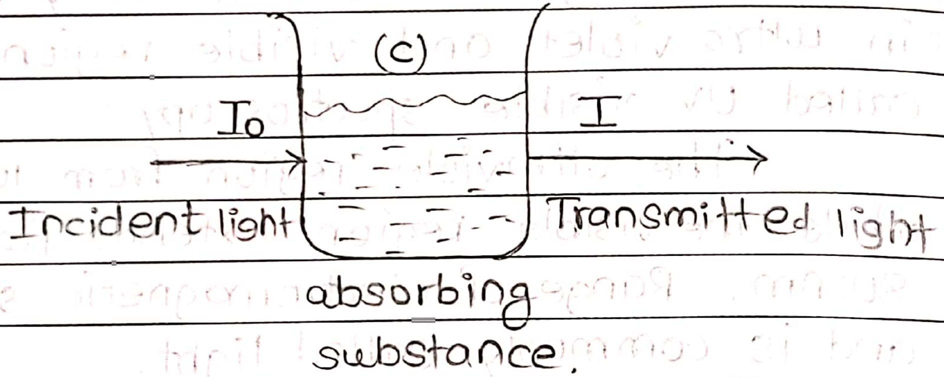
The ultraviole region from 100 to 400 nm while the visible region extends from 400 to 800 nm, Range of electromagnetic spectrum and is commonly called light.

The region from 100 to 200 nm is known as far ultraviolet, The ultraviolet light is obtained by duterium discharge lamp, while visible range radiation are obtained from a tungsten filament lamp. Ultraviolet and visible radiation are energenetic for produce transition of valence electrons from a lower to higher energy level. Hence UV visible spectroscop is often called as electronic spectroscopy.

* Beer Lambert's law :

When a beam of monochromatic light passes through and absorbing substance in a non absorbing solvent the radiation in absorbed completely or partially, so the transmitted being intensity (I) will be less than incident beam intensity (I_0)

The quantitative relation between light absorbed and the concentration as well as the optical path length (l) of the absorbing compound is given by scientist Beer and Lambert's.



Lambert's law :

When a ray of monochromatic light passes through a absorbing medium it's intensity decrease exponentially as the optical path length (l) of the absorbing medium increases.

Mathamatically it can be written as.

$$I = I_0 e^{-k_1 l} \text{ - - - - - - - - } ①$$

Beer's law :

When a ray of monochromatic light passes through a absorbing soln it's intensity decrease exponetially as the concentration of the absorbing solution increase.

Mathamatically it can be written as,

$$I = I_0 e^{-k_2 C} \quad ----- ②$$

Beer's lambert's law : combining the eq^n ① and ②

$$I = I_0 e^{-k.c.l}$$

$$----(k_1 . k_2 = k)$$

$$\frac{I}{I_0} = e^{-k.c.l}$$

$$-------- ③$$

Taking log the on both side

$$\log_e \frac{I}{I_0} = \log_e e^{-k.c.l}$$

$$\log_e \frac{I}{I_0} = -k.c.l$$

$$\log_e \frac{I_0}{I} = k.c.l$$

$$\log_{10} \frac{I_0}{I} = \frac{k}{2.303} . c.l$$

The expression is simplified by using notation A (absorbance) or sometimes E (Extinction) for ($\log_{10} I_0/I$) and a new constant ε is called molar extinction coefficient. $\frac{k}{2.303}$

The eqn takes from

$$A = \varepsilon . c . l \; - - - - - - ④$$

When the concentration is expressed in mol. per dm^3 and path length in centimet then A is called molar absorbance and ε is called molar extinction coefficient, when, $c = 1\,M$, $l = 1\,cm$, the eqn changes from molar absorbance is equal to molar extinction coefficient.

$$A = \varepsilon$$

So, molar extinction coefficient ε is defined as, the molar absorbance of 1 mole of solution of an absorbing substance in 1 cm^3 cuvette under given conditions of wavelength (λ), solvent and temperature.

When ε is measured at most absorbed wavelength it is denoted as ε_{max}. A given compound has characterstic value ε_{max} that remains constant and implies how strongly ~~is~~ it absorbs.

* Terms used in ultraviolet spectroscopy

1] Chromophore :

A chromophore is an unsaturated group of a molecule that undergoes $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition by absorbing in ultraviolet and visible, The compounds containing chromophore are called chromo~~phore~~gens.

eg. $H_{13}C_6-C=C-CH_3$ Alkene $H_3C-N=N-CH_3$ Azo.

a] $\pi \rightarrow \pi^*$

Chromophore in which olefinic bond is between two carbon atoms, eg. alkene, $(-HC=CH-)$, alkyne $(-C\equiv C-)$ etc. They show only $\pi \rightarrow \pi^*$ transitions. These transitions are some what higher energy transitions.

b] $n \rightarrow \pi^*$

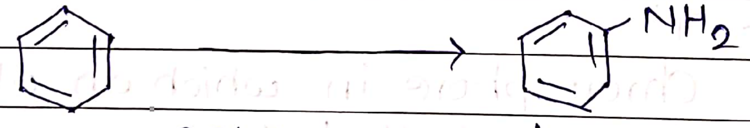
Chromophore in which an olefinic bond involves one or both hetero atoms, eg. carbonyl $(C=O)$, diazo $(N=N-)$, They show both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The $n \rightarrow \pi^*$ transitions are of low energy transitions and caused by longer wavelengths.

2] Auxochrome :

An auxochrome is an atom or a saturated group containing non-bonded or

lone pair electrons, it does ~~d~~ not absorb radiations of wavelengths greater than 200nm but when coupled to a chromogen it shifts absorption to longer wavelength.
Some common and important auxochrome are $-OH$, $-OR$, $-SH$, $-Cl$, $-Br$, $-NH_2$, $-NHR$ etc. They all contain an atom having at least one lone pair of electrons in their p-orbital.

An auxochrome offers it's lone pair of electrons for extending the conjugation of chromophore and becomes a part of new extended chromophore system.
The $-NH_2$ group although does not absorb radiations of longer wavelength, when bound to benzene ring absorption shifts to longer side.

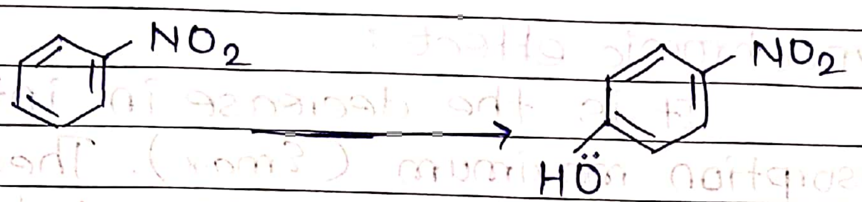


λmax = 254nm λmax = 280 nm.

③ **Bathochromic or red shift :**
The shift of absorption band to longer wavelength is called bathochromic or red shift.

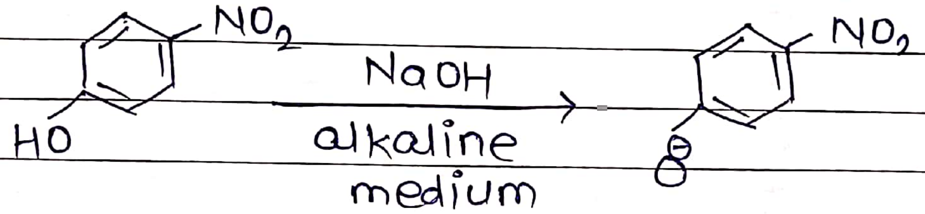
a) Bathochromic can be observed when an auxochrome is attached to a chromogen.

eg.



$\lambda_{max} = 268\,nm$ $\lambda_{max} = 318\,nm$.

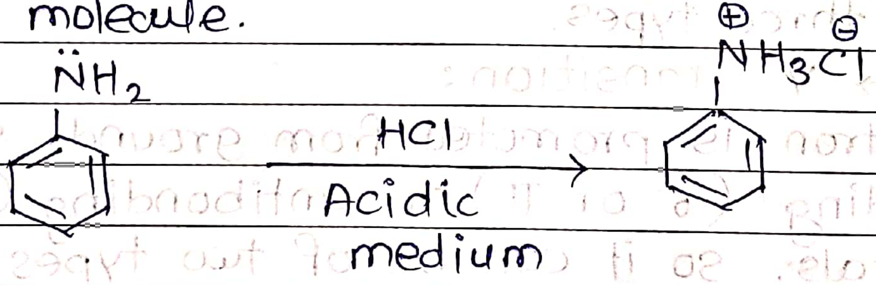
b] When the surrounding medium is a changed
eg.



p- nitrophenol p - nitrophenoxide ion

4] Hyspochromic or blue shift:
The shift of absorption band to starnger wavelength is called hyspochromic or blue shift. This shift is often noticed when.

a] Positive charge is introduced into the molecule.



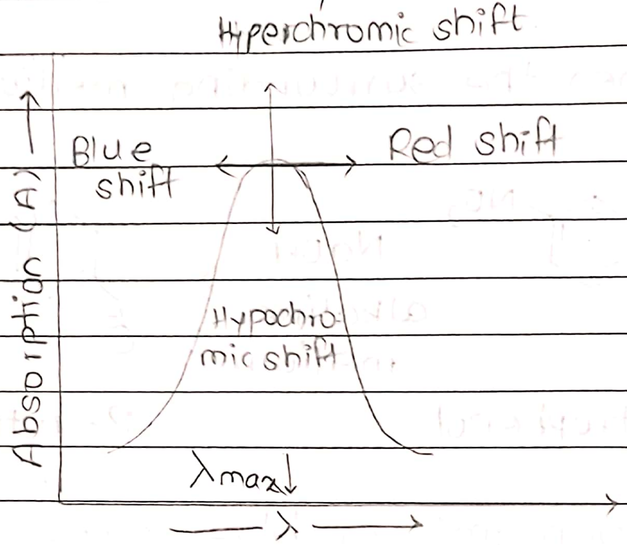
$\lambda_{max} = 280\,nm$ $\lambda_{max} = 265\,nm$

5] Hyperchromic effect:
It is decrease in the intensity of absorption maximum (ϵ_{max}). The introduction of an auxochrome usually increases the intensity of absorption.

10 07 2025

6) Hypochromic effect :

It is the decrease in intensity of absorption maximum (ε_{max}). These effects can be schematically represented as in fig.



Inter-relation between absorption effects

* Modes of electronic transition :

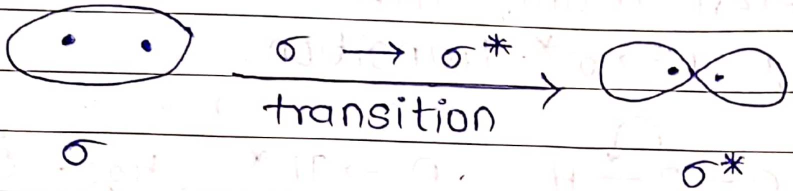
The electronic transion occurring in an absorbing molecules are broadly grouped into three types.

1. N ⟶ V Transition :

Electron is promoted from ground state bonding (σ or π) to antibonding (σ* or π*) orbitals. so it can be of two types.

i) $\sigma \rightarrow \sigma^*$ Transition :

It is the promotion of electrons from σ - bonding to σ* antibonding orbital. since the σ electrons are strongly held and transition energy (ΔE) for $\sigma \rightarrow \sigma^*$ transition is quite large, it requires the radiations of shorter wavelength below 150 nm.

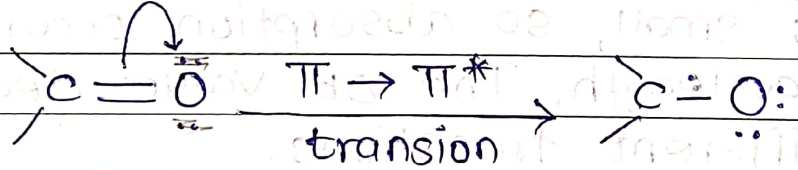


Alkanes are saturated compounds lacks π and non-bonding electrons. show it can ota only σ → σ* transitions.

ii) π → π* Transition :

It is promotion of electron from π bonding to π* antibonding orbital. The compound containing multiple bonds, eg. C=C, C≡C, C=O, C=S, C≡N etc. undergo π → π* transition. The π* electrons are delocalised so the transition energy ΔE for π → π* transition is less, hence transition Occurs at longer wavelength camparotivly, that is 180 to 210 nm.

eg.



2) N → Q Transition

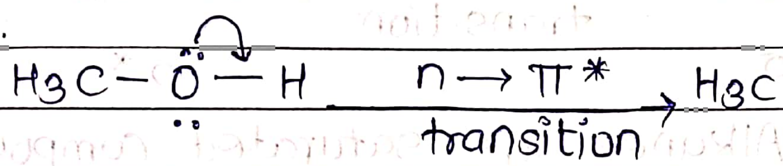
It is electron is promoted from non-bonding (n) orbital to antibonding (σ* or π* orbital, so it can be of two types

i) n → σ* Transition :

It is the promotion of electron from

non-bonding to antibonding σ^* orbital. Compound containing lone pair of electrons on hetero atoms like N, S, O, Cl, Br, I etc. undergo $n \rightarrow \sigma^*$ transition.

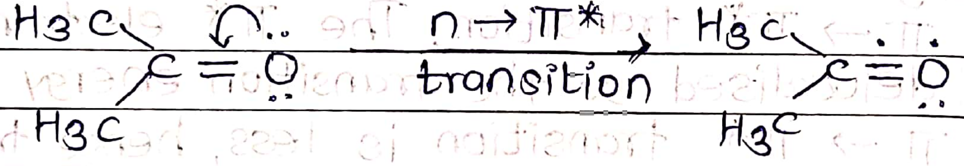
eg.



ii) $n \rightarrow \pi^*$ Transition :

It is promotion of non-bonding to antibonding ~~σ^*~~ π^* orbital, The compounds containing multiple bonds involving hetero atoms, C=N, C≡N, C=O, C=S etc. show such transition.

eg.



The transition energy (ΔE) for $n \rightarrow \pi^*$ is small, so absorption occurs at longer wavelength. The ΔE value decreases for different transitions.

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

It is obvious ($\sigma \rightarrow \sigma^*$) transitions occurs by absorbing the radiations in far ultraviolet region, while the ($n \rightarrow \pi^*$) transitions occur by absorbing the radiations in near visible region. That is, the wavelength

14 07 2025

absorbed depend on (ΔE) the molecular structure.

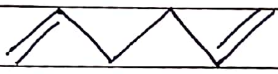
3| N→R Transition :

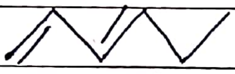
An electron from ground state is excited to one at very high energy leading to ionisation of the transition

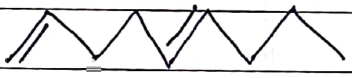
* Application of Ultraviolet spectroscopy.

1| Extent of conjugation :

Higher the λmax value longer the conjugation and vice versa. so distinction between conjugated and non-conjugated structural analysis can be made easily.


λmax 175 nm. (non-conjugated)


λmax 217 nm. (conjugated)


λmax 258 nm (extended conjugation)

2| Detection of Chromophore :

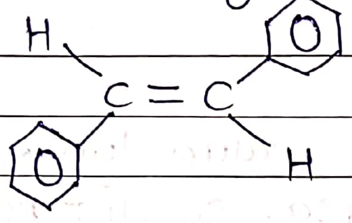
A strong absorption ($\varepsilon = 10,000 - 20,000$) usually is characteristic of $\pi \rightarrow \pi^*$ transition If absorption occurs above 200 nm a conjugated system of multiple bond is indicated.

A weak absorption ($\varepsilon = 10 - 100$) and suggests $n \rightarrow \pi^*$ transition of an isolated carbonyl group. If this absorption is found in the region of ~~217~~ 270 - 350 nm an aldehyde or ketone is probable.

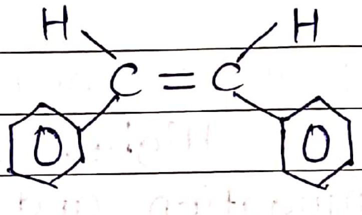
The stronger absorptions ($\varepsilon = 100 - 4000$) between 200 - 260 nm. may correspond to $n \rightarrow \sigma^*$ transitions.

3) Detection of geometrical isomers:

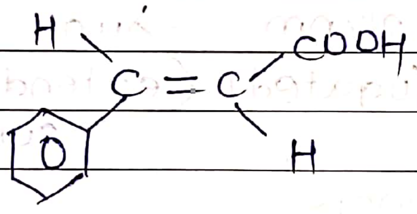
compared to cis- isomer, the trans-isomer show absorption at higher λ_{max} values with larger extinction coefficient. (ε_{max}) eg.



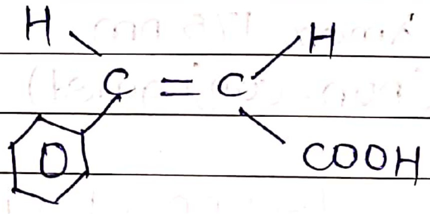
trans- stilbene
λ_{max} = 294 nm
ε_{max} = 24,000



cis- stilbene
λ_{max} = 278 nm
ε_{max} = 9,350.



trans - cinnamic acid
λ_{max} = 272 nm
ε_{max} = 15,900



cis - cinnamic acid
λ_{max} = 268 nm
ε_{max} = 10700.

4) structure of organic compounds:

UV spectroscopy is used for the structure elucidation of organic molecules. But its utility is confined to know the presence or absence of chromophore.

~~8] Detection of Impurities :~~

~~It is one of the best methods for detection.~~

8] The strength of hydrogen bonds :

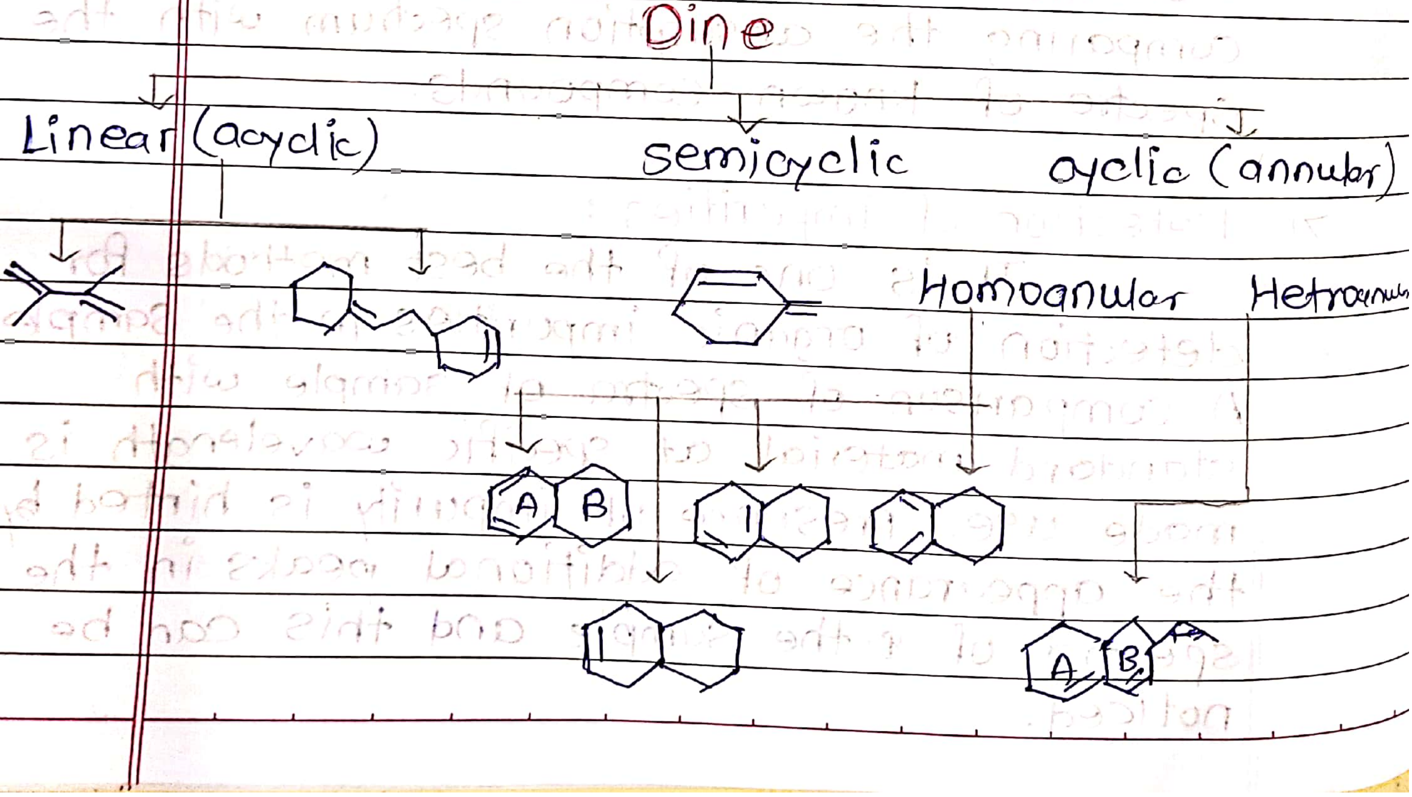
The strength of hydrogen bond can be calculated by using the UV spectrum in polar (water) and non-polar (n-hexane) solvents. The difference in λ_{max} values in water and in n-hexane should directly give the strength of hydrogen bond. consider UV spectrum of acetone.

$$\underset{126\ kcal/mole}{264.5\ nm} \xleftarrow[\text{water}]{} \text{Acetone} \xrightarrow[\text{n-hexane}]{} \underset{121\ kcal/mole}{297\ nm}$$

Thus the strength of hydrogen bond

$= (126-121)$ kcal/mole.

$= 5$ kcal/mole.



From the location of peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not etc.

5] Quantitative analysis :
UV spectroscopy is used for the quantitative determination of compounds that absorb UV radiation. This determination is based on Beer's law ~~dis~~

$$A = \varepsilon bc$$

Where, ε is extinction co-efficient,
c is concentration,
b is the length of the cell used.

6] Qualitative analysis :
UV spectroscopy is specially used for characterizing aromatic compound and aromatic compound. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

7] Detection of impurities :
It is one of the best methods for detection of organic impurities in the sample. A comparison of spectra of sample with standard material at specific wavelength is made use. Presence of impurity is hinted by the appearance of additional peaks in the spectra of ~~s~~ the sample and this can be noticed.

8) Detection of Impurities:

It is one of the best methods for detection.

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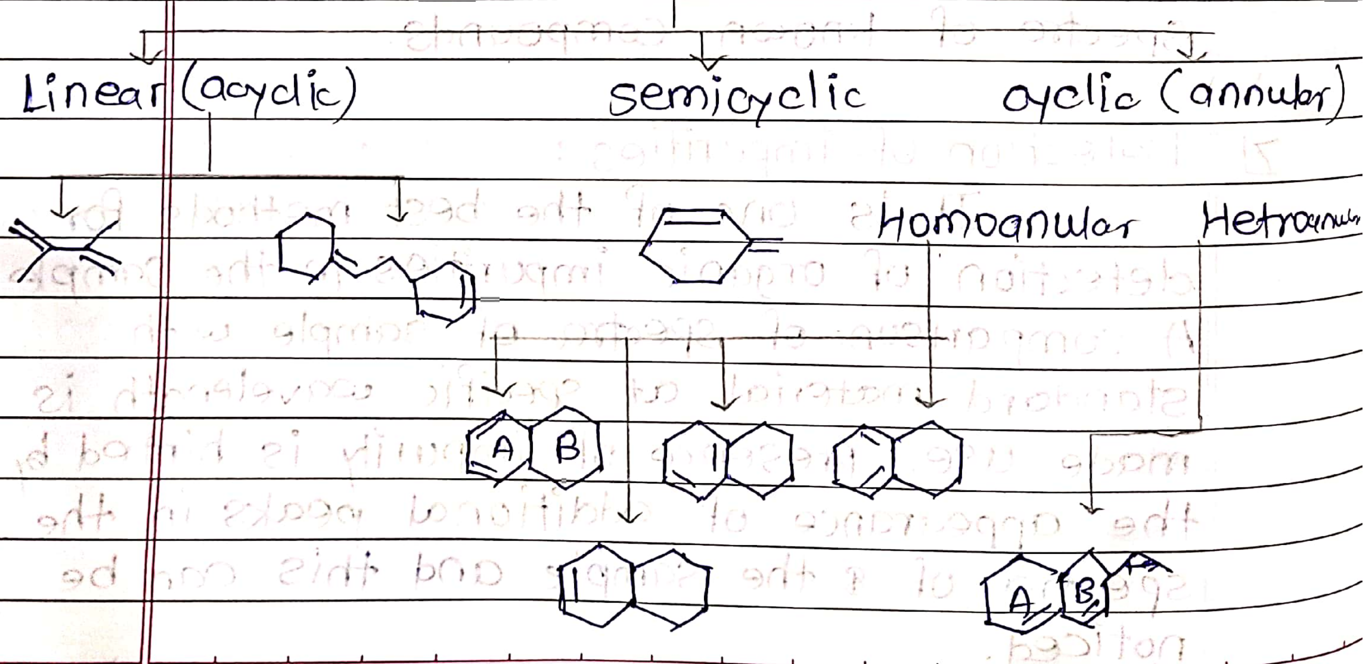
Thus the strength of hydrogen bond
= (126 − 121) kcal/mole.
= 5 kcal/mole.

Dine



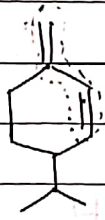
Alkyl - 5 nm
-OR - 5 nm
-OCOR - 0
X (Cl, Br, I) - 5 nm
exocyclic - 5 nm

* Examples :

1)

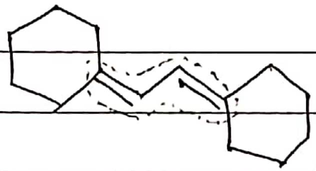
i) Base value (acyclic) = 214 nm
ii) one alkyl substituent = (1×5) = 5 nm
λ_{max} = 219 nm

2)



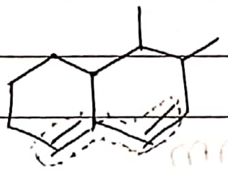
i) Base value (semicyclic) = 214 nm
ii) two alkyl substituent = 2×5 = 10 nm
iii) one C=C exocyclic = 5
λ_{max} = 229 nm

3)



i) Base value (acyclic) = 214 nm
ii) four alkyl substituent = (4×5) = 20 nm
iii) two C=C bond exocyclic = 2×5 = 20 nm
244 nm.

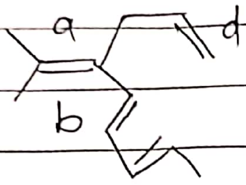
4)



i) Base value (Homoanular) = 253 nm
ii) 3 alkyl substituent = (3×5) = 15 nm
iii) Extended value = 30 nm
iv) exocyclic double bond = 5 nm
λ_{max} = 303 nm

(A and b)

5

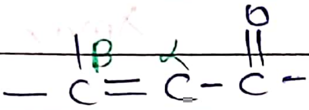


i) Base value (acyclic) = 214 nm
ii) 4 alkyl substituent = (4×5) = 20 nm
iii) Extend value = 30 nm

(b and c)

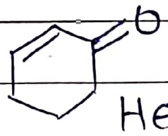
i) Base value (acyclic) = 214

Enone (α, β unsaturated carbony compound.



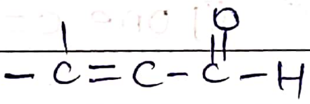
$-\overset{|\beta}{C}=\overset{\alpha}{C}-\overset{\overset{O}{\|}}{C}-$

acyclic enone
215 nm



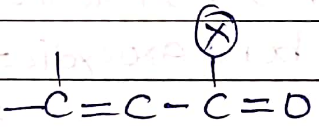
Hexocyclic 215 nm

Pentacyclic
202 nm



$-\overset{|}{C}=C-\overset{\overset{O}{\|}}{C}-H$

Aldehyde. 207 nm.



$-\overset{|}{C}=C-\overset{\overset{\textcircled{x}}{|}}{C}=O \rightarrow$ 197 nm.

X = OH, OR

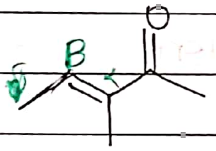
Extend conjugation = 30 nm
Homodine congugation = 39 nm
exocyclic = 5 nm.

$-\overset{|\delta}{C}=\overset{\gamma}{C}-\overset{|\beta}{C}=\overset{\alpha}{C}-C=O$ increments For each group at . . . . . position.

-R alkyl (including part of carboxylic group.

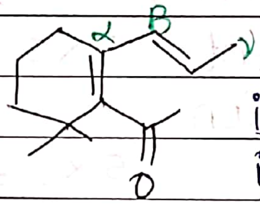
	α	β	γ	δ and above	
-R	10	12	18	18	18
-OR	35	30	17	31	
-OH	35	30	-	50	-
-SR	-	80	-	-	-
-Cl	15	12	-	-	-
-Br	25	30	-	-	-

	α	β	γ	δ	
$-O-\overset{O}{\overset{\|\|}{C}}-R$ acyloxy	6	6	-	6	-
$-NH_2$ - NHR $-NR_2$	—	95	-	-	-



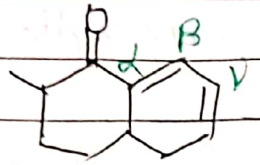
i) Base value (acyclic) = 215 nm
ii) one alkyl substituent = 10 nm
iii) one β substituent = 12 nm

237 nm

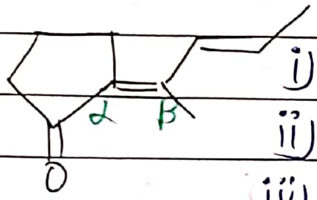


i) Base value (Hexacyclic) = 215 nm
ii) one α substituent = 10 nm
iii) one β substituent = 12 nm
iv) one δ substituent = 18 nm
v) extend = 30 nm

285 nm



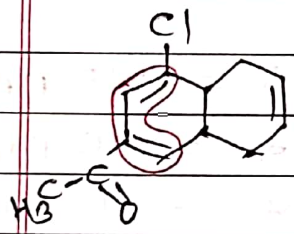
i) Base value (Hexacyclic) = 215 nm
ii) one α substituent = 10 nm
iii) one δ substituent = 18 nm
iv) Homodiene = 39 nm
v) extended = 30 nm
vi) exocyclic = 5 nm



i) Base value (pentadiene) = 202 nm
ii) one α substituent = 10 nm
iii) one β substituent = 18 nm
iv) one δ substituent = 18
v) extended = 30
vi) exocyclic = 5 nm

277 nm

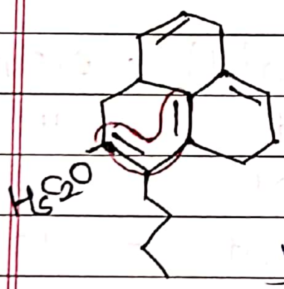
1)



i) Base value (Homodien) = 253
ii) Three alkyl substituent = 15

268 nm.

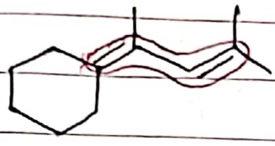
2)



i) Base value (Homodiene) 253
ii) five alkyl substituent 5 × 4 = 20
iii) Extended conjugation 30
iv) Exocyclic two 5 × 2 = 10
v) OR 6

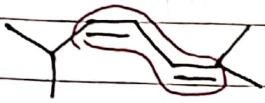
319 nm

3)



i) Base value (acyclic)	214
ii) one exocyclic	5
iii) Alkyl substitution (5 × 5)	25
	244 nm.

4)

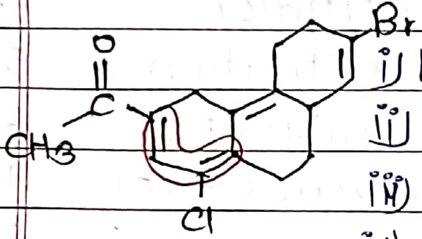


i) Base value (acyclic)	214
ii) 3 alkyl substitution (3×5)	15
	229 nm

5)

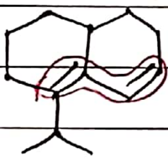
i) Base value (Homodiene)	253
ii) four alkyl substitution (4×5)	20
	273 nm

6)



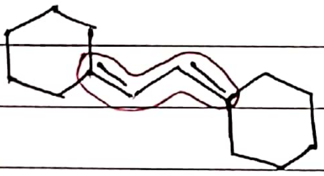
i) Base value (Homodiene)	253
ii) Extended conjugation	30
iii) Halide group (Cl)	5
iv) alkyl substitution (2×5)	10
v) acyloxy	0
vi) exocyclic (3×5)	15
	313 nm

7)



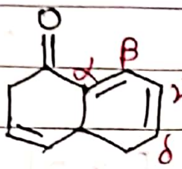
i) Base value (Heteroannular)	214
ii) Alkyl substitution (4×5)	20
iii) Exocyclic	5
	239 nm

8)



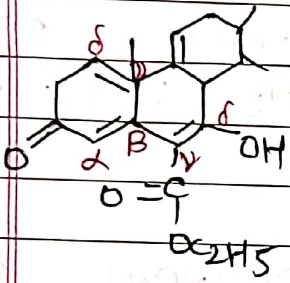
i) Base value (Acyclic)	214
ii) Alkyl four substitution (4×5)	20
iii) exocyclic (2×5)	10
	244 nm

1)



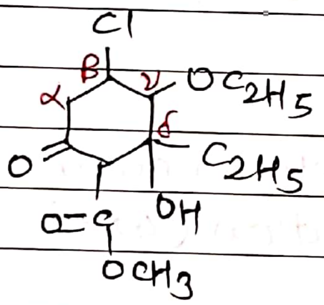
i) Base value(Hexocyclic)	215 nm
ii) one α substitution	10
iii) one δ substitution	18
iv) Exocyclic	5
v) Extended conjugation	30
vi) Homodiene	39
	317 nm

2)



i) Base value (Hexacyclic)	215
ii) one β substitution	12
iii) one γ substitution	18
iv) one δ substitution	18
v) one OH substitution	50
vi) extended conjugation	30
vii) Three exocyclic (3×5)	15
viii) Homodiene	39
	387 nm

3)



i) Base value (Hexacyclic)	215
ii) one β substitution	24
	239 nm