2

Ultraviolet (UV) and Visible Spectroscopy

2.1 Introduction

Ultraviolet and visible spectroscopy deals with the recording of the absorption of radiations in the ultraviolet and visible regions of the electromagnetic spectrum. The ultaviolet region extends from 10 to 400 nm. It is subdivided into the near ultraviolet (quartz) region (200–400 nm) and the far or vacuum ultraviolet region (10–200 nm). The visible region extends from 400 to 800 nm.

The absorption of electromagnetic radiations in the UV and visible regions induces the excitation of an electron from a lower to higher molecular orbital (electronic energy level). Since UV and visible spectroscopy involves electronic transitions, it is often called *electronic spectroscopy*. Organic chemists use ultraviolet and visible spectroscopy mainly for detecting the presence and elucidating the nature of the conjugated multiple bonds or aromatic rings.

2.2 Absorption Laws and Molar Absorptivity

A UV-visible spectrophotometer records a UV or visible spectrum (Fig. 2.1) as a plot of wavelengths of absorbed radiations versus the intensity of absorption in terms of absorbance (optical density) A or molar absorptivity (molar extinction coefficient) ε as defined by the Lambert-Beer law. According to Lambert's law, the fraction of incident monochromatic radiation absorbed by a homogeneous medium is independent of the intensity of the incident radiation while Beer's law states that the absorption of a monochromatic radiation by a homogeneous medium is proportional to the number of absorbing molecules. From these laws, the remaining variables give the following equation which expresses the Lambert-Beer law

$$\log_{10} \frac{I_0}{I} = A = \varepsilon c l \tag{2.1}$$

where I_0 is the intensity of incident radiation, I the intensity of radiation transmitted through the sample solution, A the absorbance or optical density, ε the molar absorptivity or molar extinction coefficient, c the concentration of solute (mole/litre) and l the path length of the sample (cm).

The molar absorptivity of an organic compound is constant at a given wavelength. The intensity of an absorption band in the UV or visible spectrum is usually expressed as the molar absorptivity at maximum absorption, ε_{max} or $\log_{10} \varepsilon_{max}$. The wavelength of the maximum absorption is denoted by λ_{max}.

When the molecular weight of a sample is unknown, or when a mixture is being examined, the intensity of absorption is expressed as $E^{1\%}_{1\,cm}$ (or $A^{1\%}_{1\,cm}$) value, i.e. the absorbance of a 1% solution of the sample in a 1 cm cell

$$E^{1\%}_{1\,cm} = \frac{A}{cl}$$

where c is the concentration in g/100 ml and l the path length of the sample in cm.

This value is easily related to ε by the expression

$$10\varepsilon = E^{1\%}_{1\,cm} \times \text{Molecular weight}$$

2.3 Instrumentation

The desired parameter in spectroscopy is absorbance, but it cannot be directly measured. Thus, a UV-visible spectrophotometer compares the intensity of the transmitted radiation with that of the incident UV-visible radiation. Most UV-visible spectrophotometers are double-beam instruments and consist of a radiation source, monochromator, detectors, amplifier and recording system as shown in Fig. 2.1.

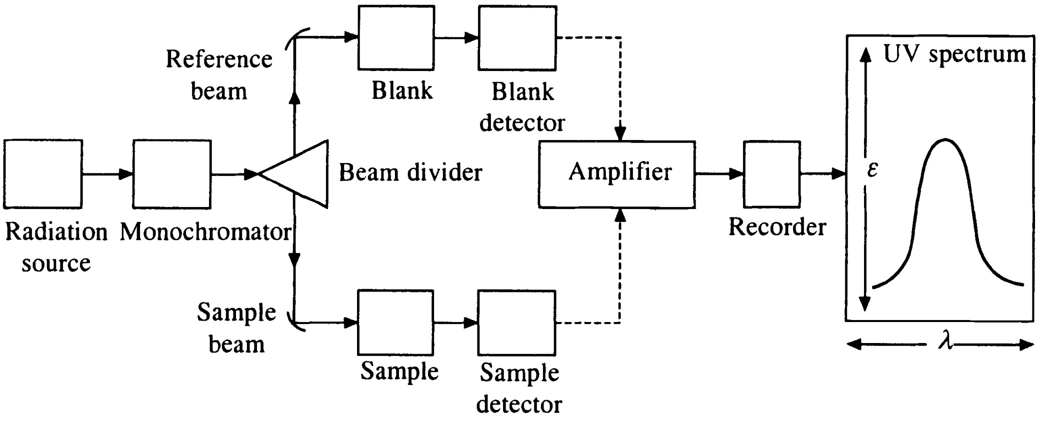


Fig. 2.1 Schematic diagram of a double-beam UV-visible spectrophotometer

(i) Radiation Source

The hydrogen-discharge lamp is the most commonly used source of radiation in the UV region (180-400 nm). A deuterium-discharge lamp is used in its place when more (3-5 times) intensity is desired. A tungsten-filament lamp is used when absorption in the visible region (400–800 nm) is to be determined.

(ii) Monochromator

It disperses the radiations obtained from the source into their separate wavelengths. The most widely used dispersing element is a prism or grating made up of quartz because quartz is transparent throughout the UV range. Glass strongly absorbs ultraviolet radiation, hence it cannot be used in this region. Glass can be satisfactorily used in the visible region. The dispersed radiation is divided by the beam divider into two parallel beams of equal intensity; one of which passes through a transparent cell containing the sample solution and the other through an identical cell containing the solvent. The former is called *sample beam* and the latter *reference beam.*

(iii) Detectors

These have photocells or photomultiplier tubes which generate voltage proportional to the radiation energy that strikes them.

(iv) Amplifier

The spectrophotometer has balancing electronic amplifier which subtracts the absorption of the solvent from that of the solution electronically.

(v) Recorder

It automatically records the spectrum as a plot of wavelengths of absorbed radiations against absorbance A or molar absorptivity ε.

2.4 Sample Handling

UV-visible spectra are usually recorded either in very dilute solutions or in the vapour phase. Quartz cells of 1 cm square are commonly used for recording the spectra. The sample is dissolved in some suitable solvent which does not itself absorb radiation in the region under investigation. Commonly used solvents are cyclohexane, 1,4-dioxane, water, and 95% ethanol. The chosen solvent should be inert to the sample. Generally, 1 mg of the compound with a molecular weight of 100–200 is dissolved in a suitable solvent and made up to, e.g. 100 ml and only a portion of this is used for recording the spectrum.

2.5 Theory (Origin) of UV-Visible Spectroscopy

UV-visible absorption spectra originate from electronic transitions within a molecule. These transitions involving promotion of valence electrons from the ground state to the higher-energy state (excited state) are called *electronic excitations* and are caused by the absorption of radiation energy in the UV-visible regions of the electromagnetic spectrum. Since various energy levels of molecules are quantized, a particular electronic excitation occurs only by the absorption of specific wavelength of radiation corresponding to the required quantum of energy.

2.6 Electronic Transitions

According to molecular orbital theory, the excitation of a molecule by the absorption of radiation in the UV-visible regions involves promotion of its electrons from a bonding, or non-bonding (n) orbital to an antibonding orbital. There are σ and π bonding orbitals associated with σ^* and π^* antibonding orbitals, respectively. Non-bonding (n or p) orbitals are not associated with antibonding orbitals because non-bonding or lone pair of electrons present in them do not form bonds. Following electronic transitions are involved in the UV-visible region (Fig. 2.2):

(i) $\sigma \rightarrow \sigma^*$ (iii) $n \rightarrow \sigma^*$ (iii) $\pi \rightarrow \pi^*$ (iv) $n \rightarrow \pi^*$

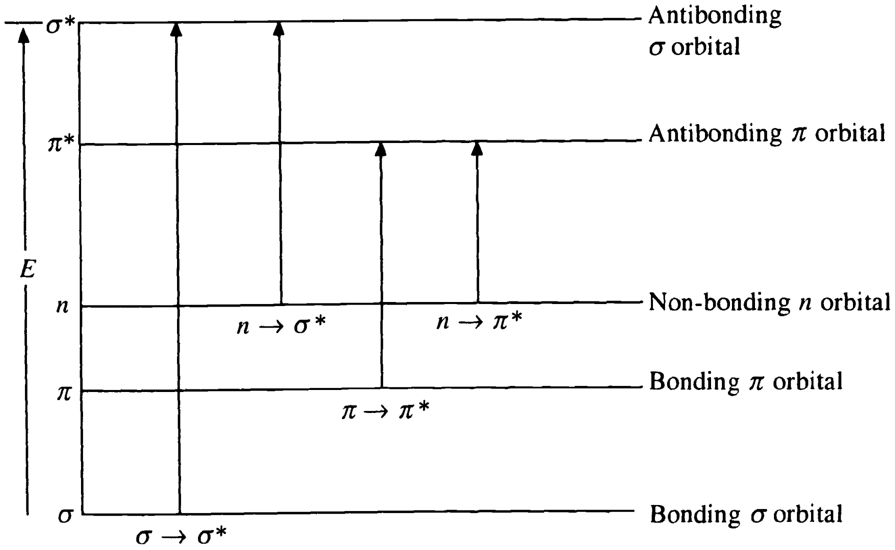


Fig. 2.2 Relative energies of electronic transitions

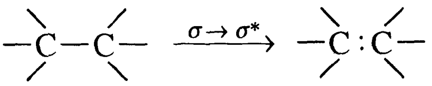
The usual order of energy required for various electronic transitions is

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

Now we will discuss the electronic transitions involved in UV-visible spectroscopy.

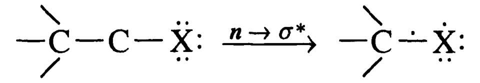
(i) $\sigma \rightarrow \sigma^*$ Transition

The transition or promotion of an electron from a bonding sigma orbital to the associated antibonding sigma orbital is $\sigma \rightarrow \sigma^*$ transition. It is a high energy process because σ bonds are generally very strong. Thus, these transitions do not occur in normal UV-visible regions (200-800 nm). For example, in alkanes only $\sigma \rightarrow \sigma^*$ transition is available and they absorb high energy UV radiation around 150 nm; ethane shows λ_{max} 135 nm. The region below 200 nm is called *vacuum UV region*, since oxygen present in air absorbs strongly at ~200 nm and below. Similarly, nitrogen absorbs at ~150 nm and below. Thus, an evacuated spectrophotometer is used for studying such high energy transitions (below 200 nm). However, this region is less informative



(ii) $n \rightarrow \sigma^*$ Transition

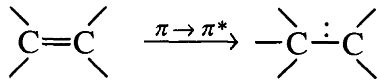
The transition or promotion of an electron from a non-bonding orbital to an antibonding sigma orbital is designated as $n \rightarrow \sigma^*$ transition. Compounds containing non-bonding electrons on a heteroatom are capable of showing absorption due to $n \rightarrow \sigma^*$ transitions. These transitions require lower energy than $\sigma \rightarrow \sigma^*$ transitions. Some organic compounds undergoing $n \rightarrow \pi^*$ transitions are halides, alcohols, ethers, aldehydes, ketones etc. For example, methyl chloride shows λ_{max} 173 nm, methyl iodide λ_{max} 258 nm, methyl alcohol λ_{max} 183 nm and water λ_{max} 167 nm



In alkyl halides, the energy required for $n \rightarrow \sigma^*$ transition increases as the electronegativity of the halogen atom increases. This is due to comparatively difficult excitation of non-bonding (n or p) electrons on increase in the electronegativity. The difficult excitation means less probability of transition. The molar extinction coefficient ε increases as the probability of the transition increases. Thus, methyl iodide shows λ_{max} 258 nm, ε_{max} 378 and methyl chloride λ_{max} 173 nm, ε_{max} ~100. Since iodine is less electronegative than chlorine, $n \rightarrow \sigma^*$ transition is more probable at low energy process in methyl iodide than in methyl chloride. Similarly, amines show both higher λ_{max} and ε_{max} than alcohols owing to lesser electronegativity of nitrogen than oxygen, e.g. trimethylamine λ_{max} 227 nm, ε_{max} 900 and methyl alcohol λ_{max} 183 nm, ε_{max} 150. Protonated trimethylamine does not show absorption due to $n \rightarrow \sigma^*$ transition, because it has no non-bonded electrons.

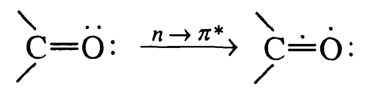
(iii) $\pi \rightarrow \pi^*$ Transition

The transition or promotion of an electron from a π bonding orbital to a π antibonding orbital is designated $\pi \rightarrow \pi^*$ transition. These type of transitions occur in compounds containing one or more covalently unsaturated groups like C═C, C═O, NO_2 etc. $\pi \rightarrow \pi^*$ transitions require lower energy than $n \rightarrow \sigma^*$ transitions. In unconjugated alkenes, this transition occurs in the range 170–190 nm; ethylene shows λ_{max} 171 nm. Similarly, unconjugated carbonyl compounds show $\pi \rightarrow \pi^*$ transition in the range 180–190 nm; acetone shows λ_{max} 188 nm.



(iv) $n \rightarrow \pi^*$ Transition

The transition or promotion of an electron from a non-bonding orbital to a π antibonding orbital is designated $n \rightarrow \pi^*$ transition. This transition requires lowest energy.



Saturated aldehydes and ketones show both types of transitions, i.e. low energy $n \rightarrow \pi^*$ and high energy $\pi \rightarrow \pi^*$ occurring in the regions 270–300 nm and 180–190 nm, respectively; acetone shows $n \rightarrow \pi^*$ at λ_{max} 279 nm. The band due to $\pi \rightarrow \pi^*$ transition is more intense, i.e. it has high value of ε than the less intense bands due to $n \rightarrow \pi^*$ transition. In addition, carbonyl compounds also exhibit high energy $n \rightarrow \sigma^*$ transition around 160 nm; acetone shows λ_{max} 166 nm.

Because of different structural environments, identical functional groups in different compounds do not necessarily absorb at exactly the same wavelength.

2.7 Formation of Absorption Bands

Since the energy required for each electronic transition is quantized, the UV-visible spectrum is expected to exhibit a single, discrete line corresponding to each electronic transition. In practice, broad absorption bands are usually observed. In a molecule, each electronic energy level (either in ground state or in excited state) is accompanied by a large number of vibrational (v_0, v_1, v_2 etc.) and rotational (r_0, r_1, r_2 etc.) energy levels which are also quantized (Fig. 2.3). In complex molecules having many atoms, there are still a large number of closer vibrational energy levels.

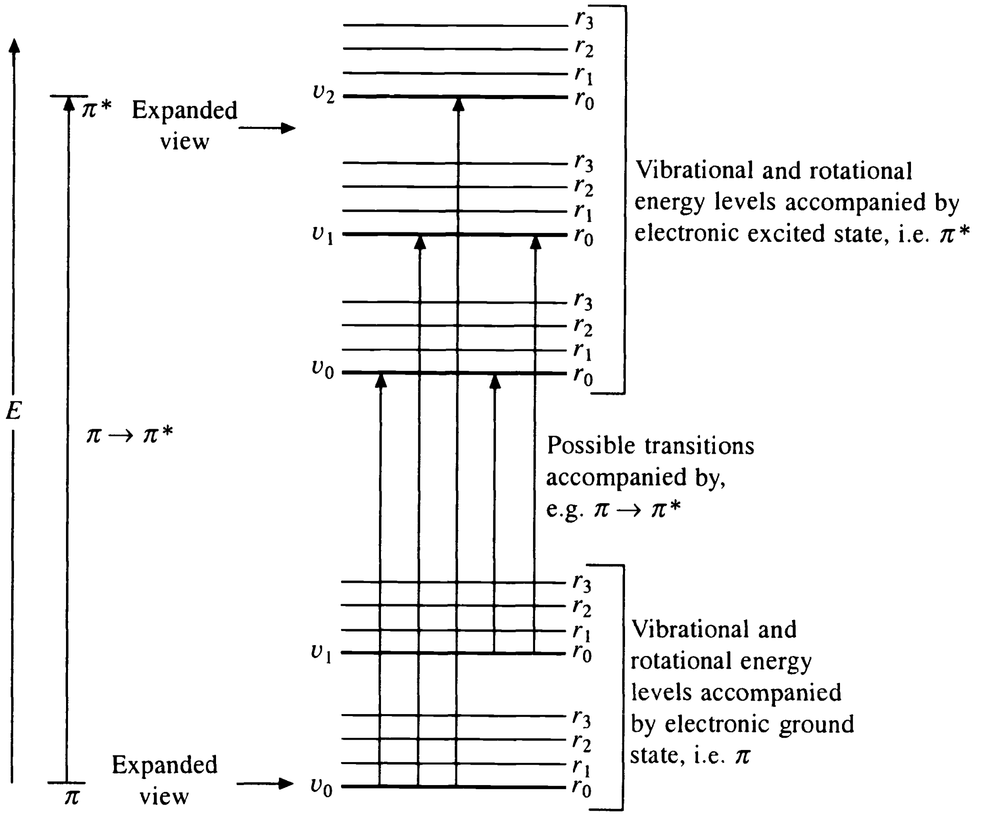


Fig. 2.3 Schematic energy level diagram of a diatomic molecule

The radiation energy passed through a sample is sufficient to induce various electronic transitions as well as transitions in accompanying vibrational and rotational energy levels. However, these transitions have very small energy differences, but the energy required to induce an electronic transition is larger than that required to cause transitions in the accompanying vibrational and rotational energy levels. Thus, the electronic absorption is superimposed upon the accompanying vibrational and rotational absorptions resulting in the formation of broad bands. More clearly, not only a single but a large number of very close wavelengths are absorbed and the closeness of the resulting discrete spectral lines causes them to coalesce to give broad absorption bands in case of complex molecules.

2.8 Designation of Absorption Bands

UV-visible absorption bands may be designated by the type of electronic transition from which they originate, e.g. $\sigma \rightarrow \sigma^*$ band, $\pi \rightarrow \pi^*$ band etc., or by the letter designation. The following letter designation was proposed because more than one band may arise due to the same type of electronic transition.

K-Bands (Conjugated; German: *Konjugierte*). These bands originate from $\pi \rightarrow \pi^*$ transitions in compounds having a π — π conjugated system (a system having at least two multiple bonds separated by only one single bond), e.g. 1,3-butadiene shows *K*-band at λ_{max} 217 nm, ε_{max} 21,000 and acrolein at λ_{max} 210 nm, ε_{max} 11,500. Aromatic compounds having a chromophoric substituent also exhibit *K*-bands in their UV spectra, e.g. acetophenone shows *K*-band at λ_{max} 240 nm, ε_{max} 13,000 and styrene at λ_{max} 244 nm, ε_{max} 12,000. Usually, *K*-band have high molar absorptivity, $\varepsilon_{max} > 10^4$.

R-Bands (Radical-like; German: *Radikalartig*). These bands originate from $n \rightarrow \pi^*$ transitions of a single chromophoric group, e.g. carbonyl or nitro group. *R*-bands have low molar absorptivity, $\varepsilon_{max} < 100$, and are also called forbidden bands. For example, acetone shows an *R*-band at λ_{max} 279 nm, ε_{max} 15; acrolein at λ_{max} 315 nm, ε_{max} 14 and acetophenone at λ_{max} 319 nm, ε_{max} 50.

B-Bands (Benzenoid bands). These bands originate from $\pi \rightarrow \pi^*$ transitions in aromatic or heteroaromatic compounds. For example, benzene shows a *B*-band at λ_{max} 256, ε_{max} 200 and acetophenone at λ_{max} 278 nm, ε_{max} 1100.

E-Bands (Ethylenic bands). Similar to *B*-bands, these are characteristic of aromatic and heteroaromatic compounds and originate from $\pi \rightarrow \pi^*$ transitions of the ethylenic bonds present in the aromatic ring. *E*-band which appears at a shorter wavelength and is usually more intense is called E_1-band. The low intensity band of the same compound appearing at a longer wavelength is called E_2-band[†]. For example, benzene exhibits E_1- and E_2-bands near λ_{max} 180 nm, ε_{max} 60,000 and λ_{max} 200 nm, ε_{max} 7900, respectively.

For more examples of *K*-, *R*-, *B*- and *E*-bands, see Tables 2.2, 2.6 and 2.7. A compound may exhibit more than one band in its UV spectrum, either due to the presence of more than one chromophore or due to more than one transition of a single chromophore. A typical UV spectrum is given in Fig. 2.4.

A band may be submerged under some more intense band. Thus, in certain

---

[†] In another notation it is designated *K*-band but we shall use the designation E_2-band for this.

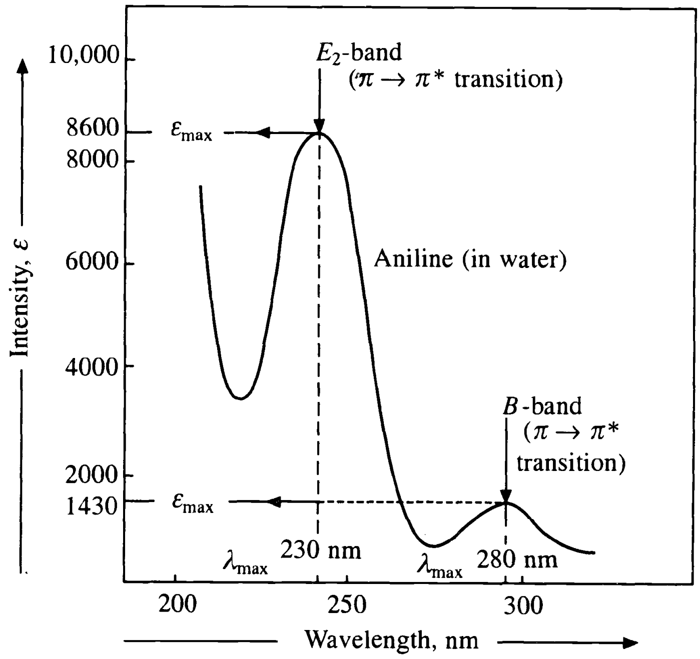


Fig. 2.4 UV spectrum of aniline showing E_2- and B-bands

cases, all the expected bands may not be observed. For example, B-bands are sometimes buried under K-bands (see Tables 2.6 and 2.7).

2.9 Transition Probability: Allowed and Forbidden Transitions

On exposure to UV or visible radiation, a molecule may or may not absorb the radiation, i.e. it may or may not undergo electronic excitation. The molar absorptivity at maximum absorption

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

where P is the transition probability with values from 0 to 1 and a the target area of the absorbing system, i.e. a chromophore.

A chromophore with a length of the order of 10 Å or 10^{-7} cm and with unit probability will have ε_{max} value of ~10^5. Thus, there is a direct relationship between the area of a chromophore and its absorption intensity (ε_{max}). Transitions with ε_{max} values > 10^4 are called *allowed transitions* and are generally caused by π → π* transitions, e.g. in 1,3-butadiene, the absorption at 217 nm, ε_{max} 21,000 results from the allowed transition. Transitions with ε_{max} values < 10^4 are called *forbidden transitions*. These are generally caused by n → π* transitions, e.g. in carbonyl compounds, the absorption near 300 nm with ε_{max} values 10–100 results from the forbidden transition.

In addition to the area of a chromophore, there are also some other factors which govern the transition probability. However, the prediction of their effects on the transition probability is complicated because they involve geometries of the lower and higher energy molecular orbitals as well as the symmetry of the molecule as a whole. Symmetrical molecules have more restrictions on their transitions than comparatively less symmetrical molecules. Consequently, symmetrical molecules like benzene have simple electronic absorption spectra as compared to less symmetrical molecules. There are very less symmetry restrictions for a highly unsymmetrical molecule, thus it will exhibit a complex electronic absorption spectrum.

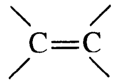
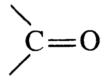
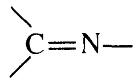
2.10 Certain Terms Used in Electronic Spectroscopy: Definitions

Chromophore

A covalently unsaturated group responsible for absorption in the UV or visible region is known as a *chromophore*. For example, C$=$C, C$\equiv$C, C$=$O, C$\equiv$N, N$=$N, NO_2 etc. If a compound absorbs light in the visible region (400–800 nm), only then it appears coloured. Thus, a chromophore may or may not impart colour to a compound depending on whether the chromophore absorbs radiation in the visible or UV region.

Chromophores like C$=$C or C$\equiv$C having π electrons undergo $\pi \rightarrow \pi^*$ transitions and those having both π and non-bonding electrons, e.g. C$=$O, C$\equiv$N or N$=$N, undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. Since the wavelength and intensity of absorption depend on a number of factors, there are no set rules for the identification of a chromophore. Characteristics of some common unconjugated chromophores are given in Table 2.1.

Table 2.1 Characteristics of some common unconjugated chromophores

Chromophore	Example	λ_{max} (nm)	ε_{max}	Transition	Solvent
 $>C=C<$	Ethylene	171	15,530	$\pi \rightarrow \pi^*$	Vapor
—C$\equiv$C—	Acetylene	150	~10,000	$\pi \rightarrow \pi^*$	Hexane
		173	6000	$\pi \rightarrow \pi^*$	Vapor
 $>C=O$	Acetaldehyde	160	20,000	$n \rightarrow \sigma^*$	Vapor
		180	10,000	$\pi \rightarrow \pi^*$	Vapor
		290	17	$n \rightarrow \pi^*$	Hexane
	Acetone	166	16,000	$n \rightarrow \sigma^*$	Vapor
		188	900	$\pi \rightarrow \pi^*$	Hexane
		279	15	$n \rightarrow \pi^*$	Hexane
—COOH	Acetic acid	204	60	$n \rightarrow \pi^*$	Water
—$CONH_2$	Acetamide	178	9500	$\pi \rightarrow \pi^*$	Hexane
		220	63	$n \rightarrow \pi^*$	Water
—COOR	Ethyl acetate	211	57	$n \rightarrow \pi^*$	Ethanol
—NO_2	Nitromethane	201	5000	$\pi \rightarrow \pi^*$	Methanol
		274	17	$n \rightarrow \pi^*$	Methanol
 $>C=N-$	Acetoxime	190	5000	$n \rightarrow \pi^*$	Water
—C$\equiv$N	Acetonitrile	167	Weak	$\pi \rightarrow \pi^*$	Vapor
—N$=$N—	Azomethane	338	4	$n \rightarrow \pi^*$	Ethanol

Auxochrome

A covalently saturated group which, when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as *auxochrome*, e.g. NH_2, OH, SH, halogens etc. Auxochromes generally increase the value of λ_{max} as well as ε_{max} by extending the conjugation through resonance. These are also called *colour enhancing groups.* An auxochrome itself does not show absorption above 200 nm. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different values of λ_{max} and ε_{max}. For example, benzene shows λ_{max} 256 nm, ε_{max} 200, whereas aniline shows λ_{max} 280 nm, ε_{max} 1430 (both increased). Hence, NH_2 group is an auxochrome which extends the conjugation involving the lone pair of electrons on the nitrogen atom resulting in the increased values of λ_{max} and ε_{max}.

Absorption and Intensity Shifts

Bathochromic Shift or Effect. The shift of an absorption maximum to a longer wavelength (Fig. 2.5) due to the presence of an auxochrome, or solvent effect is called a *bathochromic shift* or *red shift.* For example, benzene shows λ_{max} 256 nm and aniline shows λ_{max} 280 nm. Thus, there is a bathochromic shift of 24 nm in the λ_{max} of benzene due to the presence of the auxochrome NH_2. Similarly, a bathochromic shift of $n \rightarrow \pi^*$ band is observed in carbonyl compounds on decreasing solvent polarity, e.g. λ_{max} of acetone is at 264.5 nm in water as compared to 279 nm in hexane.

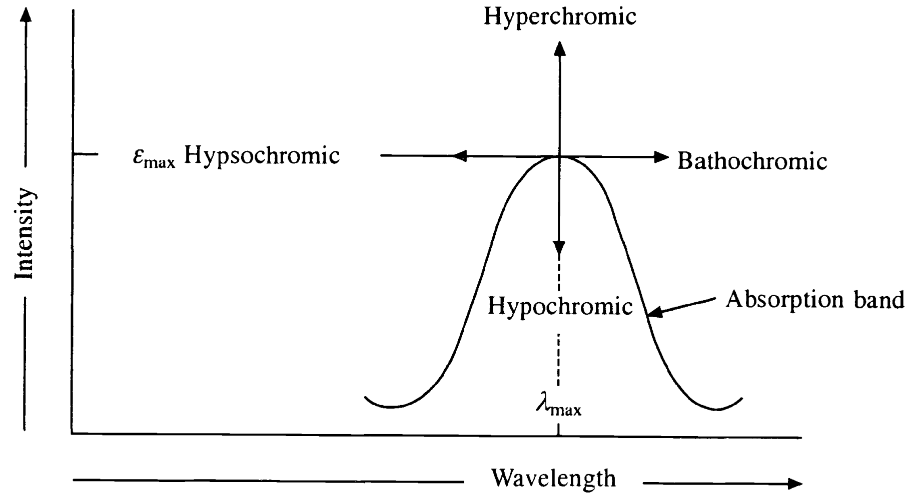


Fig. 2.5 Shifts in absorption position and intensity

Hypsochromic Shift or Effect. The shift of an absorption maximum to a shorter wavelength is called *hypsochromic* or *blue shift* (Fig. 2.5). This is caused by the removal of conjugation or change in the solvent polarity. For example, aniline shows λ_{max} 280 nm, whereas anilinium ion (acidic solution of aniline) shows λ_{max} 254 nm. This hypsochromic shift is due to the removal of $n \rightarrow \pi$ conjugation[†] of the lone pair of electrons of the nitrogen atom of aniline with the π-bonded

---

[†] A system in which an atom having non-bonding electrons is separated from a multiple bond by only one single bond is called *n-p* conjugated system.

system of the benzene ring on protonation because the protonated aniline (anilinium ion) has no lone pair of electrons for conjugation. Similarly, there is a hypsochromic shift of 10–20 nm in the λ_{max} of $\pi \rightarrow \pi^*$ bands of carbonyl compounds on going from ethanol as solvent to hexane, i.e. on decreasing solvent polarity.

Hyperchromic Effect. An effect which leads to an increase in absorption intensity ε_{max} is called *hyperchromic effect* (Fig. 2.5). The introduction of an auxochrome usually causes hyperchromic shift. For example, benzene shows *B*-band at 256 nm, ε_{max} 200, whereas aniline shows *B*-band at 280 nm, ε_{max} 1430. The increase of 1230 in the value ε_{max} of aniline compared to that of benzene is due to the hyperchromic effect of the auxochrome NH_2.

Hypochromic Effect. An effect which leads to a decrease in absorption intensity ε_{max} is called *hypochromic effect* (Fig. 2.5). This is caused by the introduction of a group which distorts the chromophore. For example, biphenyl shows λ_{max} 252 nm, ε_{max} 19,000, whereas 2,2′-dimethylbiphenyl shows λ_{max} 270 nm, ε_{max} 800. The decrease of 18,200 in the value of ε_{max} of 2,2′-dimethylbiphenyl is due to the hypochromic effect of the methyl groups which distort the chromophore by forcing the rings out of coplanarity resulting in the loss of conjugation.

2.11 Conjugated Systems and Transition Energies

When two or more chromophoric groups are conjugated, the absorption maximum is shifted to a longer wavelength (lower energy) and usually to a greater intensity compared to the simple unconjugated chromophore, e.g. ethylene shows λ_{max} 171 nm, ε_{max} 15,530 and 1,3-butadiene λ_{max} 217 nm, ε_{max} 21,000. In conjugated dienes, the π molecular orbitals of the separate alkene groups combine to give two new bonding molecular orbitals designated π_1 and π_2, and two anti-bonding molecular orbitals designated π_3^* and π_4^*. Fig. 2.6 shows the $\pi_2 \rightarrow \pi_3^*$ transition, i.e. the promotion of an electron from a highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of a conjugated diene, is of very low energy, 1,3-butadiene shows λ_{max} 217 nm

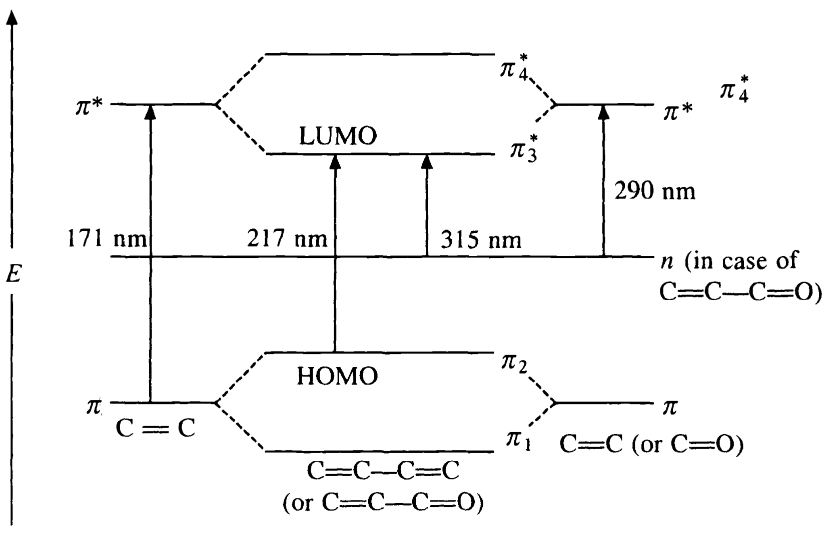


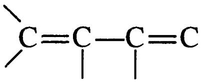
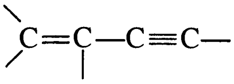
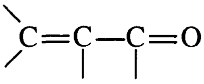
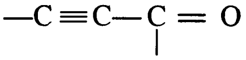
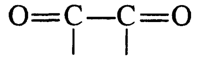
Fig. 2.6 Relative energies of electronic transitions in conjugated systems

which is lower than the $\pi \rightarrow \pi^*$ transition of an unconjugated alkene, ethylene shows λ_{max} 171 nm.

Similarly, in case of other conjugated chromophores, the energy difference between HOMO and LUMO is lowered resulting in the bathochromic shift. Thus, α,β-unsaturated carbonyl compounds show both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions at longer wavelengths (e.g. acrolein, λ_{max} 210 and 315 nm) compared to unconjugated carbonyl compounds (acetaldehyde, λ_{max} 180 and 290 nm) (Fig. 2.6).

We know that as the energy of electronic transitions decreases, usually their probability increases and so ε_{max} also increases. Since conjugation lowers the energy required for electronic transitions, it increases the value of λ_{max} and usually that of ε_{max} also. Thus, ethylene shows λ_{max} 171 nm, ε_{max} 15,530 and 1,3-butadiene λ_{max} 217 nm, ε_{max} 21,000. For more examples of various conjugated chromophores, see Tables 2.2, 2.6 and 2.7.

Table 2.2 Characteristics of some simple conjugated chromophores

Chromophore	Example	λ_{max} (nm)	ε_{max}	Transition	Solvent	Band
	1,3-Butadiene	217	21,000	$\pi \rightarrow \pi^*$	Hexane	*K*
	1,3,5-Hexatriene	258	35,000	$\pi \rightarrow \pi^*$	Hexane	*K*
	Vinyl acetylene	219	7600	$\pi \rightarrow \pi^*$	Hexane	*K*
		228	7800	$\pi \rightarrow \pi^*$	Hexane	*K*
	Acrolein	210	11,500	$\pi \rightarrow \pi^*$	Ethanol	*K*
		315	14	$n \rightarrow \pi^*$	Ethanol	*R*
	Crotonaldehyde	218	18,000	$\pi \rightarrow \pi^*$	Ethanol	*K*
		320	30	$n \rightarrow \pi^*$	Ethanol	*R*
	3-Pentene-2-one	224	9750	$\pi \rightarrow \pi^*$	Ethanol	*K*
		314	38	$n \rightarrow \pi^*$	Ethanol	*R*
 $-C\equiv C-C=O$	1-Hexyn-3-one	214	4500	$\pi \rightarrow \pi^*$	Ethanol	*K*
		308	20	$n \rightarrow \pi^*$	Ethanol	*R*
 $O=C-C=O$	Glyoxal	195	35	$\pi \rightarrow \pi^*$	Hexane	*K*
		280	3	$n \rightarrow \pi^*$	Hexane	*R*
HOOC—COOH	Oxalic acid	~185	4000	$\pi \rightarrow \pi^*$	Water	*K*
		250	63	$n \rightarrow \pi^*$	Water	*R*

Note: In general, the longer the conjugated system, the higher are the values of λ_{max} and ε_{max}.

Thus, a compound with sufficient conjugation absorbs in the visible region (400–800 nm) and becomes coloured. For example β-carotene, an orange pigment present in carrots, has eleven carbon-carbon double bonds and absorbs in the visible region (λ_{max} 450 nm, ε_{max} 14×10^4) and is coloured.

2.12 Solvent Effects

Since the polarity of a molecule usually changes with electronic transition, the position and the intensity of absorption maxima may be shifted by changing solvent polarity.

(i) $\pi \rightarrow \pi^*$ Transitions (*K*-Bands)

Owing to the non-polar nature of hydrocarbon double bonds, the $\pi \rightarrow \pi^*$ transitions of alkenes, dienes and polyenes are not appreciably affected by changing solvent polarity. The $\pi \rightarrow \pi^*$ transitions of polar compounds, e.g. saturated as well as α,β-unsaturated carbonyl compounds are shifted to longer wavelengths and generally towards higher intensity with increasing solvent polarity. The excited state in this transition is more polar than the ground state, thus, dipole-dipole interaction with a polar solvent lowers the energy of the excited state more than that of the ground state. Thus, there is a bathochromic shift of 10–20 nm in going from hexane as a solvent to ethanol, i.e. on increasing solvent polarity.

(ii) *B*-Bands

These bands also originate from $\pi \rightarrow \pi^*$ transitions, and their position and intensity are not shifted by changing solvent polarity except in case of heteroaromatic compounds which show a marked hyperchromic shift on increasing solvent polarity.

(iii) $\pi \rightarrow \pi^*$ Transitions (*R*-Bands)

It has been found that an increase in solvent polarity usually shifts $n \rightarrow \pi^*$ transitions to shorter wavelengths (higher energy). For example, acetone shows λ_{max} 279 nm in hexane, whereas in water it shows λ_{max} 264.5 nm. This can be explained on the basis that the carbonyl group is more polar in the ground state ($>\overset{\delta+}{C}=\overset{\delta-}{O}$) than in the excited state ($>\overset{\delta-}{C}=\overset{\delta+}{O}$). Thus, dipole-dipole interaction or hydrogen bonding with a polar solvent lowers the energy of the ground state more than that of the excited state resulting in the hypsochromic shift in case of unconjugated as well as conjugated carbonyl compounds with increasing solvent polarity.

(iv) $n \rightarrow \sigma^*$ Transitions

These transitions are affected by solvent polarity, especially by solvents capable of forming hydrogen bond. Alcohols and amines form hydrogen bonds with protic solvents. Such associations involve non-bonding electrons of the heteroatom. The involvement of non-bonding electrons in hydrogen bonding lowers the energy of the *n* orbital, and thus the excitation of these electrons requires greater energy resulting in the hypsochromic shift with increasing polarity.

- Polar solvents stabilize polar groups through dipole-dipole interaction or hydrogen bonding.
- If a chromophore is more polar in the ground state than in the excited state, then polar solvents stabilize the ground state to the greater extent than the excited state. Thus, there is a hypsochromic shift with increasing solvent polarity.
- If a chromophore is more polar in the excited state than in the ground state, then the former is stabilized to a greater extent by polar solvents than the latter. Thus, there is a bathochromic shift with increasing solvent polarity.

It has been found that an increase in solvent polarity usually shifts $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelengths, and $\pi \rightarrow \pi^*$ bands of polar compounds to longer wavelengths.

2.13 Woodward-Fieser Rules for Calculating λ_{max} in Conjugated Dienes and Trienes

Woodward (1941) formulated a set of empirical rules for calculating or predicting λ_{max} in conjugated acyclic and six-membered ring dienes. These rules, modified by Fieser and Scott on the basis of wide experience with dienes and trienes, are called Woodward-Fieser rules and are summarized in Table 2.3. First, we discuss the following terms used in Woodward-Fieser rules.

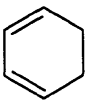
Table 2.3 Woodward-Fieser rules for calculating λ_{max} in conjugated dienes and trienes

Base value for acyclic or heteroannular diene	214 nm
Base value for homoannular diene	253 nm
Increment for each:	
Alkyl substituent or ring residue	5 nm
Exocyclic conjugated double bond	5 nm
Double bond extending conjugation	30 nm
—OR (alkoxy)	6 nm
—Cl, —Br	6 nm
—OCOR (acyloxy)	0 nm
—SR (alkylthio)	30 nm
—NR_2 (dialkylamino)	60 nm
In the same double bond is exocyclic to two rings simultaneously	10 nm
Solvent correction	0 nm
Calculated* λ_{max} of the compound	Total nm

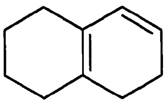
*For $\pi \rightarrow \pi^*$ transition (*K*-band).

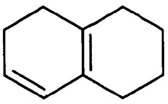
(i) Homoannular Dienes

In homoannular dienes, conjugated double bonds are present in the same ring and having *s-cis* (*cisoid*) configuration (*s* = single bond joining the two doubly bonded carbon atoms):



(I)





The *s-cis* configuration causes strain which raises the ground state energy level of the molecule leaving the high energy excited state relatively unchanged. Thus, the transition energy is lowered resulting in the shift of absorption position to a longer wavelength. Acyclic dienes exist mostly in the strainless *s-trans* (*transoid*) conformation with relatively lower ground state energy level. Thus, their absorptions appear at shorter wavelengths. For example, 1,3-cyclohexadiene

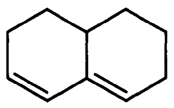
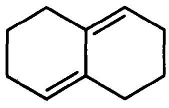
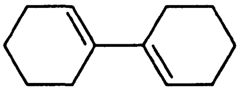
(I) shows λ_{max} 256 nm, whereas 1,3-butadiene shows λ_{max} 217 nm. Also, due to the shorter distance between the two ends of the chromophore, *s-cis* dienes give lower ε_{max} (~10,000) than that of the *s-trans* dienes (~20,000).

s-trans
1,3-butadiene
~ 97.5%
λ_{max} 217 nm

s-cis
1,3-butadiene
~ 2.5%

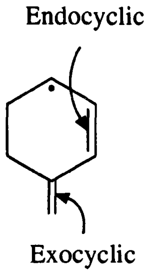
(ii) Heteroannular Dienes

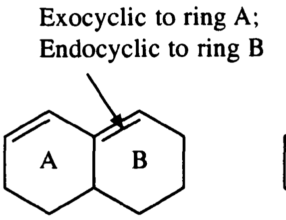
In heteroannular dienes, conjugated double bonds are not present in the same ring and these have *s-trans* (*transoid*) configurations:

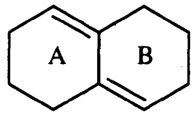
(iii) Exocyclic Conjugated Double Bonds

The carbon-carbon double bonds projecting outside a ring are called *exocyclic double bonds*. For example

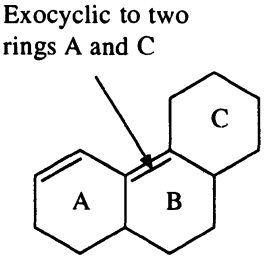




(One exocyclic double bond)



(Two exocyclic double bonds)

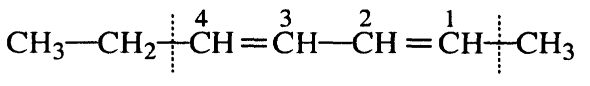


(Equivalent to two exocyclic double bonds)

Note that the same double bond may be exocyclic to one ring, while endocyclic to the other and sometimes the same double bond may be exocyclic to two rings simultaneously.

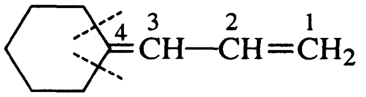
(iv) Alkyl Substituents and Ring Residues

Only the alkyl substituents and ring residues attached to the carbon atoms constituting the conjugated system of the compound are taken into account. Following examples indicate such carbon atoms by numbers and the alkyl substituents and ring residues by dotted lines:

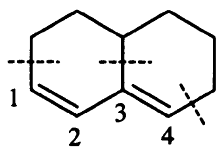


$$CH_3-CH_2 \vdots \overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H \vdots CH_3$$

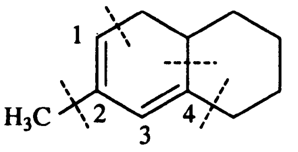
Two alkyl substituents



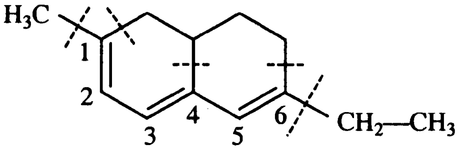
Two ring residues



Three ring residues



Three ring residues and one alkyl substituent

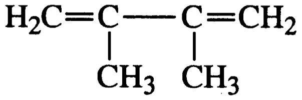


Three ring residues and two alkyl substituents

In compounds containing both homoanular and heteroannular diene systems, the calculations are based on the longer wavelength (253 nm), i.e. the homoannular diene system.

The calculated and observed values of λ_{max} usually match within ±5 nm as shown in the following examples illustrating the applications of Woodward-Fieser rules (Table 2.3).

Example 1. Using Woodward-Fieser rules, calculate λ_{max} for 2,3-dimethyl-1,3-butadiene.

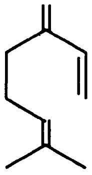


$$H_2C{=}\underset{CH_3}{\underset{|}{C}}{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

It is an acyclic diene with two alkyl substituents.
Thus, λ_{max} of this compound is

Base value	214 nm
Two alkyl substituents (2 × 5)	10 nm
Calculated λ_{max}	224 nm
Observed λ_{max}	226 nm

Example 2. Calculate the wavelength of the maximum UV absorption for

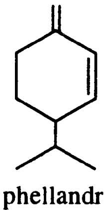


Myrcene

Since, it is an acyclic diene with one alkyl substituent, thus

Base value	214 nm
One alkyl substituent	5 nm
Calculated λ_{max}	219 nm
Observed λ_{max}	224 nm

Example 3. Predict the value of λ_{max} for

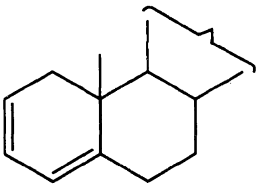


β-phellandrene

This is a heteroannular diene (conjugated double bonds are not in the same ring) with two ring residues and one exocyclic double bond, hence

Base value	214 nm
Two alkyl substituents (2 × 5)	10 nm
One exocyclic double bond	5 nm
Predicted λ_{max}	229 nm
Observed λ_{max}	232 nm

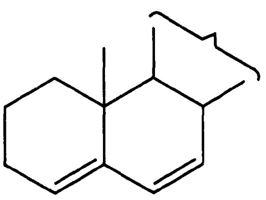
Example 4. Applying Woodward-Fieser rules, calculate the value of absorption maximum for the ethanolic solution of



This is a homoannular diene with three ring residues and one exocyclic double bond, thus

Base value	253 nm
Three ring residues (3 × 5)	15 nm
One exocyclic double bond	5 nm
Calculated λ_{max}	273 nm
Observed λ_{max}	275 nm (ε_{max} 10,000)

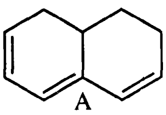
Example 5. Calculate λ_{max} for the ethanolic solution of



This is a heteroannular diene with three ring residues and one exocyclic double bond, thus

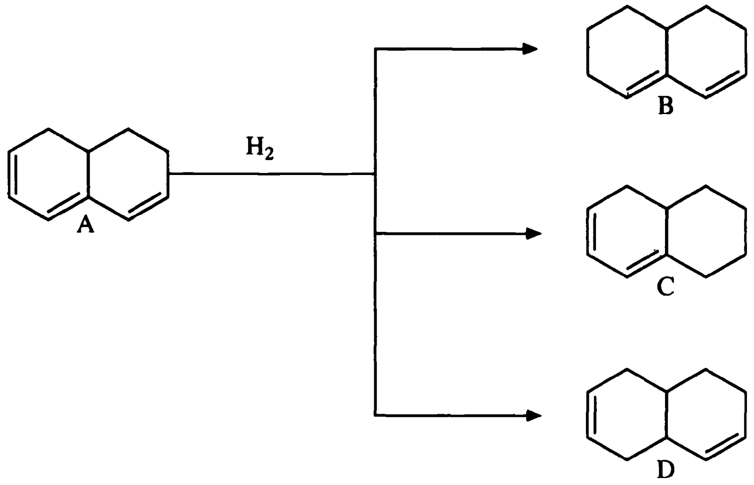
Base value	214 nm
Three ring residues (3 × 5)	15 nm
One exocyclic double bond	5 nm
Calculated λ_{max}	234 nm
Observed λ_{max}	235 nm (ε_{max} 19,000)

Example 6. Hydrogenation of one mole of the triene A with one mole of H_2 gives isomeric dienes having molecular formula $C_{10}H_{14}$. Show how UV spectroscopy and the expected λ_{max} values could distinguish these isomers:



A

The hydrogenation of one mole of the triene A with one mole of H_2 may give three isomeric dienes B, C and D with molecular formula $C_{10}H_{14}$:



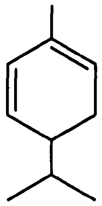
Diene B is a heteroannular conjugated diene with three ring residues and one exocyclic double bond, thus its expected $\lambda_{max} = 214 + 3 \times 5 + 5 = 234$ nm.

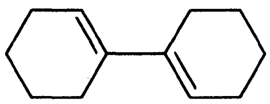
Diene C being a homoannular conjugated diene with three ring residues and one exocyclic double bond, thus its expected $\lambda_{max} = 253 + 3 \times 5 + 5 = 273$ nm.

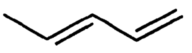
Diene D is an unconjugated diene, hence $\lambda_{max} < 200$ nm.

Thus, by comparing the expected λ_{max} values of the isomeric dienes B, C and D with their observed values of λ_{max}, we can distinguish these isomers.

Example 7. An organic compound can have one of the following structures:


(a)


(b)


(c)

The λ_{max} of the compound is 236 nm. Which is the most likely structure of the compound? Explain your choice.

Let us calculate the λ_{max} for each of these structures:

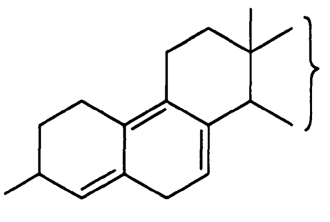
Structure (a) is a homoannular diene with two ring residues and one alkyl substituent, hence its calculated $\lambda_{max} = 253 + 3 \times 5 = 268$ nm.

Structure (b) represents a heteroannular diene with four ring residues, hence its calculated $\lambda_{max} = 214 + 4 \times 5 = 234$ nm.

Structure (c) shows an acyclic conjugated diene with one alkyl substituent, hence its calculated $\lambda_{max} = 214 + 5 = 219$ nm.

Since the given λ_{max} of the compound is 236 nm, its most likely structure is (b) because the calculated λ_{max} (234 nm) for this structure is very close to the given value (236 nm).

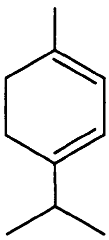
Example 8. Applying Woodward-Fieser rules, calculate the value of absorption maximum for

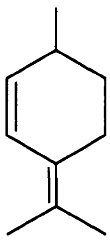


It contains both homoannular and heteroannular diene systems but the calculation of its λ_{max} will be based on the homoannular diene system. There are six ring residues attached to the carbon atoms of the entire conjugated system, one double bond extending conjugation, two exocyclic double bonds and one double bond exocyclic to two rings simultaneously. Thus, λ_{max} of this compound is calculated as:

Base value	253 nm
Six ring residues (6 × 5)	30 nm
One double bond extending conjugation	30 nm
Two exocyclic double bonds (2 × 5)	10 nm
One double bond exocyclic to two rings simultaneously	10 nm
Calculated λ_{max}	333 nm

Example 9. The following dienes have the experimental λ_{max} 243 and 265 nm in ethanol. Giving reasons, correlate the λ_{max} values to the structures (a) and (b):

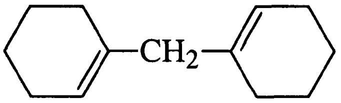

(a)


(b)

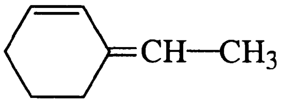
The calculated λ_{max} for (a) (a homoannular diene with two ring residues and two alkyl substituents) is $253 + 2 \times 5 + 2 \times 5 = 273$ nm. Thus, structure (a) is the diene having experimental λ_{max} 265 nm as this value is in fair agreement with the calculated λ_{max} for (a).

The calculated λ_{max} for (b) (a heteroannular diene with two ring residues, two alkyl substituents and one exocyclic double bond) is $214 + 2 \times 5 + 2 \times 5 + 5 = 239$ nm. Thus, the structure (b) is the diene having the experimental λ_{max} 243 nm because this value is in agreement with the calculated λ_{max} for (b).

Example 10. Which of the following compounds is expected to have higher value of λ_{max} and why?



(a)

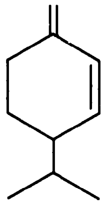


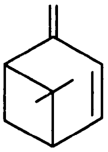
(b)

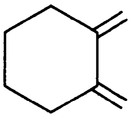
Compound (a) is an unconjugated diene. Hence, it will have $\lambda_{max} < 200$ nm. The compound (b) is a heteroannular conjugated diene with two ring residues, one alkyl substituent and one exocyclic double bond. Thus, it is expected to have λ_{max} $(214 + 2 \times 5 + 5 + 5) = 234$ nm, i.e. higher than that of the compound (a).

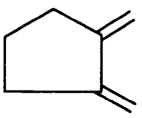
(v) Exceptions to Woodward-Fieser Rules

Distortion of the chromophore is the most important factor responsible for deviations from the predicted values of λ_{max} for dienes and trienes. Distortion of the chromophore may cause red or blue shifts depending on the nature of the distortion. Thus, the strained diene verbenene (III) has λ_{max} 245.5 nm compared to 232 nm of β-phellandrene (II), whereas the calculated value for both is 229 nm. In such bicyclic compounds, 15 nm is added as the ring strain correction to the calculated values of absorption maxima. The diene (IV) which is expected to have λ_{max} 234 nm but actually it is 220 nm (ε_{max} 10,050). This blue shift is due to the distortion of the chromophore resulting in the loss of coplanarity of the double bonds with consequent loss of conjugation. On the other hand, the expected coplanarity of the double bonds in the diene (V) is confirmed by its λ_{max} 243 nm (ε_{max} 15,800) although it still does not agree with the calculated value 234 nm.


(II)

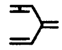

(III)


(IV)


(V)

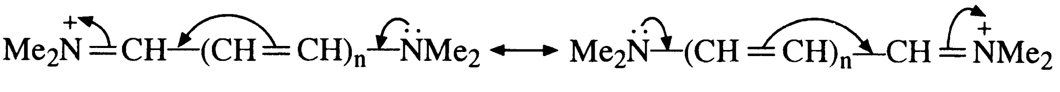
In general, if the strain in the molecule does not considerably affect the coplanarity of the conjugated system, then a bathochromic shift occurs. If the strain forces the chromophore out of coplanarity, then there is loss of conjugation and a hypsochromic shift occurs.

The change of ring size of homoannular dienes from six-membered to any other, say five- or seven-membered, leads to deviations from predicted values due to distortion of the chromophore resulting in the loss of conjugation. Thus, calculations for homoannular dienes are valid only for six-membered rings.

Woodward-Fieser rules work well only for conjugated systems containing up to four double bonds. These rules do not apply satisfactorily to cross (branched)-conjugated systems like .

2.14 Polyenes and Poly-ynes

As the number of conjugated double bond increases, the values of λ_{max} and ε_{max} also increase and several subsidiary peaks appear. For example, lycopene (the compound responsible for the red colour of tomatoes) has eleven conjugated double bonds and absorbs in the visible region (λ_{max} 474 nm, ε_{max} 18.6 × 10^4). As the chain length in conjugated polyenes increases, the value of λ_{max} for long chains also increases, but not proportionately. This is probably due to the variation in bond lengths between the double and single bonds. In the following cyanine dye analogue, the resonance leads to uniform bond length and bond order along the polyene chain. Since there is no change in bond length in the polyene chain, calculated values of λ_{max} are in agreement with the observed values.



$$Me_2\overset{+}{N}{=}CH{-}(CH{=}CH)_n{-}\ddot{N}Me_2 \longleftrightarrow Me_2\ddot{N}{-}(CH{=}CH)_n{-}CH{=}\overset{+}{N}Me_2$$

In a long chain polyene, change from *trans-* to *cis-*configuration at one or more double bonds lowers both λ_{max} and ε_{max}.

Alkynes, like alkenes, absorb strongly below 200 nm due to $\pi \rightarrow \pi^*$ transitions. When triple bond is conjugated with one or more chromophoric groups as in polyenynes and poly-ynes, radiation of longer wavelength is absorbed. For example, acetylene absorbs at 150 and 173 nm, while vinylacetylene absorbs at 219 and

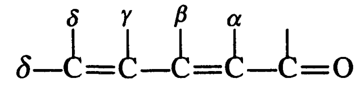
228 nm. Acetylenic compounds exhibit high intensity bands at shorter wavelength and low intensity bands at longer wavelengths, e.g. —$(C\equiv C)_3$— shows two bands at λ_{max} 207 nm, ε_{max} 1,35,000 and λ_{max} 306 nm, ε_{max} 120.

2.15 Woodward-Fieser Rules for Calculating λ_{max} in α,β-Unsaturated Carbonyl Compounds

Compounds containing a carbonyl group (C=O) in conjugation with an ethylenic groups (C=C) are called enones. UV spectra of enones are characterized by an intense absorption band (*K*-band) due to $\pi \rightarrow \pi^*$ transition in the range 215-250 nm (ε_{max} usually 10,000–20,000) and a weak *R*-band due to $n \rightarrow \pi^*$ transition in 310-330 nm region (ε_{max} usually 10-100).

Similar to dienes and trienes, there are set rules called Woodward-Fieser rules for calculating or predicting λ_{max} in α, β-unsaturated carbonyl compounds (enones). These rules first framed by Woodward and modified by Fieser and by Scott are given in Table 2.4.

Table 2.4 Woodward-Fieser rules for calculating λ_{max} in α, β-unsaturated carbonyl compounds



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

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

---

†For $\pi \rightarrow \pi^*$ transition (*K*-band).

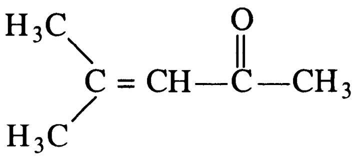
For calculated λ_{max} in other solvents, a solvent correction given in Table 2.5 must be carried out.

Table 2.5 Solvent corrections

Solvent	Correction (nm)
Ethanol	0
Methanol	0
Dioxane	+5
Chloroform	+1
Ether	+7
Hexane	+11
Cyclohexane	+11
Water	–8

Since carbonyl compounds are polar, the positions of the *K*- and *R*-bands of enones are dependent on the solvent. Hence, solvent corrections are required (Table 2.5) to obtain the calculated values of λ_{max} in a particular solvent. The ε_{max} for *cisoid* enones are usually <10,000, while that of transoid are >10,000. The calculated values of λ_{max} are usually within ±5 nm of the observed values as shown in the following examples illustrating the applications of Woodward-Fieser rules (Table 2.4).

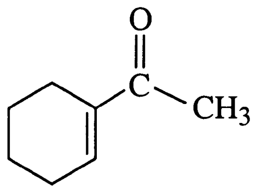
Example 1. Applying Woodward-Fieser rules, calculate the λ_{max} for the ethanolic solution of mesityl oxide



This being an acyclic α,β-unsaturated ketone with two β-alkyl substituents, the λ_{max} of this compound is calculated as

Base value	215 nm
Two β-alkyl substituents (2×12)	24 nm
Calculated λ_{max}	239 nm
Observed λ_{max}	237 nm

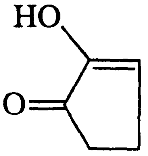
Example 2. Predict the value of λ_{max} (hexane) for



This is a six-membered cyclic α,β-unsaturated ketone with one α- and one β-alkyl substituents. Hence,

Base value	215 nm
One α-alkyl substituent	10 nm
One β-alkyl substituent	12 nm
Predicted λ_{max} (EtOH)	237 nm
Observed λ_{max} (EtOH)	249 nm
Calculated λ_{max} (hexane)	237 (EtOH)
Solvent correction	+11
	248 nm

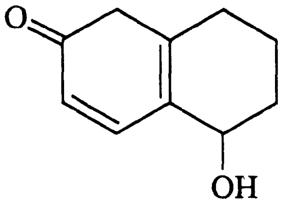
Example 3. Calculate λ_{max} (EtOH) for



It is a five-membered cyclic α,β-unsaturated ketone with one α-hydroxy and one β-ring residue. Thus,

Base value	202 nm
One α-hydroxy groups	35 nm
One β-ring residue	12 nm
Calculated λ_{max} (EtOH)	249 nm
Observed λ_{max} (EtOH)	247 nm

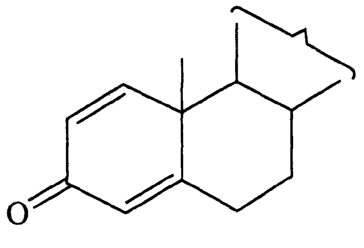
Example 4. What is the expected λ_{max} for



This being an α,β-unsaturated cyclohexenone system, hence

Base value	215 nm
Ring residues γ (1)	18 nm
δ (2)	36 nm
One homoannular diene component	39 nm
One double bond extending conjugation	30 nm
Expected λ_{max} (EtOH)	338 nm

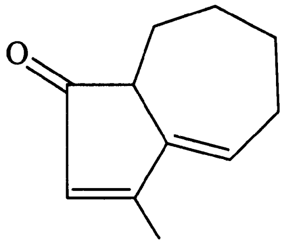
Example 5. Calculate λ_{max} for



It is a six-membered cyclic α,β-unsaturated ketone in which the carbonyl group has α,β-unsaturation on either side, i.e. there is cross (branched) conjugation in this compound. In such cases, λ_{max} is calculated by considering most highly substituted conjugated system which gives higher value of λ_{max}. Thus,

Base value	215 nm
Two β-ring residues (2 × 12)	24 nm
One exocyclic carbon-carbon double bond	5 nm
Calculated λ_{max} (EtOH)	244 nm
Observed λ_{max} (EtOH)	245 nm

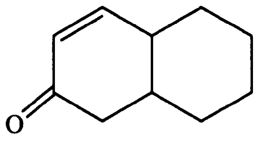
Example 6. Calculate the wavelength of the maximum UV absorption for the ethanolic solution of



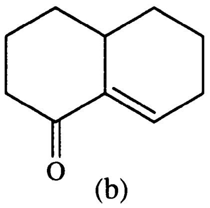
It is an α,β-unsaturated cyclopentenone system. Hence,

Base value	202 nm
One β-alkyl substituent	12 nm
One double bond extending conjugation	30 nm
One exocyclic carbon-carbon double bond	5 nm
One γ-ring residue	18 nm
One δ-ring residue	18 nm
Calculated λ_{max} (EtOH)	285 nm
Observed value (EtOH)	287 nm

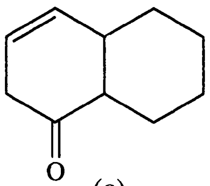
Example 7. An organic compound can have one of the following structures:



(a)



(b)



(c)

The λ_{max} of ethanolic solution of the compound is 242 nm. Which is the most likely structure of the compound? Explain your choice.

Let us calculate λ_{max} for each of the above structures.

The calculated λ_{max} (EtOH) for:

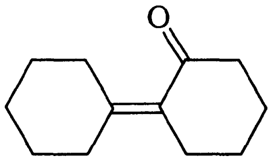
(a) 215 (base) + 12 (1 β-ring residue) = 227 nm.

(b) 215 (base) + 10(1 α-ring residue) + 12 (1 β-ring residue) + 5(1 exocyclic carbon-carbon double bond) = 242 nm.

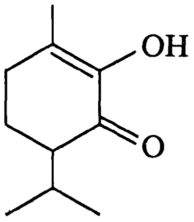
(c) It has an unconjugated system. Hence its C=C will show $\lambda_{max} < 200$ nm due to $\pi \to \pi^*$ transition, and C=O will show two bands at ~180 and 285 nm due to $\pi \to \pi^*$ and $n \to \pi^*$ transitions, respectively.

Since the given λ_{max} of the compound is 242 nm, its most likely structure is (b) because the calculated λ_{max} for this structure is equal to the given value.

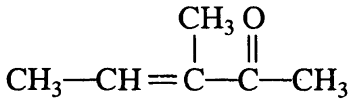
Example 8. The following α,β-unsaturated ketones have λ_{max} 236, 256 and 270 nm in ethanol. Explain which is which?



(a)



(b)



$$CH_3{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3$$

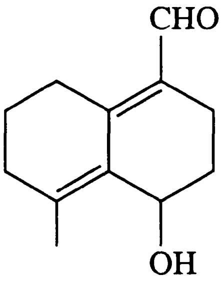
(c)

The calculated λ_{max} for (a) is 215 (base) + 10 (1 α-ring residue) + 2 × 12 (2β-ring residues) + 10 (the same C=C exocyclic to two rings) = 259 nm (EtOH). Thus, (a) is the α,β-unsaturated ketone having λ_{max} 256 nm because this value agrees with the calculated λ_{max} for (a).

The calculated λ_{max} for (b) is 215 (base) + 35(1 α-OH) + 2 × 12 (2β-ring residues) = 274 nm (EtOH). Thus, (b) is the α,β-unsaturated ketone having λ_{max} 270 nm because this value agrees with the calculated λ_{max} for (b).

The calculated λ_{max} for (c) is 215 (base) + 10 (1 α-alkyl substituent) + 12 (1β-alkyl substituent) = 237 nm (EtOH). Thus, (c) is the α,β-unsaturated ketone having λ_{max} 236 nm because this value agrees with the calculated λ_{max} for (c).

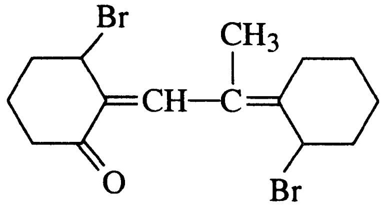
Example 9. Predict the λ_{max} for the ethanolic solution of



This compound has an α,β-unsaturated aldehyde system. Thus,

Base value	207 nm
One double bond extending conjugation	30 nm
One α-ring residue	10 nm
One β-ring residue	12 nm
One γ-ring residue	18 nm
One δ-ring residue	18 nm
One δ-alkyl substituent	18 nm
Two carbon-carbon exocyclic double bonds (2 × 5)	10 nm
Predicted λ_{max} (EtOH)	323 nm

Example 10. Calculate λ_{max} for

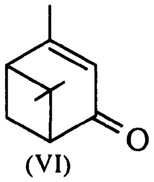


The λ_{max} for the above compound can be calculated as:

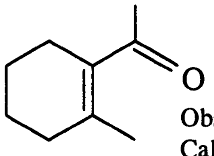
Base value	215 nm
One double bond extending conjugation	30 nm
One α-ring residue	10 nm
One γ-alkyl substituent	18 nm
Two δ-ring residues (2 × 18)	36 nm
Two exocyclic C=C (2 × 5)	10 nm
Calculated λ_{max} (EtOH)	319 nm

Similar to that of conjugated dienes and trienes (Section 2.13), there are deviations from the calculated values of λ_{max} for α,β-unsaturated carbonyl compounds also due to distortion in the chromophore. For example, verbenone (VI) shows λ_{max} 253 nm but its calculated λ_{max} is 239 nm, i.e. there is an increment of 14 nm for strain.

Thus, in such bicyclic compounds, 14 nm should be added as the ring strain correction to the calculated values of λ_{max}.



(VI)
Verbenone



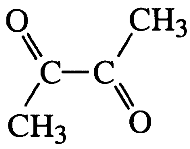
(VII)

Observed λ_{max} 243 nm, ε_{max} 1400
Calculated λ_{max} 249 nm

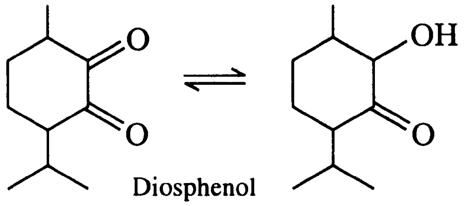
Similarly, in cyclic systems like (VII), the intensity of the K-band may be reduced to $<10^4$ due to steric hindrance which prevents coplanarity. If a carbonyl group is in a five-membered ring and the double bond is exocyclic to the five-membered ring, then the base value of 215 nm gives satisfactory results.

2.16 Dicarbonyl Compounds

Acyclic α-diketones exist in *s-trans* conformation and show the normal weak R-band and a weak K-band arising from the conjugation between carbonyl groups, e.g. biacetyl shows λ_{max} 275 nm (R-band) and ~450 nm (K-band). Cyclic α-diketones with α-hydrogen atom(s) exist almost exclusively in the enolic form. Thus, their absorption is related to α,β-unsaturated carbonyl compounds, e.g. diosphenol. In strong alkaline solution there is a bathochromic shift of 50 nm due to the formation of enolate ion because the greater the number of n electrons available for conjugation, lesser is the transition energy, i.e. longer is the wavelength of the maximum absorption. This enables the characterization of enolic structures like diosphenols (six-membered cyclic α-diketones).

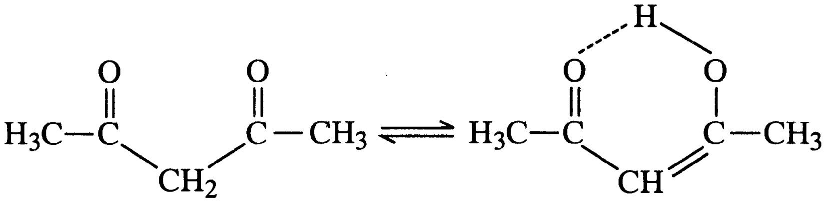


s-trans-biacetyl
λ_{max} 450 nm



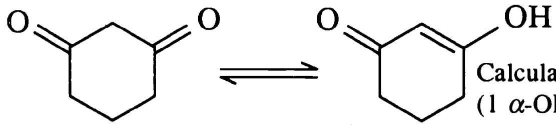
Diosphenol
Calculated λ_{max} (EtOH) = 215 (base) + 24 (2β-ring residues) + 35 (1 α-OH) = 274 nm
Observed λ_{max} (EtOH) = 270 nm

The absorption maxima of β-diketones depend on the concentration of the enol tautomer, i.e. the degree of enolization. For example, acetylacetone exists in enolic form up to 91–92% in solution in non-polar solvents or in the vapour phase. However, in this case the calculated λ_{max} 257 nm is not in good agreement with the observed value (λ_{max} 272 nm in isooctane).



λ_{max} (isooctane) = 272 nm, ε_{max} 12,000
λ_{max} (H_2O) = 274 nm, ε_{max} 2050

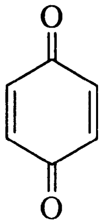
Similar to the cyclic α-diketones, cyclic β-diketones, like 1,3-cyclohexanedione exist almost exclusively in the enolic form even in polar solvents. The enolic forms show λ_{max} in the region 230–260 nm due to the $\pi \rightarrow \pi^*$ transition in the *s-trans* enone system, e.g. 1,3-cyclohexanedione shows λ_{max} (EtOH) 253 nm, ε_{max} 22,000 which is in good agreement with the calculated value (257 nm). This may be due to the difference in the configuration of enolic forms of acyclic β-diketones (*s-cis*) and that of the cyclic ones (*s-trans*). In these cases also, the formation of enolate ion in alkaline solution shifts λ_{max} into the 270–300 nm region.



1,3-cyclohexanedione

Calculated λ_{max} (EtOH) : 215 (base) + 30 (1 α-OH) + 12 (1β-ring residue) = 257 nm
Observed λ_{max} (EtOH) = 253 nm

Quinones are α-, or vinylogons α-diketones. The spectrum of *p*-benzoquinone (VIII), is similar to that of a typical α,β-unsaturated ketone and shows λ_{max} 242 nm (strong *K*-band): 281 and 434 nm (weak *R*-bands). The weak $n \rightarrow \pi^*$ transitions (*R*-bands) stretching into the visible region are responsible for imparting colour to some simple quinones and α-diketones in the diketo form.



(VIII)

λ_{max} (hexane) = 242 nm, ε_{max} 24,000 *K*-bands

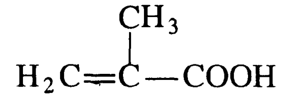
281 nm, ε_{max} 400
434 nm, ε_{max} 20
R-bands

2.17 α,β-Unsaturated Carboxylic Acids and Esters

The attachment of groups containing a lone pair of electrons to the carbonyl group, as in carboxylic acids, esters and amides, shifts the $n \rightarrow \pi^*$ transition to shorter wavelengths (200–220 nm) region with little effect on intensity. This hypsochromic shift is due to combined inductive and resonance effects. For example, compared to the *R*-band of acetaldehyde (λ_{max} 290 nm) that of acetic acid, ethyl acetate and acetamide appear at 204, 211 and 220 nm, respectively.

α, β-unsaturated acids, esters and amides display strong *K*-bands characteristic of the conjugated system. α, β-unsaturated acids and esters follow a trend similar to that of enones. Thus, we can calculate λ_{max} of their *K*-bands taking the base value 195 nm and using the data given in Table 2.4. As shown by the following examples, the calculated and observed values of λ_{max} match within ±5 nm.

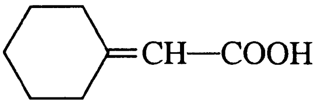
Example 1. Calculate λ_{max} for



$H_2C{=}C(CH_3){-}COOH$

Base value	195 nm
One α-alkyl substituent	10 nm
Calculated λ_{max} (EtOH)	205 nm
Observed λ_{max} (EtOH)	210 nm

Example 2. Predict the λ_{max} for



Base value	195 nm
Two β-ring residues (2 × 12)	24 nm
One exocyclic C = C	5 nm
Predicted λ_{max} (EtOH)	224 nm
Observed λ_{max} (EtOH)	220 nm

2.18 Benzene and Its Derivatives

The UV spectrum of benzene (in hexane) shows three absorption bands, viz. at 184 nm, ε_{max} 60,000; at 204 nm, ε_{max} 7900 and a broad band with multiple peaks or fine structure in the region 230–270 nm; the λ_{max} of most intense peak in this band is 256 nm, ε_{max} 200. All these bands arise from $\pi \rightarrow \pi^*$ transitions. The most intense band (E_1-band) near 180 nm originates from an allowed transition, whereas the low intensity bands near 200 nm (E_2-band) and 260 nm (*B*-band) arise from forbidden transitions in the highly symmetrical benzene molecule.

The *B*-band of benzene and many of its homologues has fine structure, specially when the spectrum is recorded in the vapour phase or in non-polar solvents (Fig. 2.7(a)). The fine structure arises from sub-levels of vibrational absorption upon which the electronic absorption is superimposed. In polar solvents, due to interactions between solute and solvent molecules, the fine structure is either reduced or destroyed (Fig. 2.7(b)).

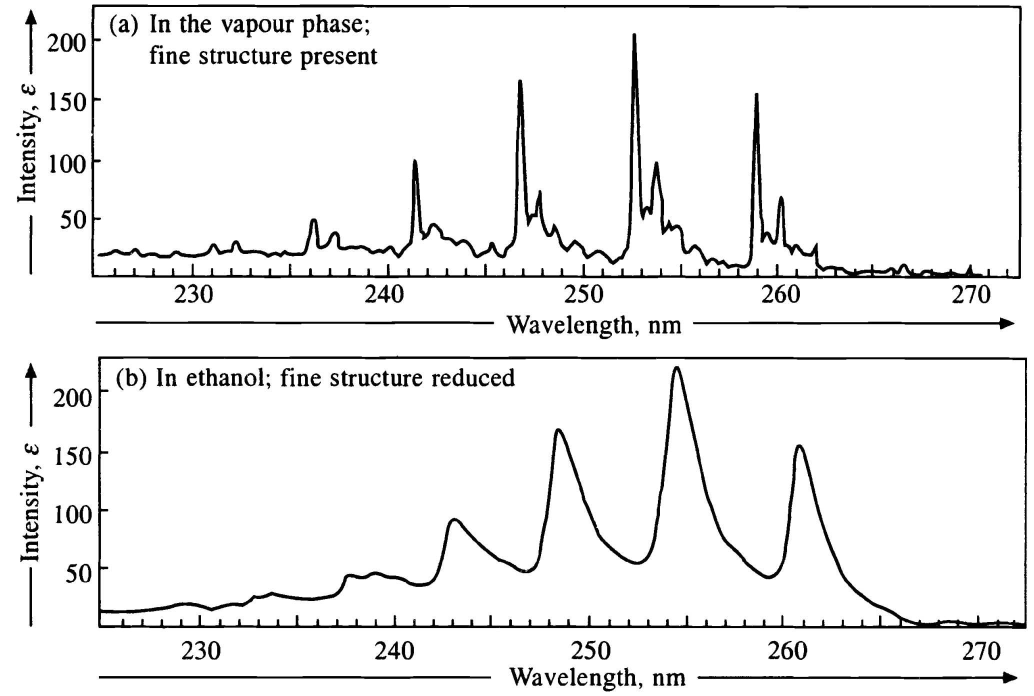
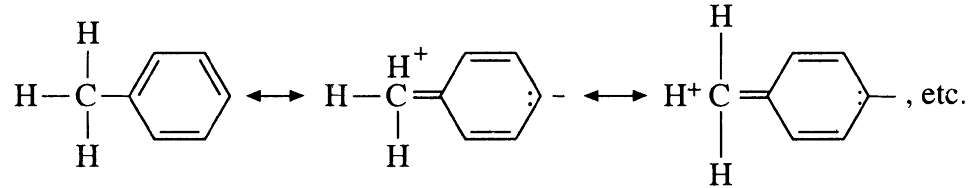


Fig. 2.7 UV spectrum of benzene showing *B*-band in: (a) vapour phase and (b) ethanol

There is a slight bathochromic shift of the *B*-band with a small increase in ε_{max} on introduction of an alkyl group into the benzene ring. This is due to hyperconjugation between the alkyl group and the π-electron system of the ring. The introduction of the second alkyl group into the *para* position is most effective in causing bathochromic shift. The *para* isomer has both the highest λ_{max} and ε_{max}, whereas the *ortho* isomer generally has the lowest λ_{max} and reduced ε_{max}. This effect is because of steric interactions between the *ortho* substituents which effectively reduce hyperconjugation.



B-band, $\lambda_{max} = 261$ nm, $\varepsilon_{max} = 225$

If substituents having non-bonding electrons such as OH, NH_2, OMe, etc. are present on the benzene ring, then because of $n \rightarrow \pi^*$, *E*- and *B*-bands are shifted to longer wavelengths with frequent increase in the intensity of the *B*-band (Table 2.6) and loss of its fine structure. The more extensive the conjugation, the less obvious is the vibrational fine structure of the *B*-band.

The spectral characteristics of phenols and aromatic amines change with the change of pH of the solution which causes protonation or deprotonation. For example, coversion of a phenol into the corresponding anion (alkaline solution of phenol) results in the shift of the E_2- and *B*-bands to longer wavelengths with an increase in ε_{max} (Table 2.6).

Table 2.6 Absorption characteristics of benzene and some of its monosubstituted derivatives Ph—*R*

R	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	Solvent
	E_2-band		*B*-band		
—H	204	7900	256	200	Hexane
—Me	206.5	7000	261	225	Water
—NH$_2$	230	8600	280	1430	Water
—NH$_3^+$	203	7500	254	160	Aq. acid
—NHAc	238	10,500	—	—	Water
—OH	210.5	6200	270	1450	Water
—O$^-$	235	9400	287	2600	Aq. alkali
—OMe	217	6400	269	1480	2% methanol
—OPh	255	11,000	272	2000	Cyclohexane
—SH	236	10,000	269	700	Hexane
—I	207	7000	257	700	Water
—Cl	209.5	7400	263.5	190	Water
—Br	210	7900	261	192	Water
	K-band		*B*-band		
—CH=CH$_2$	244	12,000	282	450	Ethanol
—C≡CH	236	12,500	278	650	Hexane
—CHO	244	15,000	280[a]	1500	Ethanol
—COMe	240	13,000	278[b]	1100	Ethanol
—NO$_2$	252	10,000	280[c]	1000	Hexane
—COOH	230	10,000	270	800	Water
—COO$^-$	224	8700	268	560	Aq. alkali
—CN	224	13,000	271	1000	Water
—COPh	252	20,000[d]	Submerged		Ethanol
—Ph	246	20,000	Submerged		Ethanol
—CH=CHPh (*cis*)	283	12,300	Submerged		Ethanol
—CH=CHPh (*trans*)	295	25,000	Submerged		Ethanol
—CH=CHCOOH (*trans*)	273	21,000	Submerged		Water

[a] *R*-band, λ_{max} 328 nm, ε_{max} 20; [b] *R*-band, λ_{max} 319 nm, ε_{max} 50;
[c] *R*-band, λ_{max} 330 nm, ε_{max} 125; [d] *R*-band, λ_{max} 325 nm, ε_{max} 180.

The larger the number of non-bonding electrons available for interaction (conjugation) with the π-electron system of the ring, smaller is the energy difference between the ground and excited states, i.e. the longer is the wavelength of absorption. Since an additional pair of non-bonding electrons in the anion is available for interaction with the π-electron system of the ring, its E_2- and *B*-band are shifted to longer wavelengths with an increase in ε_{max}. Thus, a suspected phenolic structure may be confirmed by comparison of the UV spectrum of the compound recorded in a neutral solution with that recorded in an alkaline solution (pH = 13).

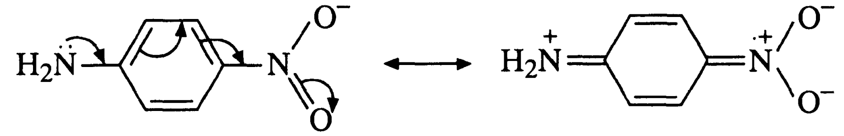
Similarly, when aniline is converted into the anilinium cation (acidic solution of aniline), the pair of non-bonding electrons of the nitrogen atom of aniline is no longer available for interaction with the π-electrons of the ring. This makes the spectral data of the anilinium cation almost identical to that of benzene

(Table 2.6). Thus, a suspected aniline derivative may be confirmed by comparison of UV spectra recorded in neutral and acid solutions (pH = 1).

The interaction between the non-bonding electron pair(s) of the heteroatom attached to the benzene ring and the π-electrons of the ring is most effective when the π-orbital of the non-bonding electrons is parallel to the π orbitals of the ring. This arrangement is considerably disturbed due to twisting in sterically crowded molecules such as N,N-dimethylaniline resulting in a hypsochromic shift in the E_2-band accompanied by a marked reduction in ε_{max}. Thus, N,N-dimethylaniline shows λ_{max} 251 nm, ε_{max} 15,500, whereas 2-methyl-NN-dimethylaniline shows λ_{max} 248 nm, ε_{max} 6360.

If an unsaturated group (chromophore) is directly attached to the benzene ring, then because of π-π conjugation, a strong bathochromic shift of the *B*-band occurs with the appearance of an intense *K*-band (ε_{max} > 10,000) in the region 200–250 nm (Table 2.6).

In disubstituted benzenes, when an electron donating group and an electron attracting group (electronically complementary groups) are *para* to each other, there is a pronounced red shift and increase in intensity of the main absorption band (*K*-band) (Table 2.7) compared to the effect of either group separately (Table 2.6). This is due to the extension of the chromophore through resonance as shown below:



λ_{max} (EtOH) = 375 nm, ε_{max} = 16,000

When two groups are *ortho* or *meta* to each other or the groups situated *para* to each other are not complementary, the absorption spectrum usually has close resemblance with that of the separate, non-interacting chromophores. For example, *p*-dinitrobenzene has λ_{max} 260 nm, ε_{max} 13,000, whereas nitrobenzene has λ_{max} 252 nm, ε_{max} 10,000. On comparing the values for *ortho, meta-* and *para-* isomers with each other (Table 2.7) and with the values for the single substituent (Table 2.6), it is clear that the effect is most pronounced when complementary groups are *para* to each other.

Table 2.7 Absorption characteristics of some disubstituted benzene derivatives *R*—C_6H_4—*R'*

R	*R'*	Orientation	*K*-band		*B*-band	
			λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
—NO_2	—NH_2	*o-*	283	5400	412	4500
—NO_2	—NH_2	*m-*	280	4800	358	1450
—NO_2	—NH_2	*p-*	381	13,500	Submerged	
—NO_2	—OH	*o-*	279	6600	351	3200
—NO_2	—OH	*m-*	274	6000	333	1960
—NO_2	—OH	*p-*	318	10,000	Submerged	
—OMe	—CHO	*o-*	253	11,000	319	4000
—OMe	—CHO	*m-*	252	8300	314	2800
—OMe	—CHO	*p-*	277	14,800	Submerged	

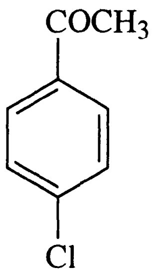
Similar to Woodward-Fieser rules, Scott formulated a set of rules for calculating the absorption maximum of the principal band of aromatic aldehydes, ketones, carboxylic acids and esters which are summarized in Table 2.8. In the absence of steric hindrance to coplanarity, the calculated values are usually within ±5 nm of the observed values.

Table 2.8 Rules for calculating λ_{max} of the principal band ($\pi \rightarrow \pi^*$ transition) of substituted benzene derivatives $R—C_6H_4—COG$

	Orientation	nm
Parent chromophore: R = H		
G = alkyl or ring residue; base value		246
G = H; base value		250
G = OH or *o*-alkyl; base value		230
Increment for each substituent:		
R = alkyl or ring residue	*o*-, *m*-	3
	p-	10
R = OH, OMe, *o*-alkyl	*o*-, *m*-	7
	p-	25
$R = O^-$	*o*-	11
	m-	20
	p-	78
R = Cl	*o*-, *m*-	0
	p-	10
R = Br	*o*-, *m*-	2
	p-	15
$R = NH_2$	*o*-, *m*-	13
	p-	58
R = NHAc	*o*-, *m*-	20
	p-	45
R = NHMe	*p*-	73
$R = NMe_2$	*o*-, *m*-	20
	p-	85
Calculated λ_{max} (EtOH) of $R—C_6H_4—COG$		Total nm

The following examples illustrate the application of these rules.

Example 1. Calculate λ_{max} for the ethanolic solution of *p*-chloroacetophenone.

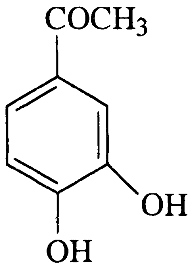


In this compound G is an alkyl group. Thus,

Base value	246 nm
Para Cl	10 nm

Calculated λ_{max} (EtOH)	256 nm
Observed λ_{max} (EtOH)	254 nm

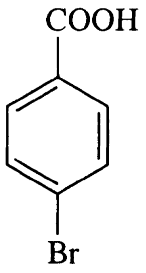
Example 2. Predict the absorption maximum for the ethanolic solution of 3,4-dihydroxyacetophenone.



In this compound *G* is an alkyl group. Thus,

Base value	246 nm
m-OH	7 nm
p-OH	25 nm
Calculated λ_{max} (EtOH)	278 nm
Observed λ_{max} (EtOH)	281 nm

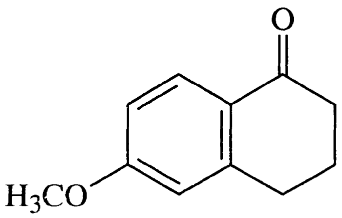
Example 3. Calculate the absorption maximum for *p*-bromobenzoic acid.



In this case *G* is OH. Thus,

Base value	230 nm
p-Br	15 nm
Calculated λ_{max} (EtOH)	245 nm
Observed λ_{max} (EtOH)	245 nm

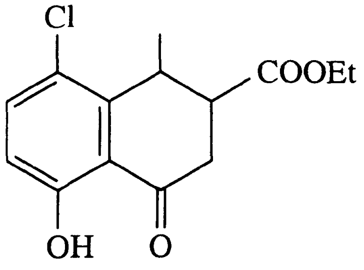
Example 4. Calculate λ_{max} for 6-methoxytetralone.



In this case *G* is a ring residue. Thus,

Base value	246 nm
o-ring residue	3 nm
p-methoxyl	25 nm
Calculated λ_{max} (EtOH)	274 nm
Observed λ_{max} (EtOH)	276 nm

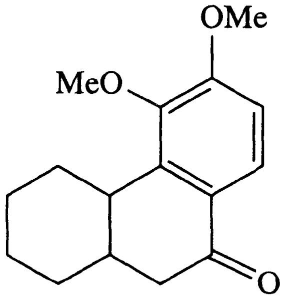
Example 5. Calculate the absorption maximum for 3-carbethoxy-5-chloro-8-hydroxyl-4-methyltetralone.



In this case *G* is a ring residue. Thus,

Base value	246 nm
o-ring residue	3 nm
o-hydroxyl	7 nm
Calculated λ_{max} (EtOH)	256 nm
Observed λ_{max} (EtOH)	257 nm

Example 6. Predict the λ_{max} for the ethanolic solution of 3,4-dimethoxy-10-oxooctahydrophenanthrene.



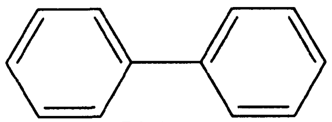
In this compound *G* is a ring residue. Thus,

Base value	246 nm
m-methoxyl	7 nm
p-methoxyl	25 nm
o-ring residue	3 nm
Predicted λ_{max} (EtOH)	281 nm
Observed λ_{max} (EtOH)	278 nm

2.19 Polynuclear Aromatic Compounds

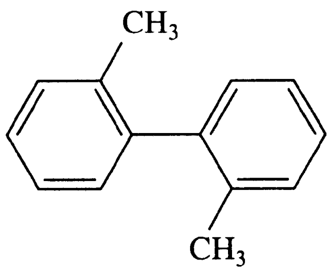
Similar to that of benzene, the spectra of polynuclear aromatics are characterized by vibrational fine-structure. Biphenyl and its derivatives have two aromatic rings in conjugation. When the rings are coplanar, the conjugation is most effective overlap of the π-orbitals, but it is least effective when the rings are twisted up to

90°. In biphenyl, the angle of twist is small, hence conjugation between the rings is not affected. Consequently, biphenyl shows a very intense (ε_{max} 19,000) absorption band at 252 nm (*K*-band). In biphenyl derivatives with bulky substituents in the *ortho* positions, the rings are forced out of coplanarity because these molecules are more stable in twisted conformations than in the planar conformation which suffers steric strain due to bulky *ortho* substituents. This results in the loss of conjugation.



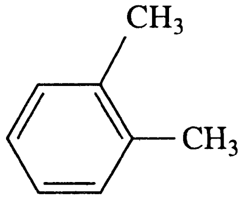
Biphenyl

K-band, λ_{max} 252 nm, ε_{max} 19,000



2,2′-dimethylbiphenyl

B-band, λ_{max} 270 nm, ε_{max} 800

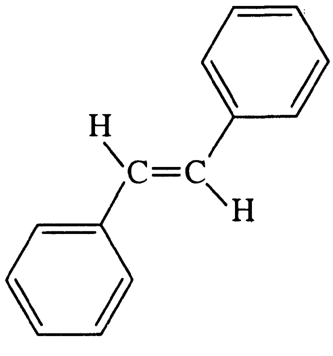


o-xylene

B-band, λ_{max} = 262 nm, ε_{max} = 270

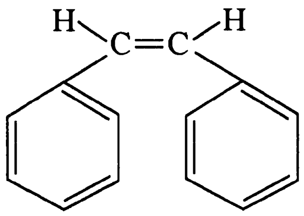
For example, the loss of conjugation due to forcing the rings out of coplanarity is reflected in the UV spectral data of 2,2′-biphenyl which are similar to those of *o*-xylene but different from that of the biphenyl which shows a very intense *K*-band.

We have seen that coplanarity is required for the most effective conjugation which lowers the transition energy resulting in a bathochromic shift accompanied by increased intensity. For example, *trans*-stilbene absorbs at a longer wavelength (295 nm) with a greater intensity (ε_{max} 25,000) compared to the corresponding band (283 nm) in *cis*-stilbene because in the latter there is the destruction of coplanarity by steric interference resulting in the loss of conjugation.



trans-stilbene

λ_{max}(EtOH) = 295 nm, ε_{max} = 25,000



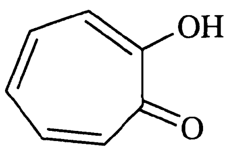
cis-stilbene

λ_{max}(EtOH) = 283 nm, ε_{max} = 12,300

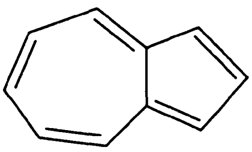
There are two common series of fused-ring aromatic compounds, viz. the linear series such as anthracene and the angular series like phenanthrene. The spectra of the linear series of compounds retain the vibrational fine structure as well as the other absorption bands typical of the benzene ring. The spectra of the angular series of compounds are relatively complicated. In both series, as the number of fused rings increases, the absorption is shifted to progressively longer wavelengths and reaches the visible region. For example, benzene absorbs at 256 nm, ε_{max} 200; naphthalene absorbs at 312 nm, ε_{max} 289, whereas pentacene absorbs in the visible region at 580 nm, ε_{max} 12,600 and is blue.

2.20 Non-benzenoid Aromatic Compounds

Spectra of non-benzenoid aromatics are considerably similar to that of benzenoid aromatics. Actually, the UV spectroscopy is one of the methods for determining whether a particular compound has aromatic character, e.g. tropolone and its derivatives absorb in the region 220–250 nm, ε_{max} ~30,000 and 340–375 nm, ε_{max} ~8000; the latter absorption has vibrational fine structure typical of aromatic systems. The UV spectra of azulene and its derivatives are complicated and consist of a number of intense bands in the UV region (up to 360 nm) and a number of relatively weak bands in the visible region (between 500 and 700 nm). As a consequence of the absorption in the visible region, azulene and most of its derivatives are blue.



Tropolone



Azulene

2.21 Heteroaromatic Compounds

In general, the spectra of heteroaromatics are almost similar to that of their corresponding hydrocarbons and their long wavelength band has fine structure analogous to the *B*-band of benzene. Thus, the absorptions of five-membered heteroaromatics are compared to that of cyclopentadiene which absorbs near 200 nm, ε_{max} 10,000 and near 238 nm, ε_{max} 3400. For example, pyrrole shows comparable absorptions at 211 nm, ε_{max} 15,000 and at 240 nm, ε_{max} 300; the latter absorption band has fine structure analogous to the *B*-band of benzene. The presence of an auxochromic or chromophoric substituent on the five-membered heteroaromatic ring causes a bathochromic shift and increased intensity of the bands of the parent molecule.

Similarly, the spectrum of a six-membered aromatic heterocycle, e.g. pyridine, is comparable with that of benzene; the only difference being that the *B*-band of pyridine (λ_{max} 270 nm, ε_{max} 450 at pH > 7) is relatively more intense and has less distinct fine structure. The transition ($\pi \rightarrow \pi^*$) resulting in the *B*-band is allowed for pyridine but forbidden for the more symmetrical benzene molecule. Pyridine shows another absorption band at 257 nm, ε_{max} 2750 (pH > 7). An increase in the solvent polarity produces a hyperchromic effect on the *B*-band of pyridine and its homologues, whereas it has little or no effect on the position or intensity of the *B*-band of benzene. This effect is due to hydrogen bonding through the lone pair of electrons of the nitrogen atom which makes pyridine molecules far less symmetrical than benzene molecules. The effect of substituents on absorption characteristics of pyridine is not clearly defined. The spectra of diazines are similar to that of pyridine.

In general, spectra of simple heteroaromatics resemble spectra of benzenoid aromatics in the sense that they consist of an absorption band of relatively higher intensity (ε_{max} 5000-15,000) at short wavelength (λ_{max} 190-240 nm) and a fine structure band of lower intensity (ε_{max} 1-400) at longer wavelength (λ_{max} 240-300 nm).

2.22 Applications of Ultraviolet and Visible Spectroscopy

A few functional groups (chromophores) may be detected by the ultraviolet and visible (electronic) spectroscopy, but it is especially useful for detecting the presence and elucidating the nature of conjugated systems including aromatic rings. In the application of the electronic spectroscopy for structural analysis, only the region above 200 nm is really useful and the region below 200 nm is hardly useful for this purpose. Some important applications of UV and visible spectroscopy to organic chemistry are summarized as follows.

(i) Detection of a Functional Group (Chromophore)

The presence or absence of a particular chromophore may be indicated by the presence or absence of an absorption band in the expected wavelength region. For example, the presence of a low intensity band in the region 270–300 nm indicates the presence of an aldehydic or ketonic carbonyl group. If the spectrum is transparent above 200 nm, it shows the absence of

(a) an aldehydic or ketonic carbonyl group.
(b) a conjugated-system.
(c) an aromatic ring.
(d) a bromine or iodine atom in the molecule.

However, an unconjugated C$=$C bond or some other atoms or groups may be present in the molecule if it does not absorb above 200 nm. Thus, no definite conclusion can be drawn regarding the structure of the molecule if it absorbs below 200 nm.

(ii) Detection of Conjugation and Elucidation of Its Nature

Compounds containing a conjugated system including aromatics are characterized by their absorptions above 200 nm. We have noted that the longer the conjugated system, the longer is the wavelength of absorption, usually accompanied by the increased intensity. Also, substitutions on a conjugated system generally cause bathochromic and hyperchromic effects. Thus, we can elucidate the nature of conjugation by comparing the values of λ_{max} and ε_{max} for the compound under study with that of a probable analogous compound.

UV spectral data for a variety of compounds are available for comparison, e.g. acyclic conjugated dienes show intense *K*-bands in region 215–230 nm (ε_{max} ~21,000). Similarly, α,β-unsaturated aldehydes and ketones show an intense *K*-band in the 215–250 nm region with ε_{max} usually 10,000–20,000, and a weak *R*-band in the region 310–330 nm (ε_{max} 10–100). Aromatic compounds are characterized by an intense band (E_2-band) near 200 nm (ε_{max} ~8000), and a weak *B*-band with fine structure near 260 nm (ε_{max} ~200). In all the above cases, additional conjugation as well as substitution generally causes bathochromic and hyperchromic effects.

A particular conjugated system may be recognized in molecules of widely varying complexities because a large portion of such molecules may be transparent in the UV region. This results in a spectrum similar to that of a much simpler molecule. For example, an α,β-unsaturated ketone moiety is easily recognized in a complex steroidal molecule 4-cholesten-3-one by resemblance of its spectrum with that of simpler mesityl oxide molecule (Fig. 2.8).

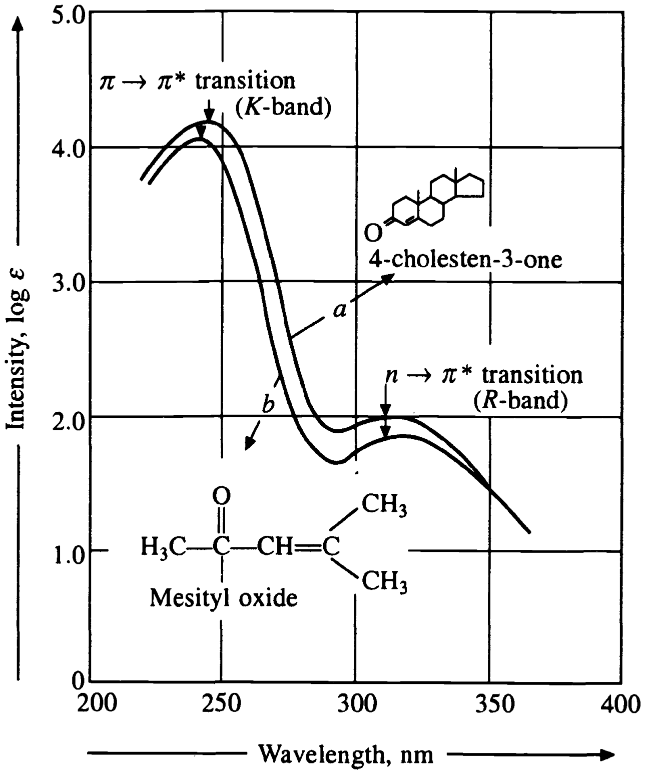


Fig. 2.8 UV spectra of (a) 4-cholesten-3-one and (b) mesityl oxide

(iii) Study of Extent of Conjugation

The values of λ_{max} and ε_{max} increase as the number of conjugated multiple bonds increases, thus the extent of conjugation can be estimated. It has been found that the absorption occurs in the visible region if a polyene has eight or more conjugated double bonds. A polyene with such a sufficient conjugation becomes coloured, e.g. β-carotene (orange) and lycopene (red) having eleven conjugated double bonds are coloured and absorb in the visible region at 450 nm, ε_{max} 14×10^4 and 474 nm, ε_{max} 18.6×10^4, respectively.

(iv) Distinction Between Conjugated and Unconjugated Compounds

In general, electronic spectroscopy can distinguish isomeric conjugated and unconjugated compounds. For example, isomeric dienes 2,4-hexadiene and 2,5-hexadiene can be readily differentiated because the former being a conjugated diene will absorb above 200 nm (227 nm), whereas the latter being an unconjugated diene will absorb below 200 nm (~170 nm). Similarly, an α,β-unsaturated ketone can be readily distinguished from its β,γ-isomer because the former having conjugated system will show both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition bands at longer wavelengths compared to that of the latter which is an unconjugated compound.

(v) Study of Strain

In molecules like 2-substituted biphenyls, there is steric strain which forces the rings out of coplanarity resulting in the loss of conjugation. This causes hypsochromic and hypochromic effects which are measures of steric strain in such molecules, i.e. the larger are these effects, the greater will be the steric strain.

(vi) Determination of Configurations of Geometrical Isomers

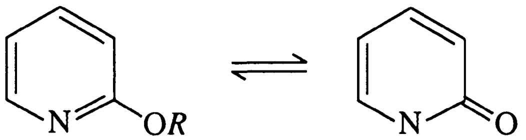
It is possible when there is loss of coplanarity of one isomer due to steric hindrance resulting in the loss of conjugation accompanied by hypsochromic and hypochromic effects. Obviously, this isomer is the *cis*-isomer in which groups are closer to each other to cause steric strain and to force the groups out of coplanarity. Thus, *cis*-isomers absorb at shorter wavelengths and have lower intensity than the *trans*-isomers, e.g. *cis*-stilbene shows λ_{max} 283 nm, ε_{max} 12,300, whereas *trans*-stilbene shows λ_{max} 295 nm, ε_{max} 25,000 (Section 2.18).

(vii) Study of Tautomerism

UV spectroscopy can be used for identifying the predominant (stable) tautomer. For example, 2-hydroxypyridine (IX, R = H) and 2-pyridone (X, R = H equilibrium has been shown to lie far to the right, i.e. 2-pyridone predominates, because the UV spectrum of the solution resembles with that of a solution of N-methyl-2-pyridone (X, R = Me) but not with that of 2-methoxypyridine (IX, R = Me).

(viii) Confirmation of Suspected Phenols and Aromatic Amines

The spectral characteristic of phenols and aromatic amines change with the change of pH of the solution. Thus, suspected phenols and aniline derivatives may be confirmed by comparison of UV spectra recorded in neutral and alkaline or acid solutions (for details, see Section 2.18).



(IX)
R = Me
$\lambda_{max} < 205$ nm ($\varepsilon_{max} > 5300$)
269 nm ($\varepsilon_{max} = 3230$)

(X)
R = Me
$\lambda_{max} = 226$ nm ($\varepsilon_{max} = 6100$)
297 nm ($\varepsilon_{max} = 5700$)
R = H
$\lambda_{max} = 224$ nm ($\varepsilon_{max} = 7230$)
293 nm ($\varepsilon_{max} = 5900$)

(ix) Study of Structural Features in Different Solvents

In certain cases, the structure of a compound changes with the change in the