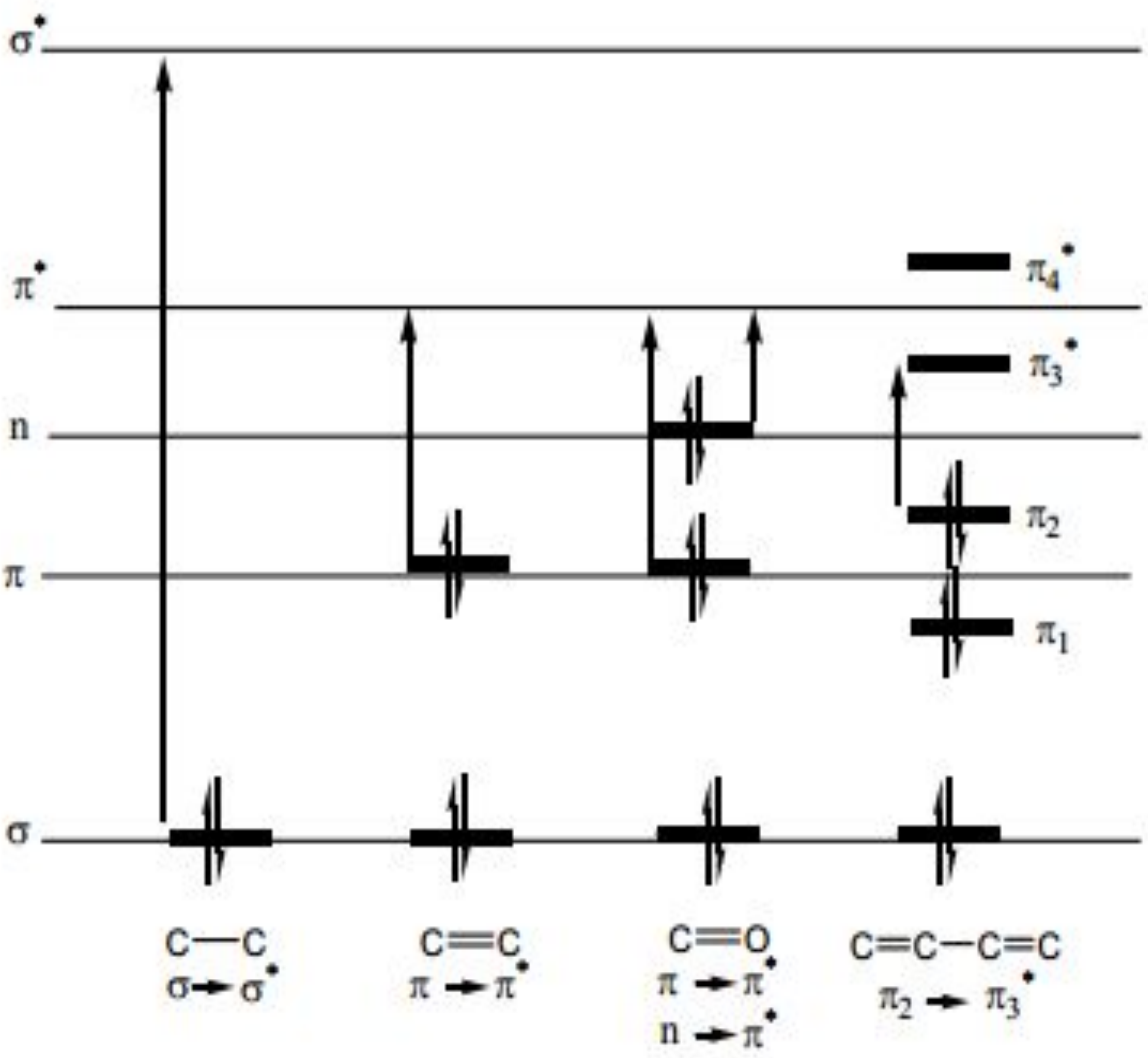
Ultraviolet – visible spectroscopy (λ 200 - 800 nm) studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from π- or non-bonding orbitals. It commonly provides the knowledge about π-electron systems, conjugated unsaturations, aromatic compounds and conjugated non-bonding electron systems etc.

This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions. Since the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule, it is also often called as electronic spectroscopy. The information provided by this spectroscopy when combined with the information provided by NMR and IR spectral data leads to valuable structural proposals.

Nature of Electronic Transitions

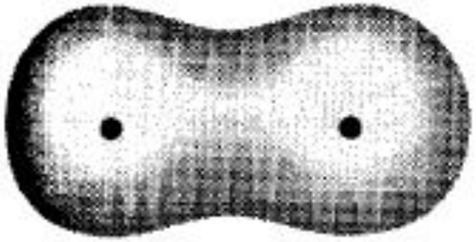
The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular 4orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding π* or σ* orbital) of greater potential energy (figure). For most molecules, the lowest-energy occupied molecular orbitals are σ orbitals, which correspond to σ bonds. The π orbitals lie at relatively higher energy levels than σ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals (π* and σ*) are orbitals of highest energy. The relative potential energies of these orbitals and vaious possible transitions have been depicted in figure.



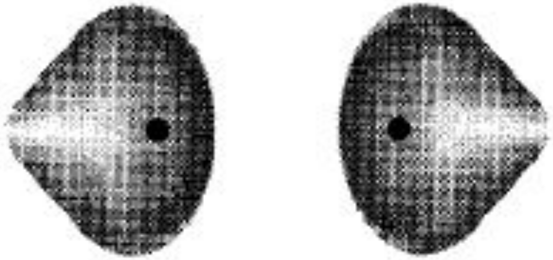
Relative energies of orbitals most commonly involved in electronic spectroscopy of organic molecules

The saturated aliphatic hydrocarbons (alkanes) exhibit only $\sigma \rightarrow \sigma^*$ transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies viz. $n \rightarrow \pi^* < n \rightarrow \sigma^* < \pi \rightarrow \pi^* < \sigma \rightarrow \pi^* < \sigma \rightarrow \sigma^*$. Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a large number of vibrational and rotational states.

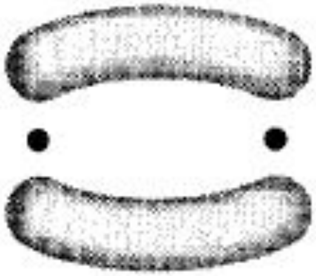
Sigma and Pi orbitals



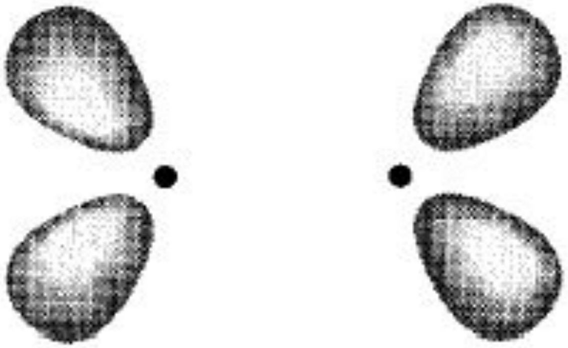
(a) σ orbital



(c) σ^* orbital

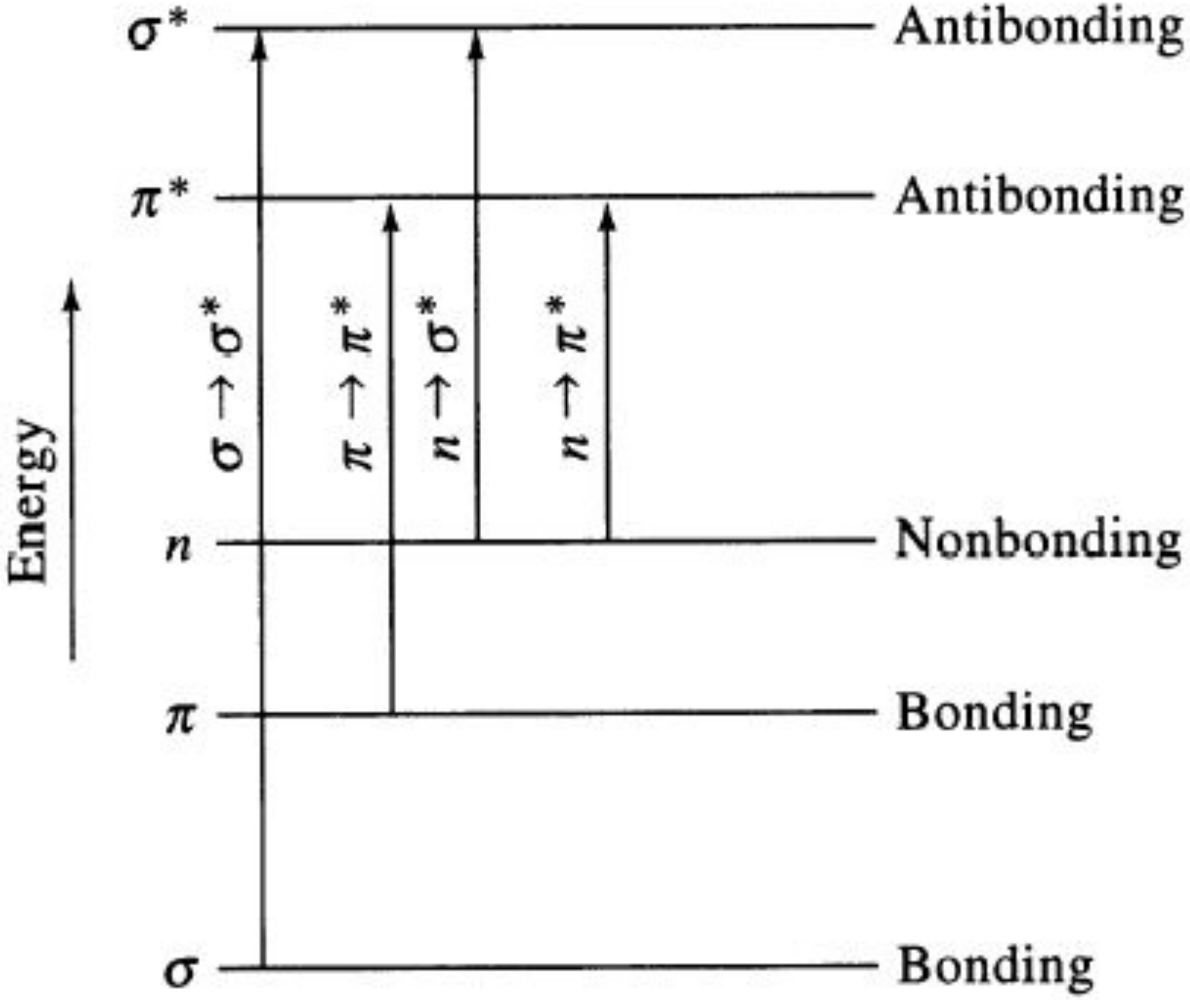


(b) π orbital



(d) π^* orbital

Electron transitions



Alkanes can only undergo $\sigma \rightarrow \sigma^*$ transitions. These are high-energy transitions and involve very short wavelength ultraviolet light (< 150 nm). These transitions usually fall out-side the generally available measurable range of UV-visible spectrophotometers (200-1000 nm). The $\sigma \rightarrow \sigma^*$ transitions of methane and ethane are at 122 and 135 nm, respectively. In alkenes amongst the available $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions, the $\pi \rightarrow \pi^*$ transitions are of lowest energy and absorb radiations between 170-190 nm.

In saturated aliphatic ketones the lowest energy transition involves the transfer of one electron of the nonbonding electrons of oxygen to the relatively low-lying π^* anti-bonding orbital. This $n \rightarrow \pi^*$ transition is of lowest energy (~280 nm) but is of low intensity as it is symmetry forbidden. Two other available transitions are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The most intense band for these compounds is always due to $\pi \rightarrow \pi^*$ transition.

In conjugated dienes the $\pi \rightarrow \pi^*$ orbitals of the two alkene groups combine to form new orbitals – two bonding orbitals named as π_1 and π_2 and two antibonding orbitals named as π_3^* and π_4^*. It is apparent that a new $\pi \rightarrow \pi^*$ transition of low energy is available as a result of conjugation. Conjugated dienes as a result absorb at relatively longer wavelength than do isolated alkenes.

Beer’s and Lambert’s Law

The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

$$\text{Log } I_o / I = \varepsilon\, c\, l$$

Where I_o = Intensity of the incident light (or the light intensity passing through a reference cell)
I = Intensity of light transmitted through the sample solution
c = concentration of the solute in mol l^{-1}
l = path length of the sample in cm

ε = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ε is numerically equal to the absorbance of a solution of unit molar concentration ($c = 1$) in a cell of unit length ($l = 1$) and its units are liters.moles^{-1} . cm^{-1}. However, it is customary practice among organic chemists to omit the units.

The ratio I / I_o is known as transmittance T and the logarithm of the inverse ratio I_o / I is known as the absorbance A.
Therefore

$$-\text{Log } I / I_o = -\log T = \varepsilon\, c\, l$$

and $$\text{Log } I_o / I = A = \varepsilon\, c\, l$$

or $$A = \varepsilon\, c\, l$$

For presenting the absorption characteristics of a spectrum, the positions of peaks are reported as λ_{max} (in nm) values and the absorptivity is expressed in parenthesis.

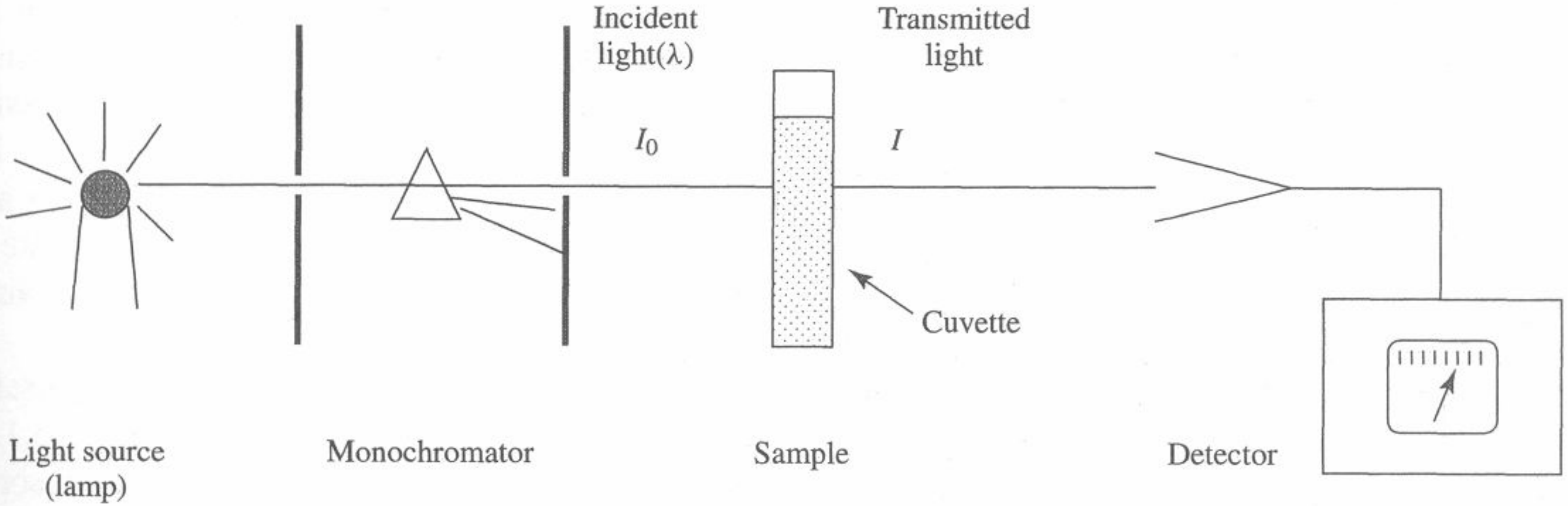


Figure 3.9. Ultraviolet/visible absorption spectroscopy experiment. Light of a single wavelength (λ) and intensity (I_0) is passed through a sample held in a cuvette. Some of this light may be absorbed by the sample. This is detected as a decreased intensity of transmitted light (I) compared to incident light. Log I_0/I is measured as absorbance

S. No.	Solvent	Cut-off wavelength (nm)
1	Acetonitrile	190
2	Water	191
3	Cyclohexane	195
4	Hexane	201
5	Methanol	203
6	95% ethanol	304
7	1,4-dioxane	215
8	Ether	215
9	Dichloromethane	220
10	Chloroform	237
11	Carbon tetrachloride	257
12	Benzene	280

Solvent Effects

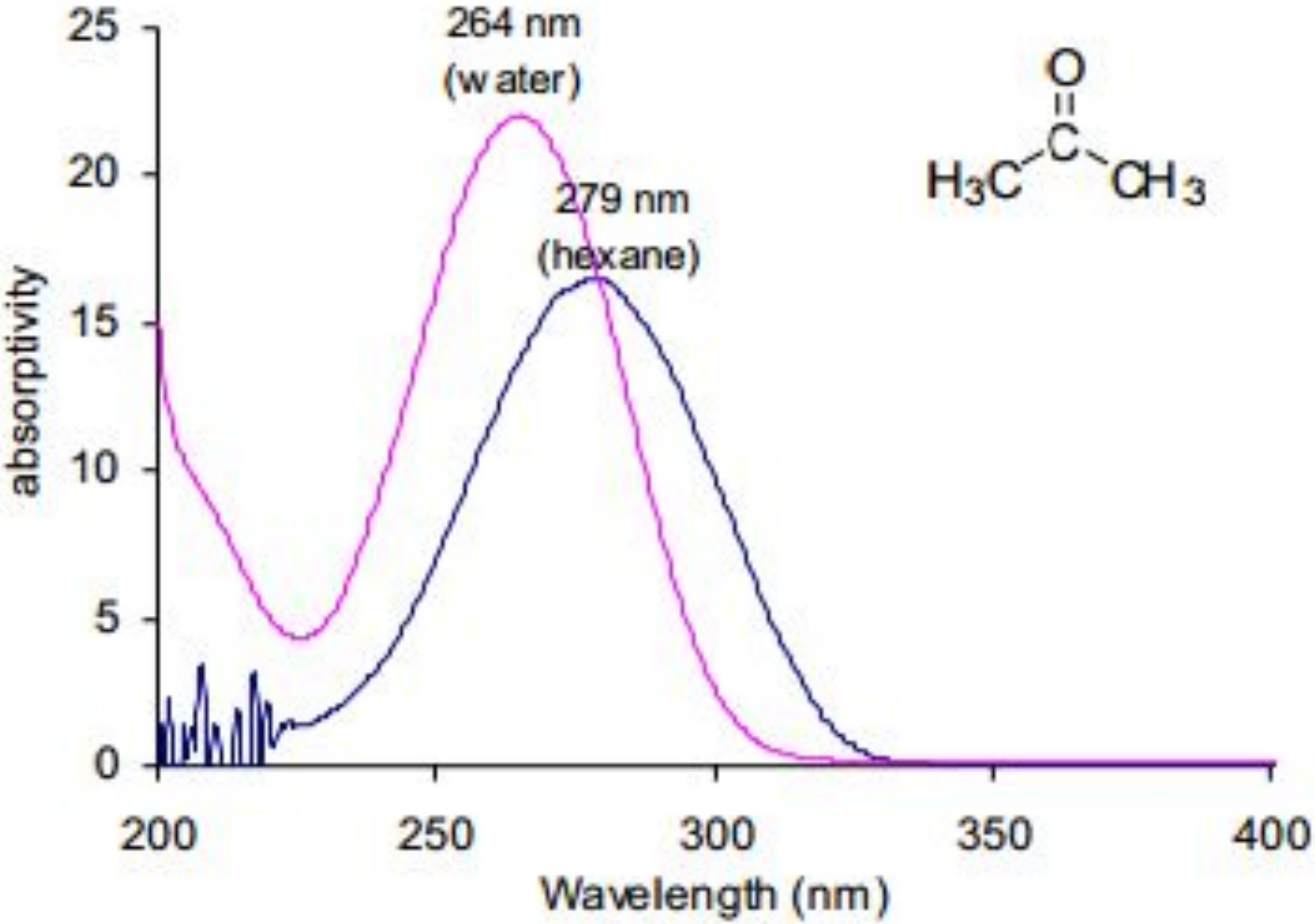
Highly pure, non-polar solvents such as saturated hydrocarbons do not interact with solute molecules either in the ground or excited state and the absorption spectrum of a compound in these solvents is similar to the one in a pure gaseous state. However, polar solvents such as water, alcohols etc. may stabilize or destabilize the molecular orbitals of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

π Æ π* Transitions

In case of π Æ π* transitions, the excited states are more polar than the ground state and the dipole-dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of π Æ π* transition andabsorption maximum appears ~10-20 nm red shifted in going from hexane to ethanol solvent.

8(ii) n Æ π* Transitions

In case of n Æ π* transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Therefore, in polar solvents the energies of electronic transitions are increased. For example, the figure 5 shows that theabsorption maximum of acetone in hexane appears at 279 nm which in water is shifted to 264 nm, with a blue shift of 15 nm.



UV-spectra of acetone in hexane and in water

Chromophore: The energy of radiation being absorbed during excitation of electrons from ground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. The group of atoms containing electrons responsible for the absorption is called chromophore. Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed in table:

Absorption maxima of simple un-conjugated chromophores

Chromophore	Transition	ε_{max}	λ_{max} (nm)
σ – bonded electrons			
(C-C, C-H etc.)	$\sigma \rightarrow \sigma^*$		~ 150
Lone pair electrons			
-O-, -N-, -S-	$n \rightarrow \sigma^*$	100-1000	~ 190
C=O, C=N	$n \rightarrow \pi^*$	15	~300
	$\pi \rightarrow \pi^*$	500	~190
R-C≡N	$n \rightarrow \pi^*$	5	~ 170
R-COOH, $RCONH_2$, RCOOR	$n \rightarrow \pi^*$	50	~ 210
π- bonded electrons			
C=C	$\pi \rightarrow \pi^*$	14000	~ 190
C≡C	$\pi \rightarrow \pi^*$	2000	~ 195
C=O	$\pi \rightarrow \pi^*$	500	~ 180

For example, alkanes contain only single bonds with only possible σ Æ σ* type electronic transitions. These transitions absorb radiations shorter than wavelengths that are experimentally accessible in usually available spectrophotometers. In saturated molecules with heteroatombearing non-bonding pairs of electrons, n Æ σ* transitions become available. These are also high energy transitions. In unsaturated compounds, π Æ π* transitions become possible. Alkenes and alkynes absorb ~ 170 nm but the presence of substituents significantly affects their position. The carbonyl compounds and imines can also undergo n Æ π* transitions in addition to π Æ π*. Amongst these, the most studied transitions are n Æ π* as these absorb at relatively longer wavelength 280-300 nm. These are low intensity (ε 10-100) transitions.

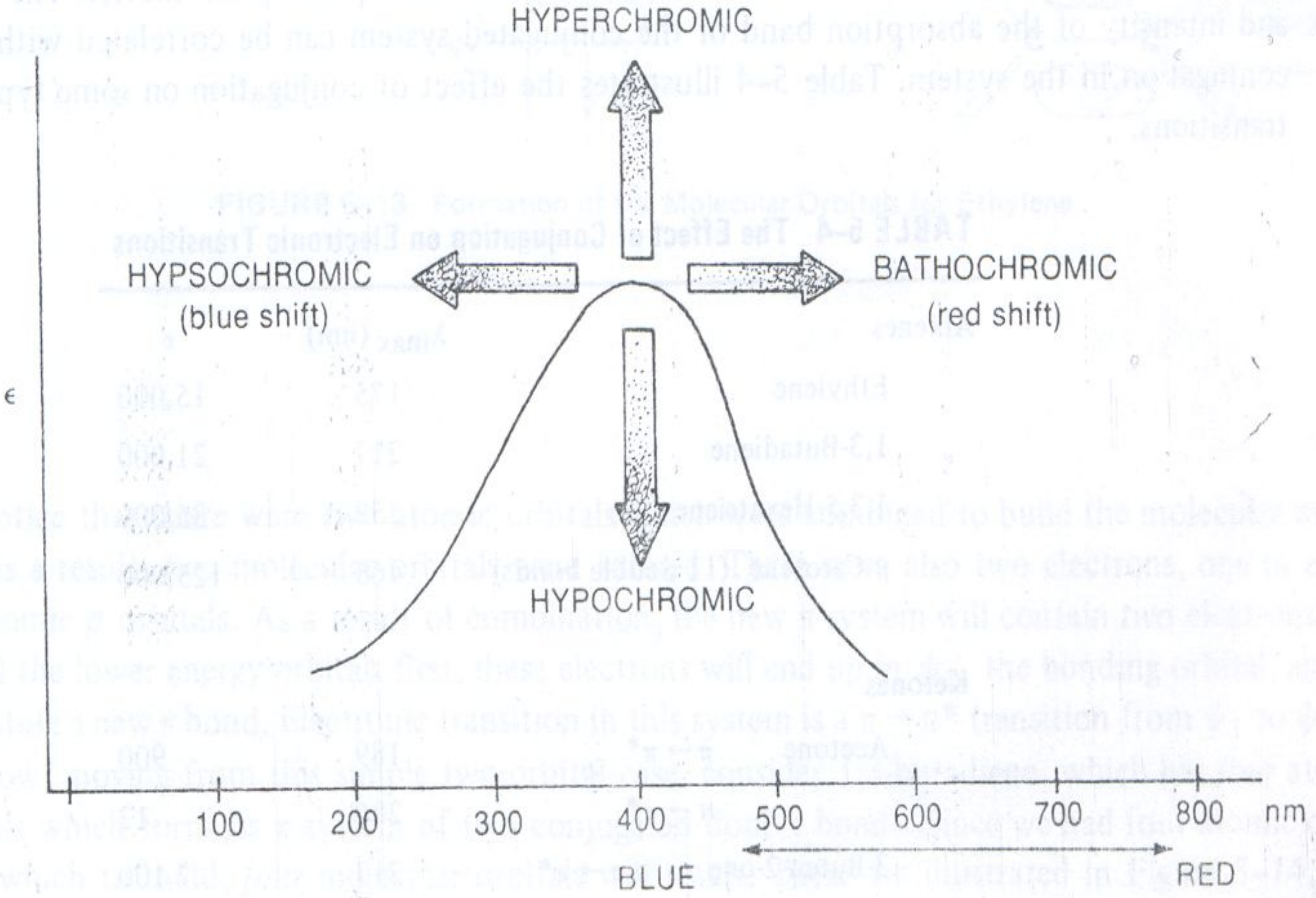
Auxochrome: The substituents that themselves do not absorb ultraviolet radiations but their presence shifts the absorption maximum to longer wavelength are called auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes.

(iii) Bathochromic Shift or Red shift: A shift of an absorption maximum towards longer wavelength or lower energy.

(iv) Hypsochromic Shift or Blue Shift: A shift of an absorption maximum towards shorter wavelength or higher energy.

(v) Hypochromic Effect: An effect that results in decreased absorption intensity.

vi) Hyperchromic Effect: An effect that results in increased absorption intensity.


HYPERCHROMIC
HYPSOCHROMIC
(blue shift)
BATHOCHROMIC
(red shift)
HYPOCHROMIC
ϵ
100
200
300
400
500
600
700
800
nm
BLUE
RED

Conjugated Dienes, Trienes and Polyenes

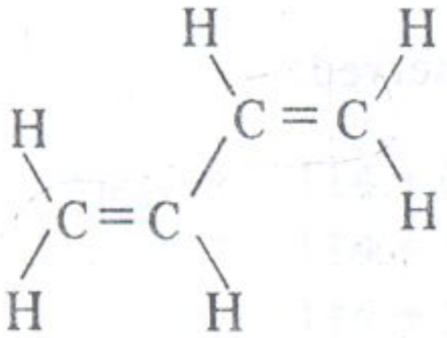
The presence of conjugate double bond decreases the energy difference between HOMO and LUMO of resulting diene. The figure 6 shows the change in energy of MO on conjugation. As a result, the radiations of longer wavelength are absorbed. The conjugation not only results in bathochromic shift (longer wavelength) but also increases the intensity of absorption. As the number of conjugated double bonds is increased, the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is progressively lowered.

Therefore, the increase in size of the conjugated system gradually shifts the absorption maximum (λmax) to longer wavelength and also increases the absorption. For example, ethylene absorbs at 10175 nm ($\varepsilon = 1000$) and the conjugation in butadiene gives a strong absorption at longer wavelength at 230 nm and with higher intensity ($\varepsilon = >1000$).

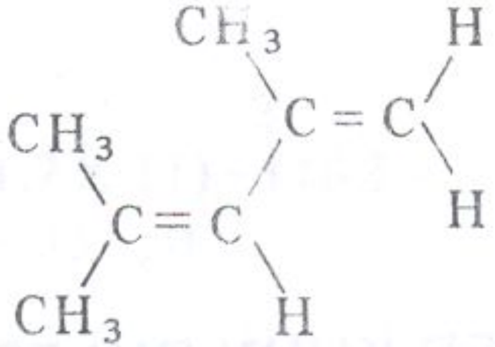
The presence of alkyl substituents on double bond also produces bathochromic shift and hyperchromic effect. These effects are additive in dienes and up to some extent in trienes. The open chain dienes can achieve s-cis or s-trans conformations and similarly diene system can behomoannular or heteroannular in cyclic systems. In 1941, Woodward suggested empirical rules for predicting the absorption of open chain and six-membered ring dienes which have been later on extended to large number of dienes and trienes (Table).

Empirical Rules for Diene and Triene absorptions

Parent open chain or heteroannular diene	214 nm
Homoannular diene	253 nm
Increments for	
(a) each alkyl substituent or ring residue	5 nm
(b) double bond extending conjugation	30 nm
(c) exocyclic double bond	5 nm
(d) lone pair conjugation	
(i) O-C(=O)-R	0 nm
(ii) O-alkyl	6 nm
(iii) S-alkyl	30 nm
(iv) –Cl, -Br	5 nm
(v) NR_2	60 nm

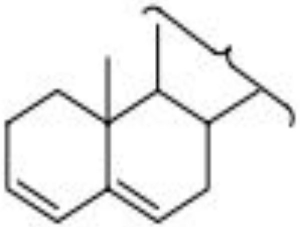


transoid:	214 nm
observed:	217 nm

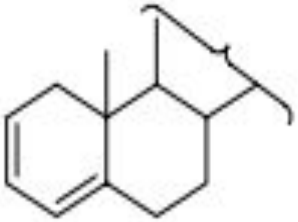


transoid:	214 nm
alkyl groups: 3 × 5 =	15
	229 nm
observed:	228 nm

For example, here the absorption maxima for dienes **1** and **2** have been calculated according to Woodward rules. The comparison of calculated λ_{max} values with observed λ_{max} values highlights the importance of these rules.



1



2

Parent value = 214 nm

Three ring residues (3 x 5) = 15

Exocyclic double bond = 5 nm

Total = 234 nm

Observed value = 235 nm

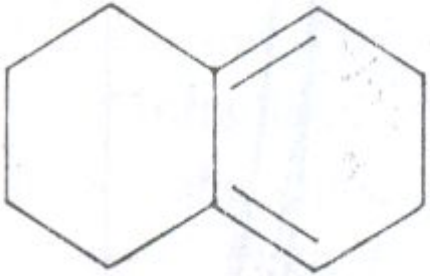
Parent value = 253 nm

Three substituents = 15 nm

Ring residue = 5

Total = 273

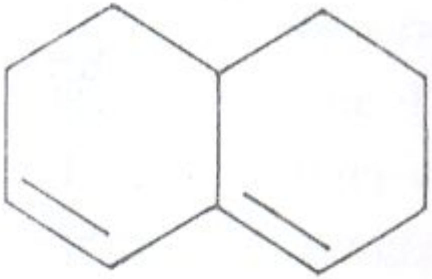
Observed value = 275 nm



Homoannular Diene
(cisoid or s-cis)

less intense, $\epsilon = 5{,}000\text{–}15{,}000$

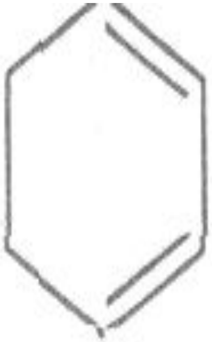
λ *longer (273 nm)*



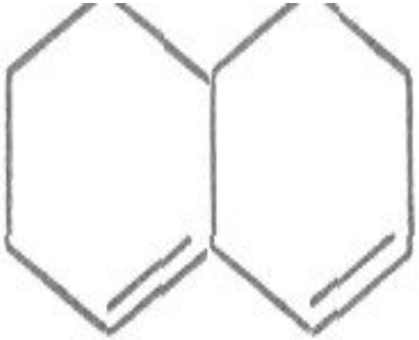
Heteroannular Diene
(transoid or s-trans)

more intense, $\epsilon = 12{,}000\text{–}28{,}000$

λ *shorter (234 nm)*



Гомоаннулярная



Гетероаннулярная

TABLE 5-5 Empirical Rules for Dienes

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253$ nm	$\lambda = 214$ nm
Increments for:		
Double bond extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
$-OCOCH_3$	0	0
$-OR$	6	6
$-Cl$, $-Br$	5	5
$-NR_2$	60	60

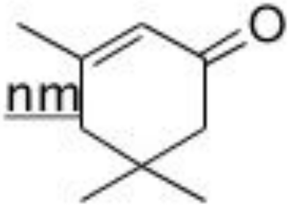
Таблица V

Правила для расчета поглощения диенов [2]

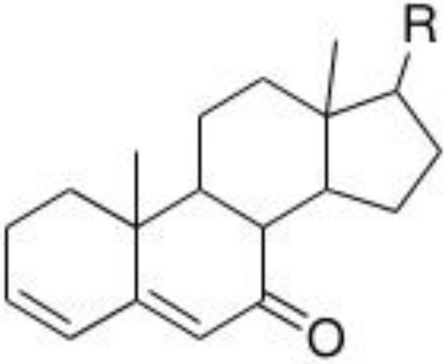
Исходное значение для	
гетероаннулярного диена	214
гомоаннулярного диена	253
Инкременты для	
сопряженной двойной связи	+30
алкильного заместителя или связи цикла	+5
экзоциклической двойной связи	+5
полярных групп: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
поправки на растворитель	+0
	$\lambda_{выч}$ равно общей сумме

Woodward-Fieser Rules - Enones

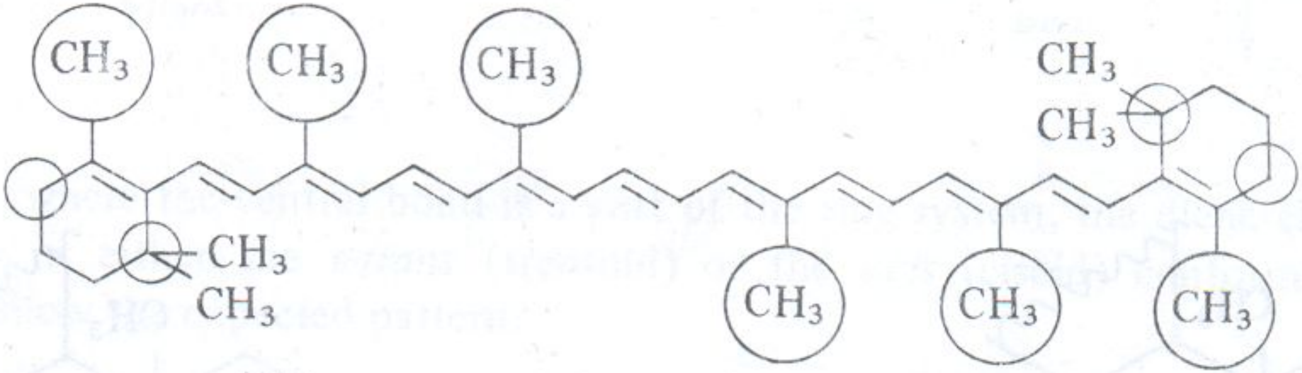
Some examples – keep in mind these are more complex than dienes



cyclic enone =	215 nm
2 x β– alkyl subs.	(2 x 12) +24
	239 nm
Experimental value	238 nm

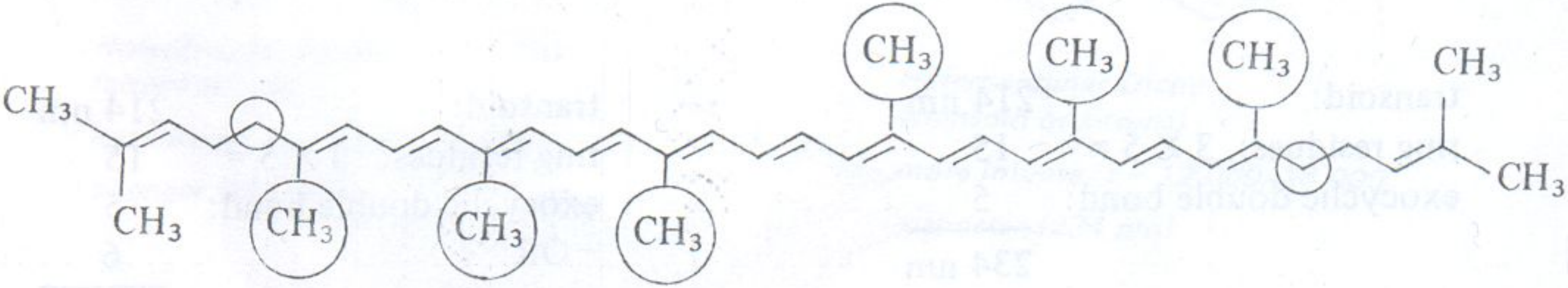


cyclic enone =	215 nm
extended conj.	+30 nm
β–ring residue	+12 nm
δ–ring residue	+18 nm
exocyclic double bond	+ 5 nm
	280 nm
Experimental	280 nm



β-Carotene, 11 Double Bonds

λ_{max} = 452 nm (hexane), ϵ = 15.2 × 10^4



Lycopene, 13 Double Bonds (11 Conjugated)

λ_{max} = 474 nm (hexane), ϵ = 18.6 × 10^4

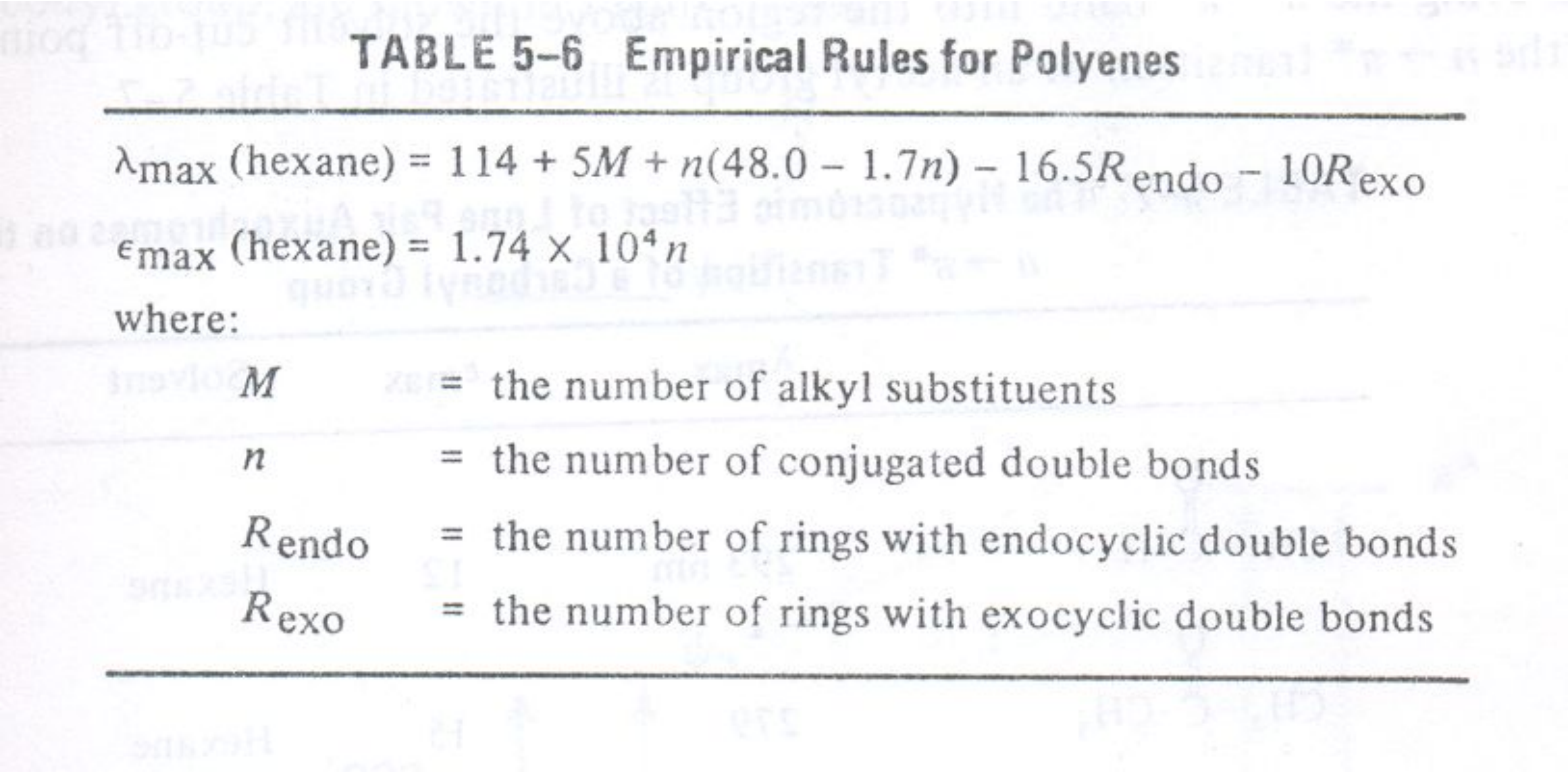


TABLE 5–6 Empirical Rules for Polyenes

λ_{max} (hexane) = $114 + 5M + n(48.0 - 1.7n) - 16.5R_{endo} - 10R_{exo}$

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

where:

M = the number of alkyl substituents

n = the number of conjugated double bonds

R_{endo} = the number of rings with endocyclic double bonds

R_{exo} = the number of rings with exocyclic double bonds

As an example, consider β-carotene:

M = 10 (see circled positions in the structure shown above)
n = 11 conjugated double bonds
R_{endo} = 2
R_{exo} = 0

Therefore:

$$\begin{aligned}
\lambda_{\text{max}} &= 114 + (5 \times 10) + 11(48.0 - 1.7 \times 11) - (16.5 \times 2) - (10 \times 0) \\
&= 114 + 50 + 11(48.0 - 18.7) - 33 - 0 \\
&= 114 + 50 + 322.3 - 33 \\
&= \boxed{453.3 \text{ CALCULATED}} \\
\epsilon_{\text{max}} &= 1.74 \times 10^4 \times 11 \\
&= \boxed{19.1 \times 10^4 \text{ CALCULATED}}
\end{aligned}$$

TABLE 5-3 Typical Absorptions of Simple Isolated Chromophores

Class	Transition	λ_{max} (nm)	log ϵ	Class	Transition	λ_{max} (nm)	log ϵ
R–OH	$n \rightarrow \sigma^*$	180	2.5	R–NO_2	$n \rightarrow \pi^*$	271	<1.0
R–O–R	$n \rightarrow \sigma^*$	180	3.5	R–CHO	$\pi \rightarrow \pi^*$	190	2.0
R–NH_2	$n \rightarrow \sigma^*$	190	3.5		$n \rightarrow \pi^*$	290	1.0
R–SH	$n \rightarrow \sigma^*$	210	3.0	R_2CO	$\pi \rightarrow \pi^*$	180	3.0
$R_2C{=}CR_2$	$\pi \rightarrow \pi^*$	175	3.0		$n \rightarrow \pi^*$	280	1.5
R–C≡C–R	$\pi \rightarrow \pi^*$	170	3.0	RCOOH	$n \rightarrow \pi^*$	205	1.5
R–C≡N	$n \rightarrow \pi^*$	160	<1.0	RCOOR′	$n \rightarrow \pi^*$	205	1.5
R–N=N–R	$n \rightarrow \pi^*$	340	<1.0	$RCONH_2$	$n \rightarrow \pi^*$	210	1.5

Carbonyl Compounds

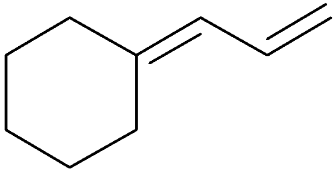
Carbonyl compounds have two principal UV radiations, the allowed π Æ π* transitions and the forbidden n Æ π* transitions. In amides, acids, esters or acid halides, the substituents viz. NR2, OH, OR, or –X on carbonyl group show pronounced hypsochromic effect on the n Æ π* transitions. The hypsochromic effect is due to inductive effect of nitrogen, oxygen or halogen atoms. The heteroatom withdraws electrons from carbonyl carbon and makes carbonyl oxygen lone pair of electrons more stabilized due to its involvement in increasing C=O bond order. As a result, the n Æ π* transition of these compounds is shifted to 200-215 nm range relative to 270 nm in aldehydes and ketones. Conjugation of the carbonyl group with double bond shifts both n Æ π* and π Æ π* transitions to longer wavelengths. The effect on π Æ π* band is more pronounced. Woodward formulated rules to predict the position of an absorption maximum inan unknown enone. These rules have been summarized in table 6.

Table: ***Empirical Rules for α, β-unsaturated ketones and aldehydes absorption maxima.***

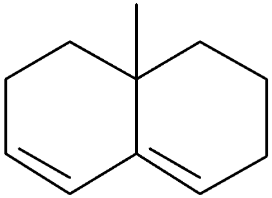
Parent acyclic ketone or six-membered		215 nm
Parent α, β-unsaturated pentanone		202 nm
Parent α, β-unsaturated aldehyde		207 nm
Increments for		
(a) a double bond extending conjugation		30 nm
(b) each alkyl group or ring residue	α	10 nm
	β	12 nm
	γ or higher	18 nm
(c) auxochrome		
(i) –OH	α	35 nm
	β	30 nm
	δ	50 nm
(ii) OCOR	α, β, δ	6 nm
(iii) OCH_3	α	35 nm
	β	30 nm
	γ	17 nm
	δ	31 nm
(iv) Cl	α	15 nm
	β	12 nm
(v) Br	α	25 nm
	β	30 nm
(Vi) NR_2	β	95 nm
(d) exocyclic double bond		5 nm
(e) Homocyclic diene		30 nm

Aromatic Compounds

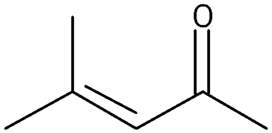
The simplest aromatic compound is benzene. It shows two primary bands at 184 (ε = 47,000) and 202 (ε = 7400) nm and a secondary fine structure band at 255 nm (ε = 230 in cyclohexane). Substituents on the benzene ring also cause bathochromic and hypsochromic shifts of various peaks. Unlike dienes and unsaturated ketones, the effects of various substituents on the benzene ring are not predictable. However, qualitative understanding of the effects of substituents on the characteristics of UV-Vis spectrum can be considered by classifying the substituents into electron-donating and electron-withdrawing groups.



Base value 217 2 x
alkyl subst. 10 exo
DB 5 total
232 Obs. 237



Base value 214 3 x
alkyl subst. 30 exo
DB 5 total
234 Obs. 235



Base value 215 2 ß
alkyl subst. 24
total 239 Obs.
237