CHAPTER 2 ULTRAVIOLET (UV) AND VISIBLE SPECTROSCOPY

ULTRAVIOLET AND visible spectroscopy (electronic spectroscopy) is primarily used to measure the multiple bond or aromatic conjugation within molecules.

Electronic Spectroscopy

- Electronic spectroscopy involves the measurement of absorption of energy when electromagnetic radiation of the proper energy is provided. An electron is promoted from the HOMO to the LUMO
- As conjugation increases, the HOMO-LUMO gap decreases and the position of the $\pi \rightarrow \pi^*$ absorption shifts to longer wavelengths (lower energy)
- Simple aldehydes and ketones like simple alkenes do not have a $\pi \rightarrow \pi^*$ absorption in the region of uv spectrum readily accessible to most spectrometers.

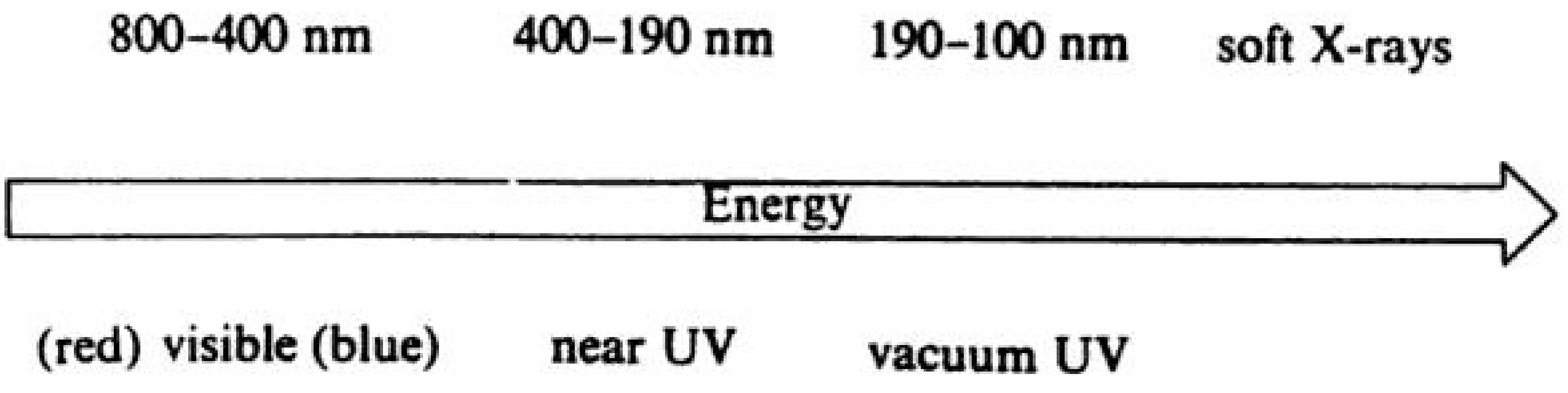
2.1 INTRODUCTION

Ultraviolet and Visible Spectroscopy

- UV/vis spectroscopy requires electromagnetic radiation of high energy.
- The visible region corresponds to 800-400 nm and ultraviolet region to 400-200 nm.

The uv region extends from 1000-4000 Å or 100-400 nanometers (nm). It should be noted that uv measurements are reported directly in nm, and the corresponding range in cm^{-1} is given in Table 1.1. The further subdivision of the uv into near uv and the far or vacuum uv is given in Scheme 2.1. The vacuum uv (below 200 nm) is so named because the molecules of air absorb radiation in this region, and thus this region is accessible only with special vacuum equipment.

On passing electromagnetic radiation in the ultraviolet and visible regions through a compound with multiple bonds, a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the



Scheme 2.1

compound. The absorption of radiation is due to the subtraction of energy from the radiation beam when electrons in orbitals of lower energy are excited into orbitals of higher energy. Since this is an electron excitation phenomenon, uv is sometimes called electronic spectroscopy. Ultraviolet spectrum records the wavelength of an absorption maximum, *i.e.*, λ_{max} and the strength of the absorption, *i.e.*, molar absorptivity (extinction coefficient ε_{max}) as defined by the combined Beer-Lambert law:

$$\log (I_0/I) = \varepsilon.l.c \text{ or } \varepsilon = A/cl$$

(the combined Beer-Lambert law)

where:

I_0 is the intensity of the incident light (or the light intensity passing through a reference cell)

I is the light transmitted through the sample solution

$\log (I_0/I)$ is the absorbance (A) of the solution (optical density, OD)

c is the concentration of solute (in mol dm^{-3})

l is the path length of the sample (in cm)

ε is the molar absorptivity (extinction coefficient).

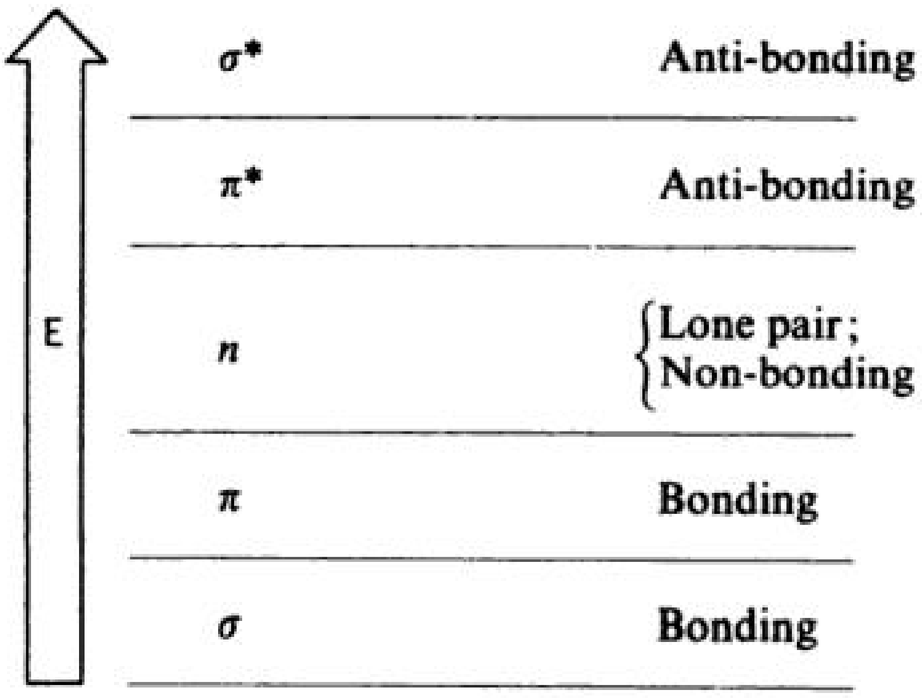
$E^{1\%}_{1\,cm}$ Absorption [$\log_{10} (I_0/I)$] of a 1 per cent solution in a cell with a 1 cm path length. This is used in place of ε when the molecular weight of a compound is not known, or when a mixture is being examined.

The molar absorptivity ε is constant for an organic compound at a given wavelength, and is reported as ε_{max} — the molar absorptivity at an absorption maximum. It may be mentioned that ε is not dimensionless, but is correctly expressed in units of 10^{-2} m^2 mol^{-1} but the units are, by convention, never expressed. Since values for ε_{max} can be very large, an alternative convention is to report its logarithm (to the base 10), $\log_{10} \varepsilon_{max}$.

In an infrared spectrum, one uses labels like strong (*s*) medium (*m*) and weak (*w*) to define the intensity of different bands, however, in discussing uv absorptions the value of ε is reported (to know, how intense the absorption is). Its value varies from 10^0–10^4 and one, considers the absorptions of the order of 10^4 very strong and those less than 10^3 as weak. The intensity of the peak is a measure of transition probability, and the peaks with low ε values often arise from transitions which are formally "forbidden".

2.2 ELECTRONIC TRANSITIONS DEFINITION OF SOME TERMS AND DESIGNATION OF UV ABSORPTION BANDS

On absorption of energy by a molecule in the ultraviolet region, changes are produced in the electronic energy of the molecule due to transitions of valence electrons in the molecule. These transitions consist of the excitation of an electron from an occupied molecular orbital, *e.g.*, a non-bonding *p* or bonding π-orbital to the next higher energy orbital, *i.e.*, an anti-bonding, π* or σ*, orbital. The anti-bonding orbital is designated by an asterisk. Thus, the promotion of an electron, *e.g.*, from a π-bonding orbital to an anti-bonding (π*) orbital is designated: $\pi \rightarrow \pi^*$ (pi to pi star). As shown, (Scheme 2.2), it is clear that $n \rightarrow \pi^*$ transition requires less energy compared to $\pi \rightarrow \pi^*$ or a $\sigma \rightarrow \sigma^*$ transition.

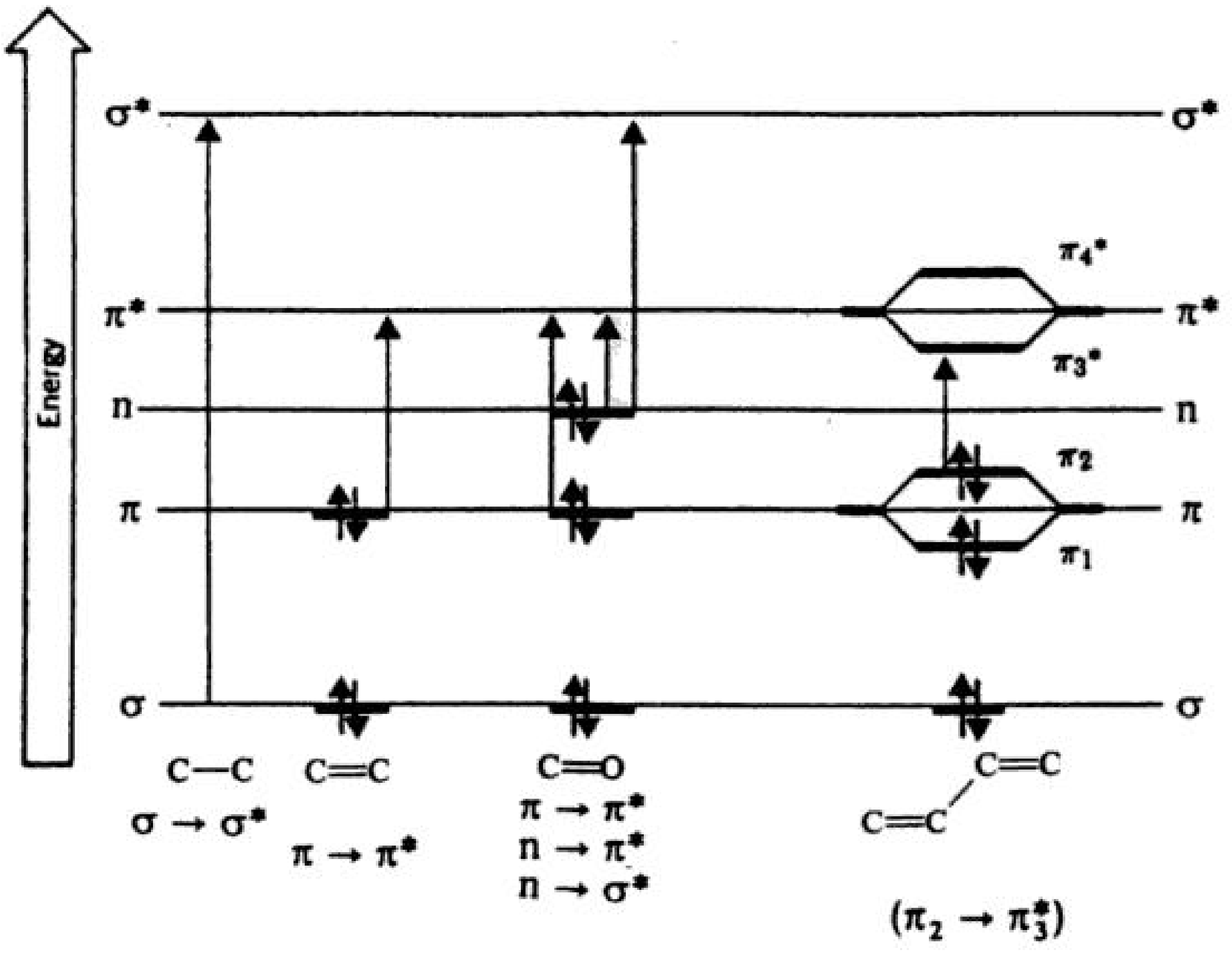


Electronic Energy Levels

Scheme 2.2

(a) The Designation of Various Transitions. In Scheme (2.2a), the relative energies of the more important orbitals are illustrated.

(i) $\sigma \rightarrow \sigma^*$ ***Transition.*** A transition of a electron from a bonding sigma orbital to the higher energy antibonding sigma orbital is designated $\sigma \rightarrow \sigma^*$ ('sigma to sigma star'). In alkanes, *e.g.*, this is the only transition available. Sigma bonds are, in general, very strong, this therefore, is a high energy process (Scheme 2.2a) and these transitions require very short



Scheme 2.2a

wavelengths, *i.e.*, high energy ultraviolet light ~ 150 nm. A study of such transition is done in vacuum ultraviolet region since below 200 nm oxygen present in air begins to absorb.

(ii) n → σ* Transition. This transition involves saturated compounds with one hetero atom with unshared pair of electrons (*n* electrons), *i.e.*, saturated halides, alcohols, ethers, aldehydes, ketones, amines, etc. These transitions require comparatively less energy than σ → σ* transitions. Water absorbs at 167; methyl alcohol at 174; methyl chloride at 169 and methyl iodide at 258 nm. In saturated alkyl halides, the energy required for this transition decreases with the increase in the size of the halogen atom (or decrease in the electronegativity of the atom). Due to the greater electronegativity of chlorine (than iodine) the *n* electrons on chlorine atom are comparatively difficult to excite. The *n* electrons on iodine atom are loosely bound. Since this transition is more probable in case of methyl iodide, its molar extinction coefficient is also higher than methyl chloride. *n* → σ* Transitions are sensitive to hydrogen bonding. Alcohols, *e.g.*, form hydrogen bonds with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus, this transition requires greater energy.

(iii) π → π* Transition (K-band). This transition is available in compounds with unsaturated centres, *e.g.*, simple alkenes, aromatics, carbonyl compounds, etc. This transition requires lesser energy then *n* → σ* transition. In a simple alkene, although several transitions are available (Scheme 2.2a), the lowest energy transition is the π → π* transition and a absorption band around 170-190 nm in unconjugated alkenes (Table 2.3) is due to this transition. In the case of, *e.g.*, saturated ketones, the most intense band around 150 nm is due to π → π* transition.

(iv) n → π* Transition (R- band). In this transition, an electron of unshared electron pair on a hetero atom is excited to π* anti-bonding orbital. This transition involves least amount of energy than all the transitions and therefore, this transition gives rise to an absorption band at longer wavelengths. In saturated aliphatic ketones, *e.g.*, the *n* → π* transition around 280 nm is the lowest energy transition (Scheme 2.2a). This *n* → π* transition is 'forbidden' by symmetry consideration, thus the intensity of the band due to this transition is low, although the wavelength is long (lower energy).

(v) Conjugated Systems and Transition Energies. In conjugated dienes, the π orbitals of the separate alkene groups combine to give new orbitals, *i.e.*, the two new bonding orbitals which are designated π_1 and π_2 and two anti-bonding orbitals which are designated $\pi^*{}_3$ and $\pi^*{}_4$. One can easily see (Scheme 2.2a) the relative energies of these new orbitals, and it is apparent that now the $\pi_2 \rightarrow \pi_3{}^*$ transition of a conjugated diene is of very low energy than π → π* transition on an unconjugated alkene. Consequently the $\pi_2 \rightarrow \pi_3{}^*$ transition of, *e.g.*, butadiene (λ_{max}, 217 nm) is bathochromically shifted relative to the π → π* transition of ethylene λ_{max} 171 nm, Table 2.4. Conjugated ketones, *i.e.*, α, β-unsaturated ketones as well, show both an *n* → π* and a π → π* transition both of lower energy, *i.e.*, at higher wavelength than those of isolated systems.

(b) Designation of Bands. One may designate the uv absorption bands by using electronic transitions or the letter designation. The band due to π → π* transition in a compound with conjugated π system is usually intense (ε_{max} > 10,000) and is frequently referred to as the *K*-band (German *Konjugierte*). The examples of the compounds in which *K*-band appears are butadiene, mesityl oxide. Benzene itself displays three absorption bands at 184, 204 and 256 nm and of these the band at 204 nm is often designated as *K*-band, and this designation is used in other benzenes as well (Table 2.7).

The *n* → π* transition (*R*-band German, *Radikal*) in compounds with single chromophoric groups *i.e.*, carbonyl or nitro are forbidden with ε value less than 100.

In conjugated systems the energy separation between the ground and excited states is reduced and the system then absorbs at longer wavelengths and with a greatly increased intensity (*i.e.*, *K*-band is intense and at longer wavelength). Moreover, due to the lessening of the energy gap, the $n \rightarrow \pi^*$ transition due to the presence of the heteroatom, *i.e.*, the *R*-band also undergoes a red shift with little change in intensity.

The ***B*-bands,** *i.e.*, benzenoid bands are characteristic of aromatic and heteroaromatic compounds. In benzene the *B*-band is at 256 nm which displays a fine structure, *i.e.*, the band contains multiple peaks. Significantly the *K*-band and *B*-band of benzenes have low intensities.

The ***E*-band**, *i.e.*, ethylenic bands are characteristic of aromatic systems like *B*-bands.

(c) Chromophores and Auxochromes. A chromophore is a covalently unsaturated group responsible for electronic absorption, *e.g.*, C=C, C=O and NO_2. Examples of simple compounds containing chromophoric groups are ethene (Table 2.3), benzene (Table 2.7) and acetone (Sec. 2.9). An auxochrome represents a saturated group containing unshared electrons which when attached to a chromophore changes both the intensity as well as the wavelength of the absorption maximum, *e.g.*, OH, NH_2, Cl. The effect of NH_2 group on λ_{max} and ε_{max} can be seen by, *e.g.*, comparing the position of *B*-band in benzene and aniline (Table 2.7); in aniline the *B*-band becomes more intense and displays itself at longer wavelength. Combining chromophores (as in 1, 3-butadiene) or extending conjugation can also significantly affect position and intensity of absorption bands (Table 2.4, also see sample problem 59, Chapter 7).

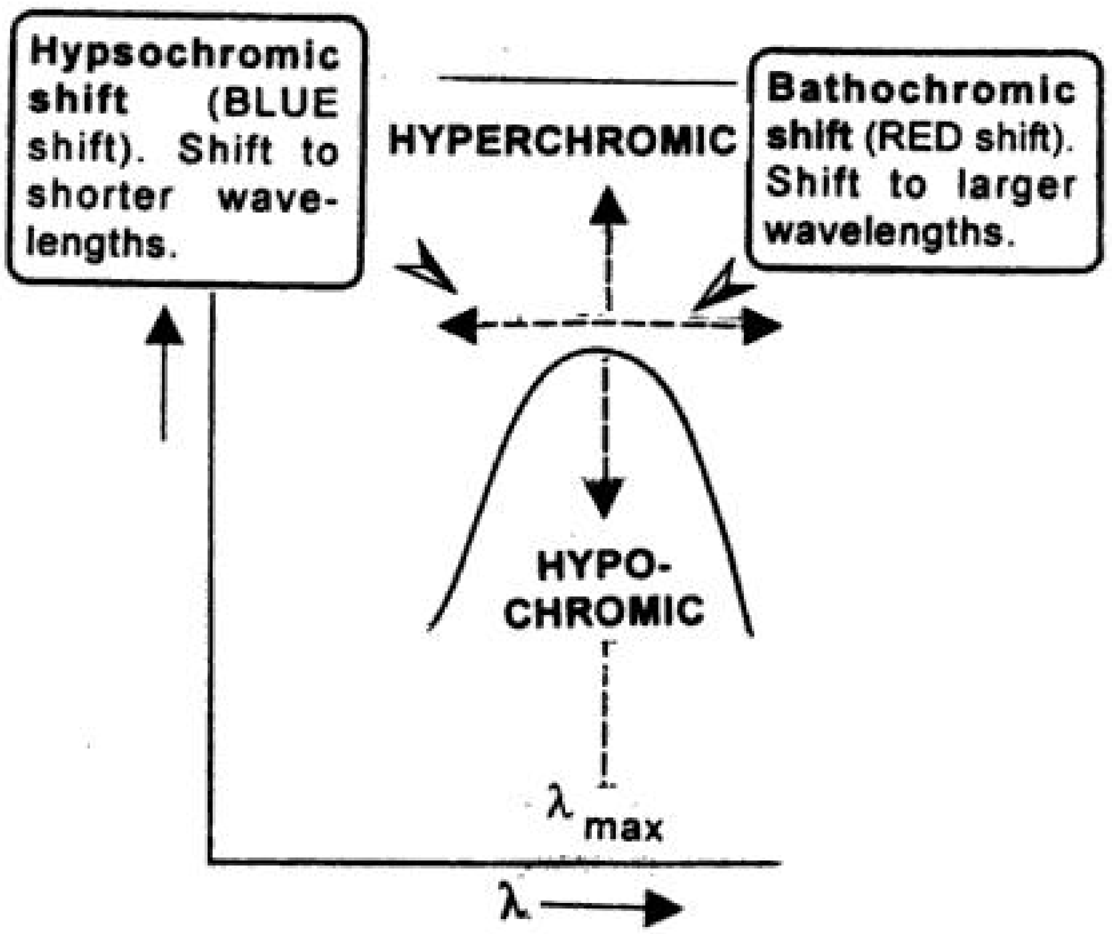
(d) Red and Blue Shifts. Groups which give rise to electronic absorption are termed *chromophores*. The term *auxochrome* is used for substituents containing unshared electrons (OH, NH, SH, halogens, etc.). When attached to π electron chromophores, auxochromes generally move the absorption maximum to longer wavelengths (lower energies). Such a movement is called a *bathochromic* or *red shift*. The term *hypsochromic* denotes a shift to shorter wavelength (*blue shift*). Increased conjugation usually results in increased intensity, termed *hyperchromism*. A decrease in intensity of an absorption band is termed *hypochromism* (Scheme 2.2b).

(e) Transition Probability—Allowed and Forbidden Transitions.

The excitation of an electron may not always take place from a bonding orbital or lone pair to an anti-bonding of non-bonding orbital, when a compound absorbs ultraviolet/visible light. The extinction coefficient, $\varepsilon_{max} = 0.87 \times 10^{20}$ P.a.

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

a = Target area of the absorbing system (*i.e.*, a chromophore).



Scheme 2.2b

The value of ε_{max} is found to be around 10^5 when the chromophore has a length of the order of 10 Å or 10^{-7} cm. A chromophore with low transition probability will have $\varepsilon_{max} < 1000$. Thus there is a direct relationship between the area of the chromophore and the absorption intensity (ε_{max}). There are some other factors as well which govern the transition probability. Depending upon the symmetry and the value of ε_{max}, the transitions may either be allowed or forbidden. The transitions with the values of (extinction coefficient) ε_{max}, more than 10^4 are usually called allowed transitions. They generally arise due to $\pi \rightarrow \pi^*$ transitions. In butadiene the absorption at 217 nm, ε_{max} 21000 is the allowed transition. There are however, other $\pi \rightarrow \pi^*$ transitions in the conjugated system and their intensities depend on the "allowedness" of the transitions.

The forbidden transition is a result of the excitation of one electron from the lone pair present on the hetero-atom to an anti-bonding π^* orbital. The $n \rightarrow \pi^*$ transition near 300 nm in case of carbonyl compounds with ε_{max} value between 10-100, is the result of forbidden transition. The values of ε_{max} for forbidden transitions are generally below 10^4.

The allowedness of electronic transitions is related not only with the geometries of the lower and higher energy molecular orbitals but also with the symmetry of the molecule as a whole. Symmetrical molecules, (*e.g.*, benzene is highly symmetrical), have more restrictions on their transitions than comparatively less symmetrical molecules. Because of this reason the electronic absorption spectrum of benzene molecule is simple.

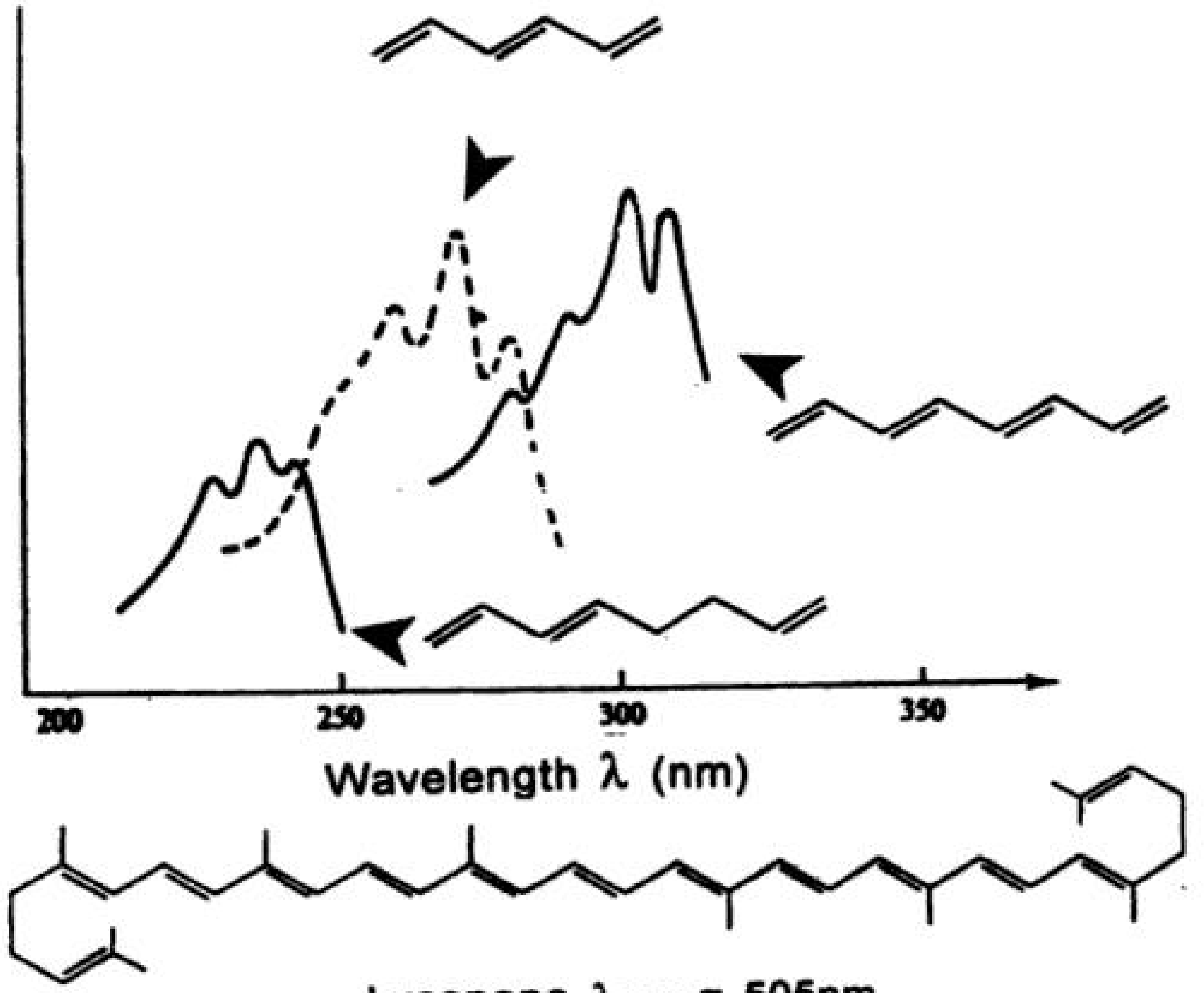
2.3 GENERAL APPLICATIONS OF ULTRAVIOLET SPECTROSCOPY — A SUMMARY

In practice, ultraviolet spectroscopy is largely limited to conjugated systems for the most part. For practical purposes the limits of visual perception may be taken as 750 nm (red) and 400 nm (violet) and therefore, ultraviolet commences around 400 nm. Organic applications of ultraviolet spectroscopy are mainly concerned in the region above 200 nm (near uv region) and hardly at all in the region below 200 nm (far uv region). Some of the most significant applications of uv spectroscopy to organic chemistry are as under.

(a) Extent of Conjugation. The longer the conjugation, the longer the maximum wavelength of the absorption spectrum as shown in the case of isomeric conjugated dienes, trienes and tetraenes (Fig. 2.1).

Sufficient conjugation shifts the absorption to wavelengths which reach the visible region of the spectrum, *i.e.,* a compound with sufficient conjugation becomes coloured. Thus lycopene, a compound which gives red colour to tomatoes has eleven conjugated double bonds (Fig. 2.1).

(b) Distinction Between Conjugated and Non-Conjugated Compounds. Generally electronic spectroscopy can differentiate conjugated



Lycopene λ_{max} = 505nm

Fig. 2.1

dienes from non-conjugated dienes, conjugated dienes from conjugated trienes, α, β-unsaturated ketones from their β, γ-analogues.

(c) Detection of a Chromophore in an Unknown Compound by Comparison of its Spectrum with that of a Known Compound. Absorption in the near ultraviolet, *i.e.,* above 200 nm is invariably associated with the presence of unsaturated groups or of atoms with unshared pairs of electrons. The saturated hydrocarbons which do not have these structural elements absorbs below 200 nm, a region not of much significance for structural study of organic compounds. Thus, interestingly, a complex steroidal molecule, cholest-4-en-3 one is easily recognised to have an α, β-unsaturated ketone moiety similar to that in mesityl oxide by their spectral resemblance (Fig. 2.2).

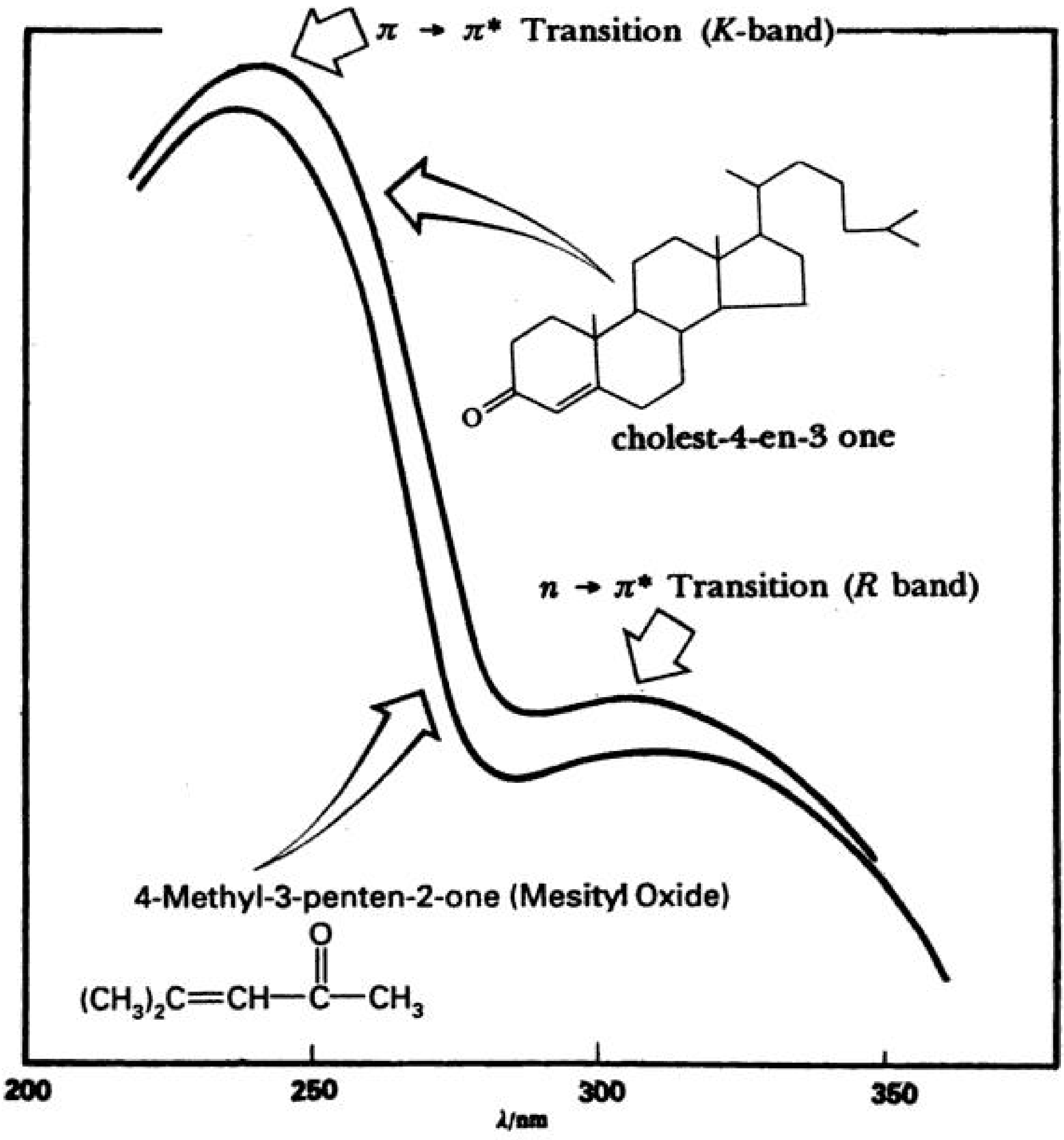
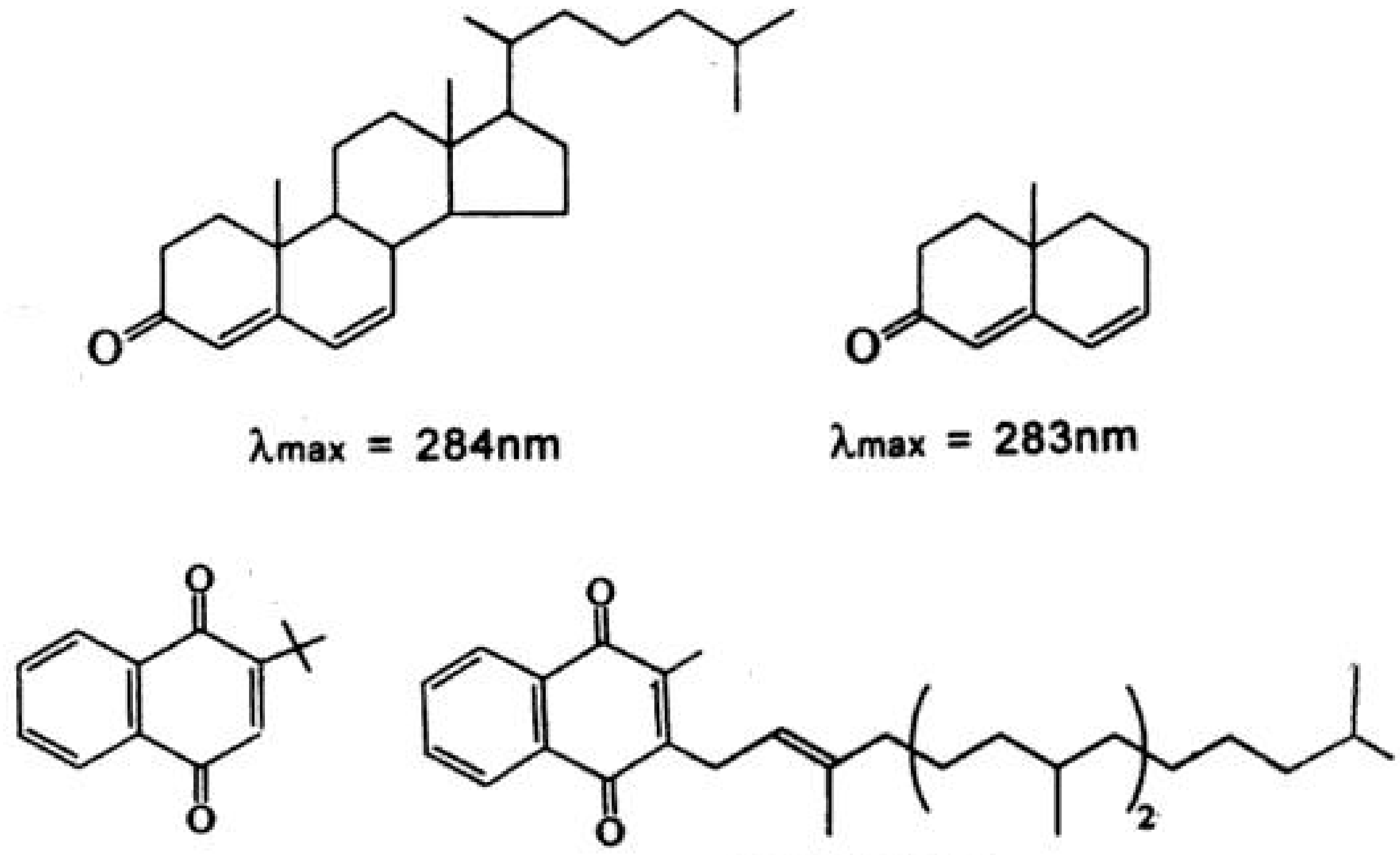


Fig. 2.2

Thus, if the UV spectrum of a known small molecule is comparable with an unknown larger molecule, the two may have the same chromophore (Scheme 2.2c).

The presence of a 1,4-naphthoquinone system was suspected (and then confirmed by other studies) to be present in vitamin K_1 since a model 1,4-naphthoquinone derivative was found to have UV spectrum similar to this vitamin (Scheme 2.2c).



2-*tert*-Butyl-1,4-naphthoquinone

λ_{max} (nm)	ε
249	19,600
260	18,000
325	2,400

Vitamin K_1

λ_{max} (nm)	ε
248	18,600
264	14,200
331	2,730

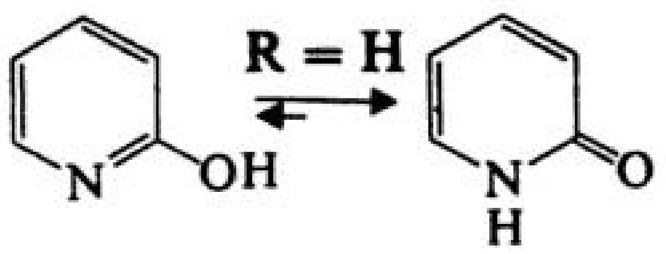
Scheme 2.2c

(d) Identification of a Chromophore (Functional Group). Simple conjugated chromophores, *i.e.,* dienes and α, β-unsaturated ketones have ε values of 10000-20000. The longer simple conjugated systems have principle maxima (usually also the longest wavelength maxima) with correspondingly higher ε values. Low intensity absorption bands around 270-350 nm with ε values of 10-100, are the result of the $n \rightarrow \pi^*$ transition of ketones (Fig. 2.2). In between these extremes, the presence of absorption bands with ε values of 1000-10000 almost always indicate the presence of an aromatic system. Several unsubstituted aromatic systems display bands with these intensities (absorption is the result of a transition with a low transition probability, low because of the symmetry of the ground and excited state). When the aromatic nucleus is substituted with groups which can extend the chromophore, strong bands appear with ε values above 10000, however, bands with ε values below 10000 are generally still present.

(e) Study of Strain. The degree of conjugation may suffer in strained molecules, *i.e.*, loss of π-orbital overlap in 2-substituted diphenyls or acetophenones. Electronic spectroscopy can therefore, be used to know the extent of such strain by correlating the change in spectrum with angular distortion. The position of absorption is also influenced in a systematic way by substituents.

(f) Study of Geometric Isomerism. The *trans* isomer absorbs at a longer wavelength and with a larger molar extinction coefficient than *cis* isomer.

(g) Study of Tautomerism. Ultraviolet spectroscopy can be used to identify stable tautomeric species (Scheme 2.3). 2-Hydroxypyridine (I, R = H); pyrid-2-one (II, R = H) equilibrium has been shown to lie far to the right, *i.e.*, the ultraviolet spectrum of the solution resembles that of a solution of *N*-methylpyrid-2-one (II, R = Me) and is different from that of 2-methoxypyridine (I, R = Me). In this equilibrium (II with an α, β-unsaturated ketone system) predominates. The uv spectrum of the solution is comparable with that of solution of *N*-methyl-pyrid-2-one (II, R = CH_3) and differs from that of 2-methoxypridine (I, R = CH_3).



2-methoxypyridine

R = Me	R = Me	R = H
λ_{max} < 205 nm (ε > 5300) 269 nm (ε 3230)	λ_{max} 226 nm (ε 6100) 297 nm (ε 5700)	λ_{max} 224 nm (ε 7230) 293 nm (ε 5900)

Scheme 2.3

(h) Study of Strutural Features in Different Solvents. The absorption maximum (λ_{max} 290 nm), *i.e.*, the *R*-band shown by chloral hydrate in hexane is not seen in spectrum of the compound measured in aqueous solution to show that structure of the compound $CCl_3.CHO.H_2O$ in hexane changes to $CCl_3CH(OH)_2$ in aqueous medium.

(i) As an Analytical Tool. In suitable cases, the reaction rates and the p*Ka* values can be determined to make UV/Vis spectroscopy a powerful analytical tool.

2.4 SPECTROPHOTOMETER AND SPECTRUM RECORDING

In modern recording spectrophotometers the intensities transmitted by solvent and solution (of the compound in the same solvent) are continuously monitored. The instrument is designed to make a comparison of the intensities of the two beams at each wavelength of the region. If the compound absorbs light at a particular wavelength, the intensity of the sample beam (I_s) will be less than the reference beam (I_R). The instrument thus records a plot of the wavelength of the entire region versus the absorbance (A) of light at each wavelength. The absorbance at a particular wavelength is defined by the equation: $A\lambda = \log (I_R/I_s)$ and such a graph is called an absorption spectrum.

For the visible and near ultraviolet region (750-350 nm). A tungsten filament lamp is used, while below 350 nm the hydrogen gas discharge lamp is a preferred source.

The spectrum below 200 nm is called the vacuum ultraviolet since the molecules of air absorb radiation in this region, air must be absent from the sample and spectrometer to record spectra in this region. Vacuum ultraviolet is, therefore, accessible only with specially, designed instruments. Ultraviolet spectrum is normally recorded with samples dissolved in solvents like water ethanol or hexane which are transparent within the wavelength range used in the study of organic compounds. Cells are normally made of quartz, since glass does not transmit ultraviolet radiation well. The solution cells can have path lengths from 1-10 cm, with 1 cm the most common.

2.5 SPECTRUM, SHIFTS OF BANDS WITH SOLVENTS

(a) The Absorption Band. Absorption bands in an ultraviolet spectrum are typically very broad when compared to an infrared or NMR spectrum. This is because, the energy put into the sample is sufficient to allow a large number of different electronic transitions to occur between the several different allowed vibrational and rotational energy levels of the molecule (Fig. 2.3). No doubt, each transition is quantized, however, the ΔE values are very close, so that complete resolution in the solution phase is not possible. Thus a broad band is displayed which consists of all these overlapped transitions. In the case of simple organic molecules, it is possible to resolve these bands in the gas phase. In other words, if only transitions in electron energy levels were involved the uv/visible spectra for all compounds would consist of fairly sharp lines, *i.e.,* very narrow absorption bands. The absorption of energy leads to electrons, initially in the ground state, moving to an excited state (an energy level of greater energy than ground state). A change in the electronic energy is accompanied by a

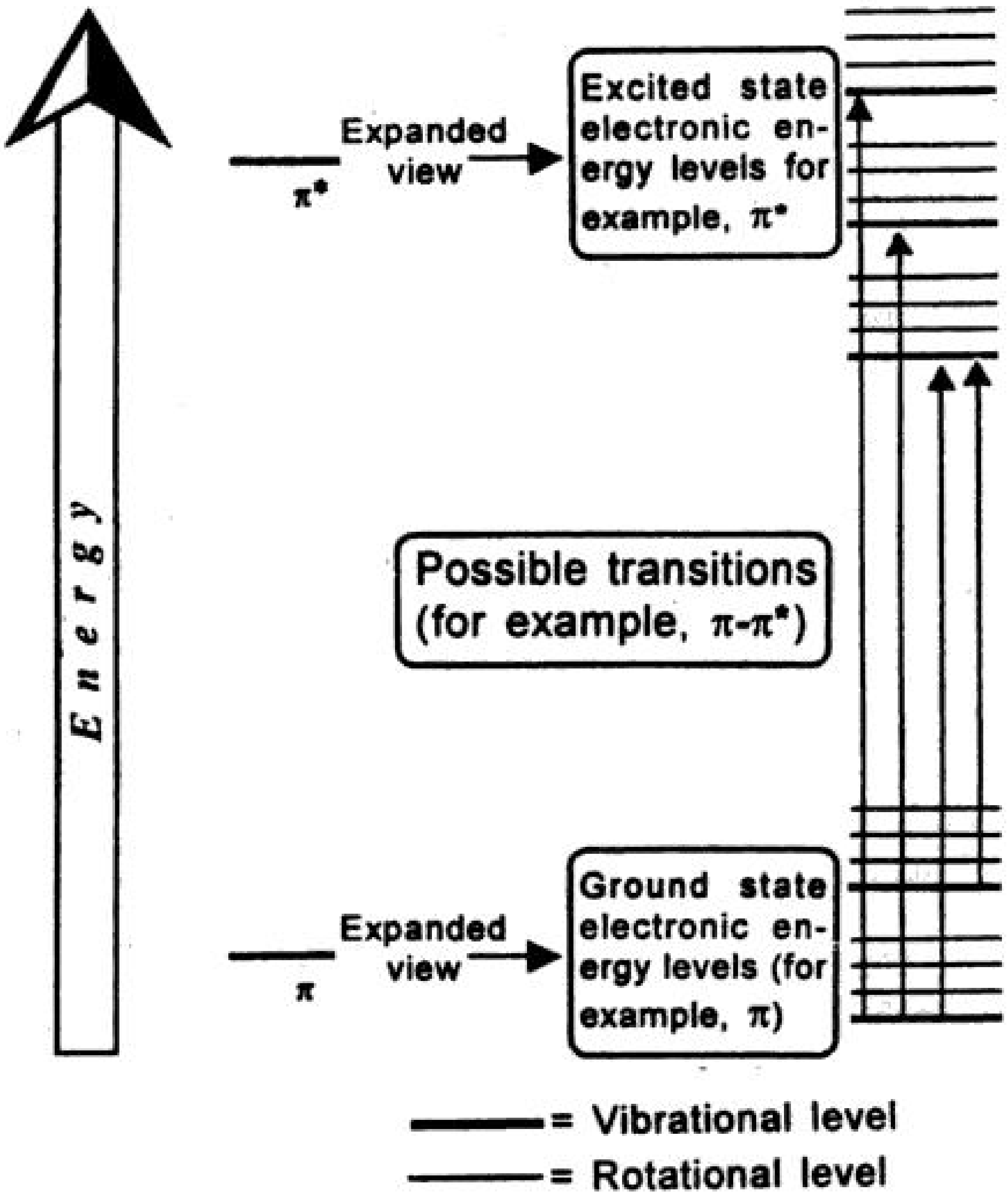


Fig. 2.3

corresponding change in the vibrational and rotational energy levels. The vibrational and rotational energy changes by themselves give rise to infrared absorption spectra. However, when they accompany ultraviolet/visible absorptions a large number of possibilities exist within each electronic state and the individual absorption bands normally become very broad. The energy transition is a change that will actually be from a vibrational energy level in the electronic ground state to one of several vibrational levels within the excited state.

The ultraviolet spectrum of an organic compound is measured from its very dilute solution, *e.g.*, 1 mg of the compound with a molecular weight of 100-200 dissolved in a solvent (which must be transparent within the wavelength range being examined) and made up to say 100 ml. A part of this solution is transferred to a cell which is placed in the spectro-photometer along with a matched cell with pure solvent. Two equal beams of ultraviolet light are passed, one through the solution of the compound and the other through the solvent. The intensities of the transmitted beams are now compared over the entire wavelength range of the instrument.

The ultraviolet spectrum of isoprene (Fig. 2.4) shows a broad absorption band in the region 210-240 nm. The absorption is at its maximum at 222.5 nm, a wavelength which is usually reported; *i.e.*, λ_{max} 222.5 nm, along with the solvent. In addition to this wavelength of maximum absorption (λ_{max}), the strength of the absorption (molar absorptivity), ε_{max} is also reported. The molar absorptivity is the proportionality constant which relates the observed absorbance (A) at a particular wavelength, λ, to the molar concentration, C of the sample and the length, l (in centimeters) of the path of the light beam through the sample cell and this quantitative relation is expressed by the Beer-Lambert equation (Sec. 2.1) which for isoprene comes out to be 10,800. The uv data for isoprene is thus recorded as λ_{max} 222.5 nm (ε = 10,800). Thus, the value of ε is an important information whose value may be worked from the Beer-Lambert law (Sec. 2.1). This equation may be gainfully rewritten as in Scheme 2.3a.

$$\varepsilon = \frac{\text{Absorbance} \times \text{Molecular weight} \times 100}{\text{Weight (mg) of the compound in 100 ml} \times \text{Path length in cm}}$$

Scheme 2.3a

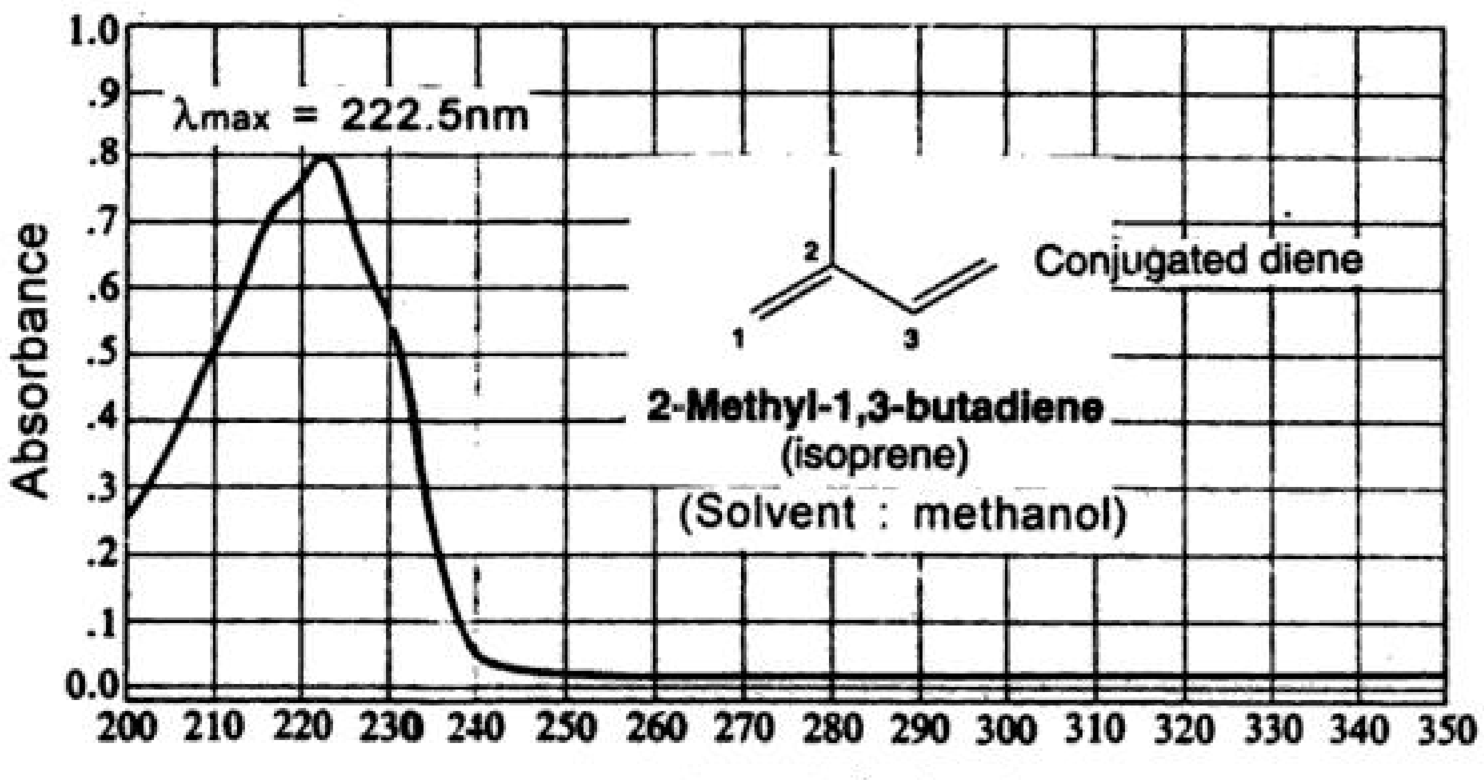


Fig. 2.4

© Sadtler Research laboratories, Division of Bio-Rad Laboratories Inc. 1979.

Thus, if the solution of the compound, *e.g.*, (C_4H_8O, 106 mg) in ethanol (100 ml) in a 1 cm long cell has a λ_{max} 295 nm and corresponding absorbance 0.28, the value of ε comes out to be:

$$\varepsilon = \frac{028 \times 72 \times 100}{106 \times 1} = 19$$

(b) Solvents Used in Ultraviolet Spectroscopy. All molecules have absorption bands (CH_4 125 nm, far uv). Therefore, the solvent must be transparent within the wavelength range being examined. Table 2.1 gives a list of some commonly used solvents, and the minimum wavelength from which they may be used in 1 cm cells.

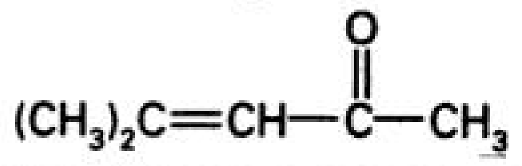
Table 2.1 : *Common Solvents Used in Ultraviolet Spectroscopy*

Solvent	Minimum wavelength for 1 cm cell, nm
Water	190
Cyclohexane	195
Hexane	200
Methanol	200
Ethanol	200
Ether	215
Methylene dichloride	220
Chloroform	240

(c) Shifts of Bands with Solvents. The transitions of polar bonds, like C=O but not ethylene, are affected by solvent polarity. As solvent polarity is increased, π → π* bands undergo red shifts. This is so since excited state is more polar than the ground state and hence stabilisation is greater relative to the ground state in polar solvents. The *n* → π* bands undergo blue shifts, since ground state with two *n* electrons receives greater stabilisation than the excited state with only one *n* electron. These opposite trends are clear by examining the data of mesityl oxide (Table 2.2). There is more on shift of bands with solvents under Section 2.9a.

Table 2.2 : *Effect of Solvent Polarity on the Spectrum of Mesityl Oxide*

Influence of Solvent on the UV λ_{max} and ε_{max} of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Excitations of 4-Methyl-3-penten-2-one (Mesityl Oxide)



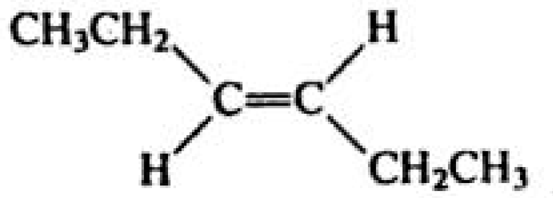
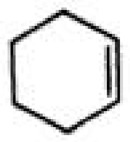
$$(CH_3)_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

Solvent	π → π* (ε)	*n* → π* (ε)
n-hexane	230 (12,600)	327 (98)
Ether	230 (12,600)	326 (96)
Ethanol	237 (12,600)	315 (78)
Water	245 (10,000)	305 (60)

2.6 THE ISOLATED DOUBLE BOND

A π → π* transition can occur in a simple unconjugated alkene like ethene, and other alkenes with isolated double bonds below 200 nm and thus is not readily measured. The alkyl substituents or the ring residues when present on the olefinic carbon atoms shift the absorption band toward, longer waves. A comparison of ethene (no alkyl substituent), 1-octene (one alkyl substitution) and *trans*-2-hexene (two alkyl substituents shows that with increasing alkyl substitution, the wavelength of absorption increase from 171 to 177 to 184 nm (Table 2.3). As might be expected cyclohexene (two ring residues on the olefinic carbons) closely resembles *trans*-2-hexene.

Table 2.3 : *Long Wavelength Absorption Maximum of Unsaturated Hydrocarbons*

STRUCTURE	λ_{max} (*nm*)	ϵ_{max}
$CH_2{=}CH_2$ Ethene	171	15,530
$CH_3(CH_2)_5CH{=}CH_2$ 1-Octene	177	12,600
 *trans*-2-Hexene	184	10,000
 Cyclohexene	182	7,600

Thus, from the wavelength of absorption, one may distinguish between di-, tri- and tetra-substituted double bonds in acyclic and alicyclic systems.

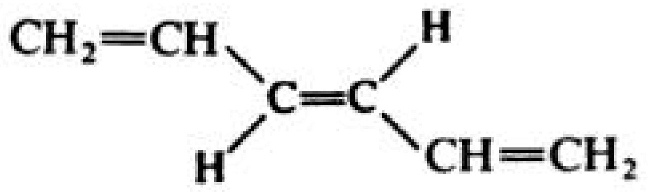
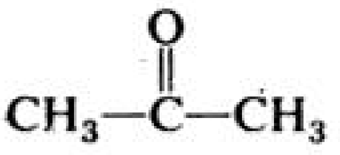
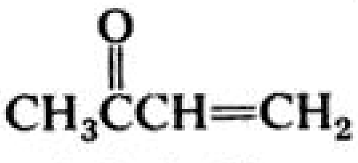
2.7 THE CONJUGATED DOUBLE BOND

Conjugation and UV/vis light absorption

Conjugation leads to lower energy (longer wavelength) $\pi \rightarrow \pi^*$ absorptions which are observable by UV/vis spectrometers. Conjugation is a mechanism to delocalize electrons—***[a way one end of the molecule may "communicate" with the other chemically]***. Electronic spectra give information on the extent of conjugation. Substituents especially those which extend conjugation decrease the HOMO-LUMO energy difference. Most organic compounds which are coloured is due to their small HOMO-LUMO gap so that absorption occurs in visible region.

Conjugation of a double bond with another double bond or a C=O group causes the absorption bands to shift to longer wavelengths with greater intensity (ε_{max}). Thus compared with the parent acyclic diene, 1,3-butadiene which has its principal maximum at 217 nm, the simple triene, *trans*-1,3,5-hexatriene absorbs at 256 nm. Thus each double bond extending the conjugation causes the absorption to occur at longer wavelength by about 40 nm in the lower polyenes (Table 2.4).

Table 2.4 : *Effect of Conjugation on uv Spectra*

STRUCTURE	λ_{max} (*nm*)	ϵ_{max}
$CH_2{=}CH_2$ Ethene	171	15,530
$CH_2{=}CH{-}CH{=}CH_2$ 1,3-Butadiene	217	21,000
 *trans*-1,3,5-Hexatriene	256	50,000
 $CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3$ acetone	187	
	$\pi \longrightarrow \pi^*$ excitations	
 $CH_3\overset{\overset{O}{\|}}{C}CH{=}CH_2$ methyl vinyl ketone	219	

When a molecule absorbs light at its longest wavelength, an electron is excited from its highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In alkenes and alkadienes the highest occupied molecular orbital is a bonding π orbital and the lowest unoccupied molecular orbital is an anti-bonding π* orbital. The wavelength of the absorption maximum depends on the energy difference between these two levels. The energy gap between highest occupied molecular orbital and lowest unoccupied molecular orbital of ethene is greater than that between the corresponding orbitals of 1,3-butadiene. Less energy is therefore, required for $\pi \rightarrow \pi^*$ transition of 1,3-butadiene than similar transition in ethene (Fig. 2.5).

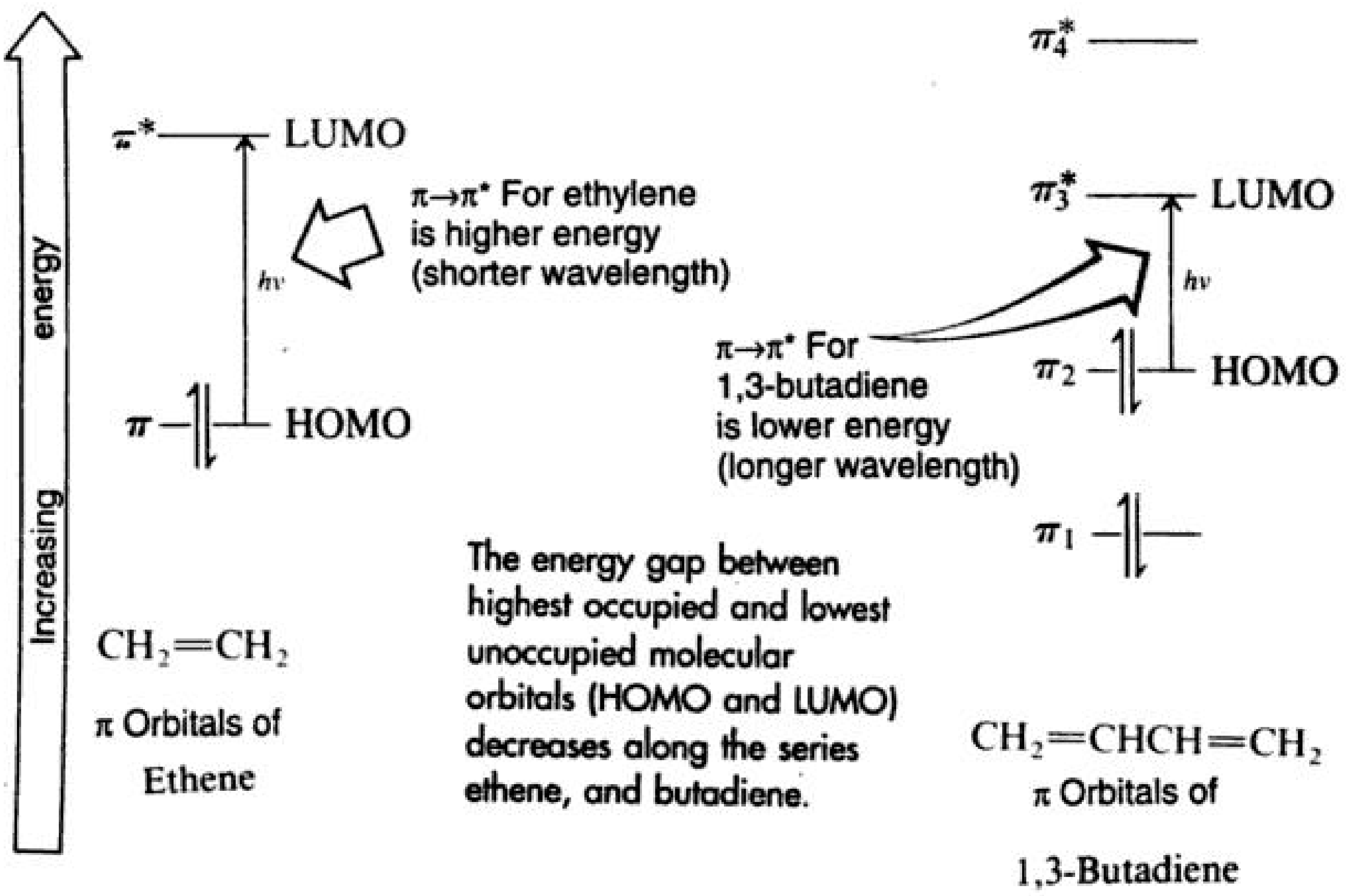
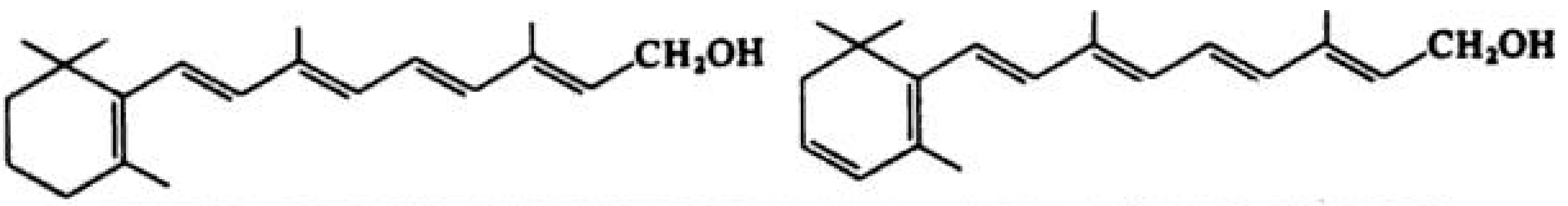


Fig. 2.5

Thus 1,3-butadiene absorbs uv radiation of longer wavelengths (less energy) while ethene requires absorption of light of greater energy (shorter wavelength). On adding more conjugated double bonds to a molecule, the energy required to reach the first excited state even decreases further. Thus, more the number of conjugated double bonds in a compound the longer will be the wavelength at which the compound will absorb light. This is seen by comparing the uv absorption data of vitamins A_1 and A_2, in latter which has an additional double bond in conjugation the position of absorption is at longer wavelength (Scheme 2.4).



Vitamin A_1	Vitamin A_2
λ_{max} =325nm(ε= 51,000)	(has two absorption maxima) λ_{max} =287nm(ε= 22,000) and 351nm (ε=41,000).

Scheme 2.4

Sufficient conjugation shifts the absorption to wavelengths that reach the visible region of the spectrum, *i.e.*, a compound with sufficient conjugation becomes coloured. Lycopene, the compound responsible for the red colour of tomatoes, has eleven conjugated double bonds (Sec. 2.2). Various structural and stereostructural features may effect the absorption of a conjugated diene and some of these factors are presented.

(a) Effect of Geometrical Isomerism and Steric Effects. In compounds where geometrical isomerism is possible *e.g.,* in stilbene, the *E*-isomer (*trans*-stilbene) absorbs at a longer wavelength with greater intensity than *Z*-isomer (*cis*-stilbene) due to steric effects (Scheme 2.5). Coplanarity is needed for the most effective overlap of the π-orbitals and increased ease of the π → π* transition. The *Z*-isomer is forced into a nonplanar conformation due to steric effects.

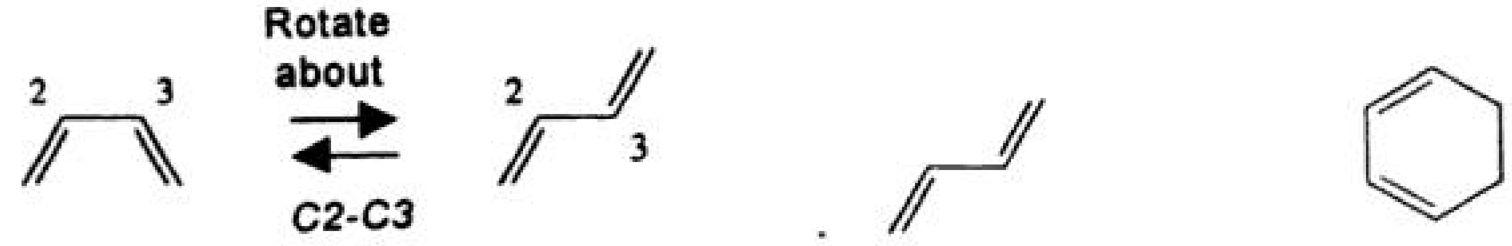
trans-stilbene
λ_{max} = 295nm, ε = 27,000

cis-stilbene
λ_{max} = 280nm, ε = 13,500

Scheme 2.5

As a rough rule of thumb, the greater the distance between the ends of a conjugated chromophore the greater is ε_{max}.

(b) Effect of *S-Cis (Cisoid)* and *S-Trans (Transoid)* Conformations. An acyclic diene largely exists in the preferred *S-trans* (*transoid*) conformation as is so in the case of butadiene (Scheme 2.6). This is so, since most acyclic dienes can rotate about their central single bond to give either a *cisoid* or a *transoid* conformation. When a diene forms a part of a ring



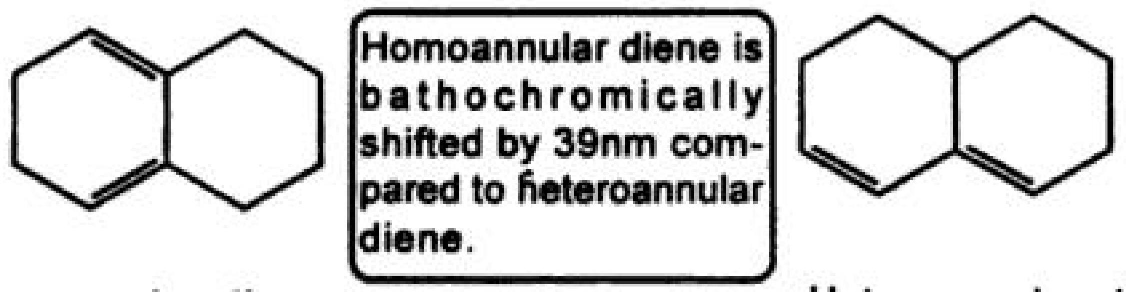
S-cis ~ 2.5% *S-trans* ~ 97.5%
1,3-Butadiene
(*S*=single bond)

1,3-Butadiene
S-trans
λ_{max} = 217nm,
ε = 21,000

1,3-Cyclohexadiene
S-cis
λ_{max} = 256nm,
ε = 8,000

Scheme 2.6

system as in 1,3-cyclohexadiene, it is forced into a (*S-cis*) *cisoid* configuration with far-reaching effects on absorption (Scheme 2.6). The wavelength of absorption is thus shifted towards the longer wavelength region and intensity is lowered in comparison with acyclic dienes. These effects are apparent from the data for 1,3,-butadiene (*S-trans*) and 1,3-cyclohexadiene (*S-cis*). Mono- and poly-cyclic dienes fall into two classes depending on whether the double bonds are in the same ring or in different rings. Members of the first class are called homoannular dienes and have the *S-cis* arrangement their absorption closely resembles 1,3-cyclohexadiene. The heteroannular dienes, the second category are *S-trans* and are spectrally related to butadiene (Scheme 2.7).



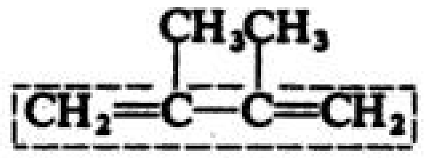
Homoannular diene is bathochromically shifted by 39nm compared to heteroannular diene.

Homoannular diene
(*cisoid* or *s-cis*)
Less intense,
ε = 5,000-15,000
λmax = 273nm

Heteroannular diene
(*transoid or s-trans*)
More intense,
ε = 12,000-28,000
λmax = 234nm

Scheme 2.7

(c) Effect of Alkyl Substitution and Ring Residues. Each alkyl substituent or ring residue attached to the conjugated diene chromophore displaces λ_{max} by about 5 nm toward longer wavelengths. Thus, compared with butadiene (λ_{max}, 217 nm), in 2,3-diemethyl-1, 3-butadiene, the two added methyl groups on C-2 and C-3 of the basic conjugated diene system result in a 5+5 or 10 nm increase in λ_{max} (Scheme 2.7a). In 1,3-pentadiene,



$CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$

2,3-Dimethyl-1,3-butadiene

λ^{calc}_{max}
217 (base value,1,3-butadiene
+ 5 x 2 **[two alkyl substituents]**
227 nm

λ^{obs}_{max} = **226 nm**

$CH_3-CH=CH-CH=CH_2$

1,3-Pentadiene

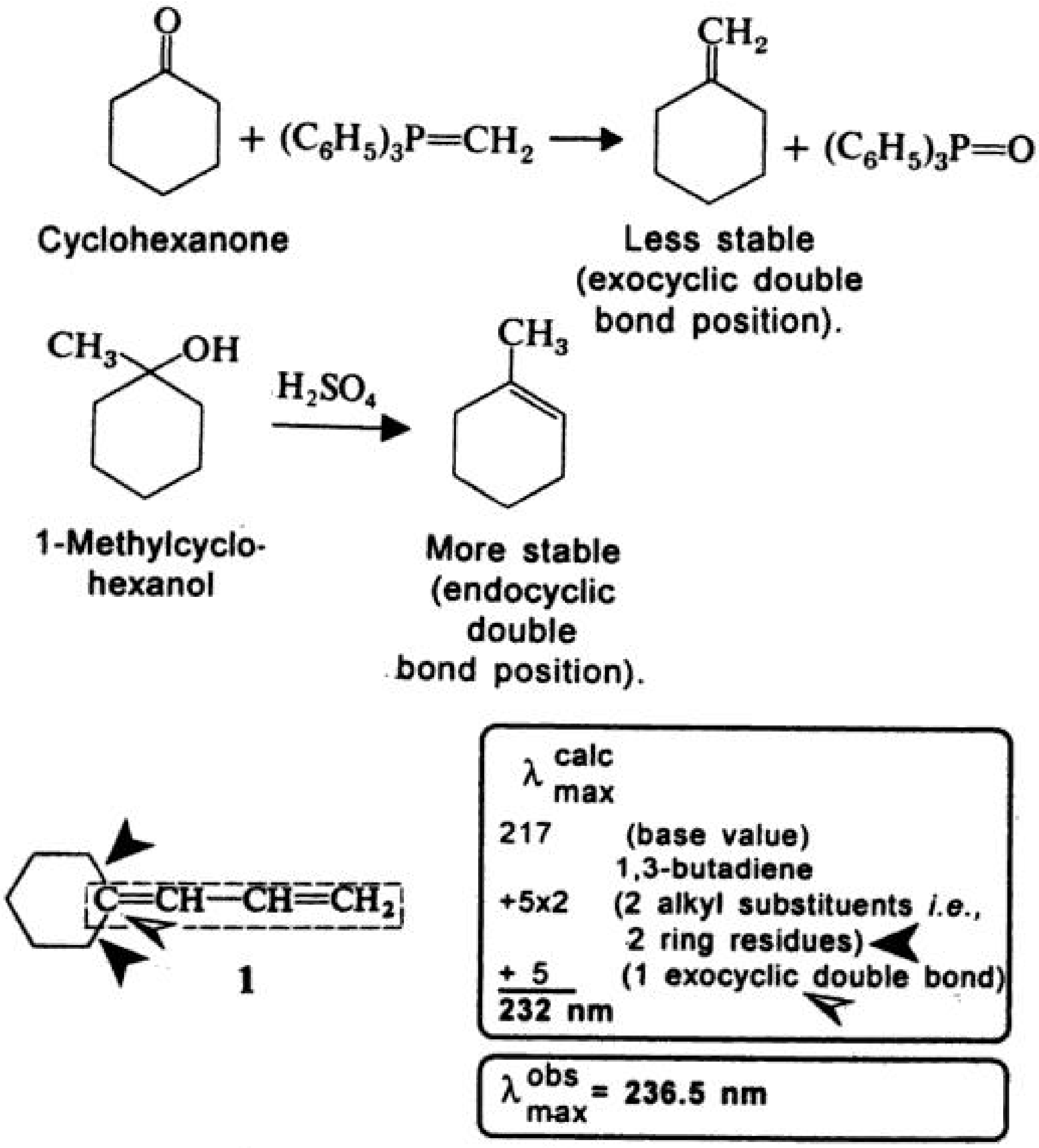
λ^{calc}_{max}
217 (base value,1,3-butadiene
+ 5 (1 alkyl substituent).
222 nm

λ^{obs}_{max} = **223 nm**

Scheme 2.7a

the observed λ_{max} is close to the calculated value. However, the *trans* isomer absorbs at a longer wavelength and with a larger molar extinction coefficient. This is generally true of *cis* and *trans* isomers, and uv spectroscopy is one of the method, that can be used gainfully to confirm the structure of geometric isomers (also see Scheme 2.5). Coplanarity is needed for the most effective overlap of the π orbitals and lower energy of the $\pi \rightarrow \pi^*$ transition. A *cis, i.e., Z* isomer, (unlike the *trans, i.e., E* isomer) adopts a nonplanar conformation due to steric effects.

(d) Effect of Exocyclic Double Bond. In, for example, 1,methylcyclohexene the double bond is inside the ring and it is recognised as the endocyclic position. This stable isomer (more substitution on the double bond) is prepared by the dehydration of 1-methyclohexanol. The less stable isomer has the double bond projecting outside the ring and is recognised as exocyclic position. This less stable isomer is prepared by the Wittig reaction from cyclohexanone (Scheme 2.8). Each exocyclic



λ_{max}^{calc}

217 (base value) 1,3-butadiene

+5x2 (2 alkyl substituents *i.e.*, 2 ring residues)

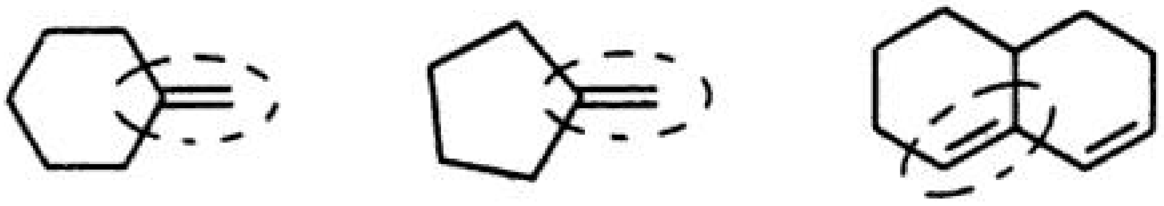
+ 5 (1 exocyclic double bond)

232 nm

λ_{max}^{obs} = 236.5 nm

Scheme 2.8

location of a double bond causes a displacement of the λ_{max} by 5 nm toward longer wavelengths (red shift). The compound 1, may be regarded as 1,3-butadiene derivative in which the two hydrogen atoms of one of the terminal CH_2 group are replaced by two ring residues (these are equal to two alkyl substituents, see fully filled arrows). These ring residues add 2 × 5 nm to the λ_{max}. Since the double bond attached to the cyclohexane is exocyclic (see the half filled arrow), therefore, additional 5 nm must be added. Thus it is important to locate the exocyclic position of a double bond in a compound (Scheme 2.8a).



The double bonds exocyclic to a ring

Scheme 2.8a

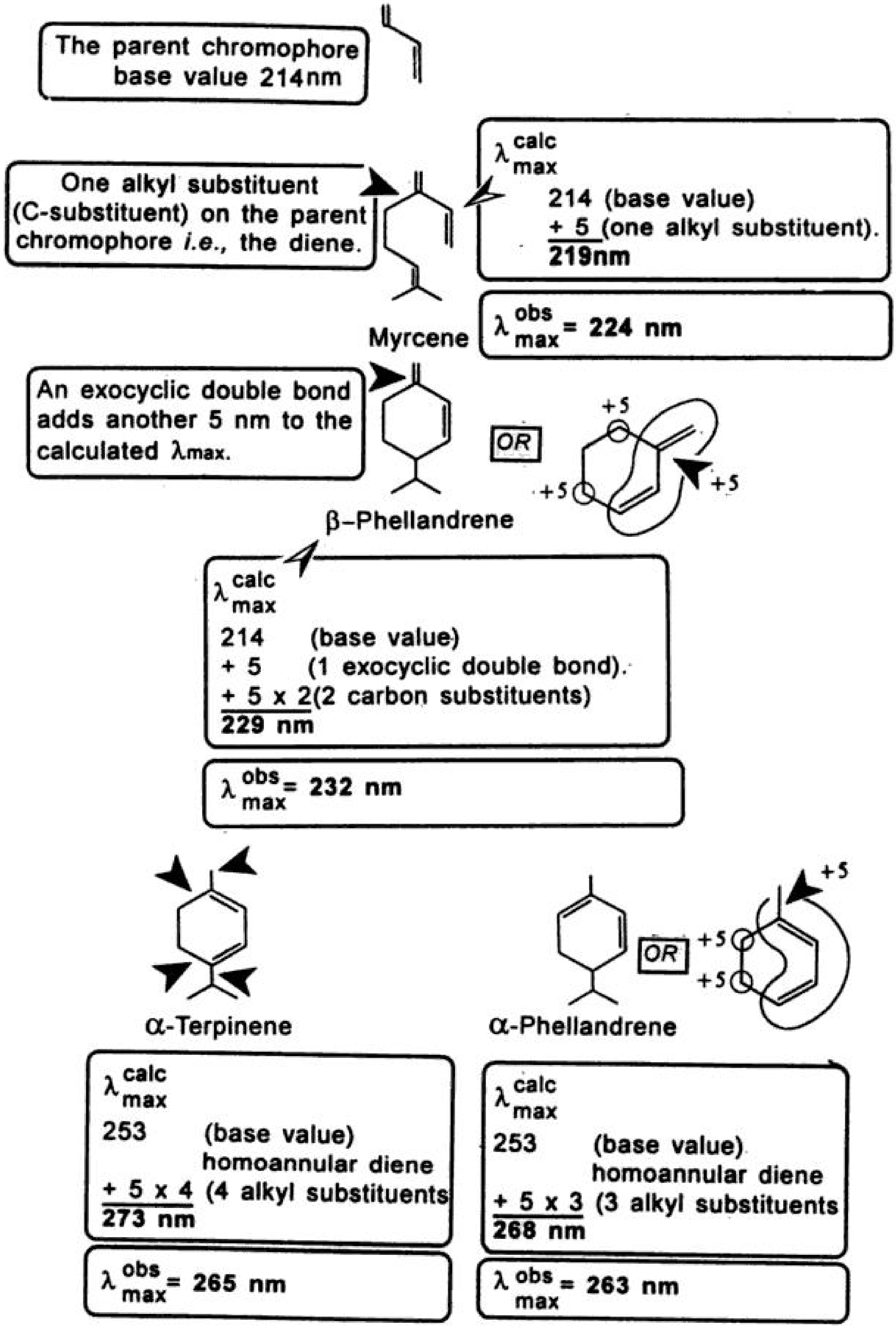
(e) Woodward-Feiser Rules (Calculation of uv Absorption Wavelength in Conjugated Dienes and Trienes). That diene absorption is in fact, influenced by structure in a surprisingly regular way, was appreciated by Woodward. He gave rules for calculating λ_{max}, which in their improved form are due to Feiser and are given in Table 2.5. Note, that unlike the base value of 217 nm used for predicting the λ_{max} values in Schemes (2.7a and 2.8), the Woodward-Fieser rules fix this value (for acyclic and heteroannular dienes) at 214 nm. (Further examples are in Chapter 7).

Table 2.5 : *Woodward and Fieser Rules for Diene and Triene Absorption*

	$\pi \rightarrow \pi^*$ Transition (*K*-band) λ_{max} (nm)
acyclic and heteroannular dienes	214 nm
homoannular dienes	253 nm
Addition for each substituent	
—R alkyl (including part of a carbocyclic ring)	5 nm
—OR alkoxy	6 nm
—Cl,—Br	5 nm
—OCOR acyloxy	0 nm
—CH=CH—additional conjugation	30 nm
if one double bond is exocyclic to one ring	5 nm
if exocyclic to two rings simultaneously	10 nm

Conjugated dienes and trienes (in ethanol) ε_{max} 6000-35000 ($\times 10^{-2}$ m^2 mol^{-1})

The calculated and experimental values of λ_{max} match within ± 5 nm, as shown by the examples (Scheme 2.9). In the case of acyclic diene,



The parent chromophore base value 214nm

One alkyl substituent (C-substituent) on the parent chromophore *i.e.*, the diene.

λ_{max}^{calc}
214 (base value).
+ 5 (one alkyl substituent).
219nm

λ_{max}^{obs} = 224 nm

An exocyclic double bond adds another 5 nm to the calculated λ_{max}.

λ_{max}^{calc}
214 (base value)
+ 5 (1 exocyclic double bond).
+ 5 x 2(2 carbon substituents)
229 nm

λ_{max}^{obs} = 232 nm

λ_{max}^{calc}
253 (base value) homoannular diene
+ 5 x 4 (4 alkyl substituents
273 nm

λ_{max}^{obs} = 265 nm

λ_{max}^{calc}
253 (base value) homoannular diene
+ 5 x 3 (3 alkyl substituents
268 nm

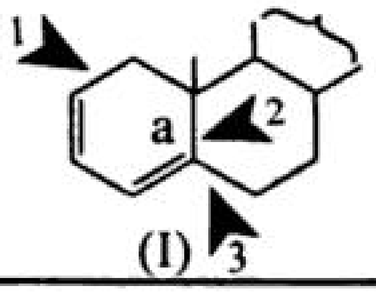
λ_{max}^{obs} = 263 nm

Scheme 2.9

myrcene there is only alkyl *i.e.,* C-substituent on the diene system. On the related monocyclic system β-phellandrene two additional factors need consideration, *i.e.,* now there are two ring residues (carbon substituents) on the diene system and one of the double bond has become exocyclic to the ring. In α-terpinene the diene is homoannular with four carbon substituents on it (shown by arrows) and these are a methyl group, an isopropyl group and two ring residues, while in α-phellandrene there are only three substituents.

Both the dienes (I and II) are homoannular and can be calculated to have a maximum at 273 nm. It may be noted that in (I), Δ^4 bond is exocyclic to ring B while none of the double bonds in (II) has exocyclic position. In (I) one has three ring residues while in (II) there are four ring residues instead, to make the total same in both the cases (Scheme 2.10).

In compounds that contain both homoannular and heteroannular diene systems the calculations are based on the homoannular diene system. When one or two double bonds extend the conjugation, in addition to adding 30 nm for each extension the carbon substituents on the entire conjugated system are taken into account as shown for compounds (IV and IVa, Scheme 2.11):



(I)

λ_{max}^{calc}

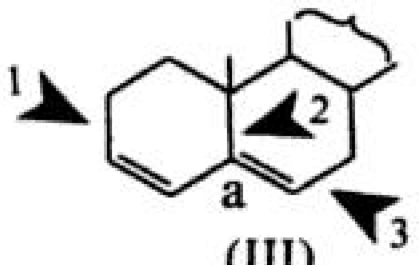
253 (base value) homoannular diene

+15 (3 ring residues,1,2,3, *i.e.,*alkyl substituents).

+ 5 (1 exocyclic double bond,*a*)

273 nm

λ_{max}^{obs} = 275 nm



(III)

λ_{max}^{calc}

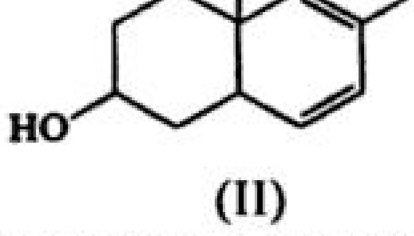
214 (base value) heteroannular diene

+15 (3 ring residues,1,2,3, *i.e.,*alkyl substituents).

+ 5 (1 exocyclic double bond,*a*)

234 nm

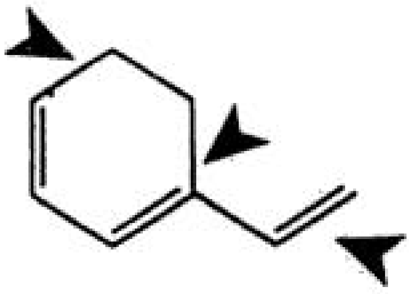
λ_{max}^{obs} = 235 nm



(II)

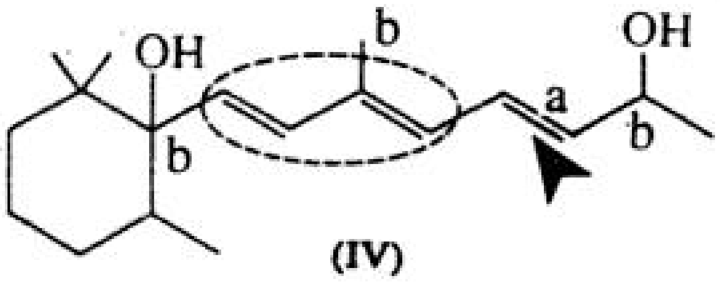
No exocyclic double bond
(the diene has four alkyl substituents.
λ_{max}^{calc} = 273 nm ; λ_{max}^{obs} = 275 nm;

Scheme 2.10



Add 30nm for the additional conjugated double bond to the base value of 214nm of acylic (*s-trans* triene).

Add 30nm for the additional conjugated double bond to the base value of 253nm of *cisoid* cyclic diene. Add also 5 x 2 for two alkyl groups.

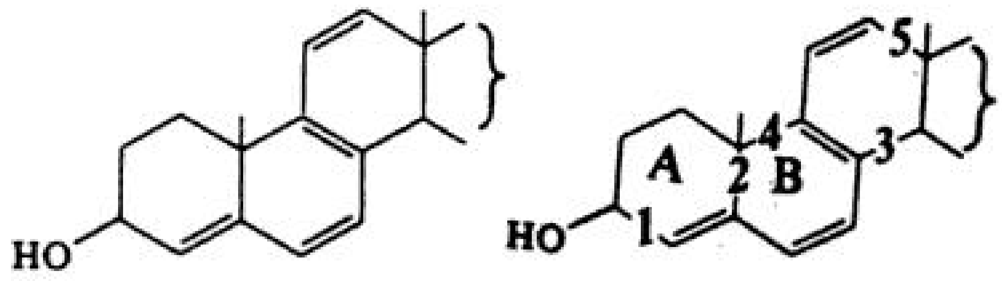


(IV)

λ_{max}^{calc}

Parent (circled)	214
double bond extending conjugation (a)	30
3 alkyl groups (b)	15
	259 nm

λ_{max}^{obs} = 263 nm



(IVa)

- The homoannular diene system in ring B. (Used as the base value).
- Two double bonds extend this conjugation.
- The double bond in ring A is exocyclic to ring B.

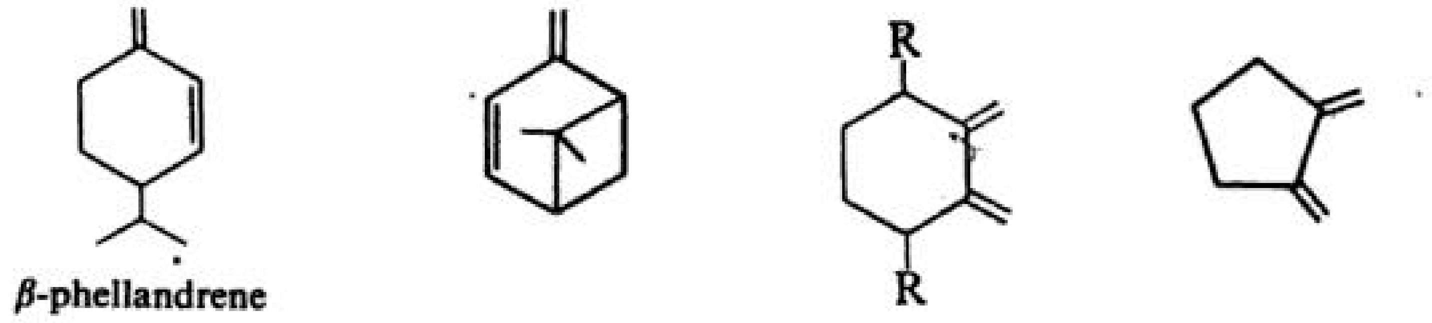
λ_{max}^{calc}

Parent chromophore (*cisoid* diene)	253
Alkyl substituents	5x5
Exocyclic double bond	5
Extended conjugation	2x30
	343nm

λ_{max}^{obs} = 355nm

Scheme 2.11

(f) Effect of Strain Around the Diene Chromophore-Exceptions to Woodward Rules. The Woodward rules for conjugated dienes do not give reliable results if strain is present around the chromophore. Thus compared to β-phellandrene (V) (Sec. 2.7e), the strained molecule verbenene (VI, Scheme 2.12) has an absorption maximum at 245.5 nm, while the calculated value for both is 229 nm. In diene (VII) the distortion of the chromophore, presumably out of planarity with consequent loss of conjugation, causes the maximum to be as low as 220 nm, (ε 10,050). Calculated absorption maximum is, 214 + 2 × 5 (exo) + 2 × 5 (alkyl) = 234. In diene (VIII, Scheme 2.12) however, the coplanarity of the diene is more likely and it gives a maximum at 243 nm (ε15800) to show that this is so, however, it still does not agree with the expected value, *i.e.*, 234 nm (Scheme 2.12).



β-phellandrene

(V) (VI) (VII) (VIII)

R=H
220 (10,050)
R=Me, <220
calcd. 234

Scheme 2.12

Electronic spectra

Ultraviolet and visible spectroscopy allows to estimate the extent of conjugation in a molecule. Peaks in electronic spectra are usually broad and reported as λ_{max} (nm). The relative intensities are given by the molar absorptivity (extinction coefficient ε).

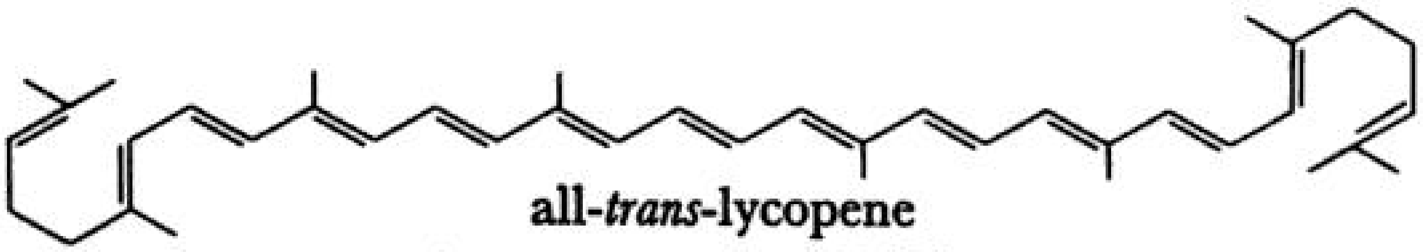
2.8 POLYENES

Among this class mention may be made of plant pigments known as carotenoids which are extended polyenes containing up to eleven conjugated double bonds. The Woodward's rules (Table 2.5) work well only for conjugated systems of 4 double bonds or less. For conjugated polyenes having more than 4, double bonds the Fieser-Kuhn rules (eq. 1) are used (Scheme 2.13). When applied to all *trans*-lycopene, one gets the results shown in eq. 2. In this compound, of the 13 double bonds only 11 are conjugated (n = 11). There are 8 substituents (methyl groups and chain residues on the polyene system (M = 8). Moreover, since in this conjugated polyene system there are no ring systems or exo- and endo-cyclic double bonds

$$\lambda_{\max}(\text{hexane}) = 114 + 5M + n(48{\cdot}0 - 1{\cdot}7n) - 16.5\,\mathrm{R}_{\text{endo}} - 10\mathrm{R}_{\text{exo}} \quad 1$$

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

n = no. of conjugated double bonds
M = no. of alkyl or alkyl-like substituents on the conjugated system
R_{endo} = no. of rings with endocyclic double bonds in the conjugated system
R_{exo} = no. of rings with exocyclic double bonds



all-*trans*-lycopene

$\lambda^{\text{obs}}_{\max}$ 504(170,000); 474(186,000) nm

$$\lambda^{\text{calc}}_{\max} = 114 + 5(8) + 11\,[48.0 - 1.7(11)] - 0 - 0 = 476 \text{ nm} \qquad 2$$

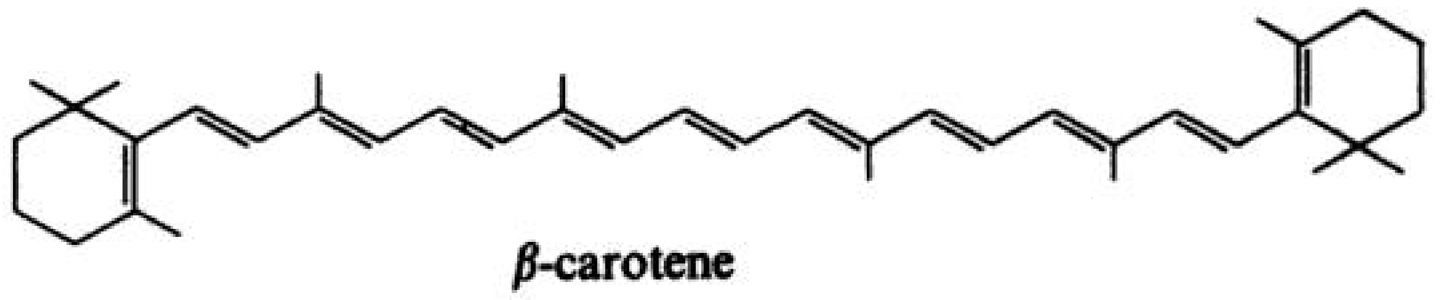
$$\lambda^{\text{obs}}_{\max} = 474 \text{ nm (hexane)}$$

$$\epsilon^{\text{cal.}}_{\max} = 1.74 \times 10^4(11) = 19.1 \times 10^4$$

$$\epsilon^{\text{obs}}_{\max}(\text{hexane}) = 18.6 \times 10^4$$

Scheme 2.13

($\mathrm{R}_{\text{exo}} = \mathrm{R}_{\text{endo}} = 0$). Similar agreement is found for all *trans* β-carotene (Scheme 2.14).



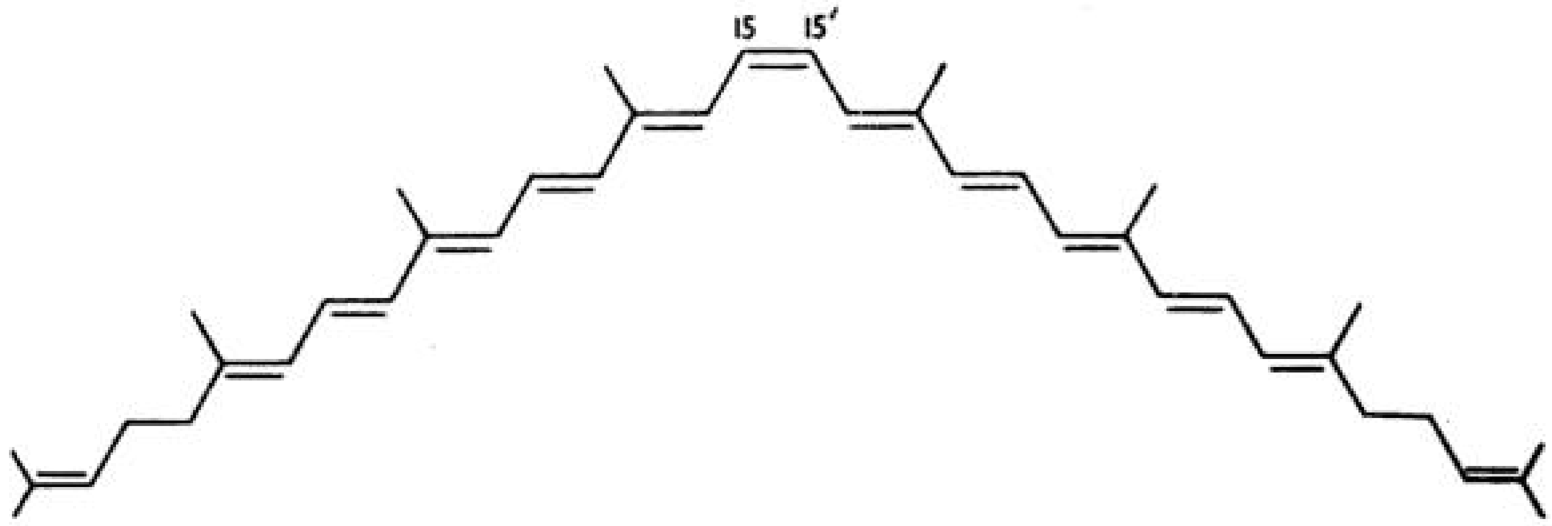
β-carotene

$\lambda^{\text{calc.}}_{\max} = 453.3$ nm $\epsilon^{\text{calc.}}_{\max} = 19.1 \times 10^4$

$\lambda^{\text{obs}}_{\max} = 452$ nm (hexane) $\epsilon^{\text{obs}}_{\max} = 15.2 \times 10^4$

Scheme 2.14

In a long-chain polyene, change from *trans* to *cis* configuration at one or more double bonds lowers both the wavelength and the intensity of the absorption maximum, as seen in the case of neolycopene A, which is stereoisomeric with all *trans*-lycopene. For neolycopene A the predicted maximum is unchanged, however, its spectrum shows an additional band at 361 nm with about one-half the intensity of the visible absorption. This band is obviously associated with the *cis* double bond in the polyene chain which is apparently breaking the conjugation at this point (Scheme 2.15).



neolycopene A

λ_{max}^{obs} 500(100,000); 470(122,000); 361(68,000) nm

Scheme 2.15

2.9 CARBONYL COMPOUNDS

(a) Saturated Carbonyl Compounds. Carbonyl groups show characteristic absorption due to non-bonding electrons on the oxygen atom. These non-bonding electrons are not tightly held as are *pi* electrons and these are, therefore, excited to anti-bonding orbitals by lower energy uv radiation. Saturated ketones and aldehydes show three absorption bands, two of which are observed in the far ultraviolet region (Scheme 2.2a). *A* $\pi \rightarrow \pi^*$ transition absorbs strongly near 150 nm; and $n \rightarrow \sigma^*$ transition absorbs near 190 nm. The third band (*R*-band, $n \rightarrow \pi^*$) appears in the near ultraviolet in the 270-300 nm region. The *R*-band is a weak symmetry forbidden band ($\varepsilon_{max} < 30$) and is due to excitation of an oxygen lone-pair electron to the anti-bonding π-orbital of the carbonyl group. This band is used for identification work (Fig. 2.6).

The introduction of polar substituents, *e.g.*, a halogen on the α-carbon in the case of an aliphatic ketone has no effect of the $n \rightarrow \pi^*$ transition. In the case of cyclic ketones, however, the presence of such substituents raise by 10-30 nm (when axial) or lower by 4-10 nm (when equatorial), the λ_{max} of the parent compound. Thus compared with parent unsubstituted steroid (I) the 6 α-bromo-derivative (II, equatorial Br) shows a decrease in λ_{max}, while the 6 β-epimer (III, axial Br) displays a wavelength shift of +26 nm with intensification of the absorption. The data may provide useful infor-

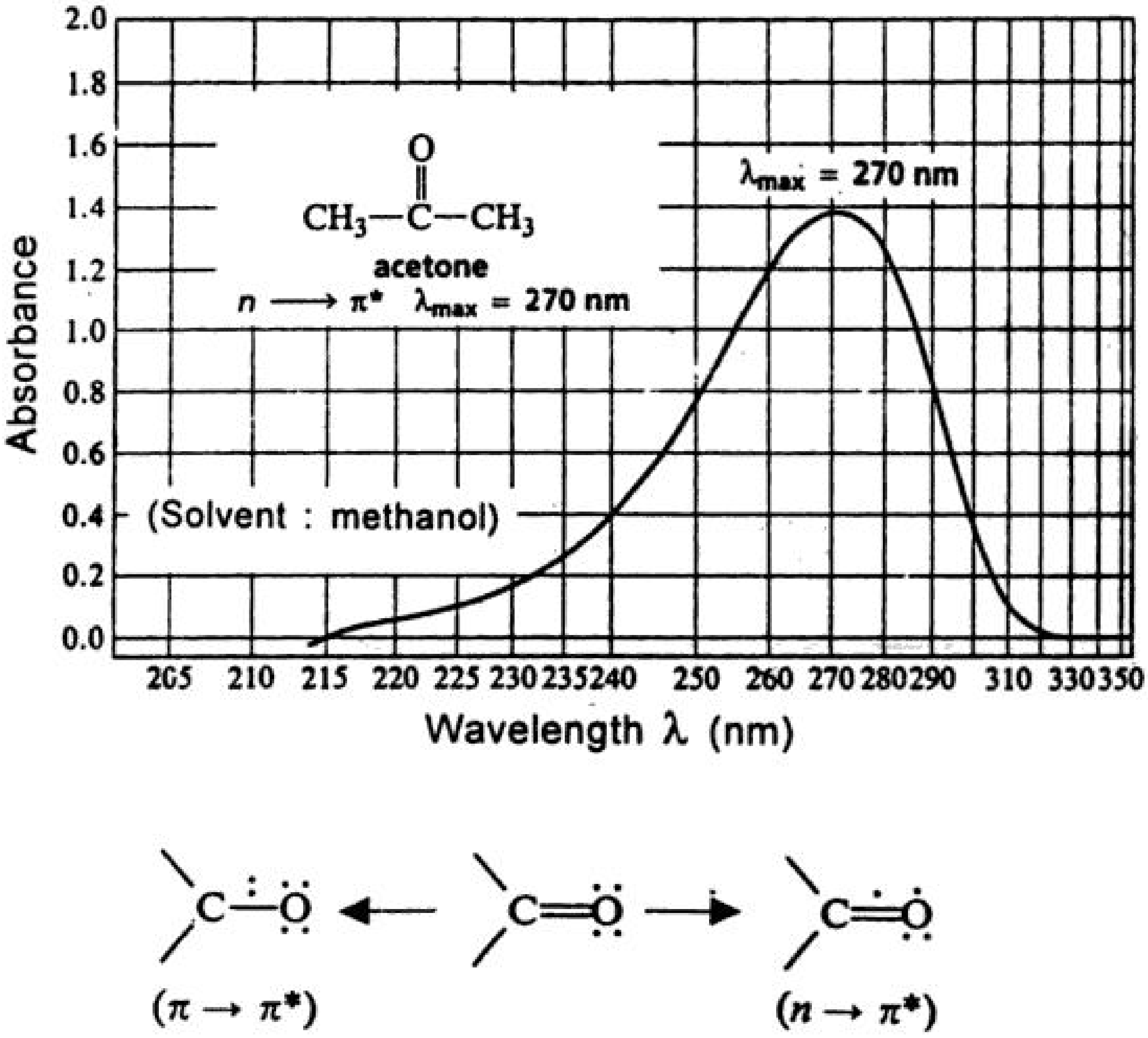
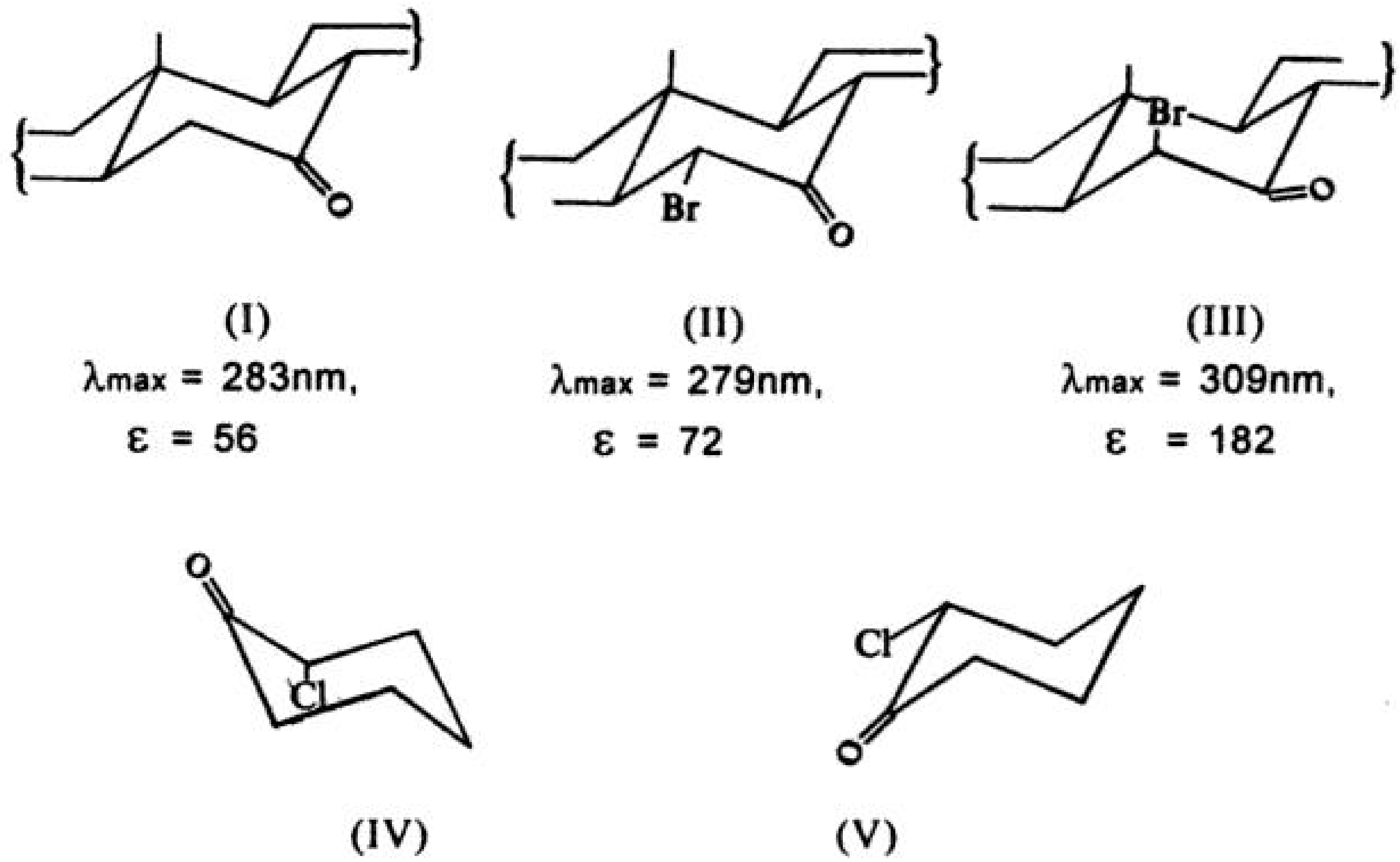


Fig. 2.6

mation to know the preferred conformation in a non-rigid system (Scheme 2.16). Thus 2-chlorocyclohexanone may have either conformation (IV) or (V). Compared with cyclohexanone (λ_{max} 282 nm), 2-chlorocyclo-hexanone absorbs at 293 nm corresponding to a shift of + 11 nm to indicate that the more important conformation is (IV).

When the carbonyl group is substituted by an auxochrome — as in an ester, an acid, or an amide — the π* orbital is raised but the *n* level of the lone-pair is left largely unaltered. As a consequence the $n \rightarrow \pi^*$ transition of these compounds is shifted to shorter wavelengths (200-220nm) range. Thus compared to acetaldehyde λ_{max} 293 nm the *R*-bands of ethylacetate, acetic acid and acetamide are shifted to 207, 204 and 220 nm respectively. The presence, therefore, of a weak band in the 275-295 nm region is positive identification of a ketone or aldehyde carbonyl group.

(b) α, β-Unsaturated Aldehydes and Ketones. Compounds in which carbon-oxygen double bond is conjugated with a carbon-carbon double bond (enones) have their absorption at longer wavelengths due to a decrease in the energy difference between ground and excited states. Thus



(I)
λ_{max} = 283nm,
ε = 56

(II)
λ_{max} = 279nm,
ε = 72

(III)
λ_{max} = 309nm,
ε = 182

(IV)

(V)

Scheme 2.16

---

both the $n \rightarrow \pi^*$ (*R*-band) and $\pi \rightarrow \pi^*$ transitions (*K*-band), for example are at longer wavelengths (lower energies) in 3-buten-2-one (methyl vinyl ketone) than in the non-conjugated acetone (Scheme 2.17). The excited state is relatively more stabilised by conjugation than the ground state, as a result, the magnitude of the energy transition is decreased.

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

acetone
$n \longrightarrow \pi^*$ λ_{max} = 270 nm
$\pi \longrightarrow \pi^*$ λ_{max} = 187 nm

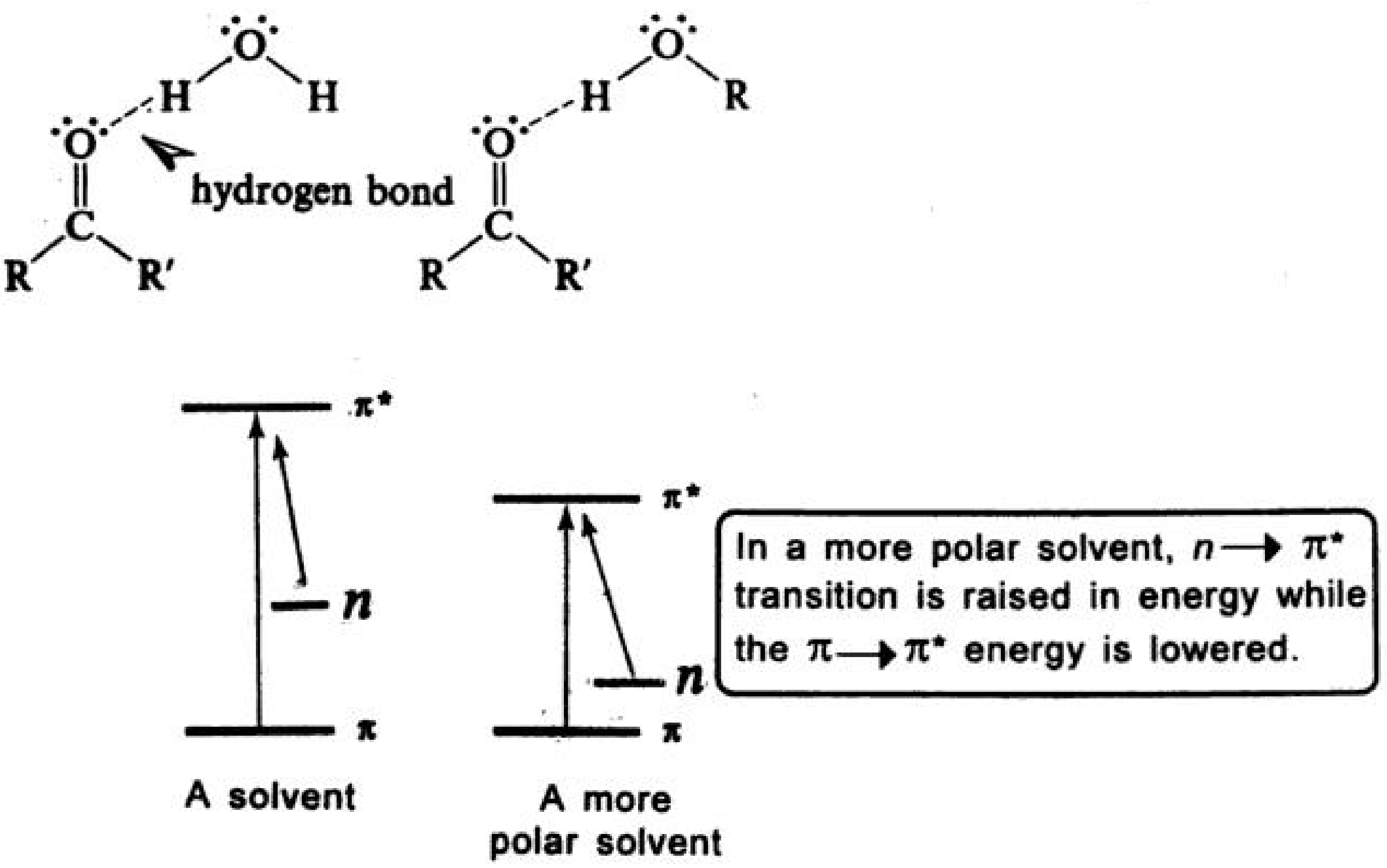
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH=CH_2$

methyl vinyl ketone
$n \longrightarrow \pi^*$ λ_{max} = 324 nm
$\pi \longrightarrow \pi^*$ λ_{max} = 219 nm

Scheme 2.17

The enones can therefore, be easily characterised by an intense absorption band (*K*-band) in the 215-250 nm region (ε_{max} usually 10,000-20,000), and a weak $n \rightarrow \pi^*$ band (*R*-band) at 310-330nm (see Fig. 2.2). The change of solvent polarity effects the wavelength of the transition.

R-bands show a blue shift on increasing the polarity of the solvent (Sec. 2.5 c). Acetone absorbs at 279 nm in *n*-hexane while in water the λ_{max} is at 264.5 nm. One can explain this blue shift on the basis of hydrogen bonding (eq I, Scheme 2.18). When the non-bonded electrons on the oxygen co-ordinate with a hydroxylic solvent, the net energy of the *n*-electrons is lowered. Thus the distance to the π^*-level will be higher and as a result



In a more polar solvent, $n \rightarrow \pi^*$ transition is raised in energy while the $\pi \rightarrow \pi^*$ energy is lowered.

Scheme 2.18

in a polar solvent the $n \rightarrow \pi^*$ transition (the *R*-band) will be of higher energy or lower wavelength (blue shift). The amount of blue shift has been used as a measure to the strength of the hydrogen bond.

The *K*-band, *i.e.*, the $\pi \rightarrow \pi^*$ transition, on the other hand shifts to longer wavelength (lower energy) in a more polar solvent. The polar excited state of the $\pi \rightarrow \pi^*$ transition is stabilised by hydrogen bonding in more polar solvent. This lowers the distance between π and π^*, with a subsequent lowering in the energy or raising the wavelength of the transition. The data for the α, β-unsaturated ketone, mesityl oxide are given in Table 2.2.

The Woodward rules (Table 2.6) again can be used to calculate the position of intense $\pi \rightarrow \pi^*$ transition (*K*-band) not the weak $n \rightarrow \pi^*$ transition (*R*-band) for α, β-unsaturated carbonyl compounds.

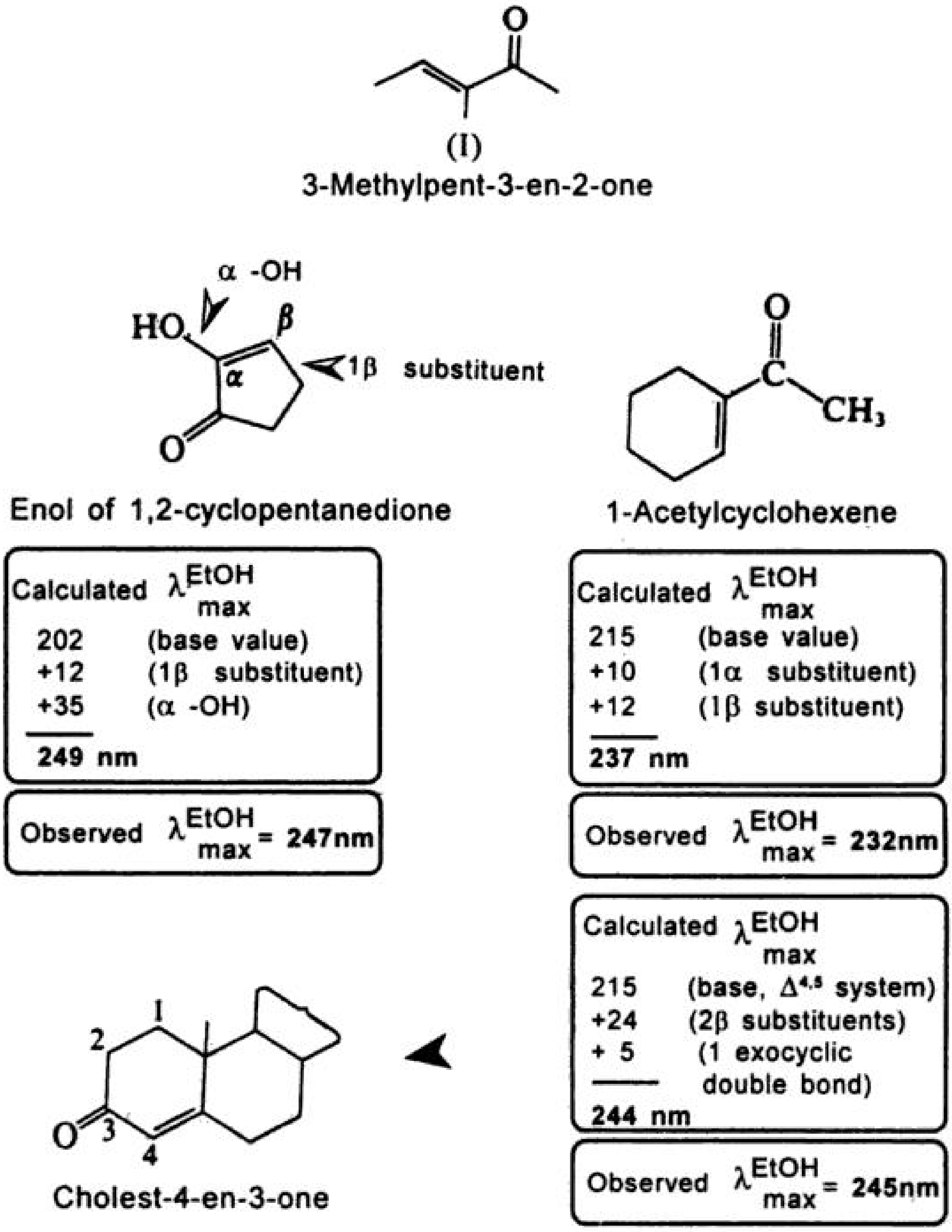
The λ_{max} for a $\pi \rightarrow \pi^*$ absorption band in the UV spectrum of compound (I, Scheme 2.19) is calculated as below. The base value is 215 nm; for one α-alkyl group add 10 nm, for one β-alkyl group add 12 nm; the total is 215 + 10 + 12 = 237 nm. This is within 1 nm of the observed value (for which ε_{max} is 4600). If the spectrum is recorded in water, λ_{max} would move to 245 nm, *i.e.*, $\pi \rightarrow \pi^*$ bands undergo a red shift. A few other examples which serve to illustrate the application of these rules to a variety of α, β-unsaturated carbonyl compounds are presented (Scheme 2.19, also see problems in Chapter 7).

Table 2.6 : *Rules for α, β-Unsaturated Aldehydes and Ketones*

λ_{max} for $\pi \rightarrow \pi^*$ transitions ε_{max} 4500-20,000 ($\times 10^{-2} m^2 mol^{-1}$)
αβ-Unsaturated carbonyl compounds (in ethanol)

Value assigned to					
ketones $-\overset{\beta}{\overset{\mid}{C}}=\overset{\alpha}{\overset{\mid}{C}}-CO-$	acyclic or 6-ring cyclic		215 nm		
	5-ring cyclic		202 nm		
aldehydes $-\overset{\mid}{C}=\overset{\mid}{C}-CHO$			210 nm		
acids and esters $-\overset{\mid}{C}=\overset{\mid}{C}-CO_2H(R)$			197 nm		
extended conjugation $-\overset{\delta}{\overset{\mid}{C}}=\overset{\gamma}{\overset{\mid}{C}}-\overset{\beta}{\overset{\mid}{C}}=\overset{\alpha}{\overset{\mid}{C}}-CO$ - etc.			add 30 nm		
homodiene component			add 39 nm		
Increments for		α	β	γ	δ
—R alkyl (including part of a carbocylic ring)		10 nm	12 nm	18 nm	18 nm
—OR alkoxy		35 nm	30 nm	17 nm	31 nm
—OH hydroxy		35 nm	30 nm	30 nm	50 nm
—SR thioether		—	80 nm	—	—
—Cl chloro		15 nm	12 nm	12 nm	12 nm
—Br bromo		25 nm	30 nm	25 nm	25 nm
—OCOR acyloxy		6 nm	6 nm	6 nm	6 nm
$-NH_2, -NHR, -NR_2$ amino		—	95 nm	—	—
if one double bond is exocyclic to one ring			5 nm		
If exocyclic to two rings simultaneously			10 nm		
"Estimated" λ_{max}^{EtOH}		Total	______		
solvent shifts					
methanol	0				
chloroform	– 1 nm				
dioxan	– 5 nm				
diethyl ether	– 7 nm				
hexane	– 11 nm				
cyclohexane	– 11 nm				
water	+8 nm				

When cross-conjugation (α, β-unsaturation on both sides of carbonyl group) is present in a compound then the value of maximum absorption is calculated by considering the most highly substituted conjugated system,



(I)
3-Methylpent-3-en-2-one

Enol of 1,2-cyclopentanedione

Calculated λ_{max}^{EtOH}
202 (base value)
+12 (1β substituent)
+35 (α -OH)
249 nm

Observed λ_{max}^{EtOH} = 247nm

1-Acetylcyclohexene

Calculated λ_{max}^{EtOH}
215 (base value)
+10 (1α substituent)
+12 (1β substituent)
237 nm

Observed λ_{max}^{EtOH} = 232nm

Cholest-4-en-3-one

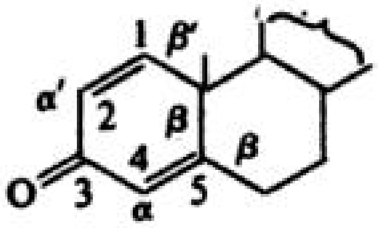
Calculated λ_{max}^{EtOH}
215 (base, $\Delta^{4,5}$ system)
+24 (2β substituents)
+ 5 (1 exocyclic double bond)
244 nm

Observed λ_{max}^{EtOH} = 245nm

Scheme 2.19

i.e., the more active monoenone chromophore. Thus, in the case of structure (I, Scheme 2.20) the calculations do not take into account the 1,2-double bond or the β group on it. The uv spectroscopy is, therefore, of value in distinguishing the structure (I) and (II). The extended dienone (II) absorbs fully 30 nm to longer waves. In the case of compound (I) the calculations taking into account the $\Delta^{1,2}$ system on the other hand gives 227 nm as the predicted value (Scheme 2.20).

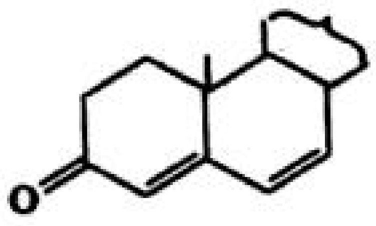
(c) Effects of Solvent Polarity. Since carbonyl compounds are polar, α, β-unsaturated carbonyl compounds show two different shifts; the π → π*



(I)
Cholesta-1,4-dien-3-one

Calculated λ_{max}^{EtOH}
215 (base, Δ^4-system)
+24 (2β substituents)
+ 5 (1 exocyclic double bond)
———
244 nm

Observed λ_{max}^{EtOH} = 245 nm



(II)

Calculated λ_{max}^{EtOH} = 280 nm

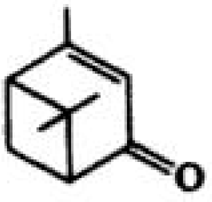
Observed λ_{max}^{EtOH} = 284 nm

Scheme 2.20

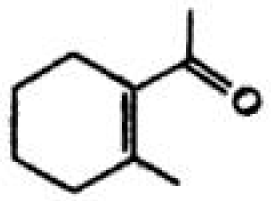
band (*K*-band) moves to longer wavelength (bathochromic, *i.e.*, red shift) while the $n \rightarrow \pi^*$ band (*R*-band) moves to shorter wavelength (hypsochromic, *i.e.*, blue shift).

(d) Effect of Structure-Strain-Steric Effect in Biphenyls and Chromophore Distortion. UV spectroscopy is highly sensitive to distortion of the chromophore whether it is brought about by ring strain or by steric hindrance. This spectroscopic technique can thus be used with advantage to demonstrate that distortion is present in a molecule. This is reflected in a marked decrease in intensity and may also lead to either a blue or a red shift of the absorption maximum.

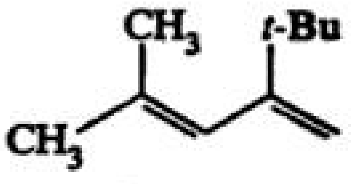
Verbenone III is calculated to have a maximum at 239 nm but actually shows a maximum at 253 nm, *i.e.*, and increment for strain of 14 nm. Compound IV displays its *K*-band at the predicted wavelength but with greatly decreased intensity. The steric hindrance in IV prevents coplanarity (Scheme 2.21).



(III)
Verbenone

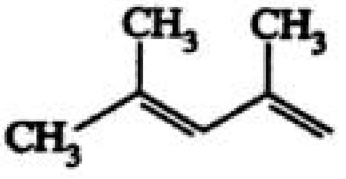


(IV)
λ_{max} = 243nm,
ε = 1400



λ_{max}^{EtOH} 225
ϵ_{max}^{EtOH} 6400

A



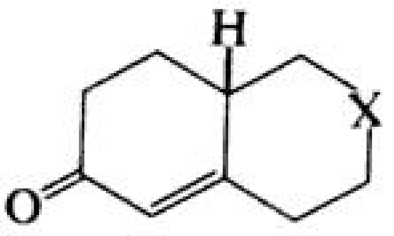
231
10,000

Scheme 2.21

Similarly, a nonbonded steric interaction between CH_3 and *tert*-butyl in (A, Scheme 2.21) is more effective than a nonbonded CH_3 and CH_3 interaction in destabilising the s-trans conformation. In the *tert*-butyl analogue, conjugation is inhibited by rotation about the sp^2-sp^2 C—C bond to give a twisted diene.

Another example of steric hindrance to conjugation is found in biphenyls. In biphenyl itself the two aromatic rings are in conjugation, the resonance energy is maximum when the rings are coplanar and will be zero when the rings are held at 90° to each other. When coplanarity and therefore, maximum π overlap of the two rings in biphenyl is severely sterically inhibited, the biphenyl derivative behaves more like the sum of the two independent aromatic chromophores (See problem 17).

(e) Non-Conjugated Interacting Chromophores. Normally the non-conjugated systems do not effect each other, as seen, *e.g.*, in the case of compound (I, Sec. 2.9, b) where cross-conjugation was successfully ignored while calculating the absorption maximum. Interestingly, however, several cases of non-conjugated interactions are known. The unsaturated ketones A display their $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions shifted in opposite directions when X becomes more electronegative. Presumably the π^* orbital is raised by transannular interaction with the $>N^+Me_2$ group, however, as the n electron is closer to the $>N^+Me_2$ group in the excited state than in the ground state, the $n \rightarrow \pi^*$ transition is of lower energy (Scheme 2.22).



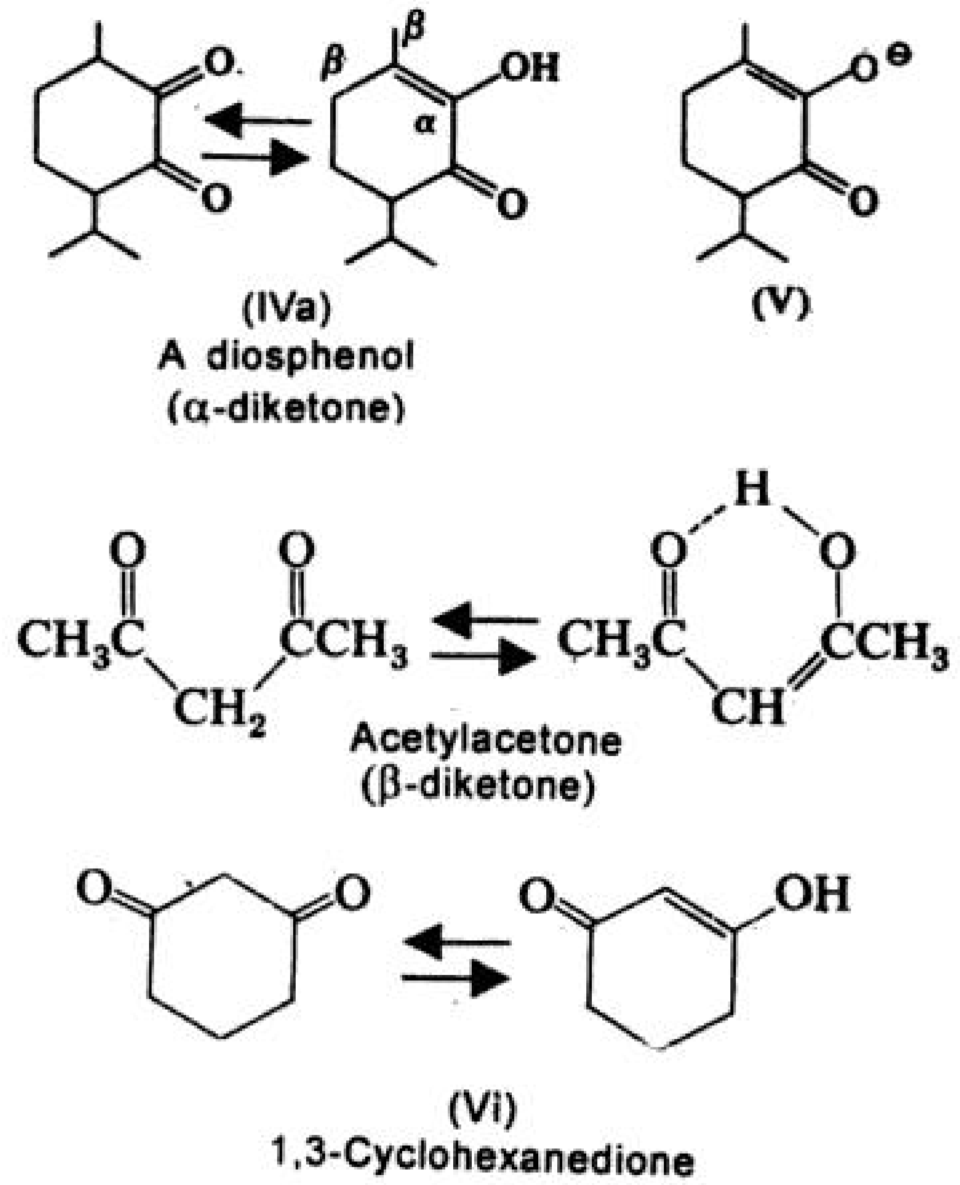
A

X	λ_{max}	
$>CH_2$	238 nm	308.5 nm
$>\overset{+}{N}Me_2$	229 nm	318.5 nm

Scheme 2.22

(f) Dicarbonyl Compounds. In cyclic α-diketones, the enolic form is generally more stable than the keto form and therefore, the absorption is related to that of an α, β-unsaturated carbonyl system. Six-membered cyclic α-diketones (IV a) known generally as diosphenols, exist in solution largely in the enolised form. In strong alkaline solution the absorption shifts to about 50 nm to longer waves, due to the formation of the enolate ion, *e.g.*, (V) to enable diosphenol structures to be characterised (Scheme 2.23).

Likewise, β-diketones are often encountered in the enolic form as seen in the case of acetylacetone. This compound exists in the enolic form to



Calculated λ^{EtOH}_{max}
215 (base value)
+24 (2β substituents)
+35 (α -OH)
274 nm

Observed $\lambda^{EtOH}_{max} = 270$ nm

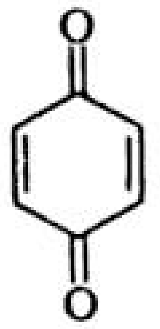
Observed $\lambda^{Isooctane}_{max} = 272$ nm
$\varepsilon = 12000$
Observed $\lambda^{H_2O}_{max} = 274$ nm
$\varepsilon = 2050$

Calculated λ^{EtOH}_{max}
215 (base value)
+12 (1β substituent)
+20 (β-OH)
257 nm

Observed $\lambda^{EtOH}_{max} = 255$ nm

Scheme 2.23

the extent of about 90% in solution in non-polar solvents and the absorption directly depends on the concentration of the enol tautomer. However, in the case of acetylacetone agreement with the calculated wavelength (257 nm) is indifferent. This may be due to the fact that the strong internal hydrogen bond forces the carbonyl group and the double bond into a configuration different from that which is present in cyclic structures, *e.g.*, in diosphenol. Cyclohexane-1,3-dione in cyclohexane (a hydrocarbon solvent) displays a weak absorption near 290 nm ($\varepsilon_{max} \sim 50$), but in ethanol it has λ_{max} 280 nm (ε_{max} 20,000). The diketone can show the equilibrium Scheme 2.23). In the hydrocarbon solvent the equilibrium lies towards the diketo form which displays itself by exhibiting the weak $\lambda_{max} = 295$ nm $n \rightarrow \pi^*$ absorption. The β-hydroxyenone tautomer is favoured in the presence of polar protic solvent and this form has the expected λ_{max} as calculated by the Woodward-Fieser rules (Scheme 2.33). Deprotonation of this enol gives the enolate anion which shows more intense absorption and at longer wavelengths than the enolic form. The formation of enolate ion in alkaline solution in these cases also shifts the strong absorption band, *e.g.*, in acetylacetone to 293 nm. Quinones represent α-, or vinylogous α-diketones. The spectrum of *p*-benzoquinone is thus found to be similar with that of a typical α, β-unsaturated ketone with the strong *K*-band appearing at 242 nm and a weak *R*-band near 434 nm (Scheme 2.24). The colour of the simpler members is due to the weak *n* → π* transition which is also present in α-diketones. The *n* → π* transitions of α-diketones in the diketo form gives rise to two bands one in the usual region near 290 nm (ε ~ 30) and a second (ε 10-30) which stretches into the visible 340-440 nm region to give yellow colour to some of these compounds.



$$\lambda_{max}^{hexane} = 242 \text{ nm } (\varepsilon\ 24\,000) \leftarrow \pi \rightarrow \pi^* \ K\text{-band}$$

$$\left.\begin{array}{l}281 \text{ nm } (\varepsilon\ 400)\\ 434 \text{ nm } (\varepsilon\ 20)\end{array}\right\} \leftarrow n \rightarrow \pi^* \ R\text{-band}$$

Scheme 2.24

2.10 AROMATIC SYSTEMS — BENZENE AND ITS SUBSTITUTION DERIVATIVES

Benzene (I) shows three absorption bands (Solid line, Fig. 2.7) at 184 nm (ε_{max} 60,000); 203.5 nm (ε_{max} 7400, often called *K*-band) and at 254 nm (ε_{max} 204, often called *B*-band). The intense band near 180 nm is a result of an allowed transition, while the weaker *K* and *B* bands near 200 and 260 nm respectively result from forbidden transitions in the highly symmetrical benzene molecule.

The *B*-band of benzene and many of its homologues show a great deal of fine structure in the vapour phase or in non-polar solvents. The fine structure originates from sub-levels of vibrational absorption upon which the electronic absorption is superimposed.

When the spectrum is determined in polar solvents, interactions occur between solute and solvent which tend to reduce the fine structure. The presence of fine structure similar to that shown in (Fig. 2.7) is indicative of the simple aromatic molecules. When benzene is substituted by simple alkyl groups the absorptions are shifted slightly to longer wavelength (Scheme 2.25) and the fine structure remains intact.

This small bathochromic shift is ascribed to hyperconjugation between the alkyl group and π system of the ring (Scheme 2.25). The second alkyl group is most effective in producing a red shift if it is in the *para* position. The *para* isomer absorbs at the longest wavelength whereas the *ortho* isomer generally absorbs at the shortest wavelength. This effect is due to steric interaction between the *ortho* substituents, which effectively

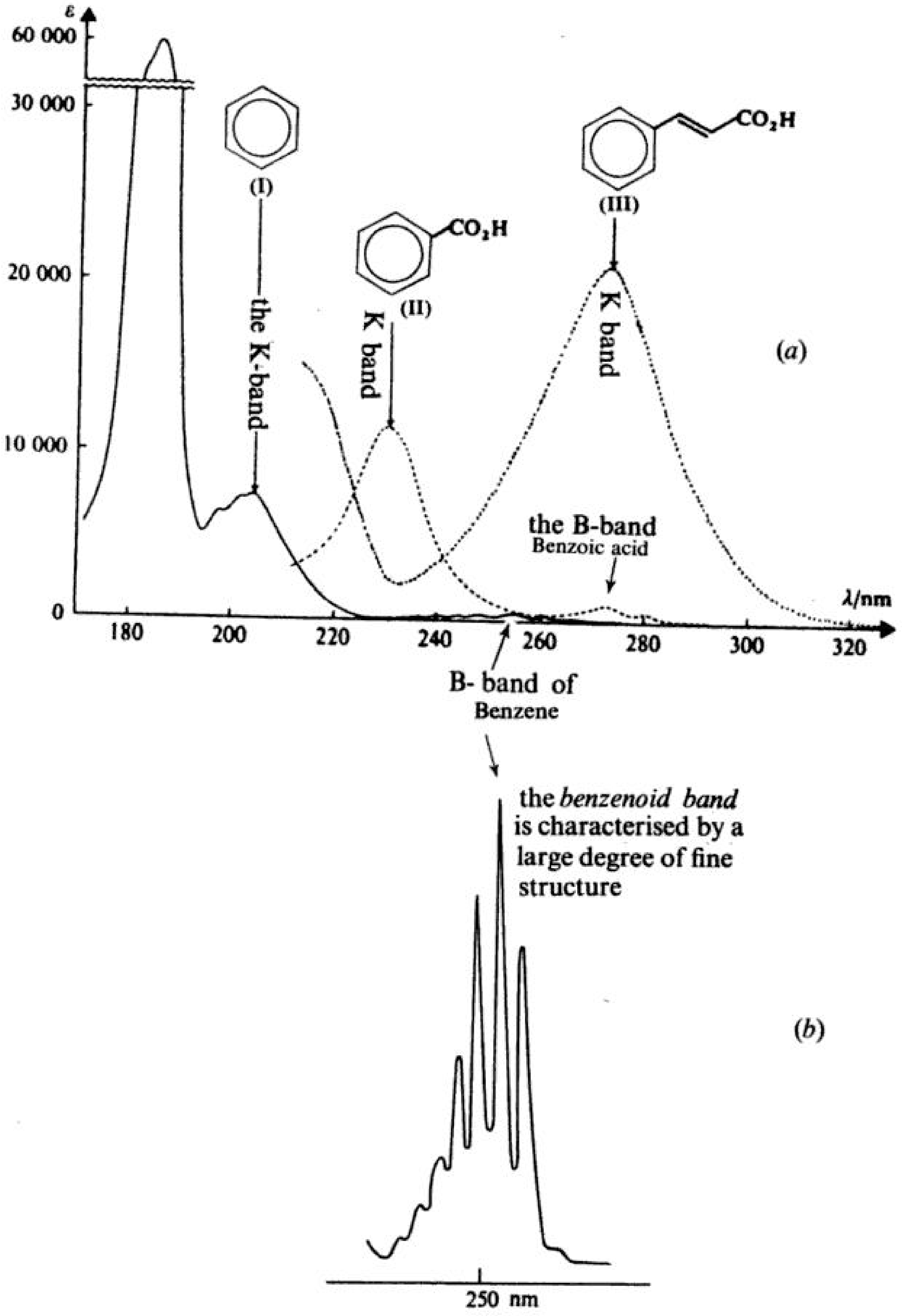
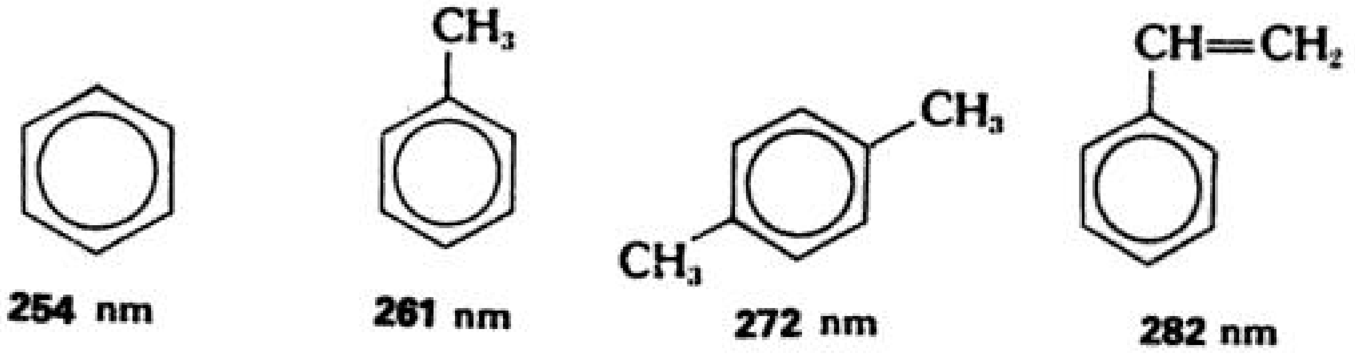
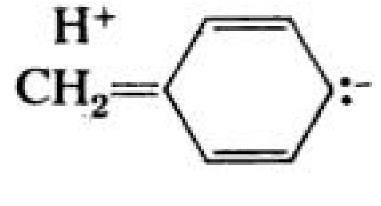


Fig. 2.7

Figure 2.6a, reproduced with permission from D.H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill 1988.)



Long-wavelength electronic absorption maxima the *B*-band *for some aromatic hydrocarbons*



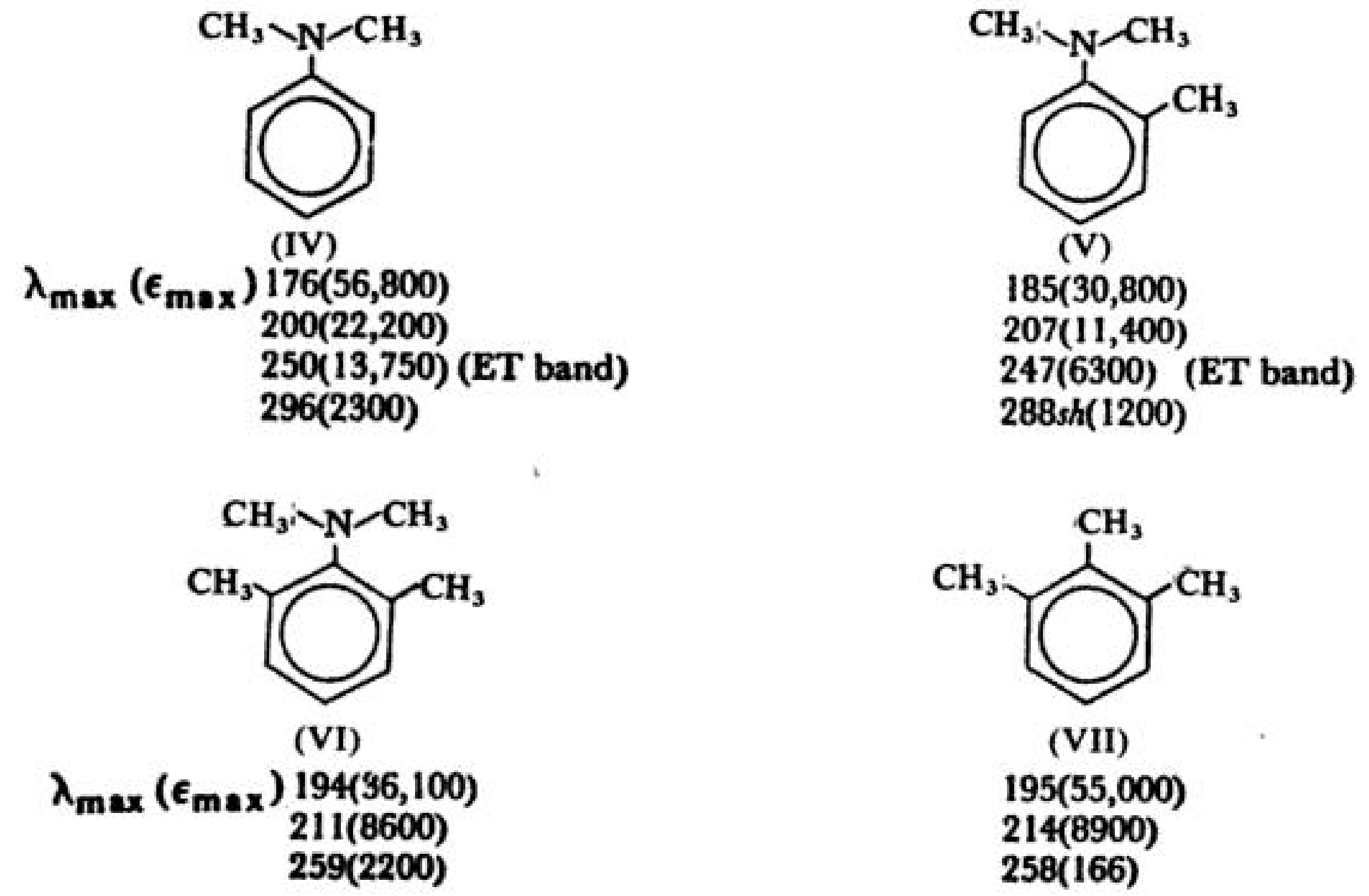
Scheme 2.25

reduce hyperconjugation. When however, non-bonding pair substituents (—OH, —NH_2, —OR, etc.) are present on the benzene ring (Table 2.7) the absorptions are shifted substantially to longer wavelengths and the fine structure of the *B*-band is either seriously diminished or wholly eliminated, because of *n* - π conjugation. When the heteroatom is attached to the benzene ring, the interaction between the non-bonding electron pair (s) on it and the π electrons of the ring is most effective when the *p* orbital of the non-bonding electrons lies parallel to the π orbitals of the ring. This arrangement is seriously disturbed due to twisting in sterically crowded molecules, *e.g.*, by the presence of bulky substitution in the *ortho* position of the molecule like dimethylaniline IV (Scheme 2.26). The absorption of dimethylaniline IV above 170 nm shows four distinct bands. Those at 176,200 and 296 nm are essentially transitions of the aromatic electrons while the fourth band, near 250 nm is due to electron transfer. The intensity of the band due to electron transfer (E.T.) is thus reduced to half in V while this band is eliminated altogether in VI. The residual absorption shown by VI constitutes the usual transitions of an aromatic system which closely resembles that of the alkyl benzene VII.

A reference to Fig. 2.7 and Table 2.7 shows how the wavelength and intensity of the absorptions peaks increase with an increase in the extent of the chromophore. On adding more and more conjugation to the benzene ring, the *K*-band (at 203.5 nm in benzene) effectively 'moves' to longer wavelength, faster than the *B*-band. Thus benzoic acid shows the *K*-band at 230 nm the *B*-band being still clearly visible at 273 nm, however, with the longer chromophore of cinnamic acid the *K*-band shifts to 273 nm and the *B*-band is completely enveloped.

Table 2.7: *λ_{max} of the substituted benzene rings Ph-R*

R	λ_{max}^{EtOH}, nm and (ε_{max})					
	the *K*-band		the *B*-band			
—H	203.5	(7400)	254	(204)		
—Cl	209.5	(7400)	263.5	(190)		
—OH	210.5	(6200)	270	(1450)		
—OMe	217	(6400)	269	(1480)		
—CN	224	(13000)	271	(1000)		
$—CO_2^-$	224	(8700)	268	(560)		
$—CO_2H$	230	(11600)	273	(970)		
$—NH_2$	230	(8600)	280	(1430)		
$—O^-$	235	(9400)	287	(2600)		
—COMe	245.5	(9800)				
$—CH{=}CH_2$	248	(14000)	282	(750)	291	(500)
—CHO	249.5	(11400)				
—Ph	251.5	(18300)				
—OPh	255	(11000)	272	(2000)	278	(1800)
$—NO_2$	268.5	(7800)				
$—CH{=}CHCO_2H$	273	(21000)				
$—CH{=}CHPh$	295.5	(29000)				



(IV)
λ_{max} (ϵ_{max}) 176(56,800)
200(22,200)
250(13,750) (ET band)
296(2300)

(V)
185(30,800)
207(11,400)
247(6300) (ET band)
288*sh*(1200)

(VI)
λ_{max} (ϵ_{max}) 194(36,100)
211(8600)
259(2200)

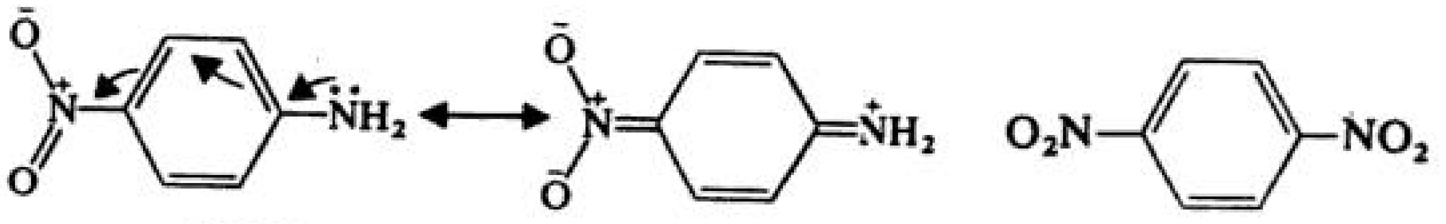
(VII)
195(55,000)
214(8900)
258(166)

Scheme 2.26

In the case of disubstituted benzenes, when electronically complementary group, *i.e.*, an amino and a nitro are situated *para* to each other as in VIII, a pronounced red shift in the main absorption band, *i.e.*, *K*-band is observed (Table 2.8). This effect of the presence of an electron donating and electron attracting groups *para* to one another leads to the extension of the chromophore through the benzene ring as shown in (VIII Scheme 2.27). This extension of the chromophore is not possible when these groups are located *ortho* or *meta* to each other or if the *para* disposed groups are not complementary as in IX. In these cases the spectrum displays close resemblance with the separate non-interacting chromophores.

Table 2.8 : *Absorption Characteristics of Disubstituted Benzenes*

Compound	$\pi \to \pi^*$ Transition *K*-band	
	λ_{max}	ε_{max}
o-NO_2 Phenol	279	6,600
m-NO_2 Phenol	274	6,000
p-NO_2 Phenol	318	10,000
o-NO_2 Aniline	283	5,400
m-NO_2 Aniline	280	4,800
p-NO_2 Aniline	381	13,500



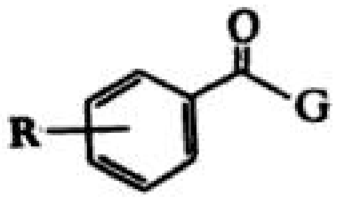
VIII
obs. λmax = 381nm

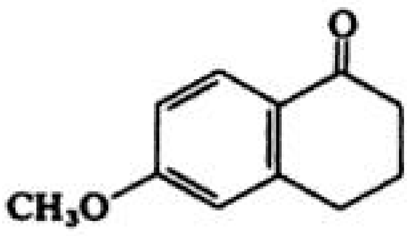
IX
261 nm

Scheme 2.27

Some quantitative assessments have been made (Table 2.9) in the case of substituted benzenes of the type R-C_6H_4-COG when the electron donating group is complemented by an electron withdrawing carbonyl group with regard to the principal band. This is explained by the use of values of table to the compounds X and XI (Scheme 2.28). Often naturally occurring aromatic compounds have a complex substitution pattern and the rules given in Table 2.9 are then of great value to assign structure. The fungal metabolic griseofulvin provides an example of this type, which contains two separate chromophores, *i.e.*, an α, β-unsaturated ketone chromophore and a substituted benzene (aromatic) chromophore. The spectrum of the dihydroderivative displays a strong band at 290 nm (ε_{max} 22,000), a weaker peak at 324 nm (ε_{max} 5300), and a shoulder near 250 nm (ε_{max} 21,000), all of which must be connected with the aromatic chromophore. The absorption of the isolated carbonyl group being negligible. The calculated

Table 2.9 : *Rules For the Principal Band of Substituted Benzene Derivatives*

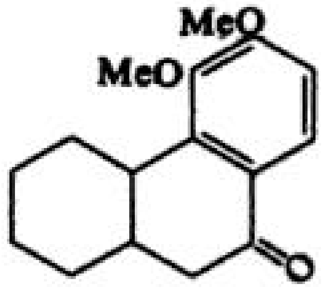
$R—C_6H_4—COG$		Calc. λ_{max}^{EtOH} *nm*
Parent chromophore:		
G = alkyl or ring residue and R = H		246
G = H and R = H		250
G = OH or O Alkyl and R = H		230
Add for R:		
alkyl or ring residue	*o,m*	3
	p	10
-OH, -OMe, -O-alkyl	*o,m*	7
	p	25
O^-	*o*	11
	m	20
	p	78
Cl	*o,m*	0
	p	10
Br	*o,m*	2
	p	15
NH_2	*o,m*	13
	p	58
NHAc	*o,m*	20
	p	45
NHMe	*p*	73
NMe_2	*o,m*	20
	p	85



(X)

Parent value 246 nm
Ortho **alkyl** 3 nm
Para **methoxyl** 25 nm

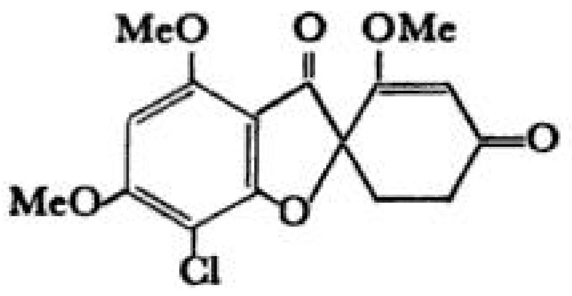
Calc: λ_{max}^{EtOH} = 274 nm Obs: λ_{max}^{EtOH} = 276 nm



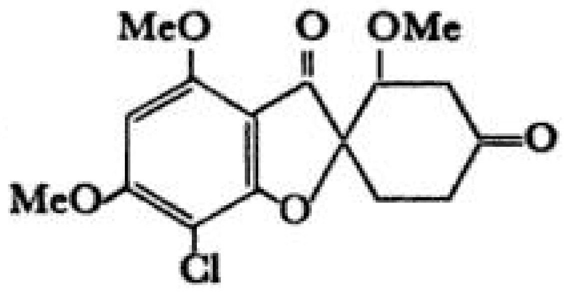
(XI)

Calc.: λ_{max}^{EtOH} = 246 + 25 + 7 + 3
= 281 nm

Obs.: λ_{max}^{EtOH} = 278 nm



griseofulvin



dihydro-derivative

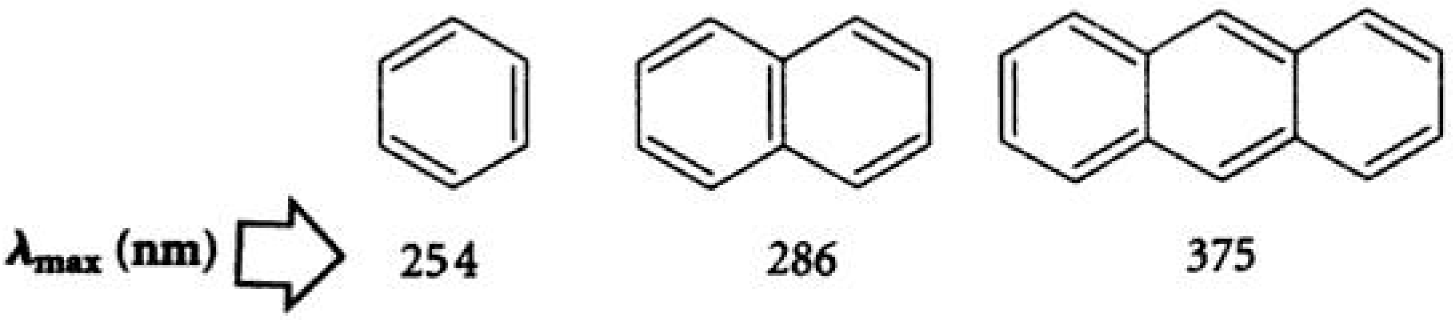
Scheme 2.28

wavelength is 246 (parent chromophore) + 2 × 7 (*o*-O Alkyl) + 0(*m*-Cl)) +25 (*p*-OCH_3) = 285 nm in agreement with the observation of an intense band at 290 nm. In griseofulvin the aromatic bands occur in essentially the same position but as expected there is additional absorption near 252 nm (ε_{max} 13,000) dut to the α, β-unsaturated ketone chromophore. The calculated λ_{max} is 257 nm. Thus the spectrum of griseofulvin is in complete accord with the assigned structure.

The values of Table 2.9 are valid only in the absence of steric hindrance to coplanarity.

2.11 POLYCYCLIC-AROMATIC HYDROCARBONS

The spectra of these compounds are highly complicated, but are uniquely characteristic of each aromatic system and thus provide useful fingerprints for identification purposes (Fig. 2.8). The introduction of relatively non-polar substituents like alkyl or acetoxyl groups have little influence on λ_{max} or ε_{max}. Thus, methylanthracenes are readily recognised to have the anthracene chromophore by a comparison of their uv spectra. As the number of condensed rings increases the absorption moves progressively to longer wavelengths (Scheme 2.29) until it occurs in the visible region, *e.g.*, in the case of pentacene λ_{max} 580 nm (blue) five benzene rings joined in a linear fashion.



Scheme 2.29

2.12 HETEROAROMATIC COMPOUNDS

Broadly speaking the spectra of heteroaromatic compounds are similar with their corresponding hydrocarbons. The absorptions of 5-membered ring heteroaromatic compounds are thus compared with that of cyclopentadiene (intense absorption near 200 nm and moderately intense absorption near 238 nm), and pyrrole, *e.g.*, displays comparable adsorption data λ_{max} 209 nm, ε_{max} 6,730 and λ_{max} 240 nm, ε_{max} 300.

Similarly the spectrum of pyridine is comparable with that of benzene, the only difference being that the *B*-band of pyridine is more intense with somewhat diminished fine structure. This transition is allowed for pyridine but forbidden for the more symmetrical benzene molecule. An increase in

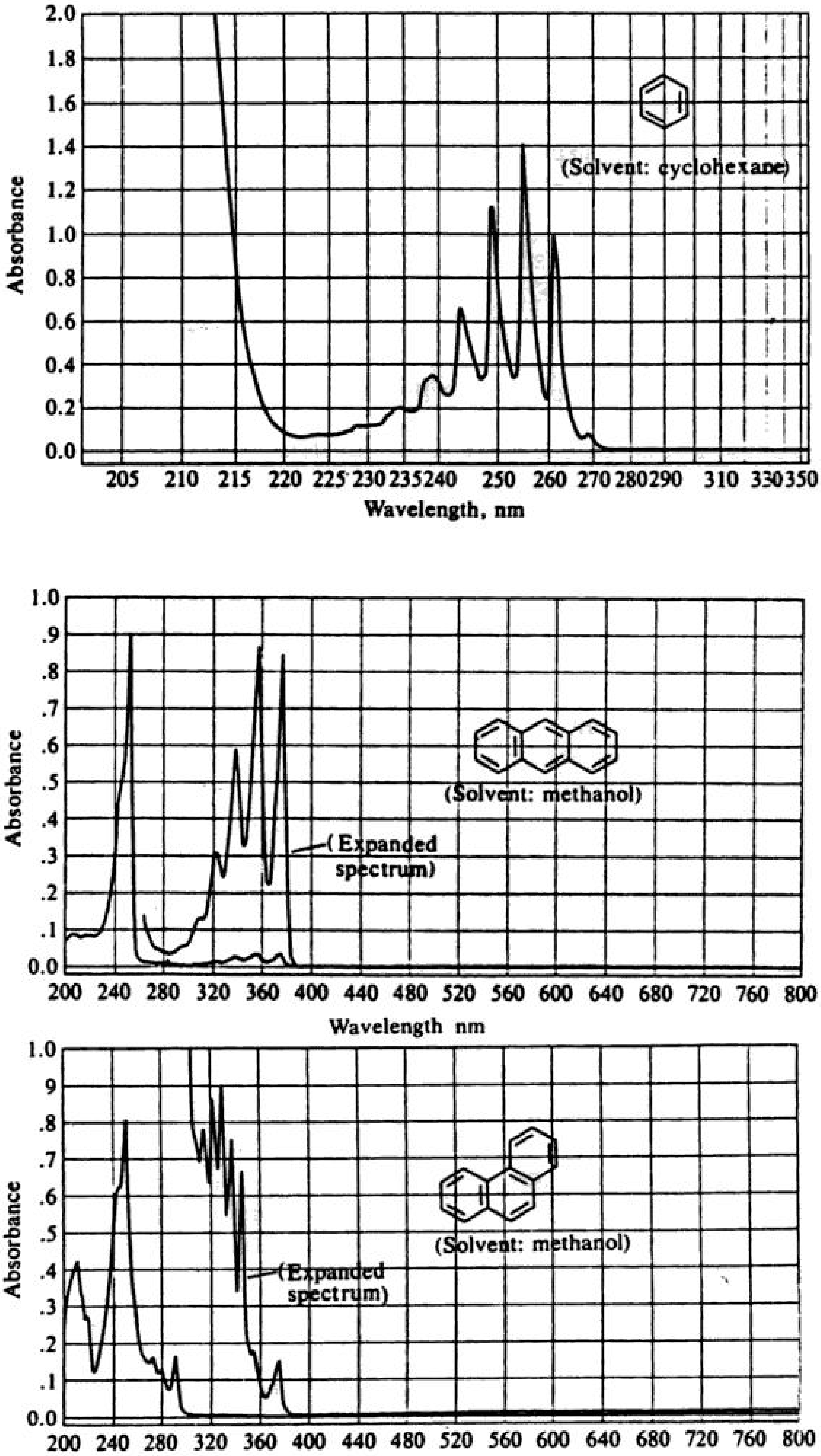

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
(Solvent: cyclohexane)
205 210 215 220 225 230 235 240 250 260 270 280 290 310 330 350
Wavelength, nm
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.0
Absorbance
(Solvent: methanol)
(Expanded spectrum)
200 240 280 320 360 400 440 480 520 560 600 640 680 720 760 800
Wavelength nm
1.0
9
.8
.7
.6
.5
.4
.3
.2
.1
0.0
Absorbance
(Solvent: methanol)
(Expanded spectrum)
200 240 280 320 360 400 440 480 520 560 600 640 680 720 760 800

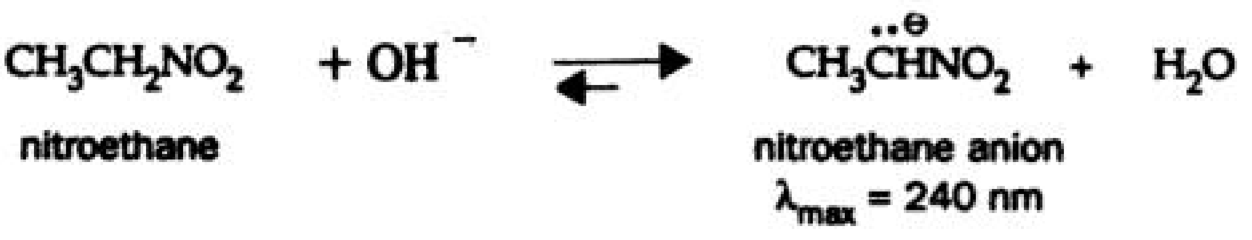
Fig. 2.8

the solvent polarity does not effect either the position or intensity of *B*-band of benzene, but produces a hyperchromic effect on this band of pyridine and its homologues. This effect is assigned to hydrogen bonding through the lone pair of electrons of the nitrogen atom. There is a possibility of the generation of tautomeric systems as seen in 2-hydropyridines. These systems tautomerise almost entirely to 2-pyridones (Sec. 2.3).

2.13 ANALYTICAL USES OF UV SPECTROSCOPY

UV/Vis spectroscopy has other uses that make it a good analytical tool. A reaction rate can be measured using UV/Vis spectroscopy provided one of the reactants or one of products absorbs UV or visible light at a wavelength where the other reactants or products have little or no absorbance. The anion of nitroethane has a λ_{max} at 240 nm, but neither H_2O nor the other reactants show any significant absorbance at this wavelength. To measure the rate at which the hydroxide ion removes a proton from nitroethane (that is, the rate at which the nitroethane anion is formed), the UV spectrophotometer is now adjusted to measure absorbance as a function of time instead of absorbance as a function of wavelength. Nitroethane is added to a quartz cell containing a basic solution, and the rate of the reaction is determined by monitoring the rate of increase in absorbance at 240 nm (Fig. 2.9).

The p*Ka* of a compound can be determined by UV/Vis spectroscopy provided either the acidic form or the basic form of the compound absorbs



$$CH_3CH_2NO_2 + OH^- \rightleftharpoons CH_3\overset{..\ominus}{C}HNO_2 + H_2O$$

nitroethane

nitroethane anion
$\lambda_{max} = 240$ nm

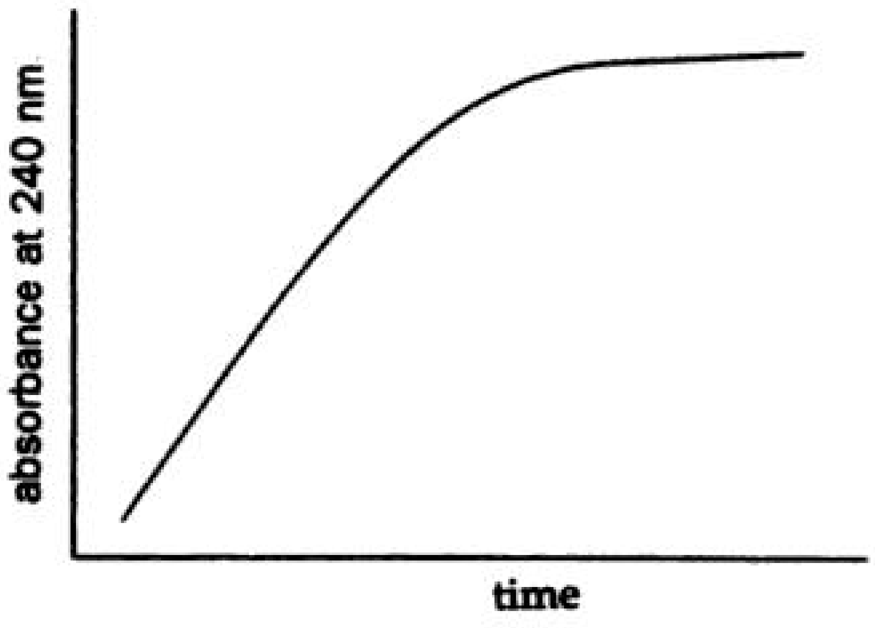


Fig. 2.9

UV or visible light. Consider the phenolate ion, it has a λ_{max} at 287 nm, if the absorbance at 287 nm is measured as a function of pH, the pKa of phenol can be known by determining the pH at which exactly one-half the increase in absorbance takes place (Fig. 2.10). At this pH, half of the phenol is converted into phenolate ion, therefore, this pH represents the p*Ka* of the compound. From the Henderson-Hasselbalch equation, one knows that the p*Ka* of the compound is the pH at which half the compound exists in its acidic form and half exists in its basic form.

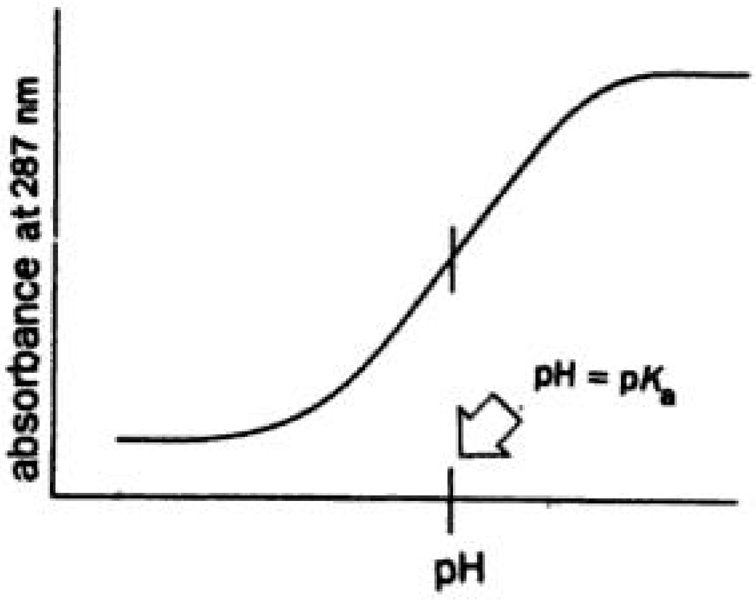
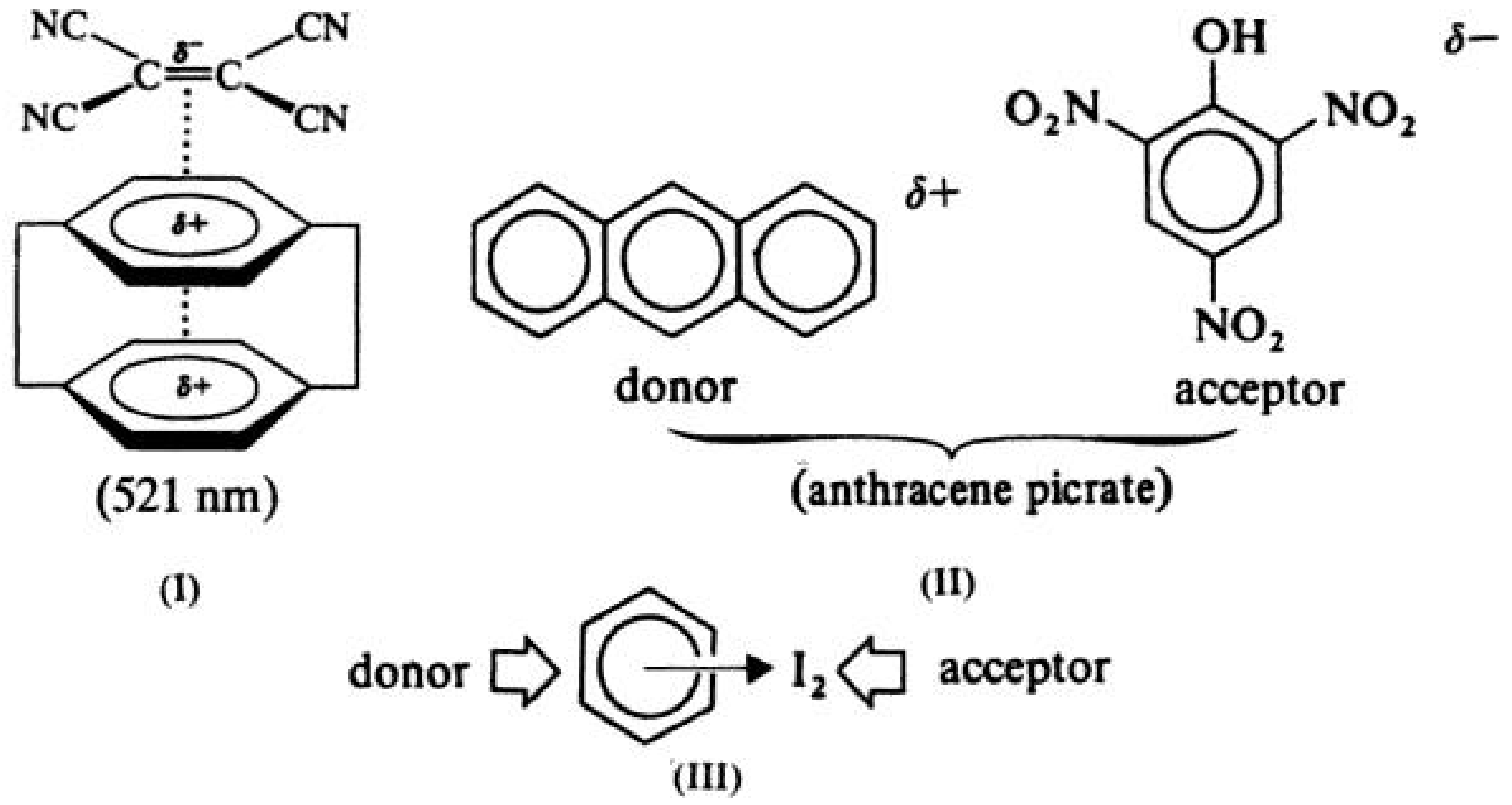


Fig. 2.10

2.14 STUDY OF CHARGE TRANSFER COMPLEXES

In these complexes, better called *EDA* complexes (Electron donor-acceptor complexes) the donor may donate an unshared pair or a pair of electrons in a π orbital of a double bond or an aromatic system. The evidence for the formation of these type of complexes is electronic spectroscopy. Such complexes generally display a spectrum (a charge-transfer spectrum) which is not the sum of the spectra of the parent individual molecules. These complexes are often coloured since the first excited state of the complex is relatively close to the ground state, consequently there is usually a peak in the visible or near UV region. Thus the colourless components TCNE and paracyclophane give a coloured complex λ_{max} 521 in CH_2Cl_2 (*I*, Scheme 2.30). Another example of such a complex is the formation of a picrate between picric acid and, *e.g.*, an aromatic hydrocarbon like anthracene (*II*, Scheme 2.30).

Lastly mention may be made of complexes in which the acceptor is, *e.g.* iodine which accepts electrons from, *e.g.*, benzene, probably via the expansion of the outer shell to hold on to 10 electrons. For the reason of complex formation iodine losses its purple colour in benzene (III, Scheme 2.30).

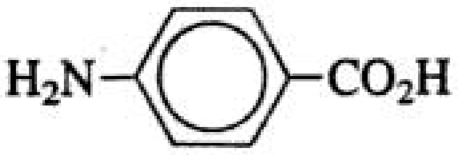


(I) (II) (III)

Scheme 2.30

2.15 USE OF SUNSCREENS

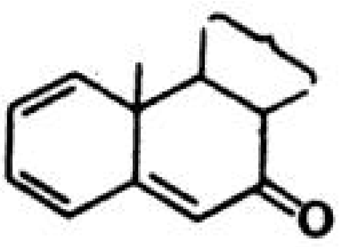
Simple substituted benzenes absorb between 250 and 290 nm (see Table 2.9). The water soluble *p*-aminobenzoic acid (PABA) has a λ_{max} at 289 nm with a high extinction coefficient of around 19,000. Due to this property PABA is used in many sunscreen lotions to protect the skin from potential cancer-causing high energy UV radiation.



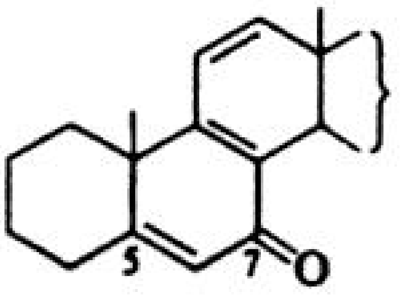
p-aminobenzoic acid
(PABA)
$\lambda_{max} = 289$ nm

EXERCISES AND PROBLEMS

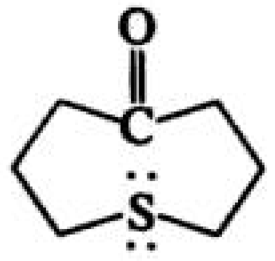
1. (a) On the basis of Woodward rules, calculate the expected position of the absorption maximum in the following trienones I and II. How you compare the calculated value with the observed values of λ_{max} 230 nm (ε18,000); 278 nm (ε 3720) and 348 nm (ε 11,000) in the case of I and at λ_{max} 256 nm and 327 nm in the case of II.



(I)



(II)

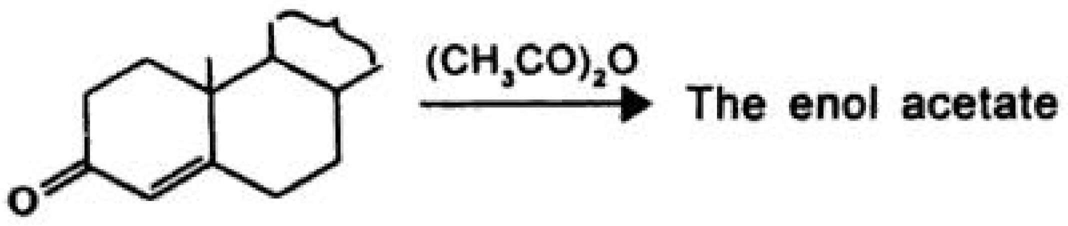


λ_{max} 238 nm, ϵ_{max} 2535

(III)

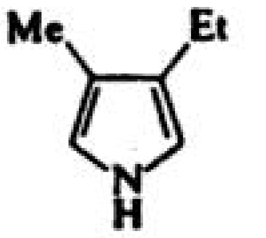
(b) The medium ring compound III shows λ_{max} 328 nm ε_{max} 2535 explain.

2. Cholest-4-en-3-one gives an enol acetate which has λ_{max} at 238 nm. Suggest the structure for the enol ester.

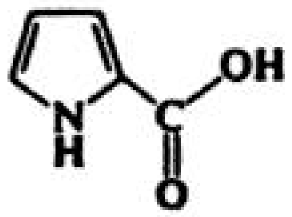


Cholest-4-en-3-one

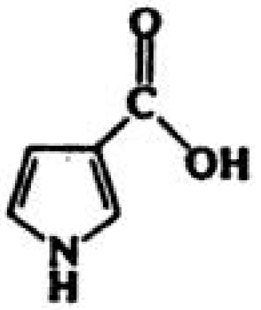
3. The pyrrole derivatives (I-III) show the indicated wavelength of absorption, explain.



(I)
λmax 203nm,
ε = 5670

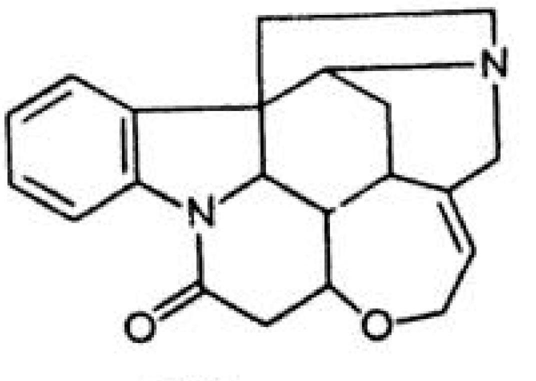


(II)
λmax 262nm,
ε = 12,000

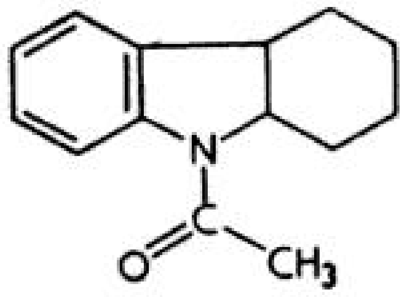


(III)
λmax 245nm,
ε = 4,800

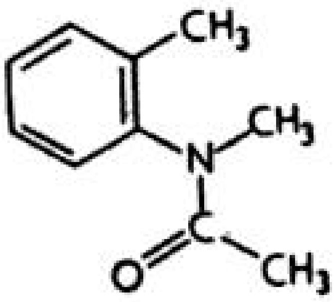
4. The absorptions by the essential chromophoric elements present in strychnine (IV) are compared with those present in two model compounds (V) and (VI). Comment on the structure and absorption.



(IV)
$\lambda_{max}(\varepsilon_{max})$ 257(16,000)
281(4200)
290(3400)

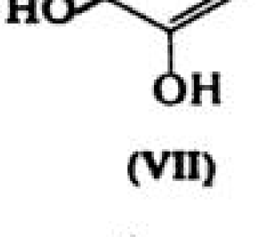


(V)
257(16,000)
281(3700)
290(3400)

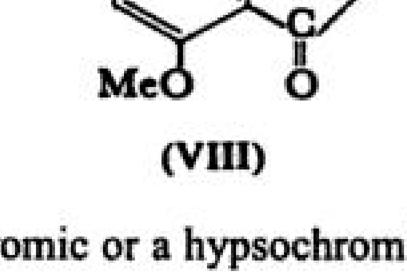


(VI)
270(300)

5. Calculate λ_{max} for the benzene derivatives (VII and VIII).



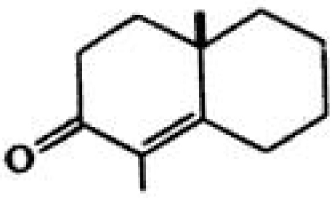
(VII)



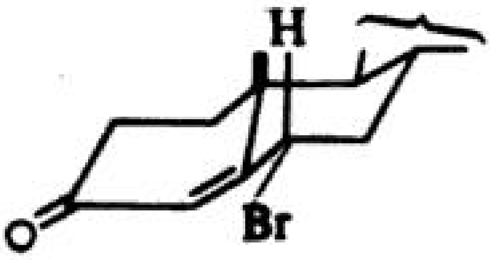
(VIII)

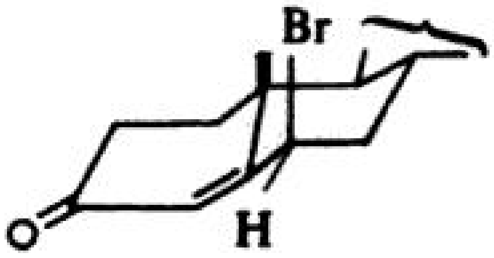
6. Which structure features may produce a bathochromic or a hypsochromic effect in an organic compound.

7. Aniline absorbs at 230 nm (ε 8600), however, in acid solution the main absorption band is seen at 203 nm (ε 7500) and is comparable with benzene. Explain.
8. Explain the substitution pattern on the following enone and calculate the position of *K*-band.

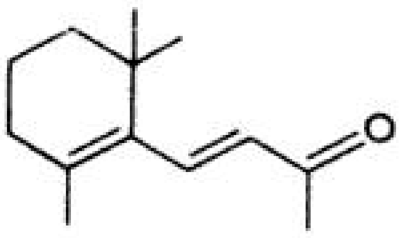


9. How ultraviolet spectroscopy can be used to distinguish between the equatorial and axial conformations shown below.

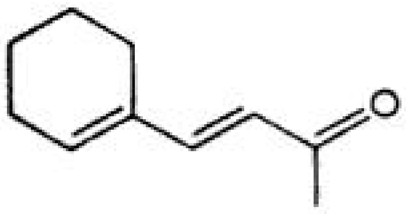




10. The position of absorption of acetone shifts in different solvents: 279 nm (hexane); 272 nm ethanol and 264.5 (water). Explain.
11. How the uv spectral data λ_{max} 296 nm, ε_{max} 10,700 and λ_{max} 281 nm, ε_{max} 20800 help in deciding between structures (IX and X).

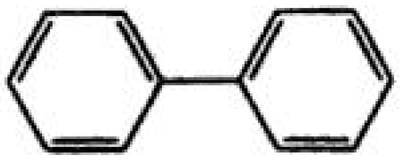


(IX)

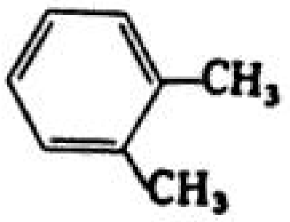


(X)

12. Which radiation, infrared or ultraviolet has (i) shorter wavelength, and (ii) lower energy?
13. What happens on absorption of infrared and uv radiation by a molecule.
14. What determines the wavelength of uv light absorption by an organic compound.
15. At what wavelength the coloured compounds absorb.
16. Which out of benzene (colourless) or quinone (yellow) has more easily promoted electrons.
17. Biphenyl shows the following uv absorption data. In its 2,2′-dimethyl derivative however, the absorption pattern becomes almost similar to *O*-xylene. Explain.

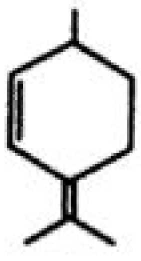


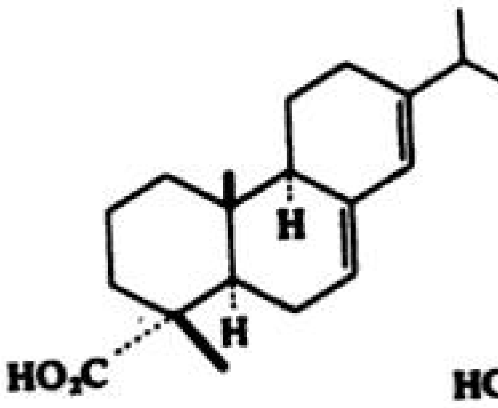
Biphenyl (planar conformation)
***K*-Band, λ_{max} 252nm, ε = 19,000**

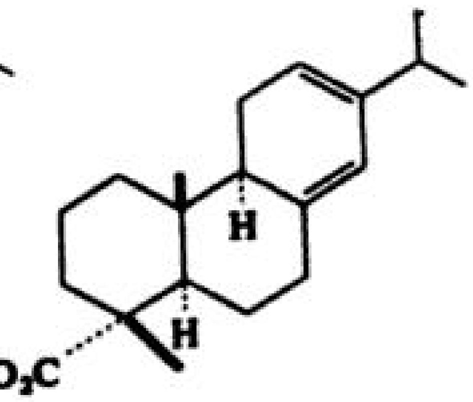


O-Xylene
λ_{max} 262nm, ε = 270

18. In the following compounds both the experimental as well as calculated λ_{max} values are given. Recalculate the expected λ_{max} for each compound and compare with the given values.

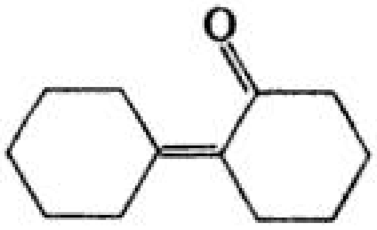


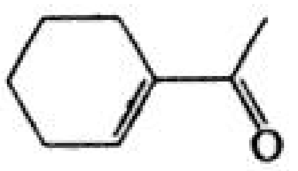


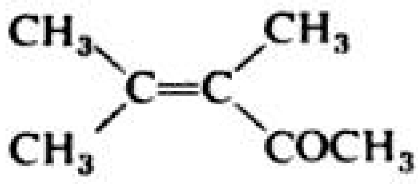


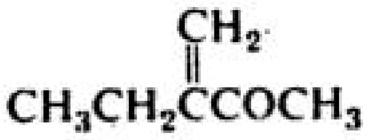
2,4(8)-*p*-Menthadiene	Abietic acid	Laevopimaric acid
λ_{max}^{obs} = 243nm,	λ_{max}^{obs} = 241nm,	λ_{max}^{obs} = 272nm,
ε =18,000	ε =26,200	ε =6,300
λ_{max}^{calc} = 239nm	λ_{max}^{calc} = 239nm	λ_{max}^{calc} = 278nm

19. The labels fell off from the four bottles of ketones shown to have the structures shown below. Measurement of the ultraviolet spectra of the contents of the four bottles gave λ_{max} at 221, 249, 233 and 258 nm. Assign structures to the appropriate λ_{max}.



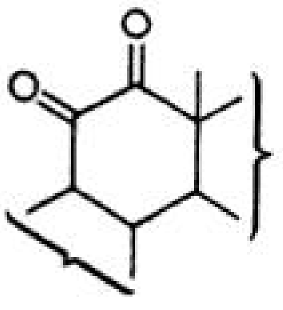




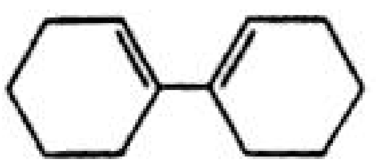


$$CH_3CH_2\overset{\overset{\displaystyle CH_2}{\|}}{C}COCH_3$$

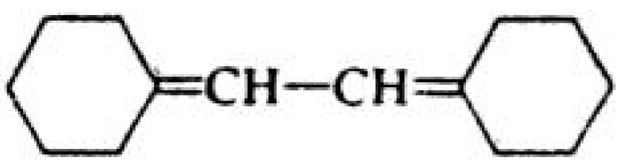
20. How will you confirm the presence of α-diketone system in the following steroid?



21. Why the λ_{max} for the diene (I) is observed at lower nm than (II).

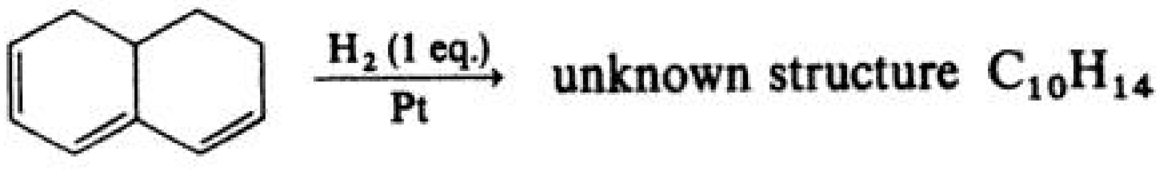


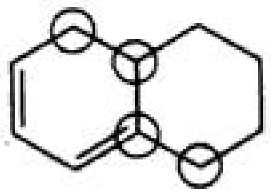
(I)

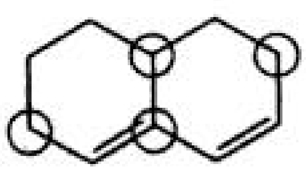


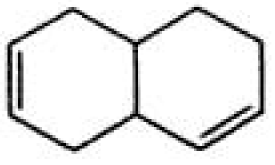
(II)

22. The following triene on partial hydrogenation gives three products, which are separated by glc. How uv spectroscopy and application of Woodward-Fieser rules will help to identify the products.



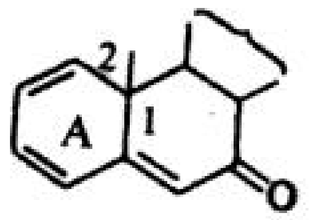






ANSWERS TO THE PROBLEMS

1. (a)



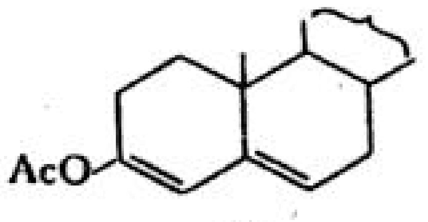
Parent value	215 nm
β-substituent 1	12 nm
ω-substituent 2	18 nm
2 × extended conjugation	60 nm
Homoannular diene component	39 nm
Exocyclic double bond (the αβ-double bond is exocyclic to ring A)	5 nm
Calc. λ_{max}	349 nm

In simple polyenes (Fig. 2.1) the long chromophore gives rise to several peaks. The longest wavelength peak (348 nm) in (I) is in excellent agreement with the predicted value.

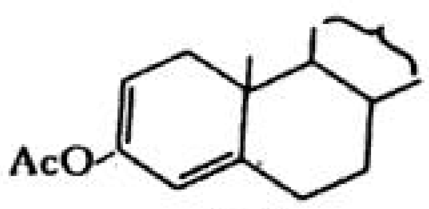
Compound (II) is a cross-conjugated trienone, the main chromophore is the linear dieneone portion as the Δ^5-double bond is not in the longest conjugated system. The calculation gives a value of 324 nm. The observed value (256 nm) may be due to the Δ^5-7-one system (λ_{max} 244 nm, *i.e.*, 215 + 2 × 12 + 5).

(b) It is apparently a non-conjugated system, however, an effective overlap of the π orbital for the C=O group and the *p* (*n*)-orbitals of the heteroatom generates transannular conjugation.

2. Of the two possible enol acetates I or II which can be formed, the structure must represent the heteroannular diene I on the basis of comparison with the position of calculated absorption maximum.



(I)



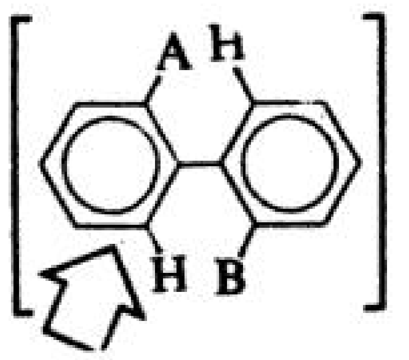
(II)

234 nm Calc. λ_{max} 273 nm

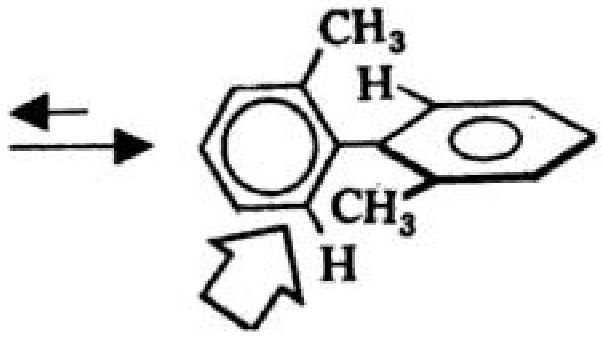
3. A simple pyrrole (I) and a pyrrole with an electron withdrawing substituent (II and III) have strikingly different absorption maxima, since the conjugation present from the nitrogen lone pair through the pyrrole ring to the carbonyl group increases the

length of the chromophore and leads to longer wavelength absorption (compare with disubstituted benzenes, Sec. 2.10).

4. This is a case of twisting in a sterically-crowded molecule. Care must be exercised in the choice of model compounds for structural work. The necessary elements of the chromophoric group in strychnine (IV) are present in *N*-methylaceto-*O*-toluidide (VI). However, this compound is not useful as a model because the *O*-methyl substituent does not allow the acetyl and phenyl groups to adopt the same relative configuration as in (IV). The hexahydrocarbazole (V) has the correct configuration and its absorption is almost indistinguishable from that of (IV).
5. For VII, 285 nm and for VIII 269 nm, the observed values are 284 and 270 nm respectively.
6. A bathochromic shift (red shift) may occur by a change of medium or by the presence of an auxochrome. A hypsochromic shift (blue shift) may be caused by a change of the medium or by such structural changes like removal of conjugation.
7. Due to the removal of conjugation of the lone pair of electrons on the nitrogen atom of aniline with the π-bond system of the benzene ring on protonation.
8. One α-substituent, two β-ring residues and one exocyclic double bond: 215 + 10 + 24 + 5 = 254 nm.
9. The long wavelength band $n \rightarrow \pi^*$ (*i.e.*, *R*-band) of α, β-unsaturated ketones is influenced by the presence of a polar group in the γ-position. The effect of an axial substituent to displace the *R*-band to longer wavelength being greater than equatorial isomer (compare the α-substituted saturated ketones).
10. This is the expected shift of the $n \rightarrow \pi^*$ transition of acetone to shorter wavelength (blue shift) by changing to solvents of increased polarity.
11. The compound with λ_{max} 296 nm has almost one half intensity, *i.e.*, ε_{max} 10,700 of this band than the other compound. This decrease in intensity is the result of steric hindrance by methyl group and its effect on the absorption of conjugated systems. Thus the compound with decreased intensity of the *K*-band is (IX).
12. The wavelengths of uv light are shorter than infrared radiation and the latter is relatively low energy radiation.
13. Absorption of infrared radiation by a molecule results in increased vibrations of covalent bonds (2-12 kcal/mole) while absorption of uv light results in electronic transitions; promotion of electrons from low energy ground state orbitals to higher energy excited state orbitals (40-70 kcal/mole).
14. The case of electron promotion. If a molecule requires more energy for electron promotion light of shorter wavelengths will be absorbed. Molecules which require less energy absorb at longer wavelengths.
15. Longer than 400 nm.
16. Quinone.
17. Although biphenyl is slightly twisted, the angle of twist is small, therefore, conjugation between the rings is not affected. Biphenyl thus shows a very intense absorption band at 252 nm (*K*-Band). Biphenyl derivatives with bulky substituents in the *ortho* positions are more stable in twisted conformations than in the planar conformation, which suffers serious non-bonded compressions from the juxtaposed substituents. The loss of conjugation in the twist conformation of 2,2-dimethylbiphenyl is reflected in its uv spectral data, which now structurally is like two moles of *O*-xylene.

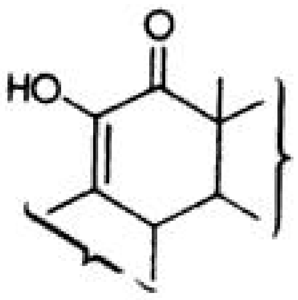


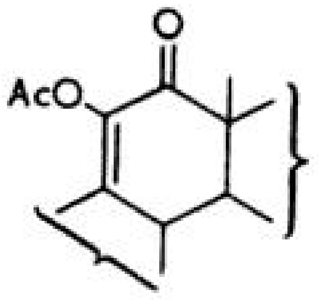
Planar conformation
(A=CH_3 and B=CH_3)
2,2'-Demethylbiphenyl



Twist conformation
2,2'-Demethylbiphenyl
B-Band, λ_{max} 270nm, ε = 800

19. (Hint) The first compound from left hand side is expected to show its λ_{max} at 259 nm. Base value 215; for one α-alkyl substituent add 10 nm for two β-alkyl groups add 2 × 12 nm; for a double bond exocyclic to two rings add 10 nm; (215 + 10 + 24 + 10 = 259 nm).
20. It will largely exist in the enolic form as revealed by the observed λ_{max} 281 nm (ε_{max} 9,700) which matches with the cal. λ_{max} (on enolisation the double bond becomes exocyclic to one ring). On acetylation the spectrum is restored to that calculated for the system now with OAc in the α-position. Further confirmation will come from the measurement of the spectrum of the enolised form in alkaline solution which will show the expected bathochromic shift of some 50 nm, *i.e.*, 281 nm → 330 nm.

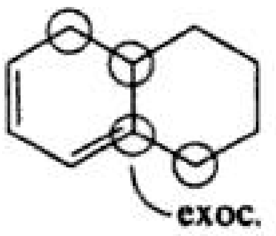


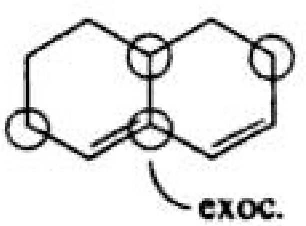


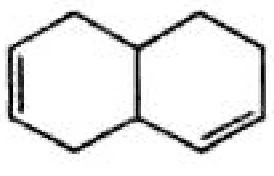
λ^{obs}_{max} = 281 nm (ϵ_{max} 9700)

λ^{calc}_{max} = $215+2\times12+5+35=279$ nm $(215+2\times12+5+6\ (OAc)=250$ nm

21. In both the dienes, there are 4 ring residues as substituents. In diene (II), the two double bonds are exocyclic, thus in it λ_{max} will be higher by 2 × 5 = 10 nm.
22. The markedly differed values are expected from each of the structures.







base value:	253 nm	217 nm	<200 nm
alkyl groups × 5:	15	15	(not conj.)
exocyc. C=C × 5:	5	5	
expected λ_{max}:	273 nm	237 nm	<200 nm

SUMMARY

1. Range of electronic spectroscopy, 200-400 nm; ultraviolet, 400-800 nm, visible.
2. A chromophore is a covalently unsaturated group (*e.g.*, C=C, C=O, NO) responsible for electronic absorption. An auxochrome is a saturated group with nonbonded electrons (*e.g.*, OH, NH_2 and Cl) which, when attached to a chromophore, changes the wavelength as well as the intensity of an absorption.

   A bathochromic shift (red shift) is the shift of absorption to a longer wavelength while a hypsochromic shift is the shift of absorption to a shorter wavelength (a blue shift).
3. Absorption of ultraviolet (200-400 nm) light leads to electronic transitions, *i.e.*, promotion of electrons from the ground-state orbitals to orbitals of higher energy. In the lowest energy transition, an electron is promoted from the highest occupied molecular orbital (HOMO) of a molecule to the lowest unoccupied molecular orbital (LUMO). Extended conjugation decreases the HOMO-LUMO energy difference and consequently λ_{max} is shifted to longer wavelengths. With extensive conjugation (as, *e.g.*, is present in lycopene) the HOMO-LUMO energy gap becomes so small that the compound has its λ_{max} in the visible range of the spectrum. The wavelength λ of absorption is inversely proportional to the energy required.

   The uv spectrum is a plot of absorbance A or molar absorptivity ε vs λ, where $\varepsilon = A/cl$. The position of maximum absorption is recorded as λ_{max}.

   The important electronic transitions are $\pi \rightarrow \pi^*$ for conjugated systems and $n \rightarrow \pi^*$. Increasing amount of conjugation results in the shift of λ_{max} toward longer wavelengths. Compounds which absorb at wavelengths longer than 400 nm appear coloured. An $n \rightarrow \pi^*$ transition requires less energy than a $\pi \rightarrow \pi^*$ or a $\sigma \rightarrow \sigma^*$ transition.
4. A low priced and a good solvent for uv spectroscopy is 95 per cent ethyl alcohol, which is transparent down to about 210 nm. Commercial absolute ethanol contains residual benezene which absorbs in the ultraviolet.
5. The transitions of polar bonds like carbonyls, but not ethylenes, are affected by solvent polarity. As solvent polarity is increased $\pi \rightarrow \pi^*$ bands undergo red shifts and $n \rightarrow \pi^*$ bands undergo blue shifts.
6. $n \rightarrow \pi^*$ Band (*R*-Band) of ketones ε 10-100, 270-330 nm, for both saturated and α, β-unsaturated ketones is one of the most important of the weak absorption bands. Its measurement requires concentrated solutions and is difficult due to the presence of nearby bands with large ε values. However, *R*-Bands are frequently important for diagnostic purposes. They are further characterised by hypsochromic or blue shift with an increase in solvent polarity.
7. The organic molecules, *e.g.*, butadiene and mesityl oxide with conjugated π-systems display *K*-bands which are due to $\pi \rightarrow \pi^*$ transitions. The aromatic molecules like, styrene, benzaldehyde or acetophenone with chromophoric substitution also show *K*-bands. These $\pi \rightarrow \pi^*$ transitions have normally high molecular absorptivity, ε_{max} more than 10,000.

   The *K*-bands ($\pi \rightarrow \pi^*$ transitions) of enone systems undergo a bathochromic shift on increasing solvent polarity while these bands of diene systems are not affected by change of solvent polarity.

8. In dienes and trienes the effect of substitution is additive and the position of λ_{max} can be predicted in open chain dienes and dienes in six-membered rings by applying Woodward-Fieser rules. The ε values are dependent on the square of the chromophore length and thus *trans*-diene maxima are more intense than those of *cis*-dienes, *i.e.*, ε for planar *S-trans* dienes: 25,000, ε for *S-cis* or homoannular dienes: 10,000-15,000. When planarity is destroyed by steric hindrance or by ring distortion, the following changes occur. Increase in ε; decrease in ε and blue shift in λ; and disappearance of conjugative effect. Calculations for homoannular dienes are only valid for six-membered rings.
9. In α, β-unsaturated aldehydes and ketones as well, the expected position of the maxima can be calculated from Woodward-Fieser-Scott rules.
10. Unlike dienes, the enone $\pi \rightarrow \pi^*$ maxima are dependent on solvent polarity. The following solvent corrections (nm) convert into value for ethanol; methanol 0; chloroform + 1; ether + 7; hexane + 11; water - 8; and dioxane + 5. For *s-trans* enones ε is usually > 10,000, while ε for *S-cis* enone is usually < 10000.
11. The presence of benzenoid bands (*B*-bands) point to the presence of aromatic or heteroaromatic system in an organic compound. Benzene, for example, shows a broad absorption band with fine structure between 230-270 nm. The *B*-bands shift to longer wavelengths than the more intense $\pi \rightarrow \pi^*$ transitions if a chromophoric group is present on the aromatic system. This is seen in the case of styrene ($\pi \rightarrow \pi^*$ transition, λ_{max} 224 nm, ε_{max} 12,000) and a *B*-band at λ_{max} 282 nm, ε_{max} 450.
12. Sharp peaks are seldom observed in an ultraviolet spectrum and instead, broad absorption bands are observed, because vibrational, and rotational effects are superimposed on the electronic transitions, so that an envelope of transitions arises.
13. Not all transitions from filled to unfilled orbitals are allowed, the symmetry considerations, *i.e.*, symmetry relationship between the two orbitals being important. When a transition is 'forbidden', the probability of that transition occurring is low, and consequently the intensity of the associated absorption band is also low.
14. The $n \rightarrow \pi^*$ transitions of aldehydes and ketones are "forbidden''. These are weak UV absorptions with values of λ_{max} between 270-330 nm.

FURTHER READING

H.H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley and Sons, Inc. New York, 1962.

I.B. Lambert, H.F. Shurvell, L. Verbit, R.G. Cooks, and G.H. Stout, *Organic Structural Analysis*, Macmillan Publishing, New York, 1976.