CHAPTER 2

Ultra-violet and Visible Spectroscopy

ULTRA-VIOLET AND VISIBLE SPECTROSCOPY

2.1 Introduction

The alternate title for this technique is Electronic Spectroscopy since it involves the promotion of electrons (σ, π, $n*$ electrons) from the ground state to the higher energy state. It is very useful to measure the number of conjugated double bonds and also aromatic conjugation within the various molecules. It also distinguishes between conjugated and non-conjugated systems; α, β-Unsaturated carbonyl compounds from β, γ-analogues; homoannular and Heteroannular conjugated dienes etc. For visible and ultra-violet spectrum, electronic excitations occur in the range 200-800 mμ and involves the promotion of electrons to the higher energy molecular orbital.

Since the energy levels of a molecule are quantised, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. Clearly, if the substance is exposed to radiation of some different value of frequency, energy will not be absorbed and thus, light or radiation will not suffer any loss in intensity. If radiation of a desired or correct frequency is passed or made to fall on the sample of the substance, energy will be absorbed and electrons will be promoted to the higher energy states. Thus, light radiation on leaving the sample after absorption will be either less intense or its intensity may be completely lost.

Substances absorbing in the visible range will appear coloured to the human eye (For visible range – See Fig. 2.1). The wavelength of particular radiation absorbed can also be expressed in terms of frequency or energy in kcal mole^{-1}.
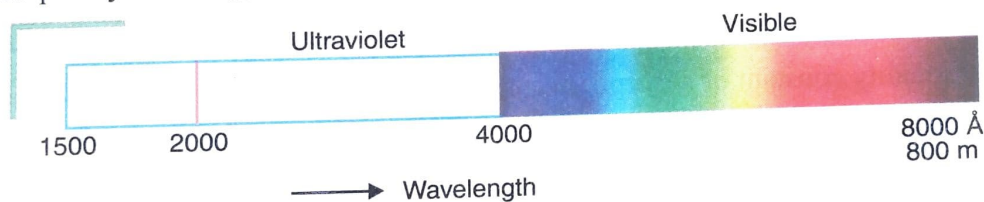

Fig. 2.1. The range of UV-visible Spectra.

$$1\mu = 10^{-4} \text{ cm}$$
$$1m\mu = 1 \text{ nm}** = 10^{-7} \text{ cm} = 10\text{Å}$$

Let us calculate the energy associated with radiations having wavelength 280 mμ.

$$\lambda = 280 \text{ m}\mu = 280 \times 10^{-7} \text{ cm}$$

We know that

$$E = h\nu$$

$$= h \cdot \frac{c}{\lambda} \qquad (h = 6.62 \times 10^{-27} \text{ ergs sec.})$$

Avogadro's number
$$N = 6.023 \times 10^{23}$$
$$4.18 \times 10^7 \text{ ergs} = 1 \text{ calorie}$$

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10} \times 6.023 \times 10^{23}}{280 \times 10^{-7} \times 4.18 \times 10^7 \times 10^3} \text{ kcal mole}^{-1}$$

$$\cong 100 \text{ kcal mole}^{-1}.$$

Note. It is not advisable to keep the compounds in ultra-violet radiations except for taking the spectrum.

A record of the amount of light absorbed by the sample as a function of the wavelength of light in mμ or nm units is called absorption spectrum which generally consists of absorption bands.

*   Non-bonding electrons.

**   nm means nanometers.

$$\ln\left(\frac{I}{I_0}\right)\Big/\ln(0.8) = \frac{-k \times 5l}{-k \times l} = 5$$

or

$$\ln\left(\frac{I}{I_0}\right) = 5 \times \ln(0.8) = \ln(0.8)^5$$

$$\frac{I}{I_0} = (0.8)^5 = 0.328$$

Taking antilogs, the fraction of the transmitted light $= \frac{I}{I_0} = (0.8)^5 = 0.328$

We know that $\frac{I}{I_0} = \frac{I_0 - I_a}{I_0} = 0.328$ or $1 - \frac{I_a}{I_0} = 0.328$

Clearly, the fraction of the incident light absorbed $= 1 - 0.328 = \mathbf{0.672}$

EXAMPLE 7. *For a solution of organic ketonic compound ($C_{10}H_{16}O$) in hexane in a 10 cm cell, the absorbance was found to 2.52. What is the concentration of the organic compound? (Given $\in_{max} = 14$).*

SOLUTION. Given that : Absorbance (A) = 2.52

$\in_{max} = 14$, cell length, $l = 10$ cm

Applying the solution: $A = \in.c.l.$

$\therefore$ Concentration, $c = \dfrac{A}{\in.l} = \dfrac{2.52}{10 \times 14} = 1.8 \times 10^{-2}$ mole L^{-1}

2.3 Measurement of Absorption Intensity

It may be noted that the intensity of absorption is directly proportional to the transition probability. An allowed transition will have ε_{max} value greater than 1000 while those having low transition probability will have its value less than 1000.

Selection Rules : The various electronic transitions which are governed by certain restrictions are called selection rules. These are:

(*i*) The transitions which involve a change in the spin quantum number of an electron during the transition do not occur. Thus, singlet-triplet transitions are forbidden.

(*ii*) The transitions between orbitals of different symmetry do not occur. For example, $n \to \pi^*$ transition is symmetry forbidden.

The wavelength of light corresponding to maximum absorption is written as λ_{max}. It can be directly read from the horizontal axis as shown in Fig. 2.2. The Figure shows the ultra-violet spectrum of vitamin *A* with vertical line showing absorbance *A* which is equal to log I_0/I.
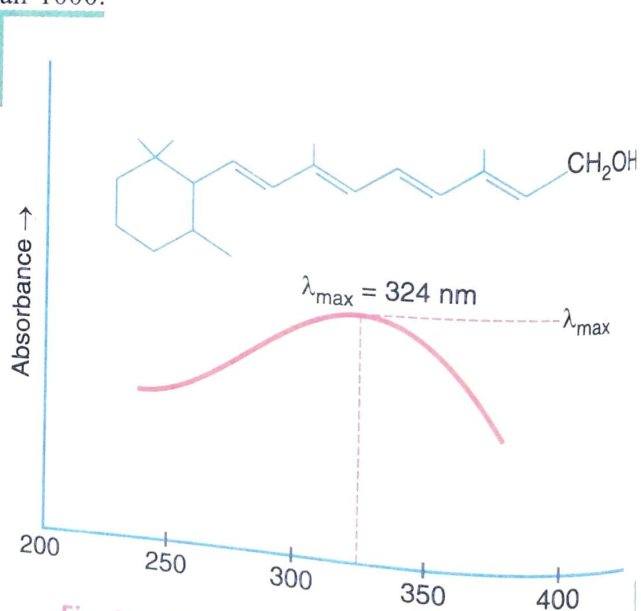
Fig. 2.2. Ultra-violet spectrum of vitamin A.

For vitamin *A*, the absorption maximum (λ_{max}) is observed at 324 nm.

2.4 Instrumentation

A spectrophotometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus, the instrument compares the intensity of the transmitted light with that of the incident light.

Usually, samples are scanned in dilute solutions. One mg of the compound under investigatio (Molecular weight 100-200) is accurately weighed and dissolved in a suitable solvent to make th solution upto 100 ml volume. A little of this solution is taken in a silica cell. The thickness of th solution in the cell should be 1 cm. When the constitution of the absorbing material is unknow the absorptivity may be sometimes expressed as $E_{1cm}^{1\%}$. Pure solvent is also taken in an exact similar cell (Reference cell). These cells are then exposed to the monochromatic beams of equ intensity in the spectrometer. After the beams pass through the sample cell as well as the referen cell, the intensities of the respective transmitted beams are then compared over the whole waveleng range of the instrument. The spectrometer electronically subtracts the absorption of the solvent i the reference beam from the absorption of the solution. Hence, the effects due to the absorptio of light by the solvent are minimised. In this way, the absorbance or the transmittance characteristi of the compound alone can be measured. The signal for the intensity of absorbance versu corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotte as absorbance A ($\log_{10} I_0/I$) against wavelength λ (abcissa). The plot is often represented as ε_{ma} (Extinction coefficient*) against wavelength.

When the sample absorbs light, its intensity is lowered. Thus, the photoelectric cells P_1 an P_2 will receive an intense beam from the reference cell and a weak beam from the sample cell. Thi results in the generation of pulsating or alternating currents which flow from the photoelectric cell to the electronic amplifier. The amplifier is coupled to a small servomotor, which in turn, is coupled to a pen recorder. Thus, it records the absorption bands automatically. Actually, the amplifier is coupled to a small servomotor which drives an optical wedge into the reference beam until the photoelectric cell receives light of equal intensities from the sample as well as the reference beams.

2.5 Formation of Absorption Bands

We expect the spectrum to consist of sharp peaks and each peak will correspond to the promotion of electron from one electronic level to another. But, actually sharp peaks are seldom observed and instead, broad absorption bands are recorded. It is due to the fact that the excitation of electrons are also accompanied by the constant vibratory and rotatory motion of the molecules. The vibratory and rotatory modes are also quantised. **A molecule in a particular electronic state is also quantised. Clearly a molecule in a particular electronic state is also accompanied by some vibrational and rotational states.** The differences between two adjacent electronic levels is more as compared to the adjacent rotational levels while the difference between the adjacent vibrational levels has some intermediate value. The electronic excitation is superimposed upon rotational and vibrational levels.
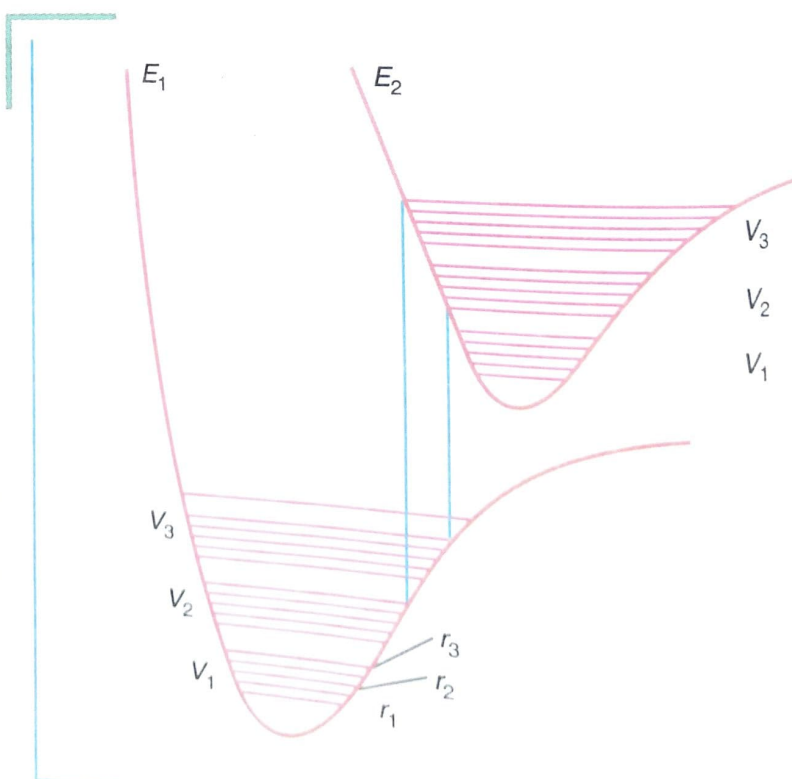
Fig. 2.4. Energy curves for a diatomic molecule.

* It is also called molar absorptivity.

Clearly, during promotion, the electron moves from a given vibrational and rotational level within one electronic mode to some other vibrational and rotational level within the next electronic mode. Thus, there will be a large number of possible transitions (close together) responsible for change in electronic, rotational and vibrational levels. Hence, not just one but a large number of wavelengths which are close enough will be absorbed resulting in the formation of bands. In more complex molecules which contain a large number of atoms, the multiplicity of vibrational sub-levels and their closeness results in the discrete bands to coalesce and thus, broad bands are observed.

2.6 Theory of Electronic Spectroscopy

When the molecule absorbs ultraviolet or visible light, its electrons get promoted from the ground state to the higher energy state. In the ground state, the spins of the electrons in each molecular orbital are essentially paired. In the higher energy state, if the spins of the electrons are paired, then it is called an excited singlet state. On the other hand, if the spins of the electrons in the excited state are parallel, it is called an excited triplet state. The triplet state is always lower in energy than the corresponding excited singlet state. Therefore, triplet state is more stable as compared to the excited singlet state. In the triplet excited state, electrons are farther apart in space and thus, electron-electron repulsion is minimised. Normally the absorption of ultraviolet or visible light results in singlet ground state to excited singlet state transition, i.e., excitation proceeds with the retention of spins. An excited singlet state is converted to excited triplet state with the emission of energy as light. The transition from singlet ground state to excited triplet state is symmetry forbidden. The higher energy states are designated as high energy molecular orbitals and also called antibonding orbitals. The highly probable transition due to absorption of quantised energy involves the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled molecular orbital. In most of the cases, several transitions occur resulting in the formation of several bands.

Types of Electronic Transitions

According to the molecular orbital theory, when a molecule is excited by the absorption of energy (UV or visible light), its electrons are promoted from a bonding to an antibonding orbital.

(i) The antibonding orbital which is associated with the excitation of σ electron is called σ*† antibonding orbital. So σ to σ* transition takes place when σ (sigma) electron is promoted to antibonding (σ) orbital. It is represented as σ → σ* transition.

(ii) When a non-bonding electron ** (n) gets promoted to an antibonding sigma orbital (σ*), then it represents n → σ* transition.

(iii) Similarly π → π* transition represents the promotion of π electrons to an antibonding π orbital, i.e., π* orbital, (See Fig. 2.5)
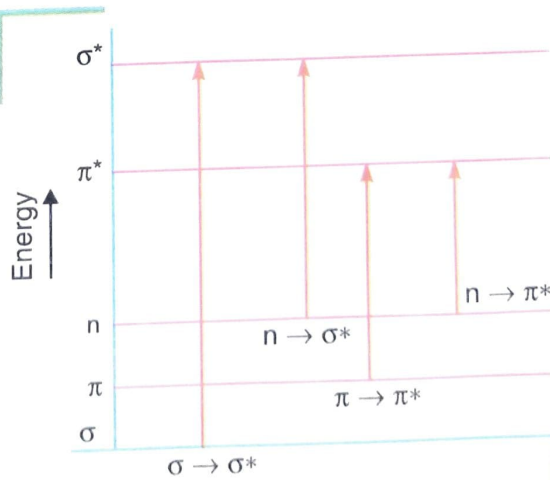

Fig. 2.5. Electronic excitation energies.

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* †called sigma asterisk.

** †Unshared pair of electrons.

Similarly, when an n-electron (non-bonding) is promoted to antibonding π orbital, it repres... $n \rightarrow \pi^*$ transition. The energy required for various transitions obey the following order :

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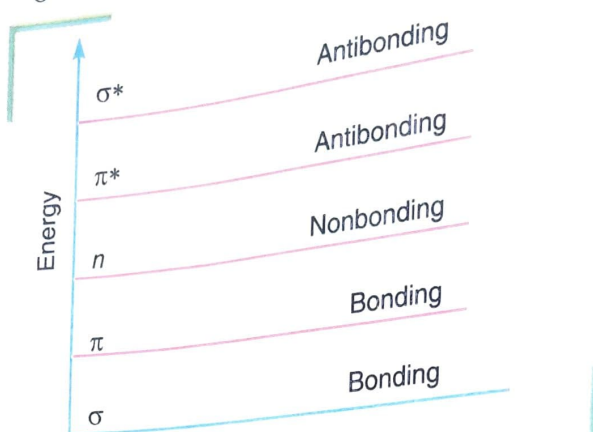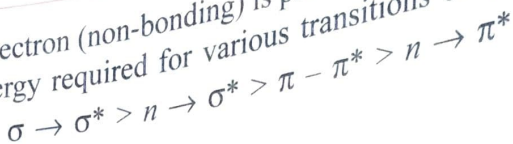

Fig. 2.6. Electronic excitation energies.

Let us now consider the various transitions involved in ultraviolet spectroscopy.

(a) $\sigma \rightarrow \sigma^*$ **transitions.** It is a high energy process since σ bonds are, in general, very strong. The organic compounds in which all the valence shell electrons are involved in the formation of sigma bonds do not show absorption in the normal ultra-violet region, i.e., 180–400 mμ. For saturated hydrocarbons, like methane, propane etc. absorption occurs near 150 mμ (high energy). Consider $\sigma \rightarrow \sigma^*$ transition in a saturated hydrocarbon :
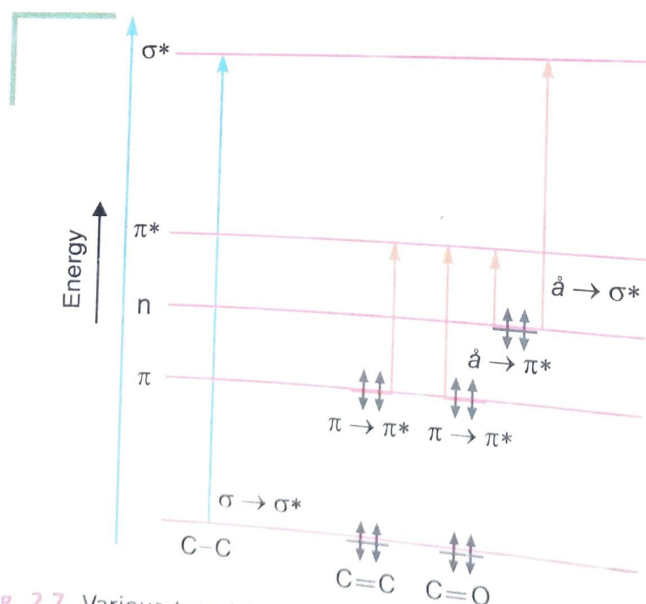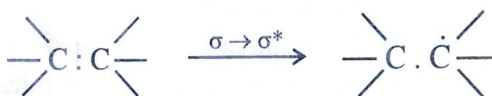
Fig. 2.7. Various transition involved in Electronic spectroscopy.

Such a transition requires radiation of very short wavelength (High energy). See Fig. 2.7. The usual spectroscopic technique cannot be used below 200 mμ, since oxygen (present in air) begins to absorb strongly. To study such high energy transitions (below 200 mμ), the entire path length must be evacuated.* Thus, the region below 200 mμ is commonly called vacuum **ultraviolet region**. The excitation of sigma bond electron to σ^* (antibonding) level occurs with net retention

of electronic spin. It is called excited singlet state which may, in turn, gets converted to excited triplet state. This region is less informative.

(b) $n \rightarrow \sigma^*$ **transition.** This type of transition takes place in saturated compounds containing one hetero atom with unshared pair of electrons (n electrons). Some compounds undergoing this type of transitions are saturated halides, alcohols, ethers, aldehydes, ketones, amines etc. Such transitions require comparatively less energy than that required for $\sigma \rightarrow \sigma^*$ transitions. Water absorbs at 167 mμ, methyl alcohol at 174 mμ and methyl chloride absorbs at 169 mμ.
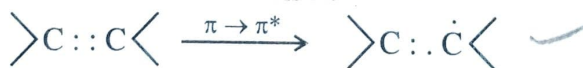
In saturated alkyl halides, the energy required for such a transition decreases with the increase in the size of the halogen atom (or decrease in the electronegativity of the atom).

$$\overset{\diagdown}{\underset{\diagup}{C}} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{X}} : \quad \xrightarrow{\;n \rightarrow \sigma^*\;} \quad \overset{\diagdown}{\underset{\diagup}{C}} - \overset{\cdot}{\underset{\cdot\cdot}{X}} :$$
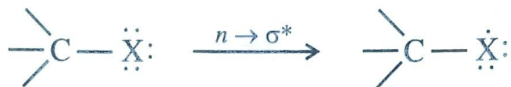
Let us compare $n \rightarrow \sigma^*$ transition in methyl chloride and methyl iodide. Due to the greater electronegativity of chlorine atom, the n electrons on chlorine atom are comparatively difficult to excite*. The absorption maximum for methyl chloride is 172–175mμ whereas that for methyl iodide is 258 mμ as n electrons on iodine atom are loosely bound. Since this transition is more probable in case of methyl iodide, its molar extinction coefficient** is also higher compared to methyl chloride.

Similarly, amines absorb at higher wavelengths as compared to alcohols and hence the extinction coefficients for amines will be larger. $n \rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus, transition requires greater energy. **Hydrogen bonding shifts the ultra-violet absorptions to shorter wavelengths.** (For details see solvent effects).

(c) $\pi \rightarrow \pi^*$ **transitions.** This type of transition occurs in the unsaturated centres of the molecule; i.e., in compounds containing double or triple bonds and also in aromatics. The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelength. A π electron of a double bond is excited to π^* orbital. For example, alkenes, alkynes, carbonyl compounds, cyanides, azo compounds etc. show $\pi \rightarrow \pi^*$ transition. Consider an alkene:

$$\overset{\diagdown}{\underset{\diagup}{C}} :: C \overset{\diagup}{\underset{\diagdown}{}} \quad \xrightarrow{\;\pi \rightarrow \pi^*\;} \quad \overset{\diagdown}{\underset{\diagup}{C}} : . \overset{\cdot}{C} \overset{\diagup}{\underset{\diagdown}{}}$$

This transition requires still lesser energy as compared to $n \rightarrow \sigma^*$ transition and therefore, absorption occurs at longer wavelengths. Absorption usually occurs within the region of ordinary ultra-violet spectrophotometer. In unconjugated alkenes, absorption bands appear around 170–190 mμ. In carbonyl compounds, the band due to $\pi \rightarrow \pi^*$ transition appears around 180 mμ and is most intense, i.e., the value of extinction coefficient is high. The introduction of alkyl group to olefinic linkage produces a bathochromic shift** of the order of 3 to 5 mμ per alkyl group. The shift depends upon the type of the alkyl group and the stereochemistry about the double bond.

(d) $n \rightarrow \pi^*$ **transition.** In this type of transition, an electron of unshared electron pair on hetero atom gets excited to π^* antibonding orbital. This type of transition requires least amount of energy out of all the transitions discussed above and hence occurs at longer wavelengths.

Saturated aldehydes $\left(\overset{R}{\underset{R}{\diagup}}C = \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : \right)$ show both the types of transitions, i.e., low energy $n \rightarrow \pi^*$ and

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* Greater the probability of a particular transition, greater the value of its molar extinction coefficient, ε_{max}.

** Shift towards longer wavelength.

high energy $\pi \rightarrow \pi^*$ occuring around 290 mμ and 180 mμ respectively. Absorption occuring lower wavelength is usually intense. In simple cases, it is quite easy to tell whether the transitie is $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ since the extinction coefficient for the former is quite low as compared that of the latter. The exact electronic structure of the molecules in the excited state (by t absorption of UV or visible light) is not known but the electronic transition involves the redistribut of electrons within the molecule. In carbonyl compounds; a high energy $n \rightarrow \sigma^*$ transition a occurs and is quite intense. Thus, in saturated carbonyl compounds, two types of transitions ta place which can be classed as :

(a) High energy transitions

    (i) $n \rightarrow \sigma^*$ (intense)

    (ii) $\pi \rightarrow \pi^*$ (intense)

(b) Low energy transition

    $n \rightarrow \pi^*$ (weak)–R*band.

In carbonyl compounds, the shift in the absorption depends upon the polarity of the solven

2.8 Transition Probability

It is not always necessary that the excitation of an electron takes place from a bonding orbit or lone pair to an antibonding or nonbonding orbital when a compound is exposed to UV or visibl light. It can be shown that

Extinction coefficient

$$\varepsilon_{max} = 0.87 \times 10^{20}. \; P.a$$

where P = transition probability with values from 0 to 1.

    a = Target area of the absorbing system, usually called a chromophore.*

It is found that the values of ε_{max} is about 10^5 when the choromophore has a length of the order of 10 Å or 10^{-7} cm. The chromophore with low transition probability will have ε_{max} value below 1000. Hence, there is a direct relationship between the area of the chromophore and the absorption intensity ε_{max}. In addition, there are some other factors also which govern the transition probability Depending upon the symmetry and the value of ε_{max}, the transitions*** can be classed as :

(a) Allowed Transitions   **(b) Forbidden Transitions**

The transitions with values of (extinction coefficient) ε_{max}, more than 10^4 are usually called allowed transitions. They generally arise due to $\pi \rightarrow \pi^*$ transitions. In Butadiene 1, 3, the absorption at 217 mμ ε_{max} 21,000 is an example of allowed transition.

The forbidden transition is a result of the excitation of one electron from the lone pair presen on the heteroatom to an antibonding π^* orbital. $n \rightarrow \pi^*$ transition near 300 mμ in case of carbony compounds with ε_{max} value between 10–100, is the result of forbidden transition. The values o ε_{max} for forbidden transition are generally below 10^4. Consider benzophenone. The two types o transitions observed in this case are :

    (i) 252 mμ

    (ii) 325 mμ ε_{max} 20,000 (allowed)

     ε_{max} 180 (forbidden).

Symmetry restrictions in Electronic transitions. The transition (allowed or forbidden) i related with the geometries of the lower and the higher energy molecular orbitals and also on th symmetry of the molecule as a whole. Symmetrical molecules have more restrictions on thei electronic transitions than less symmetrical molecules. For example, benzene is a highly symmetrica molecule. Thus, many restrictions apply to the electronic transitions of the benzene molecule an thus, its electronic absorption spectrum is simple. For a totally unsymmetrical molecule, no symmetr

*   R-bands (Radikalartig-German).

restrictions apply to the electronic transitions so that transitions may be observed among all of its molecular orbitals except among filled orbitals. Clearly, for such a substance, a complex electronic absorption spectrum will result.

Between symmetrical and totally unsymmetrical extremes, a large number of organic compounds fall which absorb light in the ultra-violet-visible region. To decide whether the transition is allowed or forbidden for such molecules, it is important to consider

(i) the geometry of the molecular orbital in the ground state

(ii) the geometry of the molecular orbital in the excited state and

(iii) the orientation of the electric dipole of the incident light that might induce the transition.

The transition will be an allowed transition if the above three factors have an appropriate symmetry relationship.

2.9 The Chromophore Concept

All those compounds which absorb light of wavelength between 400-800 mμ appear coloured to the human eye. Exact colour depends upon the wavelength of light absorbed by the compound. Originally, a chromophore was considered any system which is responsible for imparting colour to the compound. Nitro-compounds are generally yellow in colour. Clearly, nitro group is the chromophore which imparts yellow colour. Similarly, aryl conjugated azo group is a chromophore for providing colour to azo dyes. Now, the term chromophore is used in a broader way.

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region.

The absorption occurs irrespective of the fact whether colour is produced or not. Some of the important chromophores are ethylenic, acetylenic, carbonyls, acids, esters, nitrile group etc. A carbonyl group is an important chromophore, although, the absorption of light by an isolated group does not produce any colour in the ultraviolet spectroscopy. There are two types of chromophores :

(a) Chromophores in which the group contains π electrons and they undergo $n \rightarrow \pi^*$ transitions. Such chromophores are ethylenes, acetylenes etc.

(b) Chromophores which contain both π electrons and n (non-bonding) electrons. Such chromophores undergo two types of transitions i.e., $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. Examples of this type are carbonyls, nitriles, azo compounds, nitro compounds etc.

Note. In compounds of the type $\overset{\diagdown}{\underset{\diagup}{C}} - \overset{\diagup}{\underset{\diagdown}{C}}$ and $\overset{\diagdown}{\underset{\diagup}{C}} - H$ absorption occurs around 150 mμ (vacuum ultraviolet region) as result of $\sigma \rightarrow \sigma^*$ transition.

For compounds containing such atoms as $-\overset{..}{\underset{..}{O}}-$, $-\overset{..}{\underset{..}{S}}-$, $\overset{\diagdown}{\diagup}\overset{..}{N}$ absorption occurs around 190 mμ as a result of $n \rightarrow \sigma^*$ transition.

There are no set rules for the identification of a chromophore. The change in position as well as the intensity of absorption depends upon a large number of factors. Following points may be helpful :

(i) Spectrum consisting of a band near 300 mμ may contain two or three conjugated units.

(ii) Absorption bands near 270–350 mμ with very low intensity, ε_{max} 10–100 are due to $n \rightarrow \pi^*$ transitions of the carbonyl group. See table T$_2$-1.

(iii) Simple conjugated chromophores such as dienes or α, β—Unsaturated ketones have high ε_{max} values, i.e., from 10,000 to 20,000.

(iv) The absorption with ε_{max} value between 1000 to 10,000 shows an aromatic system. Although less intense, it is most characteristic of carbonyl group.

Table T$_2$-1 Simple Unconjugated Chromophores

Chromophore	Transition	Absorption max (mμ)	ε_{max}	Solvent
C=C	$\pi - \pi^*$	~175	~15000	Vapour
		(i) ~175	~10000	Hexane
—C≡C—	$\pi - \pi^*$	(ii) 196	~2000	"
		(iii) 220	~150	"
C=O	$n \rightarrow \sigma^*$	160	18000	"
	$\pi \rightarrow \pi^*$	180	10000	Hexane
	$n \rightarrow \pi^*$	285*	15	
R—NO$_2$	$\pi - \pi^*$	~200	5000	Methanol
	$n \rightarrow \pi^*$		~274	15
—C=O OH	$n \rightarrow \pi^*$	204	60	Methanol
—N=N—	$n - \pi^*$	338	~5	Ethanol
—CONH$_2$	$n \rightarrow \pi^*$	178	9500	Hexane
	$n \rightarrow \pi^*$	220	63	Hexane

When aromatic nucleus is substituted with groups which can extend the chromophore, th absorption occurs at still higher values of extinction coefficients.

Note. The presence of a compound or a functional group can be confirmed by othe spectroscopic techniques.

All compounds with the same functional group will absorb at the same wavelength with nearl the same extinction coefficient if the disturbing factors such as conjugation, substituents etc. ar absent. Some of the chromophores with their respective absorption maxima and extinction coefficient are given in Table T$_2$-1.
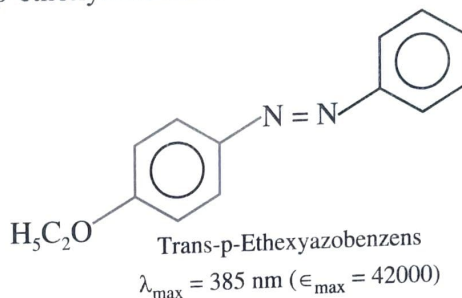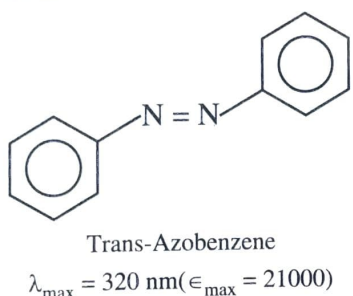
2.10 Auxochrome

An auxochrome can be defined as any group-which does not itself act as a chromophore bu whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength). The absorption at longer wavelength is due to the combination of a chromophor and an auxochrome to give rise to another chromophore. An auxochromic group is called colou enhancing group. Auxochromic groups do not show characteristic absorption above 200 mμ. Some common auxochromic groups are —OH, —OR, —NH$_2$, —NHR, —NR$_2$, —SH etc. The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons. Thus, a new chromophore results which has a different value of the absorption maximum as well as the extinction coefficient. For example, benzene shows an absorption maximum at 255 mμ [ε_{max} 203] whereas aniline absorbs at 280 mμ [ε_{max} 1430]. Hence, amino (—NH$_2$) group is an auxochrome.

Consider the following :

λ_{max} = 280 nm
($\in_{max}$ = 1430)

λ_{max} = 254 nm
($\in_{max}$ = 160)
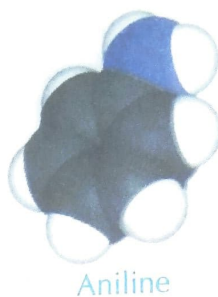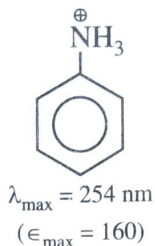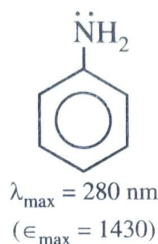
Aniline

In aniline, $-\overset{..}{N}H_2$ acts as a chromophore. But in anilinium ion, there is no lone pair on nitrogen atom.

Consider trans—Azobenzene and trans-p-ethoxyazobenzene.

Trans-Azobenzene

λ_{max} = 320 nm($\in_{max}$ = 21000)

Trans-p-Ethexyazobenzens

λ_{max} = 385 nm ($\in_{max}$ = 42000)

The presence of $-OC_2H_5$ group (an auxochrome) increases the value of λ_{max} as well as ε_{max}.

Mechanism : All auxochromic groups contain non-bonding electrons. Due to this, there is extension of conjugation of the chromophore by sharing the non-bonding electrons.

$$CH_2=CH-\overset{..}{N}(CH_3)_2 \longleftrightarrow :\overset{-}{C}H_2-CH=\overset{+}{N}(CH_3)_2$$
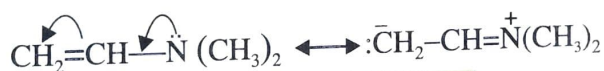
2.11 Absorption and Intensity Shifts

(a) **Bathochromic effect.** It is an effect by virtue of which the absorption maximum is shifted towards longer wavelength due to the presence of an auxochrome or by the change of solvent. (See Fig. 2.8.). Such an absorption shift towards longer wavelength is called Red shift or bathochromic shift. The $n \rightarrow \pi^*$ transition for carbonyl compounds experiences bathochromic shift when the polarity of the solvent is decreased.

(b) **Hypsochromic shift or effect.** It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength. The absorption shifted towards shorter wavelength is called **Blue shift** or hypsochromic shift.

Fig. 2.8. Absorption and intensity shifts.

It may be caused by the removal of conjugation and also by changing the polarity of the solvent. In the case of aniline, absorption maximum occurs at 280 mµ because the pair of electrons on nitrogen atom is in conjugation with the π bond system of the benzene ring. In its acidic solutions, a blue shift is caused and absorption occurs at shorter wavelength (~203 mµ).

In $-\overset{+}{N}H_3$. ion formed in acidic solution, the electron pair is no longer present and hence conjugation is removed.

(c) **Hyperchromic effect.** It is an effect due to which the intensity of absorption maximum increases *i.e.*, ε_{max} increases. For example, the B-band for pyridine at 257 mµ ε_{max} 2750 is shifted
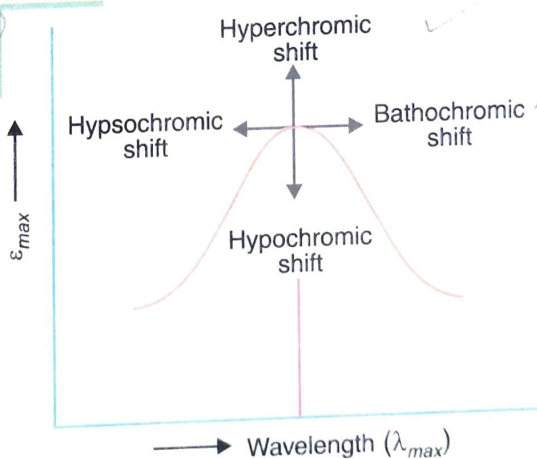
to 262 mμ ε_{max} 3560 for 2-methyl pyridine (*i.e.*, the value of ε_{max} increases). The introduction ULT
an auxochrome usually increases intensity of absorption.   attac

(*d*) **Hypochromic effect.** It is defined as an effect due to which the intensity of absorpinter
maximum decreases, *i.e.*, extinction coefficient, ε_{max} decreases. The introduction of group whiε_{max}
distorts the geometry of the molecule causes hypochromic effect. For example, biphenyl absoR-b
at 250 mμ, ε_{max} 19000 whereas 2-methyl biphenyl absorbs at 237 mμ, ε_{max} 10250 [ε_{max} decreaseapp
It is due to the distortion caused by the methyl group in 2-methyl biphenyl.   spec

2.12 Types of Absorption Bands

Following types of bands originate as a result of the possible transitions in a compound.

(*a*) **K* Bands.** K-bands originate due to $\pi \rightarrow \pi^*$ transition from a compound containing
conjugated system. Such type of bands arise in compounds like dienes, polyenes, enones et
K-bands also appear in an aromatic compound which is substituted by a chromophore. The intensi
of K-band, is usually more than 10^4. The K-band absorption due to conjugated 'enes' and 'enone
are effected differently by changing the polarity of the solvent.

Table T$_2$—2   K-band Transitions

Compound	Transition	(λ_{max} mμ)	ε_{max}
Butadiene 1,3	$\pi - \pi^*$	217	21,000
Acrolein	$\pi - \pi^*$	210	11,500
Styrene	$\pi - \pi^*$	214	12,000
Acetophenone	$\pi - \pi^*$	240	13,000
2,3 dimethyl			
Butadiene	$\pi - \pi^*$	226	21,400
Pentadiene 1, 3	$\pi - \pi^*$	223	22,600

(*b*) **R* band.** Such type of bands originate due to $n \rightarrow \pi^*$ transition of a single chromophori
group and having at least one lone pair of electrons on the hetero atom. R-bands are also calle
forbidden bands. These are less intense with ε_{max} value below 100.

Table T$_2$ – 3   R-band Transitions

Compound	Transition	λ_{max} (mμ)	ε_{max}
Acetone	$n \rightarrow \pi^*$	270	15
Acetaldehyde	$n \rightarrow \pi^*$	293	~12
Acrolein	$n \rightarrow \pi^*$	315	14
Acetophenone	$n \rightarrow \pi^*$	319	50
Methyl Vinyl			
Ketone	$n \rightarrow \pi^*$	320	~14
Crotonaldehyde	$n \rightarrow \pi^*$	322	~14

(*c*) **B-band.** Such type of bands arise due to $\pi \rightarrow \pi^*$ transition in aromatic or hetero-aromatic
molecules. Benzene shows absorption peaks between 230–270mμ. When a chromophoric group is

---

* Konjugierte-German.

* R-band or $n \rightarrow \pi^*$ transition is most characteristic for a carbonyl group of aldehyde or ketone. Fo
aldehydes, it usually appears at higher wavelengths compared to a ketone but at lower value of ε_{ma}

attached to the benzene ring, the B-bands are observed at longer wave-lengths than the more intense K-bands. For example, K-band appears at 244 mμ, ε_{max} 12000 and B-band at 282 mμ, ε_{max} 450. Out of K, B and R-bands which appear in the spectrum of an aromatic compound, R-band appears at a longer wave-length. For example, in acetophenone R-band ($n \rightarrow \pi^*$, forbidden) appears at 319 mμ ε_{max} 50 while K and B-bands appear at 240 and 278 mμ respectively. The fine spectrum of B-band in case of

(i) substituted aromatic compounds and

(ii) by the use of polar solvents

may be missing.

Table T$_2$—4 B-band Transitions

Compound	Transition	$\lambda_{max}(m\mu)$	ε_{max}
Benzene	$\pi - \pi^*$	255	215
Styrene	$\pi - \pi^*$	282	450
Toluene	$\pi - \pi^*$	262	174
Phenol	$\pi - \pi^*$	270	1450
Acetophenone	$\pi - \pi^*$	278	1110
Benzaldehyde	$\pi - \pi^*$	280	1500
Benzoic acid	$\pi - \pi^*$	270	800
Nitro-benzene	$\pi - \pi^*$	280	1000
Naphthalene	$\pi - \pi^*$	312	289
Quinoline	$\pi - \pi^*$	315	2500

(d) **E-bands.** Such bands originate due to the electronic transitions in the benzenoid system of three ethylenic bonds which are in closed cyclic conjugation. These are further characterised as E_1 and E_2-bands. E_1 and E_2 bands of benzene appear at 184 and 204 mμ respectively. E_1 band which appears at lower wave-length is usually more intense than the E_2-band for the same compound which appears at longer wavelength.

Table T$_2$–5 E-band Transitions

Compounds	E_1-band		E_2-band	
	λ_{max} (mm)	ε_{max}	λ_{max} (mm)	ε_{max}
Benzene	184	50,000	204	79,00
Naphthalene	221	133,000	286	9,300
Anthracene	256	180,000	375	9,000
Pyrrole	234	10,800	288	760
Thiophene	~270	6,300	~294	600
Quinoline	288	40,000	270	3,162

2.13 Solvent Effects

A most suitable solvent is one which does not itself absorb in the region under investigation. A dilute solution of the sample is always prepared for the spectral analysis. Most commonly used solvent is 95% Ethanol. Ethanol is a best solvent as it is cheap and is transparent down to 210 mμ.

Commercial ethanol should not be used as it contains benzene which absorbs strongly in ULT
ultraviolet region. Some other solvents which are transparent above 210 mμ are n-hexane, meth
alcohol, cyclohexane, acetonitrile, diethyl ether etc. Some solvents with their upper wavelen
limit of absorption are given in Table T_2–6.

Table T₂–6 — Solvents used in UV-spectroscopy	
Solvent	*Upper wavelength limit (mμ)*
Ethanol	210
Hexane	210
Methanol	210
Cyclohexane	210
Diethyl ether	210
Water	205
Benzene	280
Chloroform	245
THF (Tetrahydrofuran)	220
Carbon tetrachloride	265

Hexane and other hydrocarbons can be used as these are less polar and have least interaction
with the molecule under investigation. For ultra-violet spectroscopy, ethanol, water and cyclohexan
serve the purpose best.

The position and the intensity of absorption maximum is shifted for a particular chromophor
by changing the polarity of the solvent. By increasing the polarity of the solvent, compounds lik
dienes and conjugated hydrocarbons do not experience any appreciable shift. Thus, in general, th
absorption maximum for the non-polar compounds is the same in alcohol (polar) as well as i
hexane (non-polar). The absorption maximum for the polar compounds is usually shifted with th
change in polarity of the solvents. α, β- unsaturated carbonyl compounds show two different shifts

(i) $n \rightarrow \pi^*$ transition (less intense). In such a case, the absorption band moves to shorte
wave-length by increasing the polarity of the solvent. In $n \rightarrow \pi^*$ transition, the ground state is mor
polar as compared to the excited state. The hydrogen bonding with solvent molecules takes plac
to lesser extent with the carbonyl group in the excited state. For example, absorption maximum of
acetone is at 279 mμ in hexane as compared to 264 mμ in water.

(ii) $\pi \rightarrow \pi^*$ transition (intense). For such a case, the absorption band moves to longe
wavelength by increasing the polarity of the solvent. The dipole interactions with the solven
molecules lower the energy of the excited state more than that of the ground state. Thus, the valu
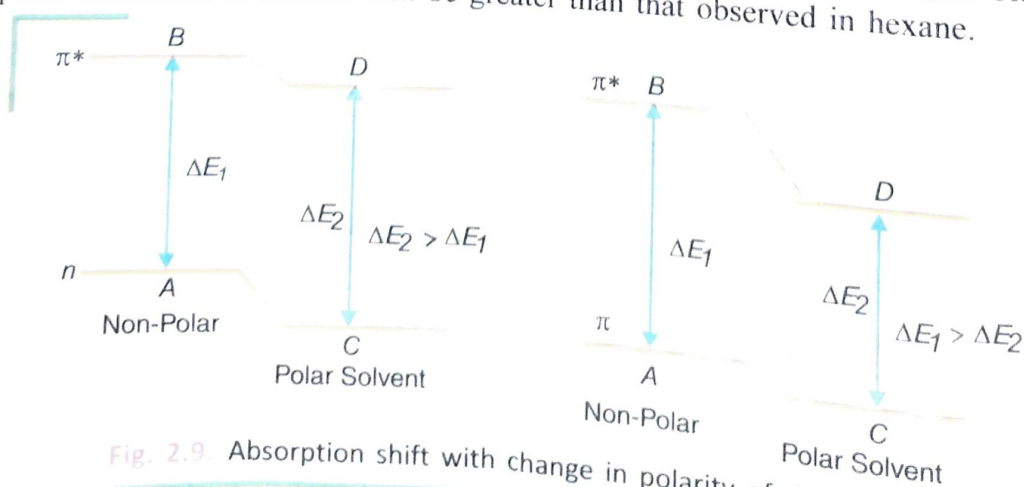of absorption maximum in ethanol will be greater than that observed in hexane.

Fig. 2.9. Absorption shift with change in polarity of the solvent.

In short, π^* orbitals are more stabilised by hydrogen bonding with polar solvents like water and alcohol. It is due to greater polarity of π^* orbital compared to π orbital. Thus, small energy will be required for such a transition and absorption shows a red shift.

$n \rightarrow \sigma^*$ transitions are also very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such associations occur due to the presence of nonbonding electrons on the hetero atom and thus, transition requires greater energy.
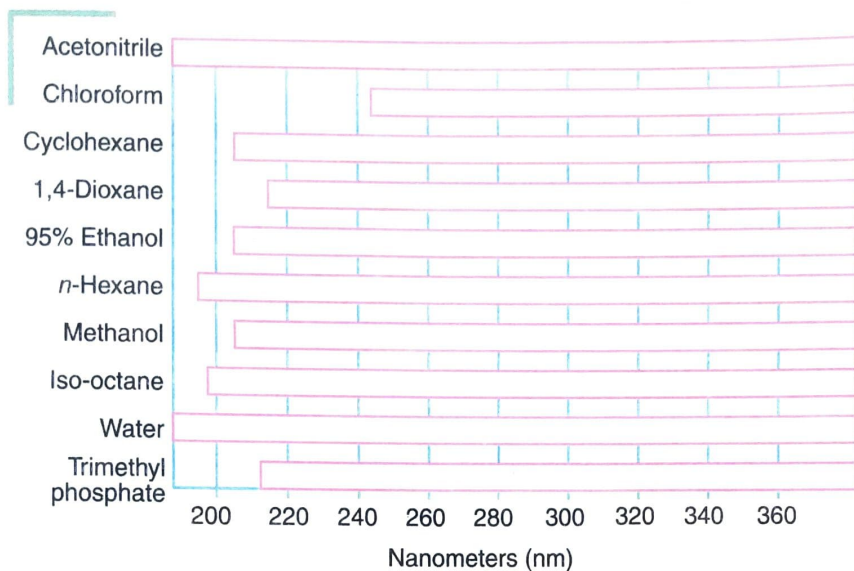
Fig. 2.10. Transparency ranges of useful solvents.

In general, we say that

(a) If the group (carbonyl) is more polar in the ground state than in the excited state, then increasing polarity of the solvent stabilises the non-bonding electron in the ground state due to hydrogen bonding. Thus, absorption is shifted to lower wavelength.

(b) If the group is more polar in the excited state, then absorption is shifted to longer wavelength with increase in polarity of the solvent which helps in stabilising the non-bonding electrons in the excited state.

It has been found that increase in polarity of the solvent generally shifts n $\rightarrow$ π^* and n $\rightarrow$ σ^* bands to shorter wavelengths and $\pi \rightarrow \pi^*$ bands to longer wavelengths.

Following points may also be noted in connection with the effect of solvent polarity on the various types of bands.

(i) **K-band.** The K-band absorption due to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent. Usually, K-bands due to conjugated dienes are not effected by changing the polarity of the solvent while these bands due to 'enones' show a red shift by increasing the polarity of the solvent.

(ii) **R-band.** The absorption shifts to shorter wavelength (blue shift) with the increase in polarity of the solvent.

(iii) **B-band.** The position as well as the intensity of the B-band is not shifted by increasing the polarity of the solvent. But in heterocyclic aromatic compounds, a marked hyperchromic shift (increase in ε_{max}) is observed by increasing the polarity of the solvent.

2.14 Effect of Temperature and Solvent on the Fineness of Absorption Band

It is known that the vibrational and the rotational states depend on temperature. As the temperature is decreased, vibrational and the rotational energy state of the molecules are also

lowered. Thus, when the absorption of light occurs at a lower temperature, smaller distribution of excited states result. It produces finer structure in the absorption band than what is noticed at higher temperature. Consider the UV spectrum of dodecapentaenoic acid in ether-alcohol solvent at 20 °C and −195 °C.
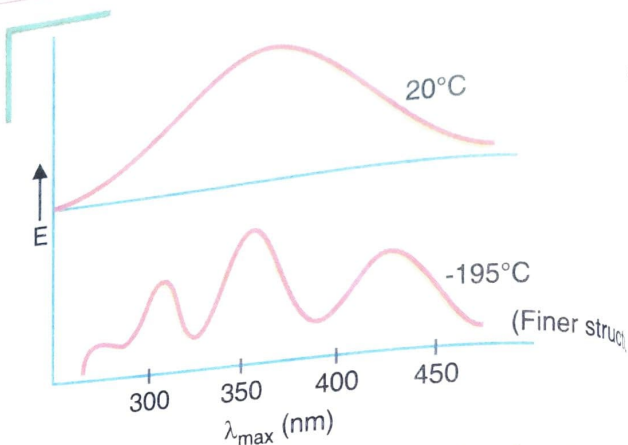
The solvent used also effects the fineness of absorption band in UV spectrum. If the dielectric constant of the solvent is high, there will be stronger solute-solvent interactions. Due to this, vibrational and rotational energy states of molecules increase and thus, the fineness of the absorption band fa

Fig. 2.10(A) Finess of absorption band.

2.15 Conjugated Dienes

The wavelength of absorption is shifted to higher values (Bathochromic shift), if two or m chromophoric groups are present in conjugation in a molecule. For example, ethylene (one dou bond) absorbs at 170 mµ ($\pi \to \pi^*$ transition) while butadiene (two double bonds in conjugati absorbs at 217 mµ. The bathochromic shift is more pronounced if the double bonds are in conjuga as compared to the isolated double bonds in which there is a little interaction between them. T absorption maximum is usually shifted 15–45 mµ towards higher wavelength in conjugated syst (compared to unconjugated) as the electron density is spread over at least four atomic centres. T value of extinction coefficient also increases. In conjugated dienes, $\pi \to \pi^*$ transition results in formation of a band, called K-band.

Table T$_2$–7 $\pi \to \pi^*$ transition (K-band)

Compound	$\lambda_{max}(m\mu)$	ε_{max}
Butadiene 1, 3	217	21,000
2,3 dimethyl butadiene	226	21,400
1,3,5, Hexatriene	254	21,400
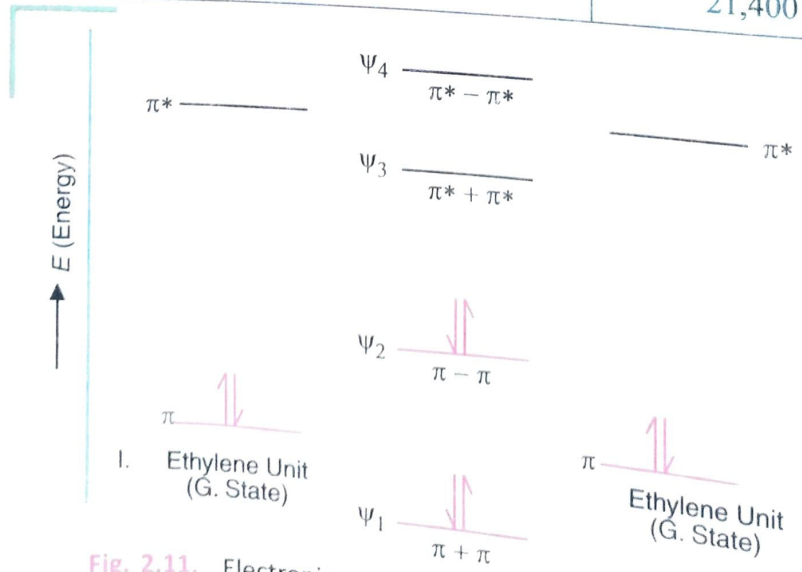
Fig. 2.11. Electronic excitations in conjugated dienes.

When ethylene molecule gets excited, it gives CH_2—CH_2 diradical. The electron cloud is spread on two carbon atoms and the absorption maximum occurs at 170 mμ.

Consider the absorption maximum of butadiene 1,3 (CH_2=CH—CH=CH_2). It consists of two ethylene units. The various excitations are shown in Fig. 2.11.

The two π bonding orbitals, one from each ethylene unit interact or mix up to give rise to two new bonding orbitals.

(i) $\pi + \pi = \pi_1$ or ψ_1–having smaller energy.

(ii) $\pi - \pi = \pi_2$ or ψ_2–having higher energy.
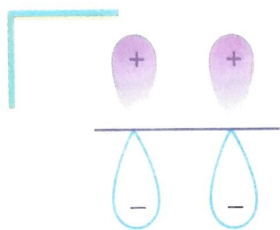
Fig. 2.12. π-bonding orbitals.
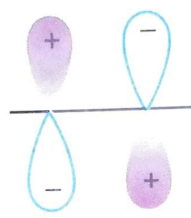
Fig. 2.13. π^* antibonding orbitals

The energy of ψ_1 is less than any one of the two combining atomic orbitals.

Also two π^* orbitals (antibonding) are formed from two ethylene units which are

(i) $\pi^* + \pi^* = \pi_1^* = \psi_3$ having smaller energy.

(ii) $\pi^* - \pi^* = \pi_2^* = \psi_4$ having higher energy.

The energies of ψ_3 and ψ_4 are compared with any one of the two (π^*) antibonding orbitals. Thus, ψ_1 can be represented as shown in the Fig. 2.14.

In this case, all the four singly filled atomic orbitals have the same spin of electrons.
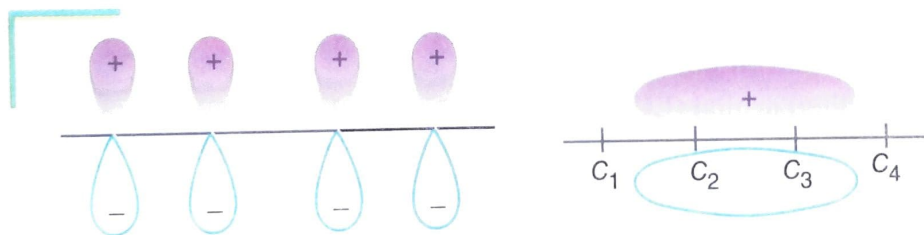
Fig. 2.14. Low energy atomic orbital (ψ_1).

Thus mixing is complete and there is no nodal plane.*

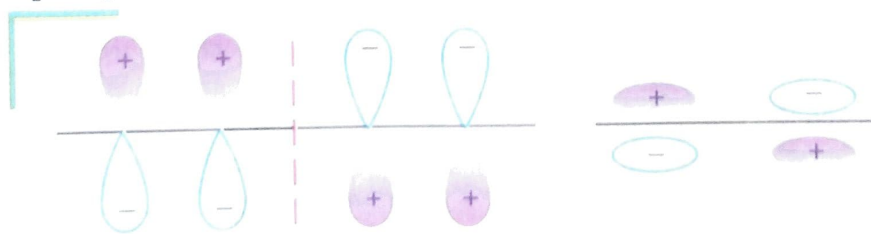$\pi - \pi = \pi_2 = \psi_2$ can be represented as shown in Figure 2.15.

Fig. 2.15. High energy bonding orbital (ψ_2)

In this case, we see one nodal plane.*

Clearly there are double bonds between C_1, C_2 and C_3, C_4 and there is a single bond between C_2 and C_3.

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* It is defined as an imaginary plane drawn perpendicular to the plane of propagation of the wave where the probability of finding the electron is zero.

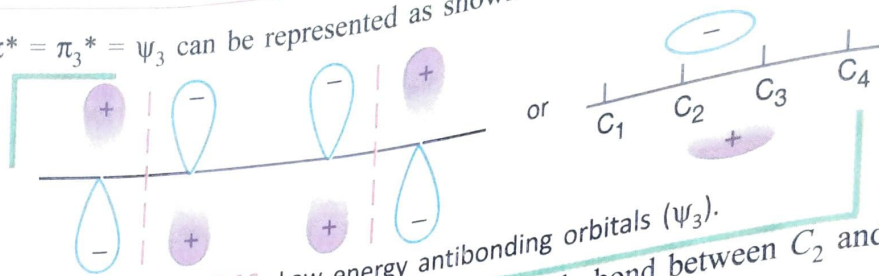$\pi^* + \pi^* = \pi_3^* = \psi_3$ can be represented as shown in Fig. 2.16.

Fig. 2.16. Low energy antibonding orbitals (ψ_3).

In this case, there are two nodal planes and one double bond between C_2 and C_3.

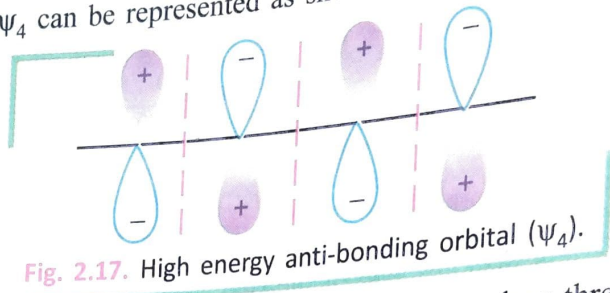$\pi^* - \pi^* = \pi_4^* = \psi_4$ can be represented as shown in Fig. 2.17.

Fig. 2.17. High energy anti-bonding orbital (ψ_4).

This structure corresponds to high energy state since it involves three nodal planes.

Thus, in butadiene, four orbitals are involved. On absorption of energy, electron jumps from π_2 to π_3^*. Since the energy difference between π_2 to π_3^* is less, absorption occurs at higher wave length. This type of transition is called $\pi \rightarrow \pi^*$ transition. **The net result is that when two double bonds are in conjugation, the energy level of higher occupied molecular orbital (HOMO) is raised and that of the lowest unoccupied molecular (antibonding) orbital (LUMO) is lowered. (See figure 2.17).**

Now this absorption corresponds to the transition y (low energy or higher wavelength). Similarly, when dissimilar chromophores are in conjugation, absorption occurs at longer wavelength as compared to the isolated chromophores. In general longer the conjugated system, smaller will be the energy needed to cause $\pi \rightarrow \pi^*$ transition and therefore, absorption

Fig. 2.18. Electronic transition in conjugated diene.

occurs at still longer wavelength. In a long conjugated system like carotene, absorption occurs in the visible region (higher wavelength region).

The values of absorption maximum (λ_{max}) as well as extinction coefficient for conjugated and unconjugated alkenes can be compared from their spectra shown in Fig. 2.19.

The values of λ_{max} and ε_{max} are more for conjugated diene as compared to those for an unconjugated alkene. A bathochromic as well as hyperchromic effect are observed when the spectrum of conjugated triene is compared to that of conjugated diene.
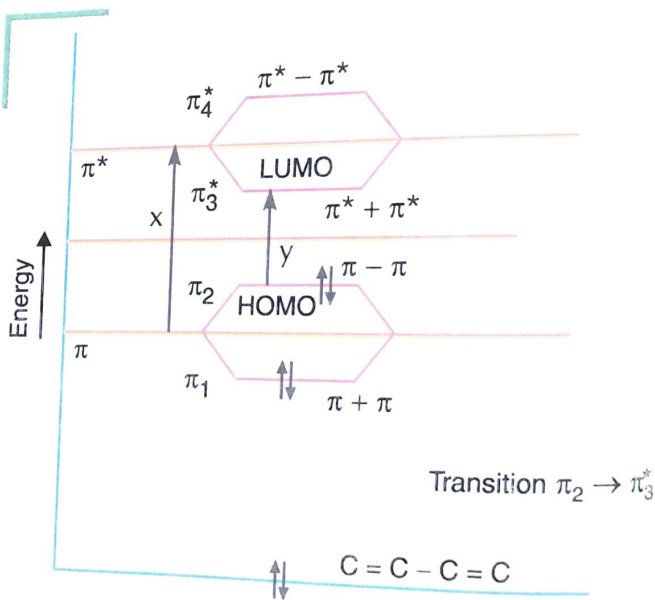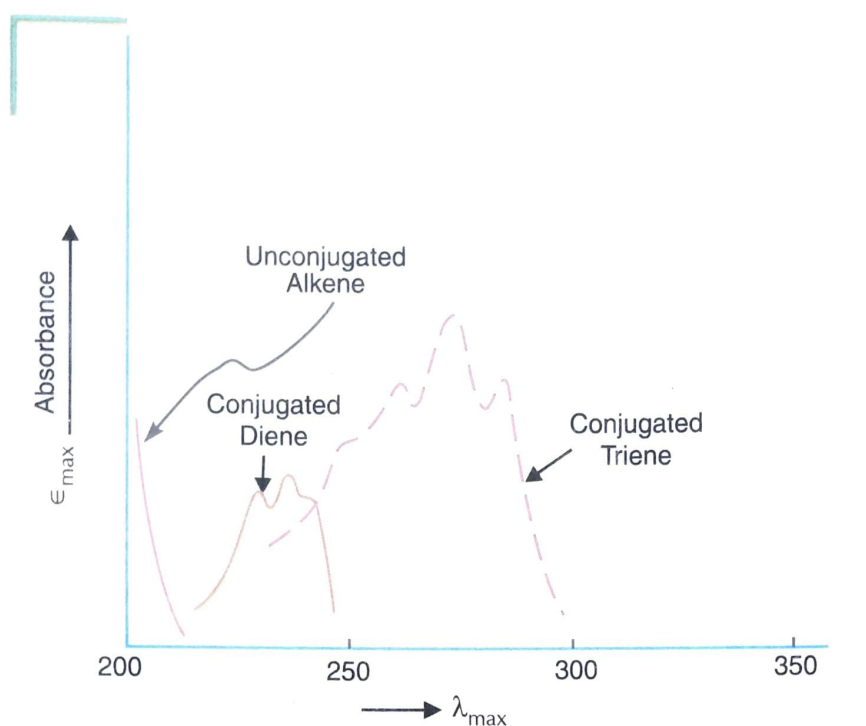
Fig. 2.19. Absorption in conjugated and un-conjugated systems.

It is important to note that greater the number of conjugated double bonds, greater is the bathochromic shift. With continuous increase in conjugation, the absorption may even shift to the visible region. As the conjugation increases, the energy gap between HOMO and LUMO decreases, (See Fig. 2.18). In case of β-carotene which contain eleven double bonds, the absorption bands appear at (*i*) λ_{max} 478 nm (ε_{max} 139000) and (*ii*) λ_{max} 452 nm (ε_{max} 122000).

2.16 Woodward-fieser Rules for Calculating Absorption Maximum in Dienes

Longer the conjugated system, greater is the wave-length of absorption maximum. The intensity of absorption [ε_{max}] also increases with the increase in the length of the chromophore (see Fig. 2.19). The conjugated polyene system appears coloured to the naked eye if there are more than five double bonds in conjugation and absorption occurs around or above 400 mμ (visible region). The presence of alkyl group on the double bond also causes bathochromic shift. Various types of double bonds in conjugation are described below :

(a) **Alicyclic dienes or dienes contained in an open chain system,** *i.e.*, where basic unit is butadiene system.

(b) **Homo-annular conjugated double bonds** are the conjugated double bonds present in the same ring. It is also called **Homodiene.** Some examples of this type are :
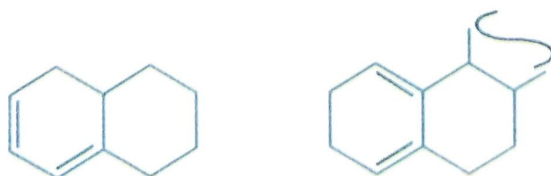
(c) **Hetero-annular conjugated double bonds** are the conjugated double bonds which are not present in the same ring. Some examples of this type are :
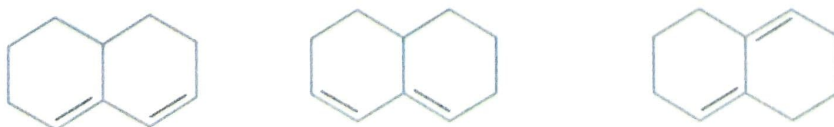
(d) **Exocyclic and Endocyclic conjugated double bonds** : Exocyclic double bond i UL double bond, part of the conjugated system, formed by any carbon atom of any ring but pre outside the ring. Endocyclic double bond is present inside the ring. Such double bonds are sh (or in the following examples :

(Exo)   (Endo)   (Exocylic double bond   (Contain two exocyclic,
                          to ring A)   double bonds)
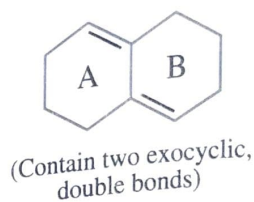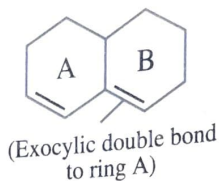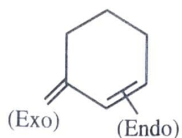
Woodward formulated certain empirical rules for calculating the λ_{max}* in case of dienes. The rules were later modified by Fieser in 1948. According to these rules, each type of diene ha certain fixed basic value and the value of absorption maximum (λ_{max}) depends upon :

(*i*) The number of alkyl substituents or ring residues on the double bond.

(*ii*) The number of double bonds which extend conjugation and

(*iii*) The presence of polar group such as —Cl, —Br, —OR, —SR etc.

Ring residue is a C–C bond, not a part of the conjugated system but attached to any one the carbon atoms of the conjugated polyene system.

The various rules for calculating the absorption maximum in case of dienes and trienes a summarised in the Table T_2–8.

Table T_2–8 **Conjugated dienes and Trienes.**

Solvent–Ethanol

Transition involved—$\pi \rightarrow \pi^*$

Parent value for Butadiene system or a cyclic conjugated diene	217 mµ
Acyclic Triene	245 mµ
Homoannular conjugated diene	253 mµ
Heteroannular conjugated diene	215 mµ
Increment for each substituent	
Alkyl substituent or ring residue	
Exocyclic double bond	5 mµ
Double bond extending conjugation	5 mµ
Auxochrome	30 mµ
—OR	
—SR	+ 6 mµ
—Cl*, —Br*	+ 30 mµ
—NR$_2$	+ 5 mµ
OCOCH$_3$	+ 60 mµ
	0 mµ

Some examples illustrating the above rules are as follows :

EXAMPLE 1. *Calculate the absorption maximum in the ultra-violet spectrum o 2, 4- Hexadiene.*

* Wavelength of absorption maximum.

** In case of a cyclic diene or diene contained in an open chain, 17 mµ are added in the basic value for chlorine as well as for bromine atom.

SOLUTION. The basic unit in 2, 4. hexadiene is butadiene. There are two alkyl substituents (one on each double bond) on it. Thus,
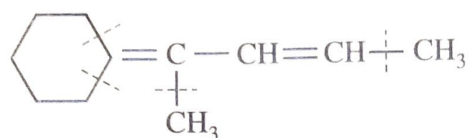
$$(CH_3—CH=CH—CH=CH—CH_3)$$

Basic value	=	217 mµ
2-alkyl substituents (2 × 5)	=	10 mµ
Calculated value	=	227 mµ

The observed value* is also found to be 227 mµ.

EXAMPLE 2. *Calculate the absorption maximum in the UV spectrum of*

It is a butadiene system. There are two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exo-cyclic double bond.

The value of absorption maximum is calculated as follows :

Basic value	=	217 mµ
2-alkyl substituents (2 × 5)	=	10 mµ
2-Ring residues (2 × 5)	=	10 mµ
1-Exocyclic double bond	=	5 mµ
Calculated value	=	**242 mµ**

The observed value is also found to be 242 mµ.

EXAMPLE 3. *Calculate* λ_{max} *for*

It is an example of heteroannular diene and there are four ring residues on the double bonds. Thus,
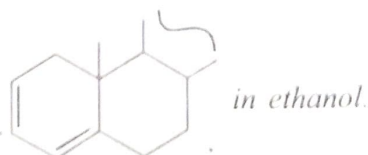
Basic value	=	215 mµ
Four Ring residues (4 × 5)	=	20 mµ
Calculated value	=	**235 mµ**

The observed value is also found to be 234 mµ,.

EXAMPLE 4. *Calculate the absorption maximum for the compound*

in ethanol.

SOLUTION. It is an example of homoannular conjugated diene and there are three ring residues on it. Moreover, it contains an exocyclic double bond in it. Thus,

Basic value	=	253 mµ
3-Ring residues (3 × 5)	=	15 mµ
1-exocyclic double bond	=	5 mµ
Calculated value	=	**273 mµ**
Observed value	=	**274 mµ**

* The calculated value and the observed value of absorption for a particular compound can differ by 5 mµ.

EXAMPLE 5. *Calculate the absorption maximum for the compound*

in ethanol.
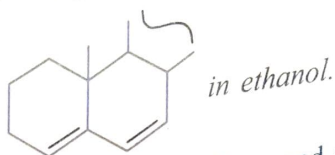
SOLUTION. It is an example of heteroannular diene and there are three ring residues in it. Moreover, it contains one exocyclic double bond in it. Thus,

Basic value	=	215 mµ
3-Ring residues	=	15 mµ
1-exocyclic double bond	=	5 mµ
Calculated value	=	**235 mµ**

The observed value of absorption maximum in the ultra-violet spectrum of this compound also found to be 235 mµ.

Note—Important. In case, both homoannular and heteroannular conjugated diene systems are present in the same compound, then calculations are based on longer wave-length, *i.e.,* for homoannular conjugated diene system (253 mµ).
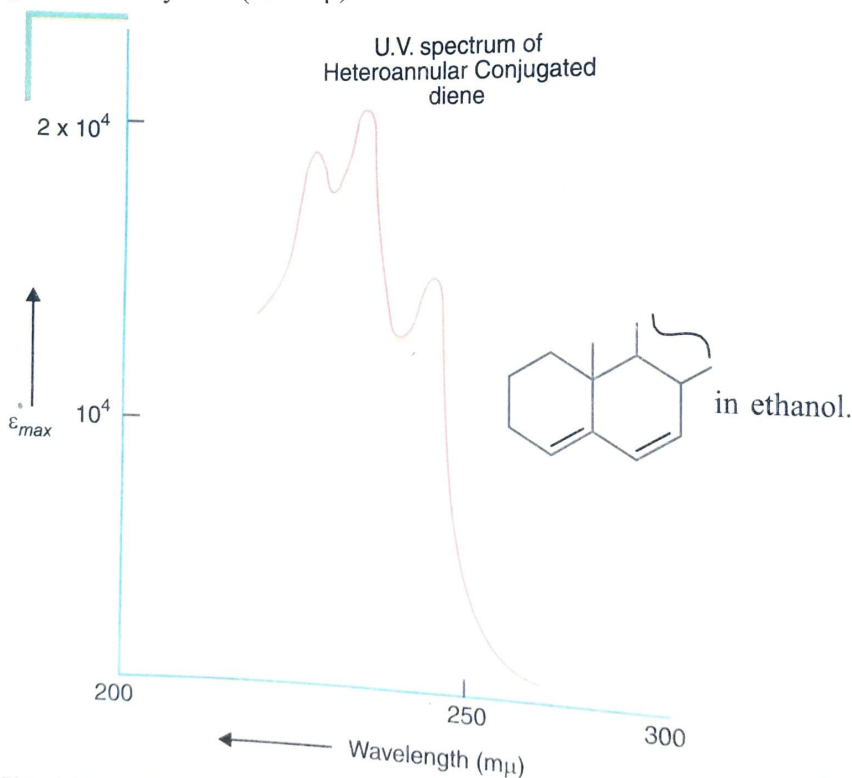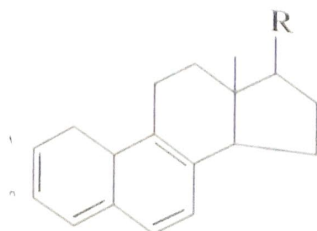

U.V. spectrum of
Heteroannular Conjugated
diene

2 x 10⁴

10⁴

ε_{max}

200

250

300

Wavelength (mµ)

in ethanol.

Fig. 2.20. UV spectrum of heteroannular conjugated diene.

EXAMPLE 6. *Calculate the value of absorption maximum for the compound*
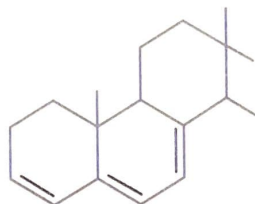
R

SOLUTION. It is a homodiene system. There are five ring residues on the double bonds, one exocyclic bond and also two double bonds which extend conjugation.

Basic value	=	253 mµ
2-double bonds extending conjugation	2 × 30 =	60 mµ
5-Ring residues	5 × 5 =	25 mµ
1-Exocyclic double bond	1 × 5 =	5 mµ
Calculated value	=	**343 mµ**
Observed value	=	345 mµ

EXAMPLE 7. *Calculate* λ_{max} *for the compound.*

SOLUTION. It is a homoannular conjugated diene system. It contains four ring residues; two exocyclic double bonds and one double bond which extend conjugation. Thus, λ_{max} for this compound is calculated as:

Basic value	=	253 mµ
4-Ring residues	(4 × 5) =	20 mµ
2-exocyclic double bonds	(2 × 5) =	10 mµ
1-double bond extending conjugation	=	30 mµ
Calculated value	=	**313 mµ**
Observed value	=	312 mµ

Bicyclic Compounds

If a diene system is present in a bicyclic compound, then due to the strain in the bicyclic compound, 15 mµ is added as the ring strain correction in the calculated value of absorption maximum.

EXAMPLE 8. *Calculate the absorption maximum in the ultraviolet spectrum of 2, 3 dimethylene bicyclo [2, 2, 1] heptane.*

SOLUTION. The value of absorption maximum for this compound is calculated as :

Basic value	=	217 mµ
2-Ring residues	(2 × 5) =	10 mµ
2-Exocyclic double bonds	=	10 mµ
1-bicyclic system (strain correction)	=	15 mµ
Calculated value	=	**252 mµ**
Observed value	=	254 mµ

2.17 Distortion of the Chromophore

Distortion of the chromophore may lead to red or blue shift depending upon the nature of distortion. The following compound whose structure is given is expected to show absorption maximum at 237 mµ but distortion of chromophore causes it to absorb at 220 mµ. The blue shift is due to the loss of conjugation as the structure is no longer coplanar (double bonds do not remain coplanar).

The change of ring size in case of simple homoannular conjugated diene leads to dep from the predicted value of 263 mµ as follows :

For cyclohexadiene, the absorption maximum can be calculated as

Basic Value $= 253$ mµ $\begin{bmatrix} \text{Homoannular} \\ \text{conjugated diene} \end{bmatrix}$

2-Ring residues $= \dfrac{10 \text{ mµ}}{263 \text{ mµ.}}$
Calculated value $= \textbf{263 mµ.}$

But, the absorption maximum for
(i) Cyclopentadiene occurs at 238.5 mµ; ε_{max} 3400
(ii) Cycloheptadiene occurs at 248 mµ; ε_{max} 7500.

The cause for the blue shift is distortion in chromophoric system which no longer rem coplanar.

2.18 POLY-enes and POLY-ynes

With the increase in the number of double bonds in conjugation, the values of absorp maximum as well as intensity increase. Note the values of absorption maximum as well as extinc coefficients in case of —(CH=CH)$_n$–where $n \geq 3$ are given below :

		λ_{max}	ε_{max}
(i) when	$n = 3$	275 mµ	30,000
(ii)	$n = 4$	310 mµ	76,500
(iii)	$n = 5$	342 mµ	122,000 etc.

Thus, as the number of double bonds in conjugation increases, the value of absorption maxim also increases but does not increase proportionally as expected. It is probably due to the variat in bond length between double and single bonds. Let us consider the cyanine dye analogue.

$Me_2 \overset{+}{N} = CH—(CH = CH)_n— \overset{..}{N} Me_2 \leftrightarrow Me_2 \overset{..}{N}—(CH=CH)_n—CH=\overset{+}{N}Me_2$
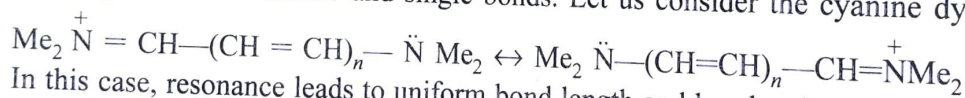
In this case, resonance leads to uniform bond length and bond order along the polyene cha As there is no change in bond length in the polyene chain, calculations give values which are ve close to observed ones.

Note. It is important to note that the change from trans to cis configuration at one or mo double bonds lower the wavelength as well as the intensity of absorption.

In case of acetylenic compounds, weak bands are observed (low intensity bands) at high wav lengths and high intensity bands occur at lower wave-lengths. Consider the absorption bands case of —(—C≡C—)$_n$—where $n \geq 3$.

		λ_{max}	ε_{max}
(i) When	$n = 3$	(i) 207 mµ	135,000
		(ii) 306 mµ	120
(ii)	$n = 4$	(i) 234 mµ	281,000
		(ii) 354 mµ	105

The ultraviolet spectrum of penta-yne is shown in the Fig. 2.21.

In Penta-yne, the absorption occurs at 260 mµ ε_{max} 352,000 and also a band at 394 m ε_{max} 120 which need a mention.

The absorption spectrum of a typical poly-yne and a typical poly-eneyne is shown in Fig. 2.2 The intensity and absorption maximum (λ_{max}) values increase with increasing conjugation an substitution. It helps in elucidating the structure of some unknown closely related compounds.
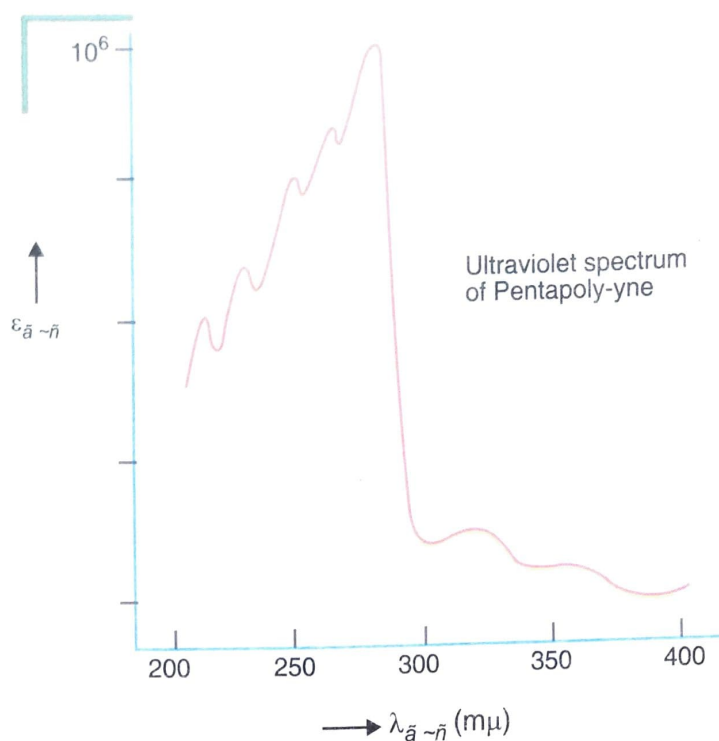
Fig. 2.21. UV Spectrum of pentapoly-yne.

Note. If a conjugated polyene contains more than four double bonds, then Fieser-Kuhn rules are used. According to this approach, both λ_{max} and ε_{max} are related to the number of conjugated double bonds as well as other structural units by the following equations.

$$\lambda_{max} = 114 \times 5\,M + n\,(48.0 - 1.7n) - 16.5\,R_{endo} - 10\,R_{exo}$$

$$\varepsilon_{max} = (1.74 \times 10^{4})n$$

where

n = no. of conjugated double bonds.

M = no. of alkyl or alkyl like substituents on the conjugated system.

R_{endo} = no. of rings with endocyclic double bonds in the conjugated system.

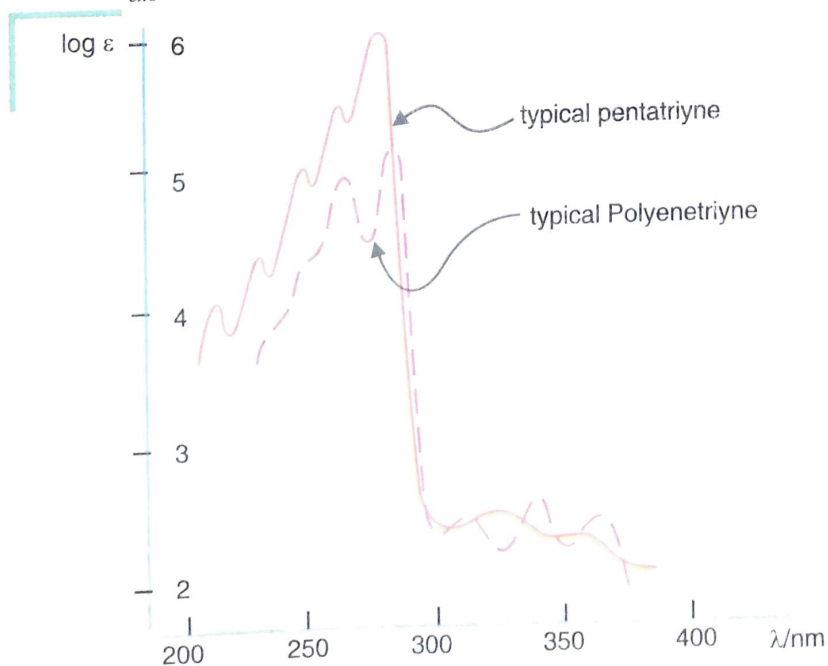R_{exo} = no. of rings with exocyclic double bonds.

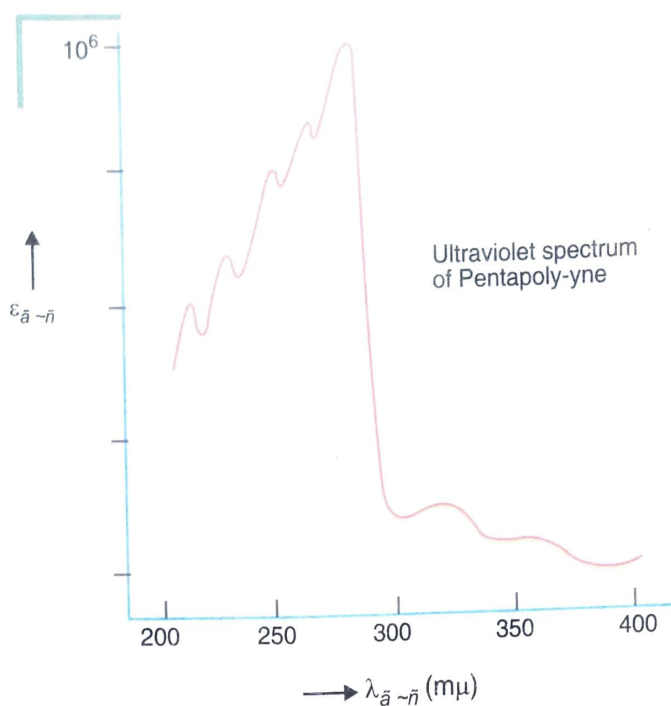Fig. 2.22. Electronic absorption spectra typical of Poly-yne and Polyeneyne Chromophores.

Fig. 2.21. UV Spectrum of pentapoly-yne.

Note. If a conjugated polyene contains more than four double bonds, then Fieser-Kuhn rules are used. According to this approach, both λ_{max} and ε_{max} are related to the number of conjugated double bonds as well as other structural units by the following equations.

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M = no. of alkyl or alkyl like substituents on the conjugated system.

R_{endo} = no. of rings with endocyclic double bonds in the conjugated system.

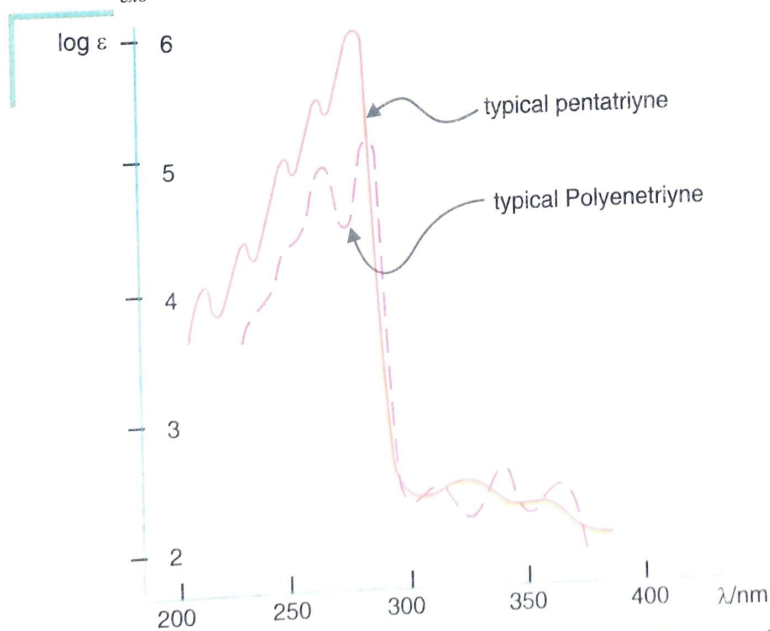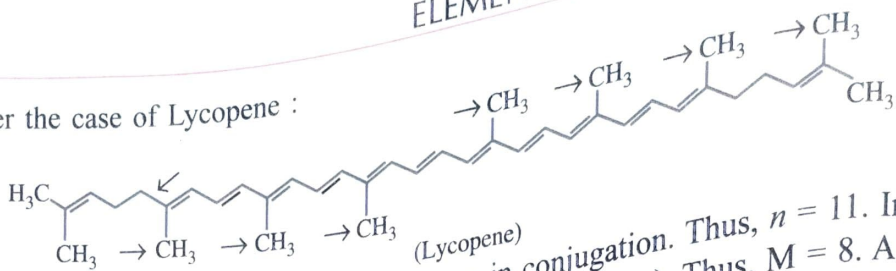R_{exo} = no. of rings with exocyclic double bonds.

Fig. 2.22. Electronic absorption spectra typical of Poly-yne and Polyeneyne Chromophores.

Consider the case of Lycopene :

(Lycopene)

In this compound, only eleven double bonds are in conjugation. Thus, $n = 11$. In addition, this, there are eight substituents (methyl groups and chain residues). Thus, $M = 8$. As there is a ring system, there are neither exo nor endocyclic double bonds in this conjugated system. λ_{max} can be calculated as under :

$$\lambda_{max} = 114 + 5(8) + 11\,[48.0 - 1.7(11)] - 0 - 0 = 476 \text{ nm}$$

The observed value of λ_{max} is found to be 476 nm (hexane)

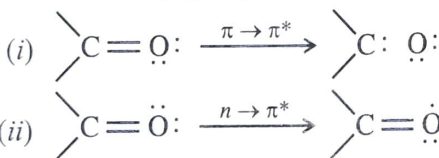$$\varepsilon_{max} \text{ (calculated)} = 19.1 \times 10^4.$$

Similarly, λ_{max} can be calculated for β-carotene.
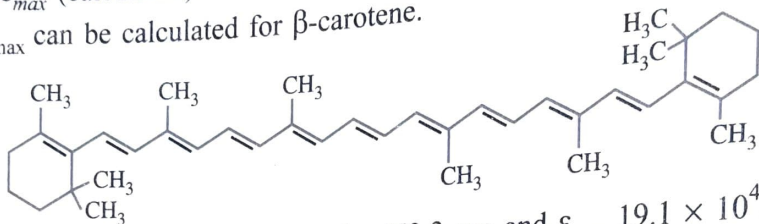
The calculated value of λ_{max} is found to be 453.3 nm and ε_{max} 19.1×10^4.

2.19 Ultra-violet Absorption in α, β-unsaturated Carbonyl Compounds

For a carbonyl group, two types of transitions occur.

(i) $\ce{C=O} \xrightarrow{\pi \to \pi^*} \ce{C : O}$

(ii) $\ce{C=O} \xrightarrow{n \to \pi^*} \ce{C=O}$

The first transition involves the promotion of one of the π electrons to an antibonding π* orbital ($\pi \to \pi^*$). It is very intense and corresponds to shorter wavelength. The second transition
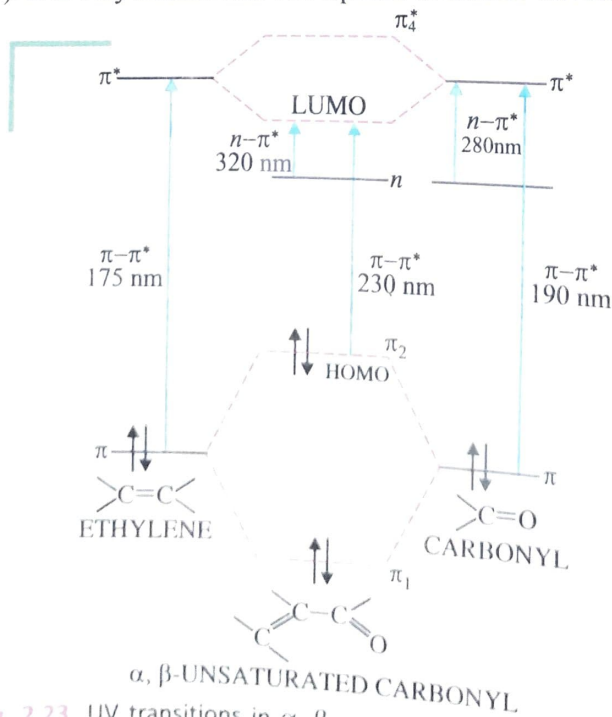

Fig. 2.23. UV transitions in α, β-unsaturated carbonyl compounds.

$(n \rightarrow \pi^*)$ involves the promotion of one of the non-bonding paired electron to π_3^* orbital. It is less intense and corresponds to longer wave-length. It is called R-band. (See Fig. 2.23).

In α, β-unsaturated carbonyl compounds, the double bond and the carbonyl group are in conjugation. The spectra for such compounds are simple summation of ethylene and carbonyl chromophores. A bathochromic shift is observed if two chromophoric groups are conjugated as π electron cloud is spread over at least four carbon atoms. There is a $\pi \rightarrow \pi^*$ transition due to ethylene unit which is in conjugation with carbonyl group.

In α, β-unsaturated carbonyl compounds where ethylene and carbonyl groups are conjugated, both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions show bathochromic shifts. The various transitions involved are shown above in Fig. 2.23. From the energy level diagram, it is clear that π_2 (HOMO) energy level is higher than either of the π levels of C=C and C=O. The π_3^* (LUMO) energy level is lower than that of π^* level of C = C and C = O chromophores. Since the energy difference between (HOMO) and (LUMO) is less, the $\pi \rightarrow \pi_3^*$ transition shows bathochromic effect. Similarly, $n \rightarrow \pi^*$ transition (R-band) also shows bathochromic shift.

$n \rightarrow \pi^*$ **transition in aldehydes and ketones.** Aldehydes and ketones show a weak forbidden band in the range 275 to 300 mμ due to the excitation of an oxygen lone electron to π^* orbital. Aldehydes and highly substituted ketones absorb at upper end of the range. Polar substituents on α-carbon atom in axial or equitorial position raise or lower the extremes of this range respectively. When the carbonyl group is substituted by an auxochrome as in an ester, amide etc. the π^* orbital is raised while n level of lone pair is hardly altered. Due to this, the $n \rightarrow \pi^*$ transition in these compounds is shifted to lower wave-length range (200—215 mμ). Clearly, a weak band at 275 to 300 mμ [ε_{max} 10–100] is a positive identification of aldehydic or ketonic carbonyl group.

α, β--unsaturated carbonyl compounds show slightly stronger $n \rightarrow \pi^*$ band or series of bands in the 300–350 mμ range. The positions as well as the intensity of $n \rightarrow \pi^*$ bands are influenced by the transannular* interactions and also by the solvent.
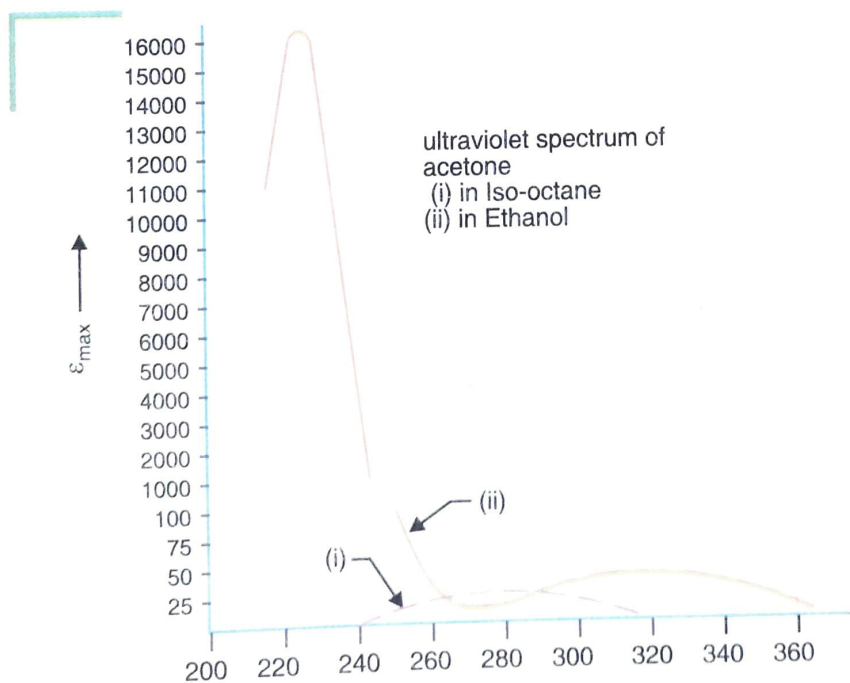

Fig. 2.24. UV spectrum of acetone in (i) Iso-octane (ii) Ethanol.

Axially substituted isomers absorb at longer wavelength than equitorially substituted isomers.
α, β-unsaturated acids, esters show bathochromic shift but absorb at comparatively shorter

---

* Trans-annular interaction arises due to the presence of apparently non-conjugated C=O and C=C groups in a compound.

wavelengths. α, β-unsaturated amides have been shown to absorb at lower values than corresponding acids. The absorption occurs usually in the inaccessible region. It is important note that the positions of $\pi \to \pi^*$ and $n \to \pi^*$ transition in carbonyl compounds vary with nature of the solvent used. (See Fig. 2.24).

By increasing the polarity of the solvent, $\pi \to \pi^*$ transition experiences a red shift w $n \to \pi^*$ transition undergoes a blue shift. The changing polarity of the solvent brings abo change in the energy difference between the levels involved in the transitions. The shift is du the change in the stability of the ground or the excited electronic states. The absorption du $n \to \pi^*$ transition experiences a blue shift as the degree of hydrogen bonding between the carbo group and the solvent increases by increasing the polarity of the solvent. In other words, the ene of n electrons is strongly lowered by hydrogen bonding and thus, greater energy is required promoting n electrons of π^* level.

A comparison in the ultra-violet spectra of un-conjugated carbonyl compounds (see Fig. 2. reveals that the value of absorption maximum for carbonyl group experiences a bathochromic well as hyperchromic effects in conjugated carbonyl compound as compared to an un-conjugat carbonyl compound.
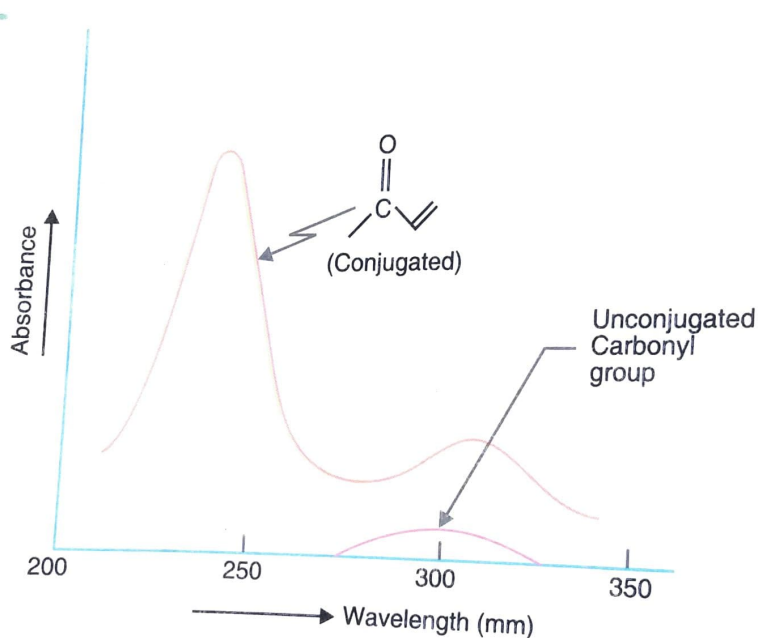

Fig. 2.25. UV Absorption spectra for conjugated and unconjugated carbonyl compounds.

2.20 Woodward-fieser Rules for Calculating Absorption Maximum in α, β-unsaturated Carbonyl Compounds

Woodward and Fieser framed certain empirical rules for estimating the absorption maximum for α, β-unsaturated carbonyl compounds. The rules were later modified by Scott and are as follows :

(a) The basic value of α, β-unsaturated ketone is taken as 215 mμ. The α, β-unsaturated ketone may be acyclic or six membered.

For a compound, = CH—COX, basic value is 215 mμ, if X is an alkyl group. If X=H, basic value becomes 207 mμ. The basic value is 193 mμ if X is OH or OR.

(b) If the double bond and the carbonyl group are contained in a five membered ring (cyclopentenone), then for such an α, β-unsaturated ketone, the basic value becomes 202 mμ. The ε_{max} for such compounds are generally above 10,000.

The structural increments for estimating λ_{max} for a given α, β-unsaturated Carbon compound are as follows :

(i) For each exocyclic double bond   + 5 mµ

(ii) For each double bond endocyclic in
    five or seven membered ring except
    cyclo-pent-2 enone   + 5 mµ

(iii) For each alkyl substituent or ring residue at the
                        α-position   + 10 mµ
                        β-position   + 12 mµ
                        γ- or δ- or higher position   + 18 mµ

(iv) For each double bond extending conjugation   + 30 mµ

(v) For a homoannular conjugated diene.   + 39 mµ

(vi) Increments for various auxochromes in the various α-, β-, γ- etc. positions are given the following Table T_2-9.

Table T_2-9 Chromophore increments in Carbonyl Compounds

| Chromophore | Increment in nm (or mµ) for position w.r.t. the carbonyl group | | | |
	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	—	—
—NR$_2$	—	+ 95	—	—

Making use of the above rules, the absorption maximum for the various α, β-unsaturate compounds can be estimated.

EXAMPLE 1. *Calculate λ_{max} (Ethanol) for the given structure :*

$$CH_3 \diagdown C = CH - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$
$$CH_3 \diagup$$
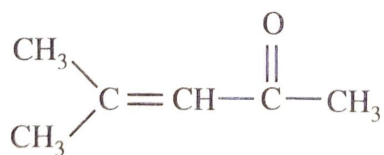
SOUTION. The basic value for acyclic α, β-unsaturated ketone is 215 mµ. In this structure we see two β-alkyl substituents. The value of absorption maximum is thus calculated as :

Basic value   = 215 mµ

2β–alkyl substituents (2 × 12)   = 24 mµ

Calculated value   = **239 mµ**

The observed value is found to be 237mµ ε_{max} 12,500.

EXAMPLE 2. *Calculate λ_{max} for the given structure.*

Basic value

2β-ring residues (2 × 12)

1 exocyclic double bond

Calculated value

The observed value is found to be 241 mµ.

$$= 215 \text{ m}\mu$$
$$= 24 \text{ m}\mu$$
$$= \underline{5 \text{ m}\mu}$$
$$= 244 \text{ m}\mu$$

EXAMPLE 3. *Calculate* λ_{max} *for the given structure.*

SOLUTION.   Basic value = 215 mµ

OH substitution at

α- position = 35 mµ

2β-substituents (one alkyl

and one ring residue) = 24 mµ

Calculated value = **274 mµ**

Observed value = 275 mµ

EXAMPLE 4. *Calculate* λ_{max} *for the following structure.*

SOLUTION. It is an α, β-unsaturated cyclopentenone system.

Basic value =	202 mµ
1 β-alkyl substitution =	12 mµ
1 exocyclic double bond =	5 mµ
1 double bond extending conjugation =	30 mµ
1 γ-ring residue =	18 mµ
1 δ-ring residue =	18 mµ
Calculated value =	**285 mµ**
Observed value =	287 mµ

EXAMPLE 5. *Calculate* λ_{max} *for the given structure*

SOLUTION. Basic value = 215 mµ

α-ring residue = 10 mµ

δ-ring residue = 18 mµ

1 exocyclic double bond = 5 mµ

Homoannular conjugated diene = 39 mµ

1 double bond extending conjugation = 30 mµ

Calculated value = **317 mµ**

Observed value = 319 mµ

EXAMPLE 6. *Calculate* λ_{max} *for the given structure*

SOLUTION. Basic value = 215 mµ

1 β-ring residue = 12 mµ

1 (δ + 1) ring residue = 18 mµ

2 (δ + 2) ring residues

(2 × 18) = 36 mµ

2 double bonds extending conjugation (2 × 30) = 60 mµ

2 exocyclic double bonds (2 × 5) = 10 mµ

Calculated value = **351 mµ**
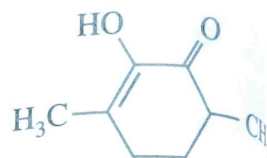
Observed value = 354 mµ
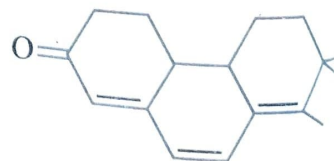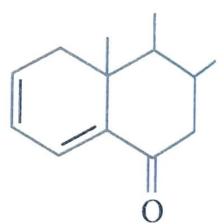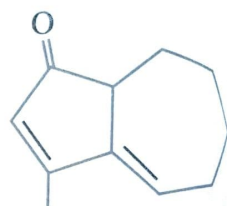
It may be noted that the value of absorption maximum is shifted due to the change in the polarity of the solvent, *i.e.*, absorption maximum is solvent dependent. More polar solvents will experience hydrogen bonding with the carbonyl group and $n \rightarrow \pi^*$ transition will experience blue shift. Sovent corrections may be noted as follows :

$$
\begin{aligned}
\text{Hexane} &= \quad + 11 \text{ m}\mu \\
\text{Dioxane} &= \quad + 7 \text{ m}\mu \\
\text{Methanol} &= \quad 0 \text{ m}\mu \\
\text{Water} &= \quad - 8 \text{ m}\mu \\
\text{Chloroform} &= \quad - 1 \text{ m}\mu
\end{aligned}
$$

After making the necessary solvent corrections, the value of absorption maximum is obtained in ethanol.

In case there is a cross conjugation in a compound, *i.e.*, the carbonyl group has α, β-unsaturation on either side; then the value of absorption maximum is estimated by considering the most highly substituted conjugated system. Consider the following example.

In ring B, the carbonyl group is conjugated on either side but conjugated system is highly substituted towards ring C. Thus, the value of absorption maximum is calculated as follows :

|		
Basic value	=	215 mμ
1 α-ring residue	=	10 mμ
1 β-ring residue	=	12 mμ
1 δ-ring residue	=	18 mμ
1 double bond extending conjugation	=	30 mμ
Homoannular conjugation diene	=	39 mμ
Calculated value	=	**324 mμ**
Observed value	=	327 mμ
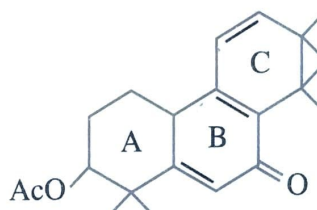
For such compounds, the value of the extinction coefficient is usually high.

Quinones. In quinones, weak $n \rightarrow \pi^*$ transitions are responsible for imparting colour to some simple quinones. The absorption values in π-quinone are :

(*i*) 242 mμ	ε_{max}	24,000
(*ii*) 281 mμ	ε_{max}	400
(*iii*) 434 mμ	ε_{max}	20

α-Diketones and α-keto Aldehydes. Acyclic α-diketones such as biacetyl, exist in the S-trans conformation (with a dihedral angle, 180°). The spectrum of biacetyl shows the normal weak R-band at 275 nm and weak band near 450 nm. The second band (at 450 nm) is formed as a result of interaction between the carbonyl groups.
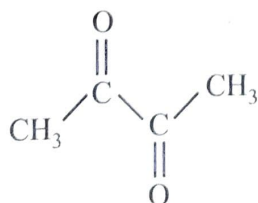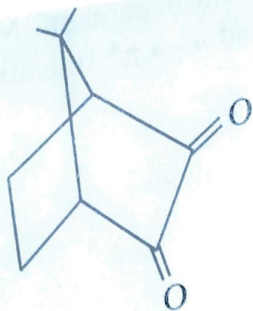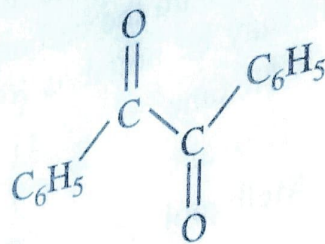

$$\lambda_{max} = 450 \text{ nm}$$
$$\varepsilon_{max} = 10$$

The position of the long wave length band of α-diketones incapable of enolisation reflects the effect of coplanarity upon resonance and thus depends upon the dihedral angle between the carbonyl groups.
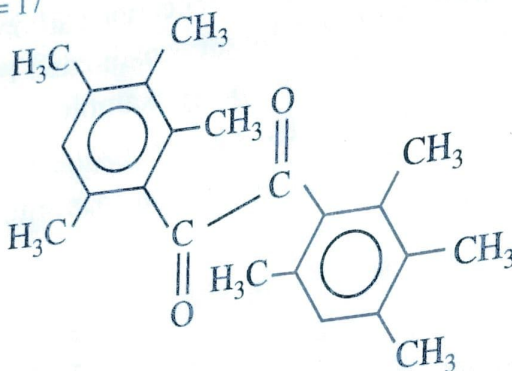
ELEMEN

Consider the following:

Camphoquinone
(I)
Dihedral angle 0-10°
$\lambda_{max} = 488$ nm
$\varepsilon_{max} = 17$

Benzil
(II)
Dihedral angle = 90°
$\lambda_{max} = 370$ nm
$\varepsilon_{max} = 40$

Isoduril
(III)
Dihedral angle = 180°

β-Diketones. The ultraviolet spectra of β-diketones depend on the degree of enolisation. T possibility of intra-molecular hydrogen bonding stabilises the enolic form in acetylacetone. T enolic species exists to the extent of 15% in aqueous solution. In the vapour phase or in soluti in non-polar solvents it exists to the extent of 91-92%. The absorption depends directly on t concentration of the enol tautomer.
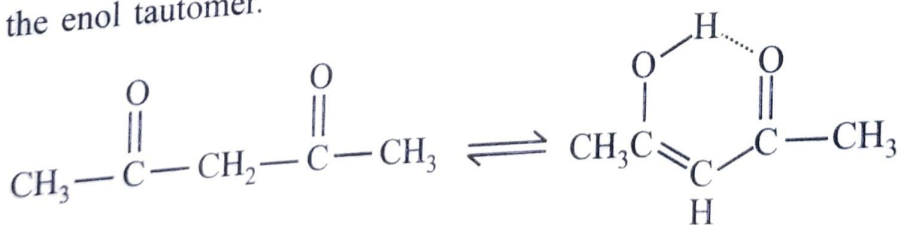
λ_{max} (in H_2O) = 274 nm, ε_{max} = 2050
λ_{max} (in Iso-octane) = 272 nm, ε_{max} = 12000

Cyclic β-diketones such as cyclohexane dione exists almost exclusively in the enolic for even in polar solvents. The enolic structures show strong absorption in the 230-260 nm region d to $\pi - \pi^*$ transition in the S-trans enone system.

(enone)
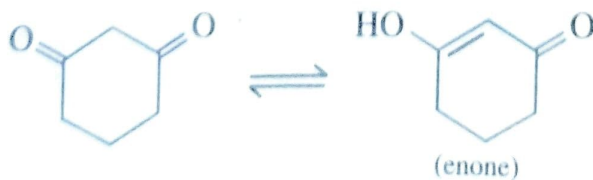
2.21 Compounds With *N* To *O* Bonds

Four groups, *viz.*, nitro, nitroso, nitrates and nitrites contain multiple nitrogen to oxygen linkages. These structures show weak absorption in the near ultraviolet region resulting from $n \rightarrow \pi^*$ transition. The sulphur atom in sulphones has no lone pair electrons and the lone pairs of electrons associated with the oxygen atom appear to be tightly bound. Saturated sulphoxides absorb near 220 nm with intensities of the order of 1500.

Table T$_2$-10 Absorption of compounds containing Nitrogen-Oxygen linkages.

Compound	$n \rightarrow \pi^*$ transition (R-band)		Solvent
	λ_{max}	ε_{max}	
Nitromethane	275 nm	15	Heptane
2-Methyl-2 nitropropane	280.5	23	Heptane
Nitrosobutane	300	100	Ether
	665	20	
Octyl nitrate	270	15	Pentane
n-Butyl nitrite	218	1050	Ethanol

2.22 Benzene and Its Derivatives

The B-band at 254 mµ in ultraviolet spectrum of benzene shows a great deal of fine structure in the vapour phase. The fineness of the structure diminishes if we scan it in hexane solution and is almost completely destroyed in ethanol solution (See Fig. 2.26). In hexane solution, benzene shows absorptions at 184 mµ. ε_{max} 60,000; 204 mµ ε_{max} 7400 and 254 mµ ε_{max} 204. The band at 254 mµ is the result of forbidden transitions in highly symmetrical benzene molecule. Benzene shows a series of low intensity bands between 230 and 270 mµ.
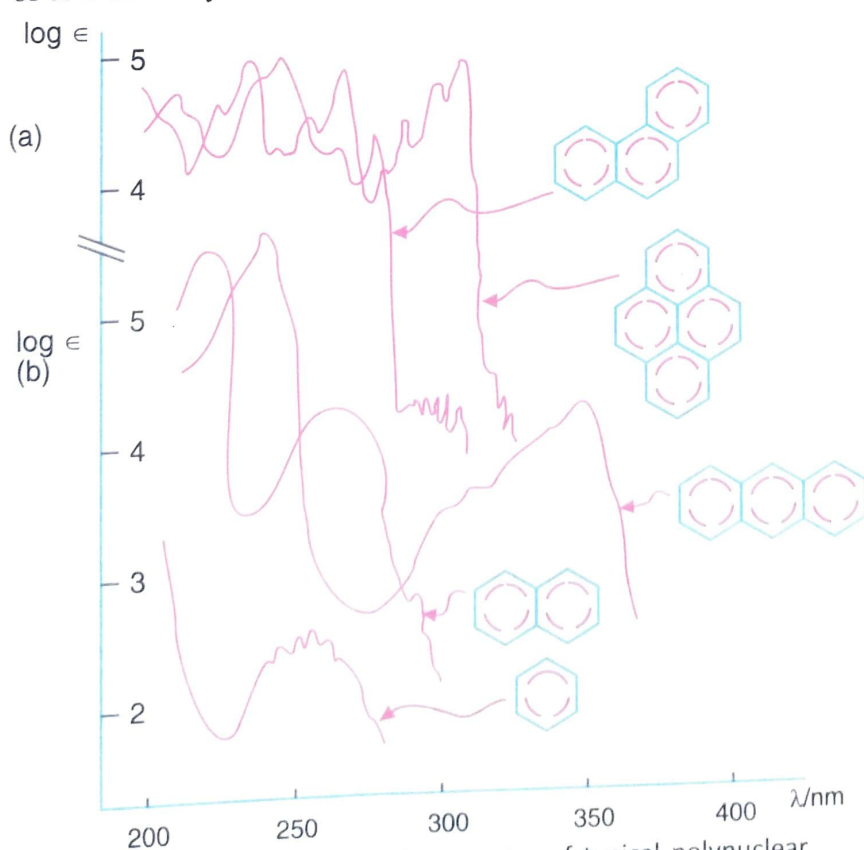

Fig.2.26. Electronic absorption spectra of typical polynuclear aromatic hydrocarbons (in hexane).

It has been noted that absorption maximum for poly-nuclear aromatic hydrocarbons mo longer wavelength. Comparing the ultra-violet spectrum of benzene with naphthalene, we see the value of absorption maximum as well as extinction coefficient are more for naphthale compared to those of benzene. Naphthalene absorbs at 480 mμ ε_{max} 11000 while anthra absorbs at still higher value. Pentacene absorbs at 580 mμ ε_{max} 12600 and appears blue.

2.23 Rules for Calculating Absorption Maximum for Derivatives of Acyl Benzenes

Like Woodward Fieser rules, Scott devised a set of rules for calculating the absorption maxim for the derivatives of acyl benzenes. These rules help in estimating the position of absorp maximum in ethanol in a number of monosubstituted aromatic ketones, aldehydes, acids and est

For a compound of the type
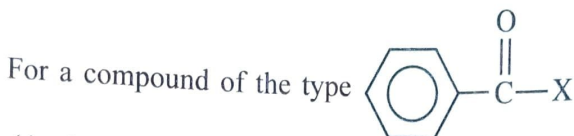
(i) the basic value is 246 mμ if X is an alkyl group or alicyclic residue.
(ii) If X is hydrogen atom, the basic value becomes 250 mμ and
(iii) the basic value is 230 mμ if X is OH or OR. The structural increments in mμ for furt p- substitution on the aromatic ring in the ortho, meta and para positions are given in th Table T_2 –11.

Table T_2–11 Auxochrome acting as a Substituent

Auxochrome	Increment in mμ Position of the Substituent		
	Ortho	Meta	Para
Alkyl	+ 3	+ 3	+ 10
OH, OR	+ 7	+ 7	+ 25
Cl	0	0	+ 10
Br	+ 2	+ 2	+ 15
NH₂	+ 13	+ 13	+ 58
NHAc	+ 20	+ 20	+ 45
NR₂	+ 20	+ 20	+ 85
O⁻	+ 11	+ 20	+ 75

Note. It is important to note that the effect of the para substituent is more pronounced for th bathochromic shift.

EXAMPLE 1. *Calculate the absorption maximum in ethanol for p-chloroacetophenone.*

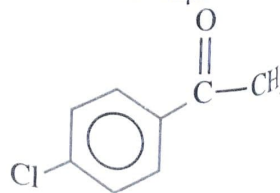**SOLUTION.** In this case, X is an alkyl group and thus the basic value is 246 mμ.

Basic value	=	246 mμ
Cl-substitution at para position	=	10 mμ
Calculated value	=	256 mμ

The observed value is found to be 254 mm.

EXAMPLE 2. *Calculate the absorption maximum for the following compound.*

SOLUTION. Basic value	=	246 mμ
OH substitution at meta	=	7 mμ
OH substitution at para	=	25 mμ
Calculated value	=	**278 mμ**
Observed value	=	281 mμ
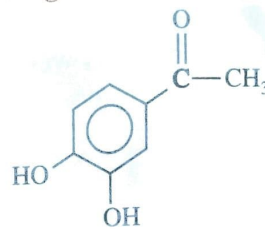
EXAMPLE 3. *Calculate the absorption maximum for the following compound.*

SOLUTION. Basic value	=	230 mμ
Br substitution at para	=	15 mμ
Calculated value	=	**245 mμ**
Observed value	=	245 mμ

In disubstituted benzenes,

(*a*) When electronically complementary groups such as —NH_2 and —NO_2 are substituted para to each other, there is a pronounced bathochromic shift in the main absorption band compared to the effect of either substituent considered separately. For example, *p*-nitroaniline absorbs at 375 mμ ε_{max} 16000. It is due to the extension of the chromophore from the electron donating group to the electron withdrawing group through the benzene ring.

(*b*) When the two groups in the para positions are not complimentary or are ortho or meta to each other, then the absorption spectrum is close to that of the separate non-interacting chromophores. For example, *m*-dinitrobenzene absorbs at 200 mμ ε_{max} 13000.

2.24 Absorption Spectra of Condensed Ring Systems

The range of absorption maximum for polycyclic hydrocarbons is very great and spectra are usually complicated (See Fig. 2.26, page 47). Such spectra are useful as finger prints. Moreover, the relatively non-polar substituents have a very small effect on the shape and position of the absorption peak of parent hydrocarbon. Identification of polycyclic hydrocarbon is usually done by comparison.

The condensed systems are classified into

(*a*) **Cata-condensed system.** In cata-condensed system, no carbon atom belongs to more than two rings. Benzene, naphthalene etc. are the examples.

(*i*) *Linear cata-condensed compounds.* These are Naphthalene, Anthracene etc.

(*ii*) *Bent cata-condensed compounds.* These include phenanthrene type molecules.

The spectra of cata-condensed hydrocarbons resemble benzene. Bathochromic shift is observed with the increase in the number of rings in the structure. For example, benzene absorbs at 254 mμ ε_{max} 204. Naphthalene absorbs at 312 mμ ε_{max} 289, while pentacene absorbs in the visible region.

(*b*) **Peri-condensed system.** In peri-condensed systems, a carbon atom belongs to more than two rings. An example is **coronene.**

Peri-condensed rings show absorptions at longer wave-lengths as compared to cata-condensed structures.

Coronene shows absorptions at 305 mμ, 342 mμ and 428 mμ.
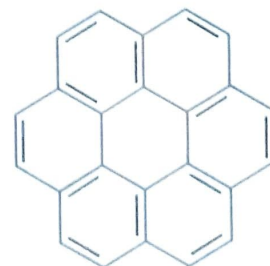
Coronene

2.25 Heterocyclic Compounds

The ultra-violet spectrum of five-membered heterocyclic aromatic compounds can be compared with cyclopentadiene. It has been observed that in these compounds, a forbidden band (R-band)

due to $n \rightarrow \pi^*$ transition is also observed with very low value of ε_{max}. For example, in furan U observe a band at 252 mμ ε_{max} 10,000. The chromophoric or auxochromic substitution b about bathochromic as well as hyperchromic shift.

Table T$_2$ –12 Heterocyclic compounds.

Compound	λ_{max} (mμ)	Intensity ε_{max}
Furan	200	10,000
	252	1
2-Nitro furan	225	3,400
	315	8,100
Pyrrole	183	–
	211	15,000
Pyrrole 2-aldehyde	252	5,000
	290	16,500
Thiophene	231	7,100
2-Bromothiophene	236	9,100

In six-membered heterocyclic compounds, the ultra-violet spectrum of pyridine can distinguished from that of benzene as its B-band is more intense than that of benzene. Moreov B-band in pyridine shows a marked increase in intensity* with the increase in polarity of t solvent (UV spectrum of pyridine is shown in Fig. 2.27). On the other hand, this band for benze is little effected in position as well as intensity. The presence of substitution in pyridine usual brings hyperchromic effect. For example, the B-band for pyridine at 275 mμ ε_{max} 2750 is shift to 262 mμ ε_{max} 3560 for 2 methyl pyridine and to 263 mμ ε_{max} 3650 for 2-chloro-pyridine.
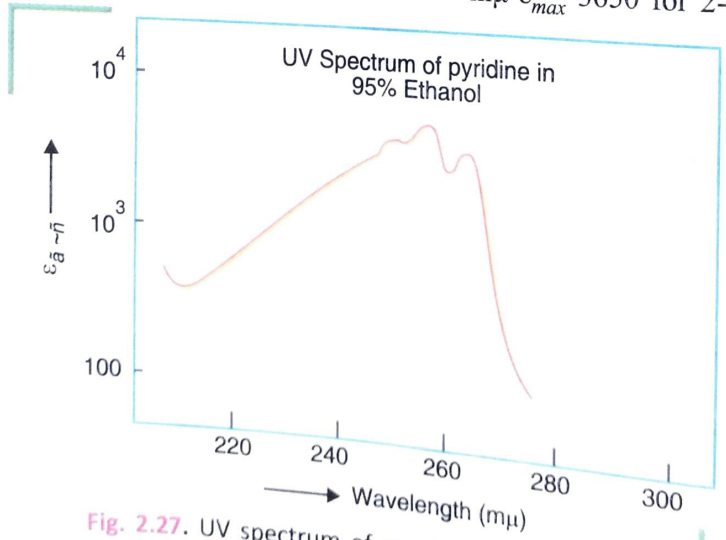

Fig. 2.27. UV spectrum of pyridine in 95% ethanol.

In some cases, like hydroxy pyridines, hypochromic shifts are also observed. Sometimes, change in pH brings about a marked change in the absorption maximum of the substance which is clearly due to the change in the chromophore. The change in chromophore is explained as th shifting of equilibrium to one of the tautomeric forms with the change in pH. Thus, a substance existing in tautomeric forms can be carefully diagnosed for the preference of one form over th

* It is due to hydrogen bonding through the lone pair of electrons on nitrogen in pyridine with solven molecules.

other by this technique. For example, 2-hydroxy pyridine and Pyridone-2 exist in tautomeric equilibrium.

2 Hydroxy Pyridine	Pyridone-2
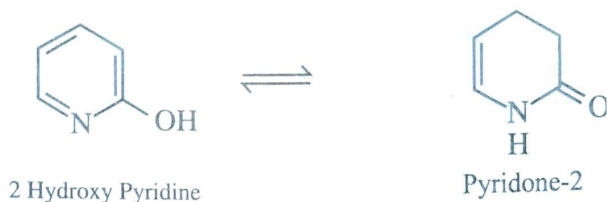
The spectra of these compounds were shown to favour pyridone-2 which is an α, β-unsaturated ketone. Clearly, the equilibrium is shifted towards right.

2.26 Steric Hindrance and Coplanarity

Woodward rules give reliable results only for those compounds in which there is no strain around the chromophore. We know that in the case of extended conjugation, the position of absorption depends upon the length of the conjugated system. Longer the conjugated system, higher will be the absorption maximum and larger will be the value of the extinction coefficient. If, in a structure, the π electron system is prevented from achieving coplanarity, there is a marked shift in the absorption maximum and extinction coefficient. The departure in the value of absorption maximum calculated from the empirical rules is due to steric crowding which distorts the geometry of the chromophore. Thus, the conjugation is reduced by reduction in the π orbital overlap. Consider the cases of biphenyl and substituted biphenyl. The π → π* transition for diphenyl which readily achieves coplanarity absorbs at 250 mµ ε_{max} 19,000 but in 2-methyl diphenyl, π → π* transition undergoes blue shift and diminished intensity as the two rings remain no longer coplanar. The absorption maximum for 2-methyl diphenyl is 237 mµ ε_{max} 10250. Also nitro benzene absorbs at 252 mµ ε_{max} 8620 while orthonitro-toluene absorbs at 250 mµ ε_{max} 5950 due to reduction in coplanarity.

If the compound containing alkene chromophore is capable of existing as geometrical isomers, the trans-isomer is found to absorb at longer wave-length with higher value of extinction coefficient as compared to cis-isomer. It is due to more effective π orbital overlap possible in the trans-isomer which, thus, achieves coplanarity of π electron system more readily. Consider the case of cinnamic acid. It exists in two isomers :

|	
(Cis)	(Trans)
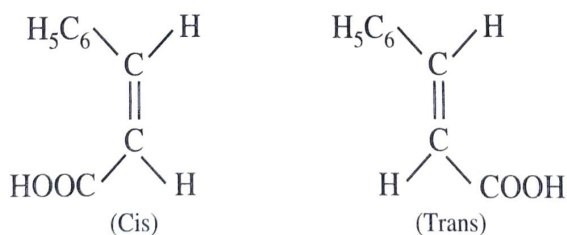
Due to greater crowding in cis-form (both bulky groups are on the same side), the geometry of the alkene chromophore is distorted and departure from coplanarity results. Thus, π → π* transition in cis-cinnamic acid takes place at lower wave-length with lower extinction coefficient.

(i) Trans-cinnamic acid absorbs at 272 mµ ε_{max} 15900.

(ii) Cis-cinnamic acid absorbs at 268 mµ ε_{max} 10700.

Slight steric hindrance to coplanarity about a single bond has a very little effect on the position and intensity of the absorption maximum. If the steric hindrance to coplanarity about a single bond is more, then, there is a marked decrease in intensity and may accompany a red or blue shift. The absorption maximum of 2, 5 dimethyl-p-nitro aniline occurs at 385 mµ ε_{max} 4840 showing a red shift and marked decrease in intensity as compared to p-nitroaniline which absorbs at 375 mµ ε_{max} 16000. A blue shift is observed in case of 2, 4, 6 trimethyl acetophenone which absorbs at 242 mµ ε_{max} 3200 as compared to p-methyl acetophenone at 252 mµ ε_{max} 15000. Out of cis-and

trans-*stilbenes*, a distortion in coplanarity in cis-stilbene is due to steric hindrance. This results in lowering the value of absorption maximum at lower extinction coefficient. Thus, a band which appears at 295 mμ ε_{max} 25000 in trans-stilbene has a value 283 mμ ε_{max} 12300 in cis-stilbene.

H₅C₆ / C = C / H ... H₃C₆ C H
(Cis-stilbene)

In some cases, steric hindrance to coplanarity about the double bond raises the ground state energy level but leaves the excited state rela... unchanged. This results in a bathochromic shift from the expected value.
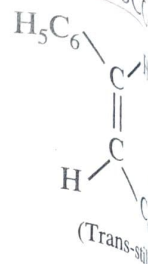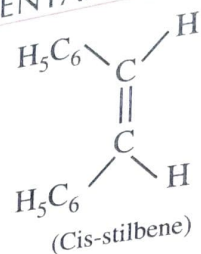
2.27 Fluorescence and Phosphorescence

Fluorescence is the light of comparatively longer wavelength emitted from a molecule and op... it has absorbed light of different and short wavelength.

Anthracene is a colourless substance and its electronic absorption spectrum lies in the u... violet region. But it is found that pure samples of anthracene when viewed in the ultra-violet l... give off a blue-visible light. This light is called **fluorescence.** The emission of light or fluoresce... stops atonce when the irradiating light is removed. On the other hand, the phenomeno... phosphorescence is said to occur when the substance continues to emit the radiation of lon... wavelength even when the irradiating light is removed. To study the phenomenon of fluoresce... and phosphorescence, let us study the one electron excitation process (see Fig. 2.28).
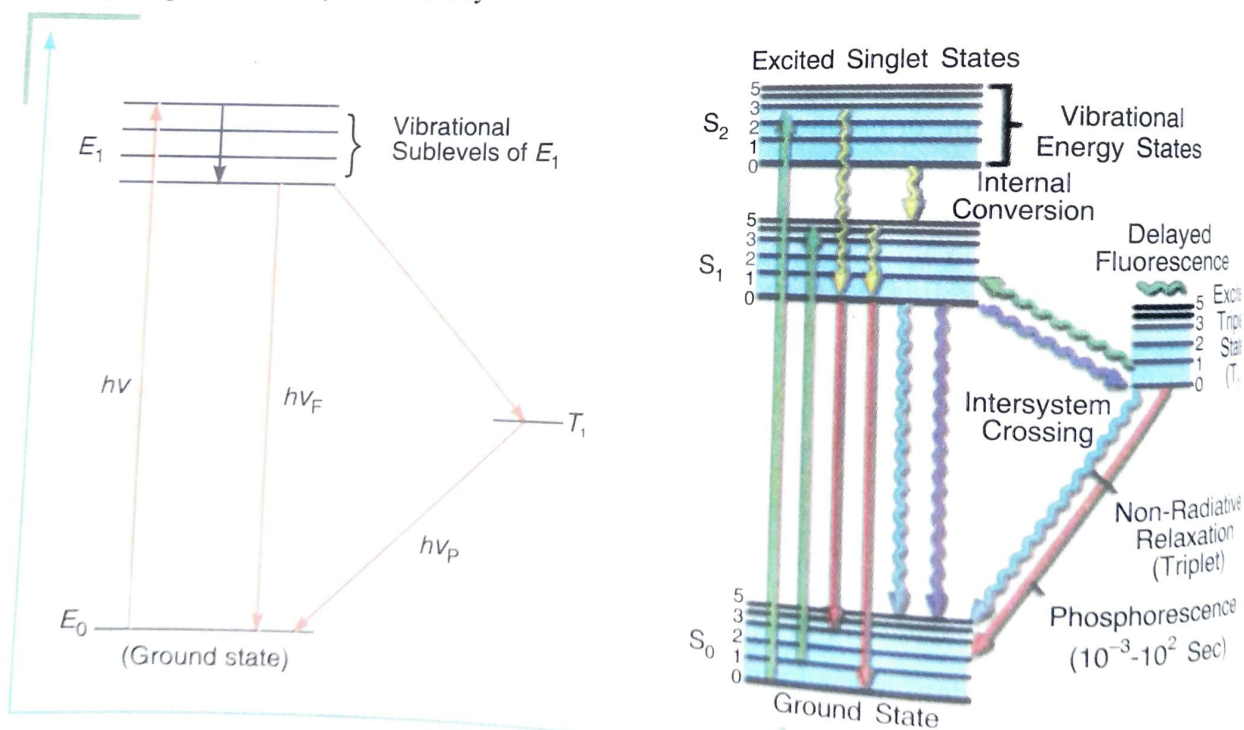

Fig. 2.28. Mechanism of Fluorescence and Phosphorescence.

When the molecule in the ground state absorbs light ($h\nu$), its one electron gets promoted fr... the ground state molecular orbital to one of the vibrational sub-levels of the first excited st... molecular orbital (E_1) or to the higher excited states E_2, E_3 etc. When the electron returns fr... E_1 to E_0, it emits radiation which is of longer wavelength or lower energy than $h\nu$. It is called h... called **fluorescent radiation**.

In another mode, the energy may be lost from E_1 to T_1 and then from T_1 to the ground sta... E_0. The main difference between E_1 and T_1 is the electron spin orientation. The spins of the tw... electrons must be anti-parallel which originally occupy the ground state molecular orbital. Th...