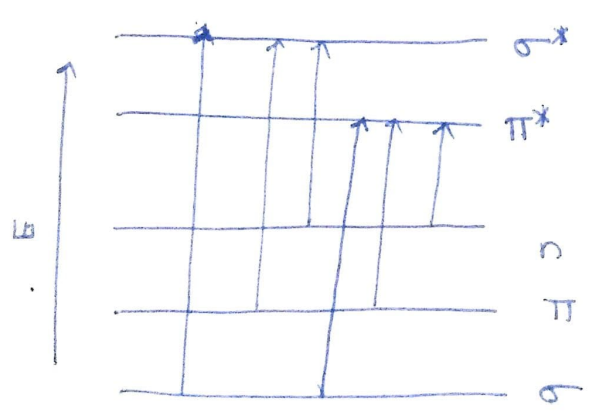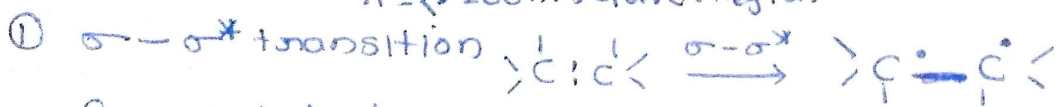# Ultra violet - Visible Spectroscopy - YR Sharma

In UV-visible spectroscopy involves electronic excitation to higher energy molecular orbital occurs in the region of 200-800 nm excitation of electrons are also accompanied by the constant vibratory and rotatory motion of the molecules. Thus a large number of wavelengths which are close enough will be absorbed resulting in the formation of bands, which will be usually broad bands. Normally absorbtion of UV or visible light results singlet ground state to excited singlet state transition. (excitation proceeds with relaxation of spins) An excited singlet state is converted in to excited triplet state with the emmission of E as light. The transition from singlet ground state to excited triplet state is symmetry forbidden. The highly probable transition due to absorbtion of quantised energy involves the promotion of one electron from HOMO to LUMO.

Types of electronic transitions

$$\sigma \to \sigma^* > \pi \to \sigma^* > \boxed{\pi \to \sigma^*} > n \to \sigma^* > \pi \to \pi^* > n \to \pi^*$$

$\lambda = \langle 200\,nm$ (far UV region)

$\lambda \geq 200\,nm$ (near UV and visible region)

① $\sigma - \sigma^*$ transition $\quad >\overset{|}{\underset{|}{C}} : \overset{|}{\underset{|}{C}} < \overset{\sigma - \sigma^*}{\longrightarrow} >\overset{.}{C} \overset{\bullet}{\underline{\quad}} \overset{.}{C} <$

Saturated hydrocarbons like methane, propane etc absorb near 150 nm (high E). Such transition requires radiation of very short wavelength. To study transition below 200 nm

air must be evacuated bec² oxygen present in air begins to absorb strongly in this region. thus region below 200 nm is called vacuum uv region. This region is less informative

(2) $n \rightarrow \sigma^*$ transition

This type of transition take place in saturated compounds containing one hetero atom with unshared pair of electrons. $(n \ \bar{e}s)$ like halides, alcohols, ethers aldehydes, ketones, amines etc.

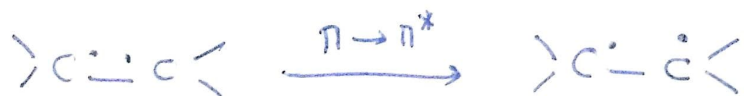eg: $H_2O - 167$ nm , $CH_3-OH - 174$ nm , $CH_3-Cl - 169$ nm.

$CH_3-I - 258$ nm

→ in Methyl iodide bec² of less of Electronegativity of Iodine in comparison to Cl 'n' electrons are free to excite, thus will have lower E (higher λ) for excitation.

→ Amines $(\ddot{N})$ absorbs at higher λ than alcohols $(\ddot{O})$ bec² EN of N is less than O.

→ Alcohols and amines form hydrogen bond through non bonded $\bar{e}s$, thus uv absorption occur at shorter wavelength.

(3) $\pi \rightarrow \pi^*$ transition

This type of transitions occurs in the unsaturated compounds like double or trible bonded and in aromatics.

$$\underset{>}{C} \vdots \underset{<}{C} \xrightarrow{\pi \rightarrow \pi^*} \underset{>}{C} \dot{-} \dot{C} \underset{<}{}$$

alkenes — 170- 190 nm.
$>C=O$ — 180 nm.

(4) $n \rightarrow \pi^*$ transitions

lowest E transition., [longest λ transition]

$$\underset{R}{\overset{R}{>}} C = O$$

$n \rightarrow \pi^* = 290$ nm
$n \rightarrow \pi^* = 180$ nm.

The molar extinction coefficient of $n \rightarrow \pi^*$ is usually less

than $\pi \to \pi^*$.

→ The values for allowed transitions E_{max} will be more than 10^4

eg: Butadiene $\pi \to \pi^*$ - 217 nm ($E_{max} = 21,000$)

The E_{max} for forbidden transitions will be lesser than 10^3.

eg: $\rangle C = O$ compd $n \to \pi^*$ - 300nm ($E_{max} = 100$).

Chromophores

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or visible region. eg: Ethylenic, acetylenic, carbonyl, acids, esters, nitrile etc.
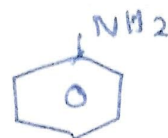
Chromophore	Transition	Absorption max	E_{max}	Solvent
$\rangle C = C \langle$	$\pi - \pi^*$	~175 nm	~15000	Vapour
		~175nm	~10,000	Hexane
$\rangle C \equiv C \langle$	$\pi - \pi^*$	~196 nm	~2000	,,
		220	~130	,,
$\rangle C = O$	$n \to \sigma^*$	~160	18,000	,,
	$\pi \to \pi^*$	~180	10,000	,,
	$n \to \pi^*$	~285	15.	
	$n \to \pi^*$	200	5000	Methanol
	$n \to \pi^*$	274	15000	
R— NO_2	$n \to \pi^*$	204	60	Methanol
-C-OH $\parallel$ O	$n \to \pi^*$	338	5	Ethanol
-N=N-	$n \to \pi^*$	178	9500	Hexane
-C-NH₂ $\parallel$ O				

Auxochrome (colour enhancing group)

An auxochrome can be defined as any group which does not itself act as a chromophore, but whose presence brings about a shift of the absorbtion bands towards the red end of the spectrum. eg: OH, OR, NH_2, NHR, NR_2, SH etc
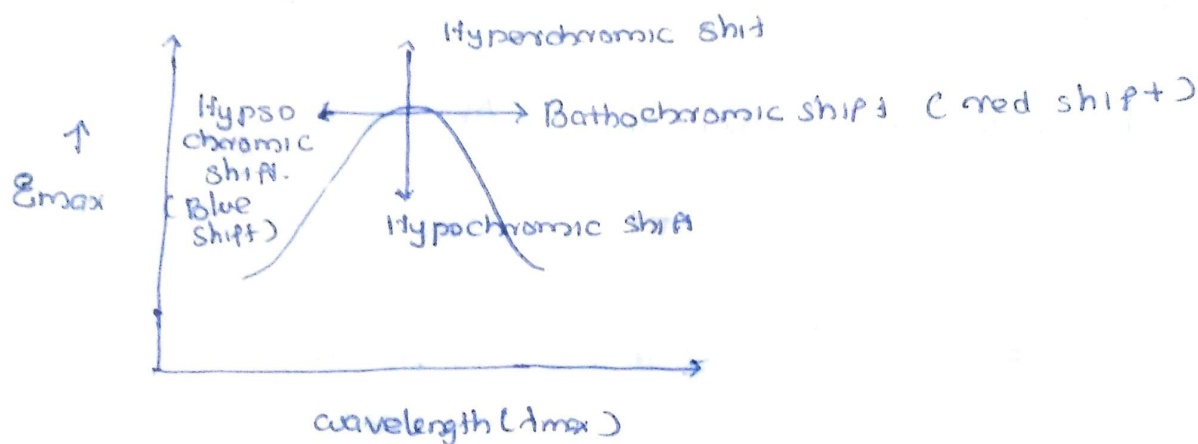

$\lambda max = 255\,nm$ ($\varepsilon max = 203$)

$\lambda max = 280\,nm$ ($\varepsilon max = 1430$)

Absorbtion and intensity shifts

Hyperchromic shit

Hypso chromic shift. (Blue Shift)

εmax ↑

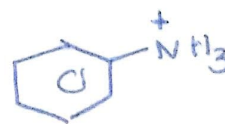Bathochromic shift (red shift)

Hypochromic shift

wavelength (λmax)

→ when polarity of solvents ↓ is decreased $n-\pi^*$ transition for Carbonyl compds experience bathochromic shift.

→ Removal of conjugation results blue shift (hypsochromic shift)
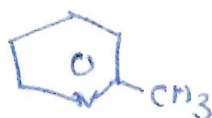

$\lambda max = 280\,nm$

In acidic soln of aniline →

$\lambda max = 203\,nm$.

→ The introduction of an auxochrome usually increases intensity of absorption εmax (Hyperchromic shift).

B-band - $257\,nm$ ($\varepsilon max = 2750$)

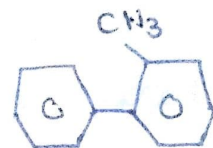$262\,nm$ ($\varepsilon max = 3560$)

→ The introduction of group which distorts the geometry of the molecule causes hypochromic shift

biphenyl - 250 nm (ε_{max} = 19000)

2-methyl biphenyl
- 237 nm (ε_{max} = 10250)

Solvent effects

A dilute soln of the sample is always prepared for spectral analysis. Most commonly used solvent is 95% ethanol as it is cheap and transparent down to 210 nm.

→ Absorption maximum for non polar compounds is same in alcohol (polar) as well as hexane (non polar). The absorption maximum for the polar compds is usually shifted with the change in polarity of the solvents.

→ In α, β unsaturated carbonyl compds, $n \rightarrow \pi^*$ transition (less intense) band moves to shorter wavelength by increasing polarity of the solvent, where as $\pi \rightarrow \pi^*$ transition (intense) absorption band moves to longer wavelength by increasing the polarity of the solvent.

→ In general increase in the polarity of the solvent generally shifts $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelength and $\pi \rightarrow \pi^*$ bands to longer wavelength.

Conjugated dienes

The wavelength of absorption is shifted to higher values (Bathochromic shift) if two or more chromophoric groups present in a molecule

$CH_2 = CH_2$ $\pi \rightarrow \pi^*$ - 170 nm.

$CH_2 = CH - CH = CH_2$ $\pi \rightarrow \pi^*$ - 217 nm

$CH_2 = CH - CH = CH - CH = CH_2$ - 254 nm

When two double bonds are in conjugation the energy levels of HOMO is raised and LUMO is lowered so energy gap decreases, wavelength of absorption increases.

Woodward Fieser rules for calculating Absorption Maximum in Dienes

Longer the Conjugated System, greater is the wave length of absorption maximum (λ_{max}) and intensity of absorption (ε_{max}). various types of double bond in conjugation are
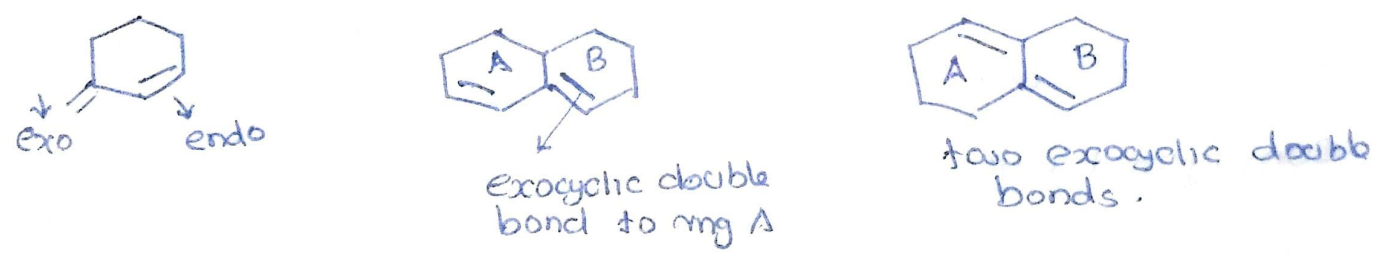
(a) Alicyclic dienes or dienes contained in an open chain system - where basic unit is butadiene system.

(b) Homo-annular conjugated double bonds - conjugated double bonds present in the same ring, also called homodiene.

(c) Hetero annular conjugated double bonds - conjugated double bonds, which are not present in the same ring

(d) Exocyclic and endocyclic conjugated double bonds

exo   endo

Exocyclic double bond to ring A

two exocyclic double bonds.

Woodward formulated certain empirical rules for calculating the λ_{max} in case of dienes. These rules were later modified by Fieser in 1948. According to these rules each type of diene has a certain fixed basic value and the value of absorption max (λ_{max}) depends upon:

(1) The no of alkye substituents or ring residues on the double bond.

(2) The no of double bonds which extend conjugation

(3) The presence of polar groups such as Cl, Br, OR, SR etc
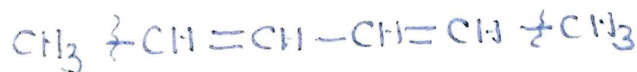
Table -1   Conjugated dienes and triens

Solvent - Ethanol
Transition involved - $\pi \to \pi^*$

1. Parent value for butadiene system or a cyclic conjugated diene	217 nm
2. Homoannular conjugated diene	253 nm
	215 nm
3. Heteroannular conjugated diene	245 nm
4. Acyclic triene	
5. Increments for each substituent	
alkyl substituent or ring residue	5 nm
Excocyclic double bond	5 nm
Double bond extending conjugation	30 nm
6. Auxochrome corrections	
— OR	+ 6 nm
— SR	+ 30 nm
— Cl, Br	+ 5 nm
— NR_2	+ 60 nm
— O COCH_3	0 nm

Problems

① Calculate λ_{max} of 2,4 -hexadiene

$$CH_3 \underset{}{\neq} CH = CH - CH = CH \underset{}{\neq} CH_3$$

Basic value = 217 nm

2 alkyl subst = $2 \times 5 = 10$ nm
_____

Calculated value = 227 nm   observed = 227 nm

②

$$= C - CH = CH \underset{}{\neq} CH_3$$
$$\underset{}{\downarrow}$$
$$CH_3$$

Basic value = 217 nm
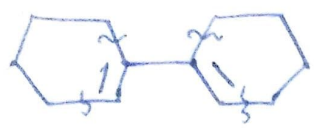
2 alkyl substituents = 2×5 = 10 nm

2 ring residues = 2×5 = 10 nm

1-exocyclic double bond = 5 nm

Calculated = 242 nm   observed = 242 nm.

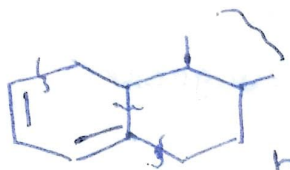3.

— It is a heteroannular diene

Basic value = 215 nm

4 ring residues = 4×5 = 20 nm

Calculated value = 235 nm   observed = 234 nm

4. Calculate λmax

in ethanol.
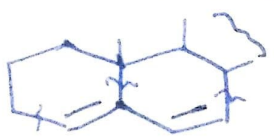homoannular diene

Basic value = 253 nm

3 ring residues = 3×5 = 15 nm

1-exocyclic double bond = 5 nm

Calculate = 273 nm   Observed = 274

5.

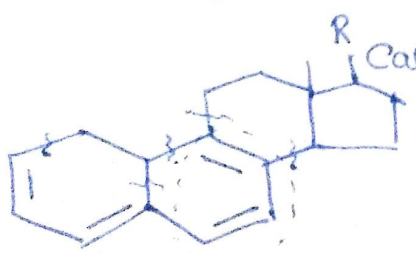heteroannular conj diene

Basic value = 215 nm

3 ring residues = 3×5 = 15 nm

1-exocyclic double bond = 5 nm

Calculated value = 235 nm   Obs - 235 nm

6.

If both homoannular and heteroannular conjugate diene system are present in the same compound, then calculations are based on longer wavelength ie homoannular conj. diene - 253 nm

$\cdot$ above system homodiene system

Basic value = 253 nm

2 double bond
    extending conjugation = 2×30 = 60 nm
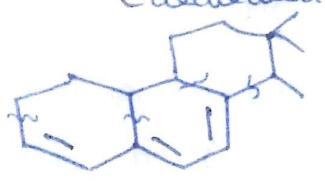
5 ring residues = 5×5 = 25 nm

1-excocyclic double bond = 5 nm
——————————————
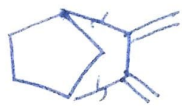   Calculated = 343 nm   Obs – 345 nm

7.

Basic value = 253 nm

4 ring residues = 4×5 = 20 nm

2-excocyclic double = 2×5 = 10 nm
    bonds

1-double bond extending = 30 nm
    conjugation
——————————————
    calculated value = 313 nm   obs – 312 nm

8.   For bicyclic system strain correction 15 nm is to be added

Basic value = 217 nm

2 ring residues = 2×5 = 10 nm.

2 Exocyclic double bond = 10 nm

bicyclic strain correction = 15 nm
——————————————
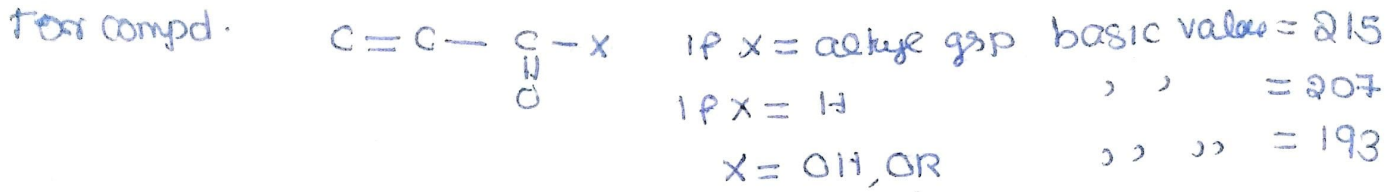   Calculated = 252 nm   obs – 254

9.

Basic value = 253 nm

2 ring residue = 10 nm
——————————————
    263 nm.

Woodward – Fieser rules for calculating absorption maximum in α, β-unsaturated carbonyl compounds

1. The basic value of α, β unsaturated ketone is 215 nm. The α, β unsaturated ketone may be a cyclic or six membered. For compd.

   $C = C - \underset{\underset{O}{||}}{C} - X$

   If X = alkyl grp   basic value = 215

   If $X = H$,, ,,   = 207

   $X = OH, OR$,, ,, ,,   = 193

2. If the double bond and the carbonyl groups are contained in a five membered ring (cyclopentanone), then for such an α, β unsat ketone the basic value is = 202 nm.

3. Structural increments

   (1) exocyclic double bond   = +5 nm

   (2) endocyclic double bond
        in 5 or 7 membered ring   = +5 nm.
        Except cyclo-pent-2-enone

   (3) For each alkyl Substituent
        Or ring residue at the
        α- position   = +10
        β- position   = +12
        γ, δ or higher postn   = +18

   (4) double bond extend conjgn   = +30

   (5) Homoanular conjugated diene   = +39

4. Auxochrome increments

	α	β	γ	δ or higher
— OH	+35	+30	—	+50
— OAc	+6	+6	+6	+6
—Cl	+15	+12	—	—
— Br	+25	+35	—	—
— OR	+35	+30	17	31
— SR	—	+85	—	—
—NR₂	—	+95	—	—

Problems

① Calculate λ_{max} (ethanol) for the given structure.

$$CH_3\underset{CH_3}{\overset{CH_3}{C}}\overset{\beta}{=}\overset{\gamma}{CH}-\overset{\delta}{\underset{O}{\overset{O}{C}}}-CH_3$$
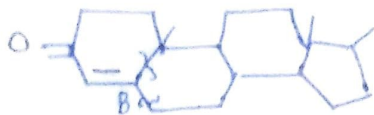
Basic value = 215 nm

2 β-alkyl Substituents = 2×12 = 24 nm

Calculated value = 239 nm   obs = 237 nm

②

Basic value =   215 nm
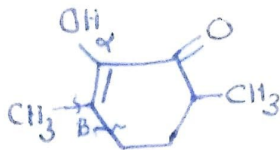
2 β-ring residues = 2×12 = 24 nm

1 exocyclic double bond = 5 nm

Calculated value = 244 nm   Obs = 241 nm

③

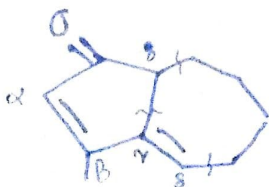Basic value =   215 nm

OH Substn at α postn = 35 nm

2 β substituents (one   = 24 nm
alkyl and one ring residue)

calculated   274 nm   obs - 275 nm

④

It is a cyclopentanone System

Basic value =   202 nm

1 β alkyl Substn =   12 nm

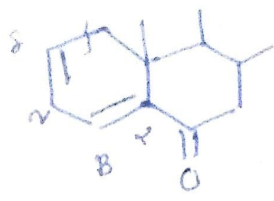1 exocyclic double =   5 nm
bond

1 double bond ext. conjgn = 30 nm

1 γ-ring residue = 18 nm

1 δ-ring residue = 18 nm

Calculated = 285 nm
Value
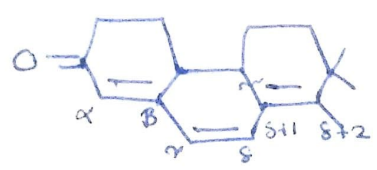
obs - 287 nm

⑤

Basic value	= 215 nm
α ring + 8 ring residue	= 10 + 18 = 28 nm
1-exocyclic double bond	= 5 nm
Homoannular conjugated diene	= 39 nm
1-double bond extending conjugation	= 30 nm

Calculated = 317 nm   Obs - 319 nm

⑥

Basic value	= 215 nm
1 β-ring residue	= 12 nm
1 δ+1 ring residue	= 18 nm
2 (δ+2) ring residue	= 2×18 = 36 nm
2 double bond extending Conjugation	= 2×30 = 60 nm
2 exocyclic double bonds	= 2×5 = 10 nm

Calculated value = 351 nm   obs - 354 nm

⑦

If the α,β-unsaturation on either side, then the value of absorption max is estimated by considering the most highly substituted conjugated system

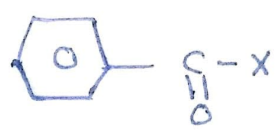|	
Basic value	= 215 nm
1 α ring residue	= 10 nm
1 β ring residue	= 12 nm
1 δ ring residue	= 18 nm

i double bond extend conjugation $= 30$ nm

Homoannular conjugated diene $= 39$ nm

calculated $= 324$ nm   Obs $- 307$ nm.

Rules for calculating Absorbtion Maximum for derivatives of acyl benzenes

Like woodward Fieser rules, Scott devised a set of rules for calculating the absorption maximum for the derivatives of acyl benzenes. For a compd of type
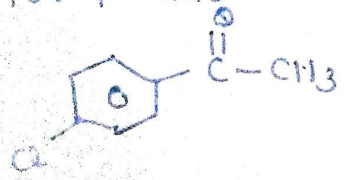

(1) basic value $= 246$ If $X =$ alkyl, alicyclic residue.

$= 250$ If $X = H$

$= 230$ $X = OH, OR$.

② Structural increments for auxochromes.

Auxochrome	ortho	meta	para
alkyl	+3	+3	+10
OH, OR	+7	+7	+25
Cl	0	0	+10
Br	+2	+2	+15
NH_2	+13	+13	+58
NHAc	+20	+20	+45
NR_2	+20	+20	+85
$\bar{O}$	+11	+20	+75

Problems

① Calculate the absorption maximum in ethanol for p-chloro acetophenone
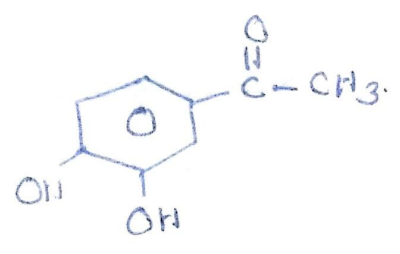
Basic value - 246 nm

Cl at para postn - $\dfrac{10 \text{ nm}}{256 \text{ nm}}$ Obs - 254 nm.

(2)

Basic value   = 246 nm

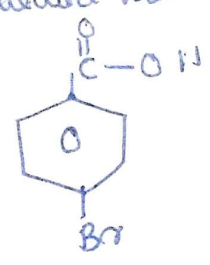OH at meta   = 7 nm

OH at para   = $\dfrac{25 \text{ nm}}{278 \text{ nm}}$

Calculated value = 278 nm   Obs - 281 nm.

(3)

Basic value = 230 nm

Br at para = $\dfrac{15 \text{ nm}}{245 \text{ nm}}$

Calc value = 245 nm   Obs value = 245

11. Bathochromic effect: It is an effect due to which the absorption maximum is sh towards longer wavelength due to the presence of auxochrome or by the change of sol. Increase in conjugation causes bathochromic shift.

12. Hypsochromic shift or effect: Due to this, absorption maximum is shifted to sh wavelength. It is due to reduction in conjugation or change in the polarity of solvent.

13. A good solvent in U.V.: Spectroscopy is one which is low priced and is transparent d to 210 nm. Polar bonds like carbonyl are effected by solvent polarity. With increase in sol polarity, $n \rightarrow \pi^*$ transitions undergo blue shift while $\pi \rightarrow \pi^*$ transitions undergo red shift.

14. In ultra-violet spectrum: Sharp peaks are seldom observed but instead broad bands observed. The reason is that vibrational and rotational effects are superimposed on the electr transitions.

2.33   Short Questions with Answers

1. **Define the term 'spectroscopy'.**

Ans. Spectroscopy involves the interaction between electromagnetic radiation and the substa under investigation.

2. **Why is absorption and not emission spectroscopy used to study the spectra of orga compounds?**

Ans. Emission spectroscopy cannot be used since the emission of radiation from an orga compound requires very high temperature. Organic compounds are low melting and th generally decompose at high temperatures.

3. **What is the effect of ultra-violet or visible light on the organic compound?**

Ans. When the substance under investigation is subjected to the action of UV or visible radiati then it causes changes in the electronic energy levels within the molecule.

4. **What do you mean by absorption of radiation in a spectrum or a record?**

Ans. Absorption of radiation at a particular wavelength leads to decrease in the perc transmission to appear in the spectrum as a dip, called a peak or an absorption ban

5. **What do you mean by a spectrum or record of the spectrum?**

Ans. The spectrum of a compound represents a graph of either wavelength or frequen continuously changing over a small portion of the electromagnetic spectrum versus ei percent transmission or absorbance.

6. **Define Absorbance.**

Ans. Absorbance is a measure of the absorption of radiation by a sample.

$$A = \log\left(\frac{\text{original intensity}}{\text{Intensity}}\right) = \log\frac{I_0}{I} = \epsilon\, cl.$$

7. **What is the effect of hydrogen bonding on ultra-violet absorption?**

Ans. Hydrogen bonding shifts the ultra-violet absorptions to shorter wave lengths.

8. **What do you mean by a good solvent in UV spectroscopy and what is its effect absorption maximum?**

Ans. A good solvent in ultra-violet or visible spectroscopy is one which is low priced and transparent down 210 nm. Polar bonds like carbonyl are affected by solvent polarity. W increase in solvent polarity, $n \rightarrow \pi^*$ transitions undergo blue shift (towards short wa length) while $\pi \rightarrow \pi^*$ transition undergo red shift.

9. **Tell whether a molecule can undergo more than one electronic shift.**

Ans. Depending upon the wavelength of light used, a molecule can undergo all the possib

electronic transitions. For example, acetaldehyde (CH_3CHO) can undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions.

10. **What happens to the excited molecule when radiation is cut off?**

Ans. In that case, the excited molecule gives off energy and returns to the ground state. The process is called deactivation. The excited molecule may undergo a chemical change depending upon the nature of the molecule. Cis-trans isomerisation is an example of the type.

11. **For the detection of aldehydes and ketones, which transition is more authentic, $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$.**
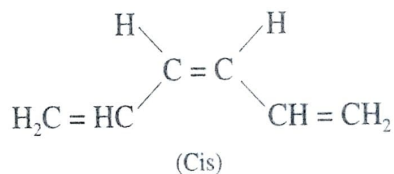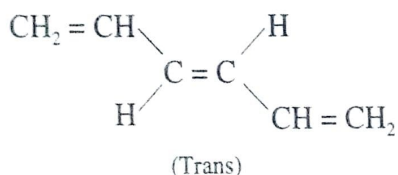
Ans. $n \rightarrow \pi^*$ with low value of extinction coefficient ($\in_{max}$).

12. **Describe the shift in absorption ($n \rightarrow \pi^*$) when a more polar solvent is used.**

Ans. When a more polar solvent is used, the excitation of n electrons to π^* orbital requires more energy. Thus, the shift is towards shorter wavelength.

13. **How will you distinguish between cis and trans-1, 3, 5-Hexatriene.**

Ans. The structure of hexatrienes are:

(Trans)   (Cis)

cis-isomer absorbs at lower wavelength, because the bulky groups on the same side cause repulsive interactions resulting in the reduction in conjugation.

14. **Which spin state is observed at the instant of excitation?**

Ans. Excitation occurs very rapidly ($<10^{-13}s$) and thus, there is no time for the excited electron to change its spin (Franck Condon Principle). Clearly, singlet ground state (S_0), gives singlet excited state (S_1).

15. **For which isomer, $\pi \rightarrow \pi^*$ transition occurs at high wavelength and higher extinction coefficient: cis-stilbene or trans-stilbene.**

Ans. Trans-stilbene absorbs at higher wavelength. The reason is that coplanarity is needed for the most effective overlap of π-orbitals and thus, increased ease of $\pi \rightarrow \pi^*$ transition. It is possible in case of trans-isomer.

16. **What structural features may produce bathochromic or hypsochromic effect in an organic compound?**

Ans. A bathochromic or red shift is caused by the change of solvent or the presence of an auxochrome. A hypsochromic (or blue) shift is caused by the change of solvent or by the structural changes such as reduction in conjugation.
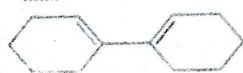
17. **Aniline absorbs at 280 nm ($\in_{max}$ 8600) but in acidic solution, the main absorption band is seen at 203 nm ($\in_{max}$ 7500) which is comparable to benzene. Explain.**

Ans. In the acidic medium, aniline is converted to anilinium ion. Thus, due to removal of conjugation of lone pair of electrons on nitrogen atom of aniline with π-bond system of benzene, the hypsochromic shift takes place.

18. **Which out of benzene (colourless) or quinone (yellow) has more easily promoted electrons?**

Ans. Quinone.

19. **Why the λ_{max} for the diene (I) is observed at lower nm than II?**
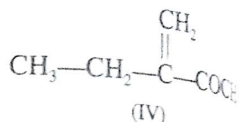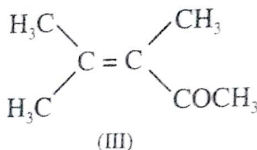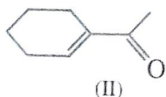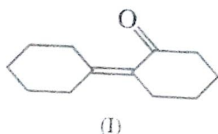
Ans. In both the dienes, there are four ring residues as substituents. In diene (II), the double bonds are exocyclic. Thus, λ_{max} for II will be higher by 2×5 nm or 10 nm

20. **Which of the following compounds would be suitable or unsuitable as a solvent use in recording UV spectra of organic compounds?**

    (a) Cyclohexane (b) Iodoethane (c) benzene (d) diethyl ether.

Ans. Cyclohexane or diethyl ether do not absorb above 200 nm and hence can be used as solvent But benzene and iodoethane absorb above 200 nm and thus, cannot be used as solvents

21. **Following four ketones are filled in four bottles and their labels are removed Measurement of ultra-violet spectra of the contents of four bottles give λ_{max} 249, 237 and 258 nm. Assign structures to the appropriate λ_{max}.**

(I)   (II)   (III)   (IV)

Ans. (i) **For compound I**

$$
\begin{aligned}
\text{Basic value} &= 215 \text{ nm} \\
\text{one } \alpha\text{-ring residue} &= 10 \text{ nm} \\
\text{two } \beta\text{-ring residue} &= 24 \text{ nm} \\
\text{exocyclic DB to two rings} &= \underline{10 \text{ nm}} \\
\lambda_{max} &= 259 \text{ nm}
\end{aligned}
$$

(ii) **For compound II**

$$
\begin{aligned}
\text{Basic value} &= 215 \text{ nm} \\
\text{one } \alpha\text{-alkyl} &= 10 \text{ nm} \\
\text{one } \beta\text{-ring residue} &= \underline{12 \text{ nm}} \\
\lambda_{max} &= 237 \text{ nm}
\end{aligned}
$$

(iii) **For compound III**

$$
\begin{aligned}
\text{Basic value} &= 215 \text{ nm} \\
\text{one } \alpha\text{-alkyl} &= 10 \text{ nm} \\
\text{two } \beta\text{-alkyls} &= \underline{24 \text{ nm}} \\
\lambda_{max} &= 249 \text{ nm}
\end{aligned}
$$

(ii) **For compound IV**

$$
\begin{aligned}
\text{Basic value} &= 215 \text{ nm} \\
\text{one } \alpha\text{-alkyl} &= \underline{10 \text{ nm}} \\
\lambda_{max} &= 225 \text{ nm}
\end{aligned}
$$

22. **Calculate the concentration in $\mu g \text{ ml}^{-1}$ of a solution of organic compound (mol mas 211.2) in 0.11 M HCl giving an absorption at its λ_{max} 281 nm of 0.612 in 4 cm cel The molar absorptivity at 281 mm is 5372.**

Ans. We know the relation: $A = \varepsilon c.l.$

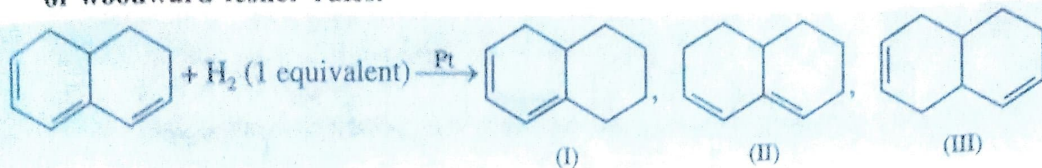Substituting the values, we get

$$0.612 = 5372 \times c \times 4$$

$$c = \frac{0.612}{5372 \times 4} = 0.0000\ 2848 \text{ mol } l^{-1}$$

$$= 0.00002848 \times 211.2 = 0.002848 \text{ gm } l^{-1}$$

$$= 2.848 \text{ } \mu g \text{ ml}^{-1}.$$

23. **The following triene on partial hydrogenation gives three products, which are separated by chromatography. How can you identify the products by the application of woodward-fesher rules.**

Ans. (*i*) **For compound I**

$$Basic\ value = 253\ nm$$
$$3\ Ring\ residue = 15\ nm$$
$$1\ exocyclic\ DB = 5\ nm$$
$$\lambda_{max} = \overline{273\ nm}$$

(*ii*) **For compound II**

$$Basic\ value = 214\ nm$$
$$3\ Ring\ residue = 15\ nm$$
$$1\ exocyclic\ DB = 5\ nm$$
$$\lambda_{max} = \overline{234\ nm}$$

(*ii*) **For compound III**

As the compound is not conjugated, λ_{max} occurs below 200 nm.

24. **How will you identify the following compounds from the given spectral data. λ_{max} 296 nm, ϵ_{max} 10700 and λ_{max} 281 nm, ϵ_{max} 20800?**

Ans. We see that the compound with λ_{max} 296 nm has half intensity as compared to the other compound. The decrease in intensity is due to steric hindrance by methyl group and its effect on the absorption of conjugated system. Thus, the compound I has decreased intensity.

25. **Benzene is colourless but its isomer, fulvene is yellow. How will you explain it?**
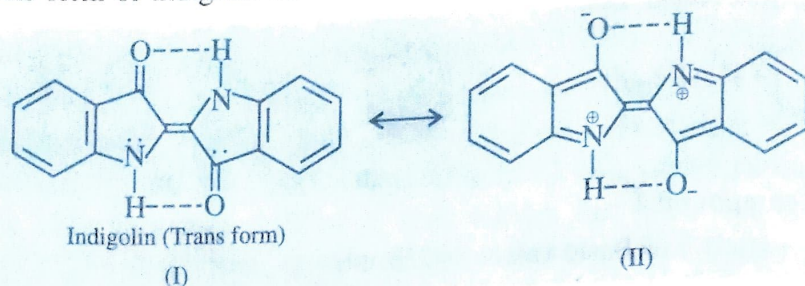
Ans. The formula of fulvene is ⬡=CH₂. It is an isomer of benzene (C_6H_6). Resonance stabilises the ground state of benzene compared to its excited state whereas fulvene is stabilised in the excited state. Thus, the electronic excitation energy required for fulvene is lower than that for benzene. As a result of this, fulvene absorbs at higher wavelength which makes it yellow in colour. Benzene absorbs at lower wavelength and is colourless.

26. **o-Nitroacetanilide is deep yellow but para-nitro acetanilide is yellow. Why is the colour of 'o'-isomer deeper?**

Ans. The ortho isomer exhibits intramolecular hydrogen bonding whereas the para Isomer shows intermolecular hydrogen bonding. Internal or intramolecular hydrogen bonding stabilises the excited state of a molecule to the greater extent than the intermolecular hydrogen bond. Clearly, the electronic excitation energy required for o-isomer is smaller and thus, absorption occurs at longer wavelength and result in deepening of the colour.

27. **Why is Indigotin dark blue in colour?**

Ans. The trans form of indigotin can be written as in the following resonating structures

Indigolin (Trans form)
(I)   (II)

The resonating structure II is more stable in the excited state. Also the internal hydrogen bonding gives further stability in the excited state. Thus, the transition from HOMO LUMO is very low. As a result λ_{max} for the electronic transition is high and indigo shows dark blue colour.

FURTHER READING

1. *A.I. Scott, Interpretation of the ultra-violet spectra of natural products.* Pergamon, Oxford 1964. It is an authoritative work on Wood-ward rules *etc.*

2. C. Nordling, *Angew, Chem. int.* Ed. II (1972), 83 (Review of E.S.C.A.).

3. C.N.R. Rao, *Ultraviolet and visible spectroscopy. Chemical applications.* Plenum Press 1975.

4. I. Fleming and D.H. William, *Spectroscopic methods in organic chemistry.* Mc-Graw Hill 1973.

5. Nachod and Zuckkerman, Determination of organic structure by physical methods Academic press—(Five volumes).

6. UV Atlas of organic compounds, Butterworths, London, 1965. (A collection of the spectra of about 1,000 compounds).

7. Ultra-violet reference spectra, Sadtler Research laboratories, 3314–20 spring garden s Philadelphia, Pa.

8. B.M. Trost, *Problems in spectroscopy : Organic structure determination by NMR, UV visible and mass spectra,* Benjamin, 1967.

REVIEW QUESTIONS

1. (a) Define Electronic spectroscopy. What is its absorption range? Write the relationship between wavelength, frequency and wave number.

   (b) Calculate the energy associated with the radiations having wave number 3×10^4 per cm.

2. (a) What are absorption laws? How is an ultraviolet spectrum plotted ?

   (b) Explain quantisation of energy.

   (c) Write a short note on Electromagnetic spectrum.

3. Describe briefly how an ultraviolet spectrum can be scanned for a pure organic compound? What are absorption bands formed instead of sharp lines in the spectrum?

4. (a) Detail the chemistry of electronic spectroscopy. Give the various types of transitions involved in this technique with one example in each case.

   (b) Explain the effect of polar solvents on (i) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

5. (a) Define the following terms :

   (i) Bathochromic shift   (ii) Hypsochromic shift

   (iii) A Chromophore   (iv) Hyperchromic effect.