

UV-VIS spectroscopy
or
Electronic Spectroscopy (Part-II)

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Effect of substituents

The attachment of substituent groups (other than H) can modify the position and intensity of an absorption band.

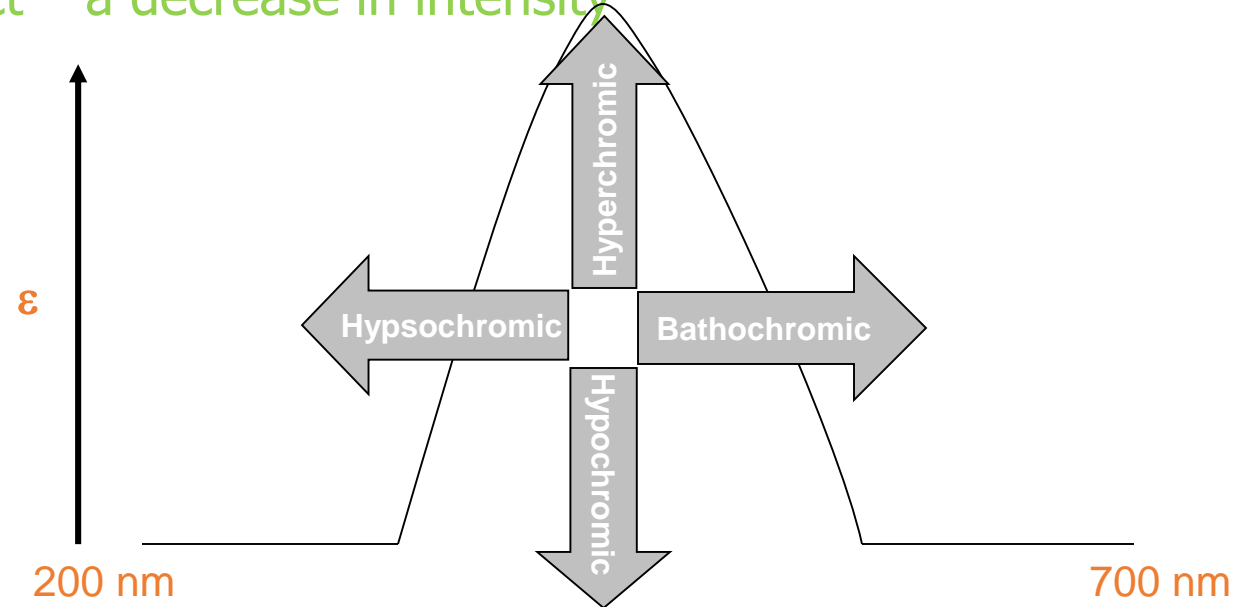
Certain substituents that do not absorb in the UV-Vis region but when attached to a chromophore bring about a shift of the absorption band towards the red end of the spectrum (longer wave length) are called *auxochromes*.

Common auxochromes include alkyl, hydroxyl, alkoxy and amino groups and the halogens

Substituent Effects

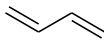
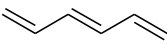
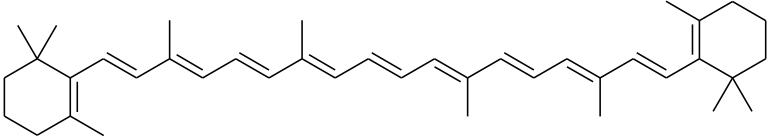

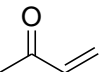
General – Substituents may have any of four effects on a chromophore

1. **Bathochromic shift (red shift)** – a shift to longer λ ; lower energy
2. **Hypsochromic shift (blue shift)** – shift to shorter λ ; higher energy
3. **Hyperchromic effect** – an increase in intensity
4. **Hypochromic effect** – a decrease in intensity



Substituent Effects

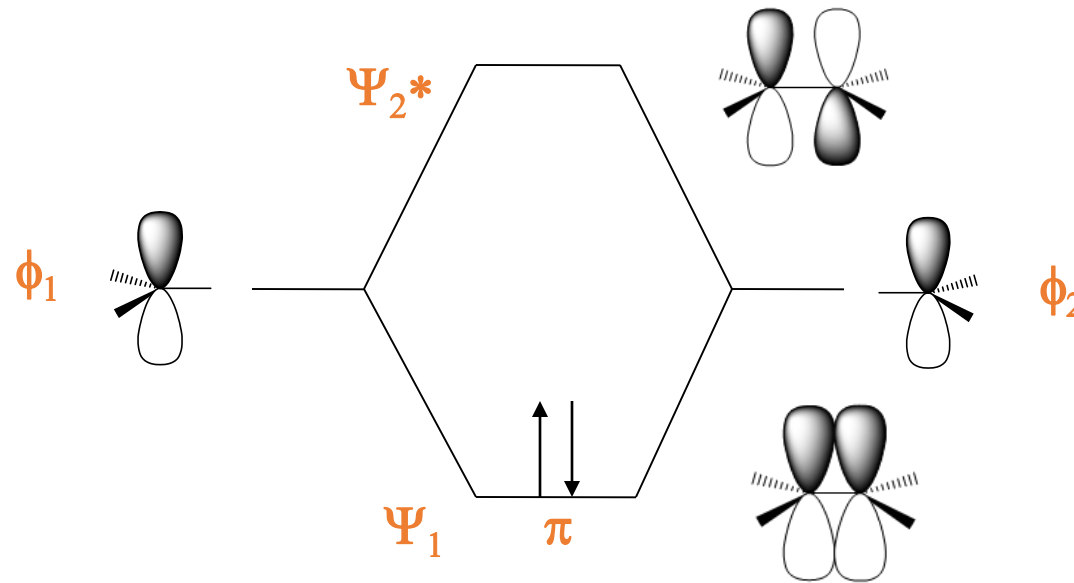
Conjugation - most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore

	λ_{max} nm	ϵ
$\text{H}_2\text{C}=\text{CH}_2$	175	15,000
	217	21,000
	258	35,000
 β-carotene	465	125,000
	$n \rightarrow \pi^*$ 280 $\pi \rightarrow \pi^*$ 189	12 900
	$n \rightarrow \pi^*$ 280 $\pi \rightarrow \pi^*$ 213	27 7,100

Conjugation of Alkenes

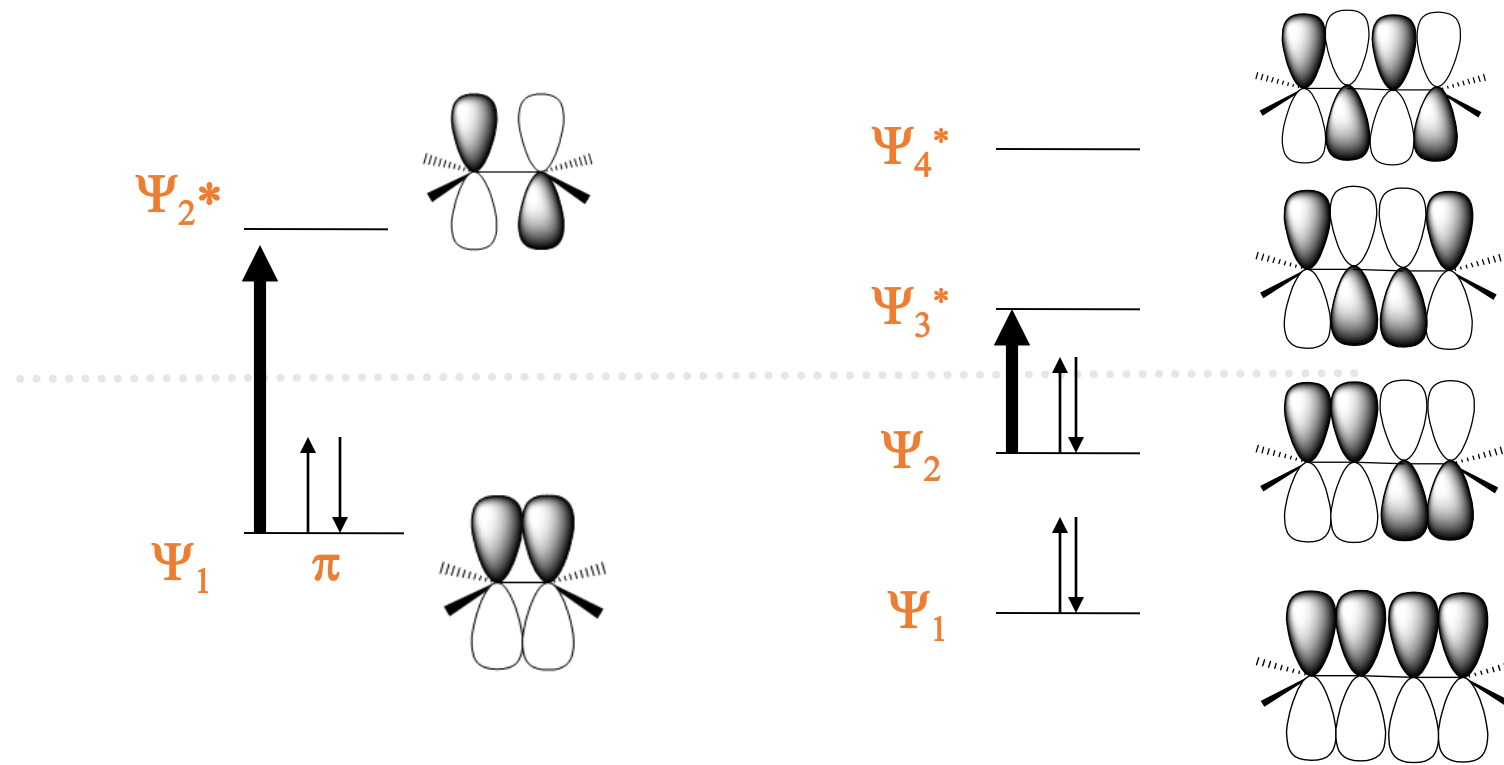
The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation

From molecular orbital (MO) theory two atomic p orbitals, ϕ_1 and ϕ_2 from two sp^2 hybrid carbons combine to form two MOs Ψ_1 and Ψ_2^* in ethylene



Conjugation of Alkenes

When we consider butadiene, we are mixing 4 p orbitals giving 4 MOs of an energetically symmetrical distribution compared to ethylene

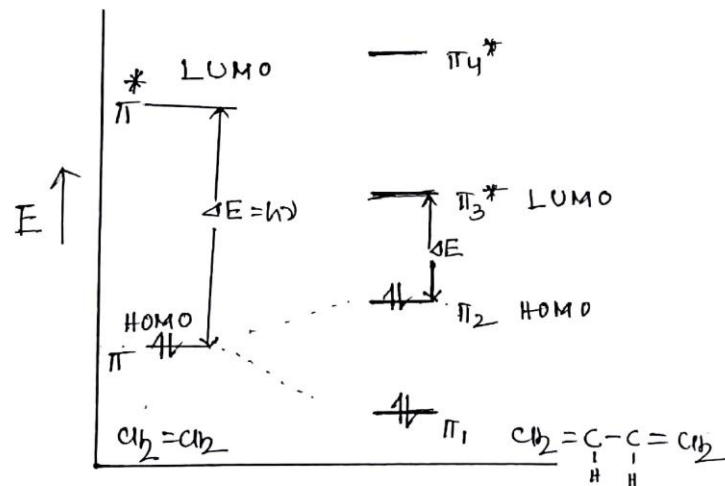


ΔE for the HOMO \rightarrow LUMO transition is **reduced**

Different types of conjugation and their effect. (11)

π - π Conjugation \Rightarrow Systems containing alternating π bonds are responsible for this type of conjugation, involving the overlap of π orbitals. Due to this conjugation the energy difference between ground state and excited state decrease and the λ_{max} as well as intensity of absorption increase. This band is called as the K-band.

As the energy gap between HOMO & LUMO decreases $n \rightarrow \pi^*$ transition due to the presence of hetero atom also shifts towards longer wave length, but a very small shift of intensity (R band)

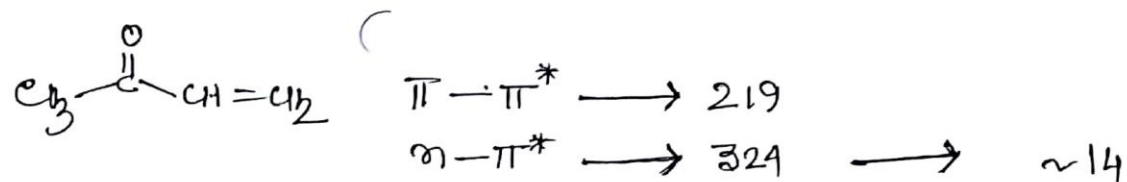
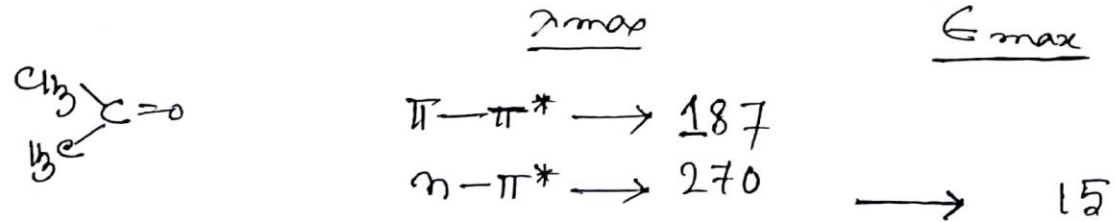


As the no of conjugation increases the length of π -conjugated system increase, which further decrease the energy gap between HOMO and LUMO. So with the increasing no of conjugation the system will move towards higher and higher λ_{max} values.

As the no of conjugation increases the length of π -conjugated system increase, which further decrease the energy gap between HOMO and LUMO. So with the increasing no of π -conjugation the system will move towards higher and higher λ_{max} values.

<u>Compound</u>	<u>λ_{max}</u>	<u>ϵ_{max}</u>
<chem>C=C</chem>	171	15
<chem>C=CC=C</chem>	217	21000
<chem>C=CC=CC=C</chem>	258	35000
B-carotene (11 Double bonds)	465	125,000.

Some $n \rightarrow \pi^*$ transitions also suffer.

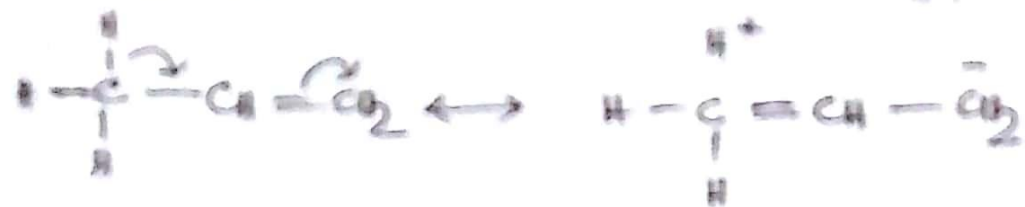


1. $\pi \rightarrow p$ Conjugation The conjugation of a lone pair of electrons from a heteroatom with an unsaturated π electron system results a $\pi \rightarrow p$ conjugation. This increases λ_{max} but ϵ_{max} remains almost-unchanged.

<u>System</u>	<u>λ_{max} (nm)</u>	<u>ϵ_{max}</u>
<chem>C=C</chem>	175	10^3
<chem>CC(=O)C=C</chem>	190	10^3
<chem>(CC(=O))2C=C</chem>	230	10^3

c. $\pi \rightarrow \sigma$ Conjugation (hyperconjugation)

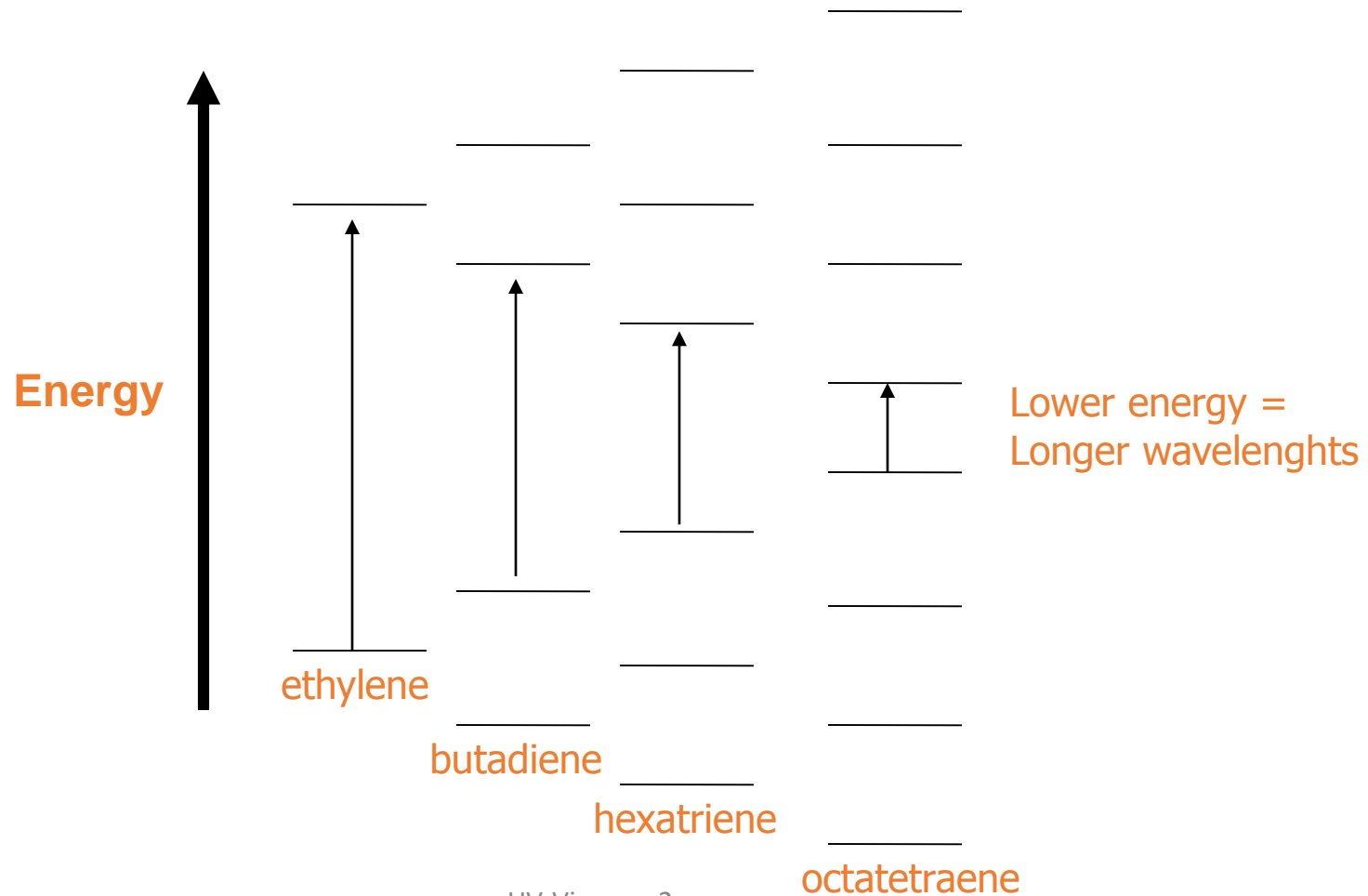
Alkyl substituents when attached to the unsaturated system results very small shift towards longer wave length. This is attributed to hyperconjugation.



	λ_{max}	ϵ_{max}
$\text{H}_2\text{C}=\text{CH}=\text{CH}=\text{CH}_2$	217	$\sim 2.1 \times 10^3$
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	223	$\sim 2.4 \times 10^3$
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	227	$\sim 2.3 \times 10^3$

Conjugation – of Alkenes

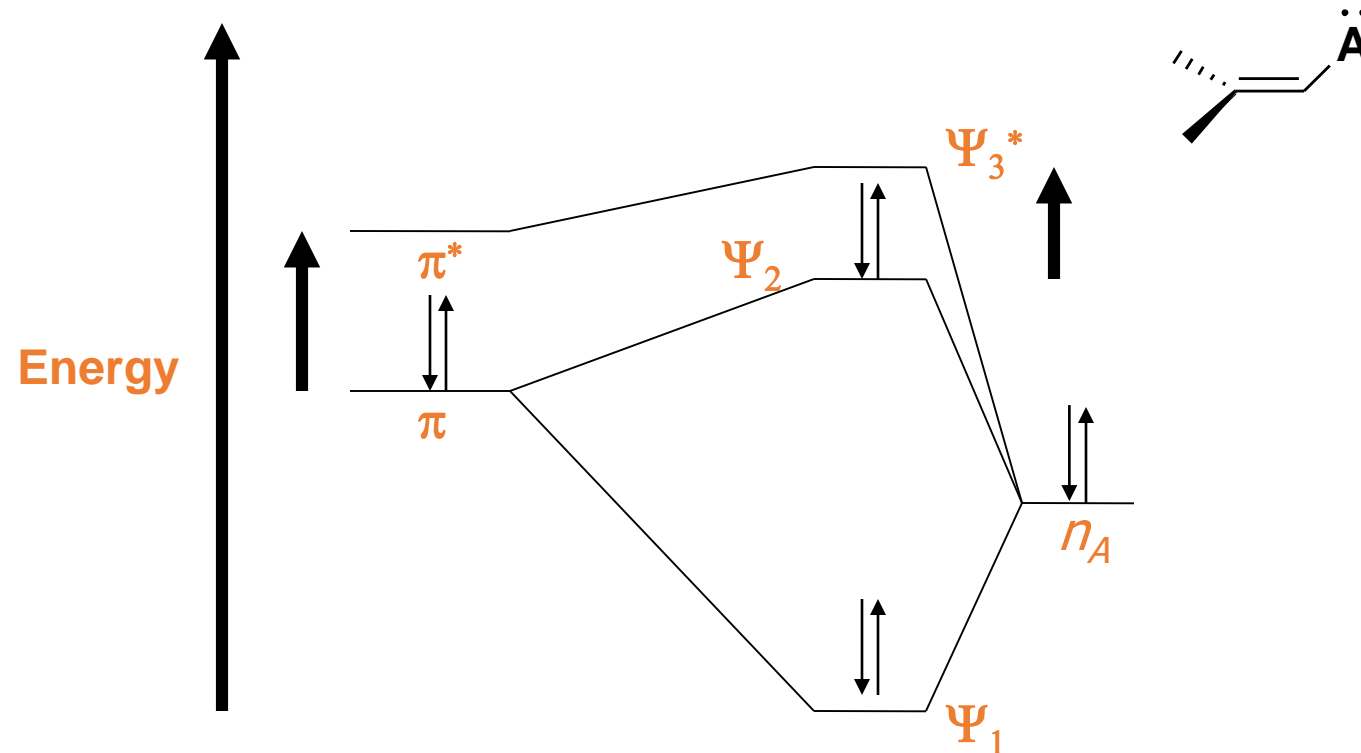
Extending this effect to longer conjugated systems the energy gap becomes progressively smaller thereby making it absorb at higher wavelengths.



Conjugation of Alkenes

Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems - auxochromes

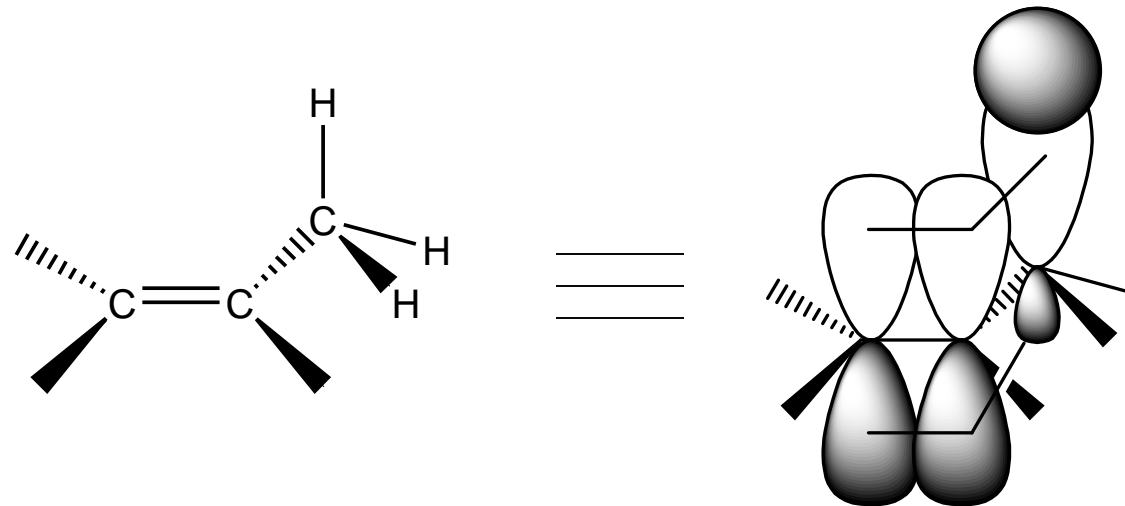
Here we create 3 MOs - this interaction is not as strong as that of a conjugated p-system



Conjugation of Alkenes

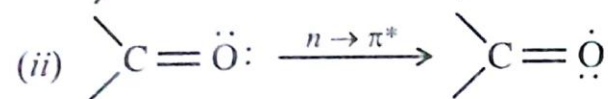
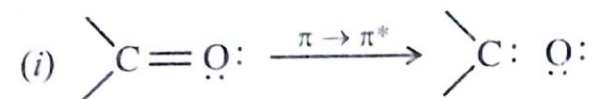
Methyl groups also cause a bathochromic shift, even though they are devoid of π - or n -electrons

This effect is thought to be through what is termed “hyperconjugation” or sigma bond resonance



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

For a carbonyl group, two types of transitions occur.



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

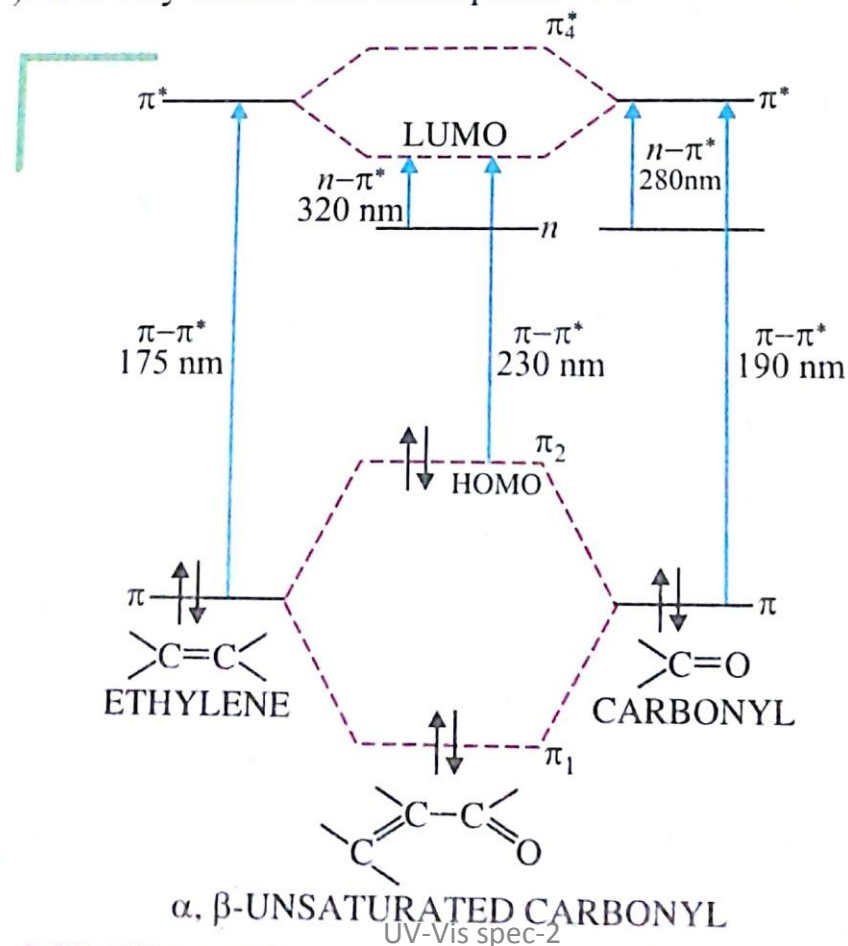


Fig. 2.23. UV transitions in α, β -unsaturated carbonyl compounds.

A comparison in the ultra-violet spectra of un-conjugated carbonyl compounds (see Fig. 2.25) reveals that the value of absorption maximum for carbonyl group experiences a bathochromic as well as hyperchromic effects in conjugated carbonyl compound as compared to an un-conjugated carbonyl compound.

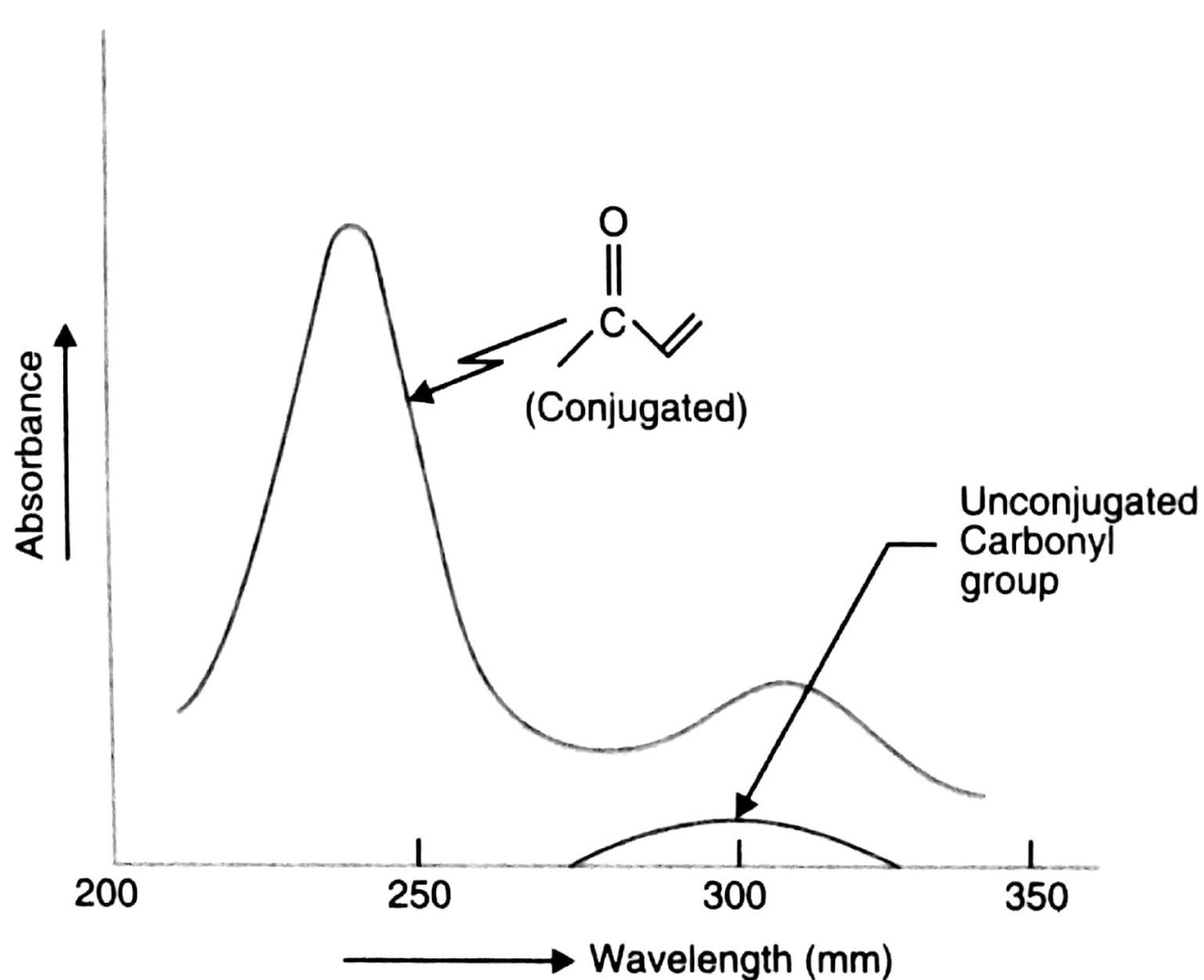


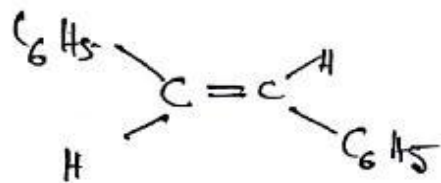
Fig. 2.25. UV Absorption spectra for conjugated and unconjugated carbonyl compounds.

twist to conformation

①

Effect of geometrical isomerism and steric effect -

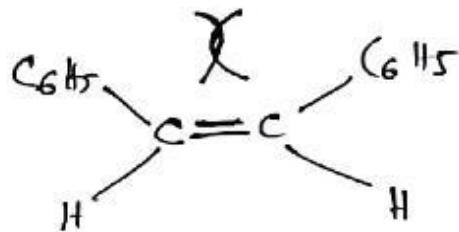
cis-Stilbene vs trans-Stilbene



Trans Stilbene

$$\lambda_{max} = 295 \text{ nm}$$

$$\epsilon \approx 27,000$$



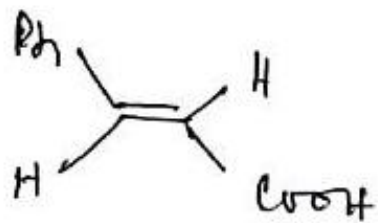
cis Stilbene

$$\lambda_{max} = 280 \text{ nm}$$

$$\epsilon \approx 13,500$$

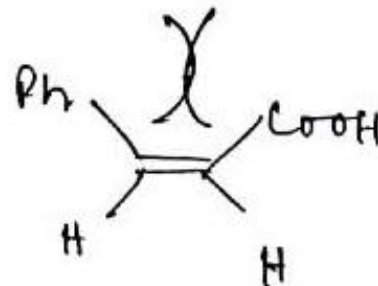
In cis isomer, the two phenyl rings are very close to each other and due to repulsion the two Ph rings are slightly out of plane from the C=C. Thus effective overlap/conjugation is reduced. Thus λ_{max} for cis < λ_{max} of trans ($\pi \rightarrow \pi^*$ overlap is much more effective)

Similar to:



$$\lambda_{\max} = 272 \text{ nm}$$

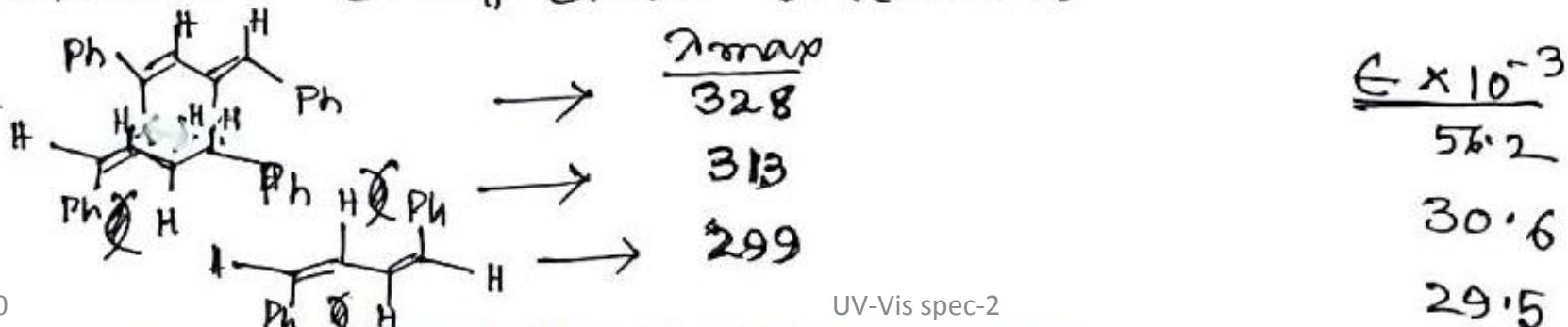
$$(\epsilon_{\max} = 16000)$$



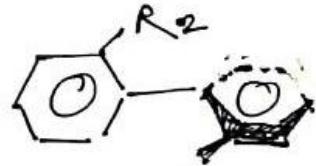
$$\lambda_{\max} = 268 \text{ nm}$$

$$(\epsilon_{\max} = 10,700)$$

1,4 Diphenyl butadiene (DPBD) shows the effect of change in geometrical isomerism and hence steric hindrance on the spectra of conjugated olefins. With increasing steric hindrance the wavelength of absorption and extinction coefficient decreases.



In case of biphenyls also steric hindrance reduce the scope of conjugation. Biphenyl derivatives with bulky groups at ortho position force the compound to take twist conformation so as to avoid the repulsive interaction between the ortho substituents. This loses coplanarity of the system and reduces the extent of conjugation. Thus λ value also decrease.



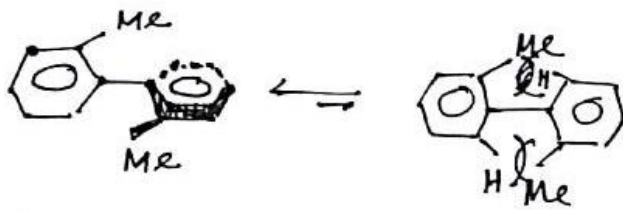
Twist conformation

When $R_1 = R_2 = \text{Me}$ or larger groups.

$$\left. \begin{array}{l} R_1 = \text{H} \\ R_2 = \text{H} \end{array} \right\} \lambda_{\text{max}} = 249$$

$$\left. \begin{array}{l} R_1 = \text{H} \\ R_2 = \text{Me} \end{array} \right\} = 237$$

$$\left. \begin{array}{l} R_1 = \text{Me} \\ R_2 = \text{Me} \end{array} \right\} = 220$$



Twist.

Regular

More stable

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.

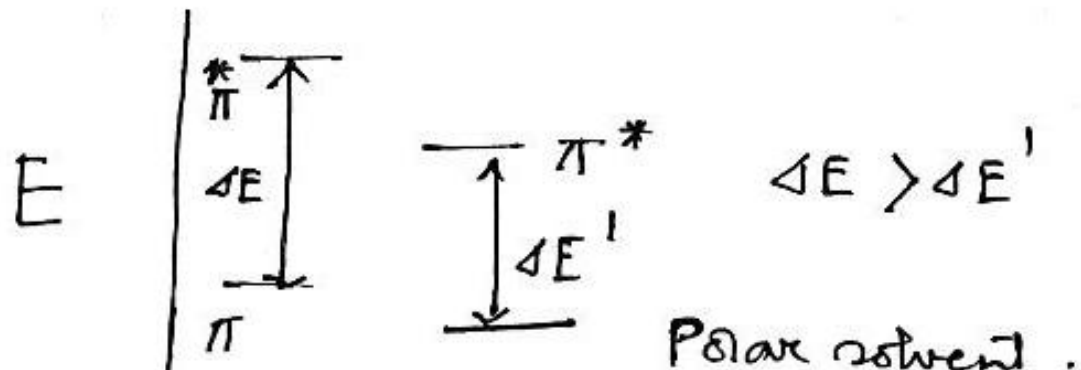
(i) $\pi \rightarrow \pi^*$ Transitions

In case of $\pi \rightarrow \pi^*$ 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 $\pi \rightarrow \pi^*$ transition and absorption maximum appears ~10-20 nm red shifted in going from hexane to ethanol solvent.

Solvent effect -

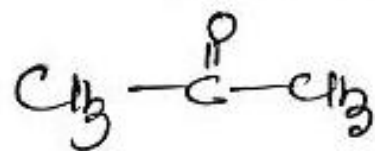
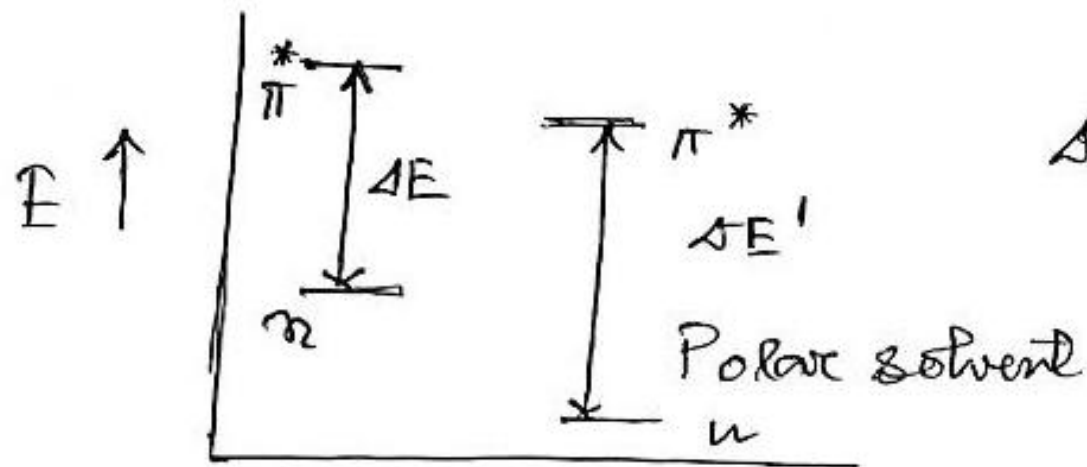
$\pi \rightarrow \pi^*$ transition.

Here the excited state is of more polar than the ground state, so polar solvents should stabilise the excited state more than the ground state. Thus the energy gap between ground state and excited state (HOMO - LUMO) decreases and λ_{max} increases. Thus in case of $\pi \rightarrow \pi^*$ transition polar solvents will increase the λ_{max} values (Bathochromic or red shift)



$n \rightarrow \pi^*$ transition

In this case the ground state is more polar than the excited state. The ground state is thus more stabilised than the excited state. ΔE increases and λ_{max} decreases (hypsochromic or blue shift)



$\lambda_{max} =$

CH_2Cl_2
278 nm

C_2H_5OH
270 nm

H_2O
265 nm

λ_{max} decreases.

(ii) $n \rightarrow \pi^*$ Transitions

In case of $n \rightarrow \pi^*$ 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 the absorption maximum of acetone in hexane appears at 279 nm which in water is shifted to 264 nm, with a blue shift of 15 nm.

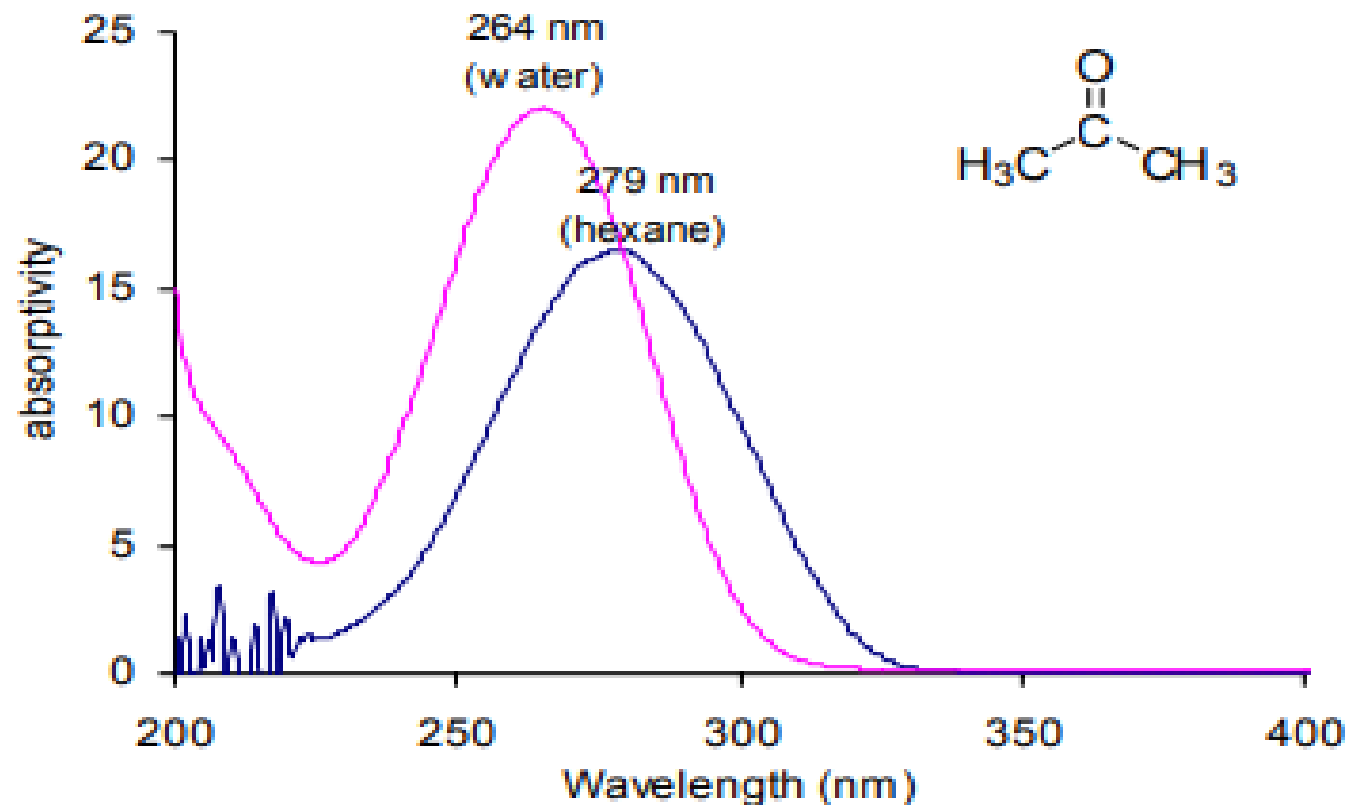
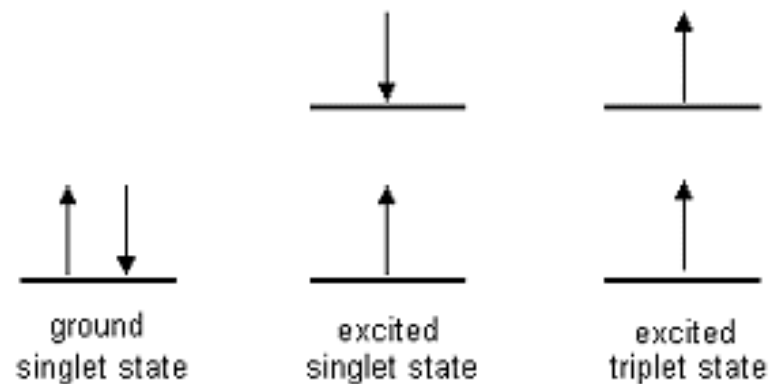


Figure 5 : UV-spectra of acetone in hexane and in water

More Complex Electronic Processes

- **Fluorescence:** absorption of radiation to an excited state, followed by emission of radiation to a lower state of the same multiplicity (singlet to singlet transition.)
- **Phosphorescence:** absorption of radiation to an excited state, followed by emission of radiation to a lower state of different multiplicity (triplet to singlet transition)
- **Singlet state:** spins are paired, no net angular momentum (and no net magnetic field)
- **Triplet state:** spins are unpaired, net angular momentum (and net magnetic field)

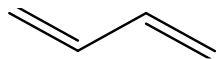


IV. Structure Determination

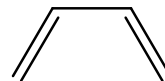
A. Dienes

1. General Features

For acyclic butadiene, two conformers are possible – *s-cis* and *s-trans*



s-trans



s-cis

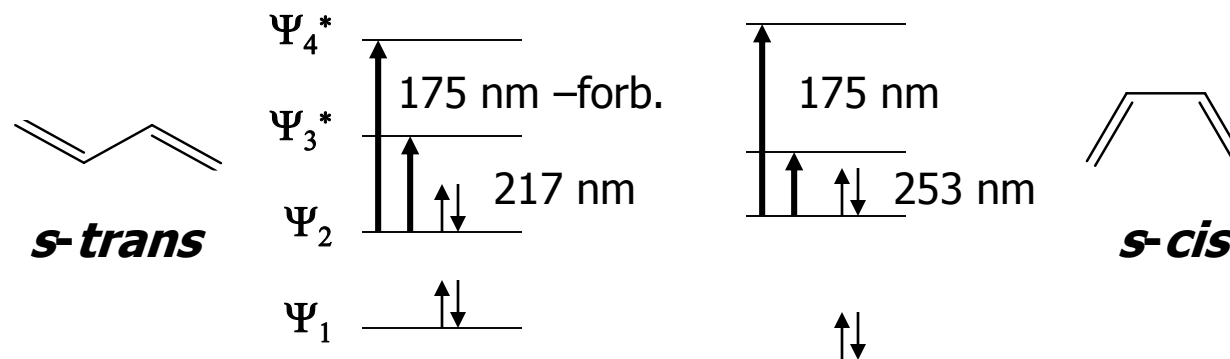
The *s-cis* conformer is at an overall higher potential energy than the *s-trans*; therefore the HOMO electrons of the conjugated system have less of a jump to the LUMO – lower energy, longer wavelength

Structure Determination

A. Dienes

1. General Features

Two possible $\pi \rightarrow \pi^*$ transitions can occur for butadiene $\Psi_2 \rightarrow \Psi_3^*$ and $\Psi_2 \rightarrow \Psi_4^*$



The $\Psi_2 \rightarrow \Psi_4^*$ transition is not typically observed:

- The energy of this transition places it outside the region typically observed – 175 nm
- For the more favorable *s-trans* conformation, this transition is forbidden

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption

Structure Determination

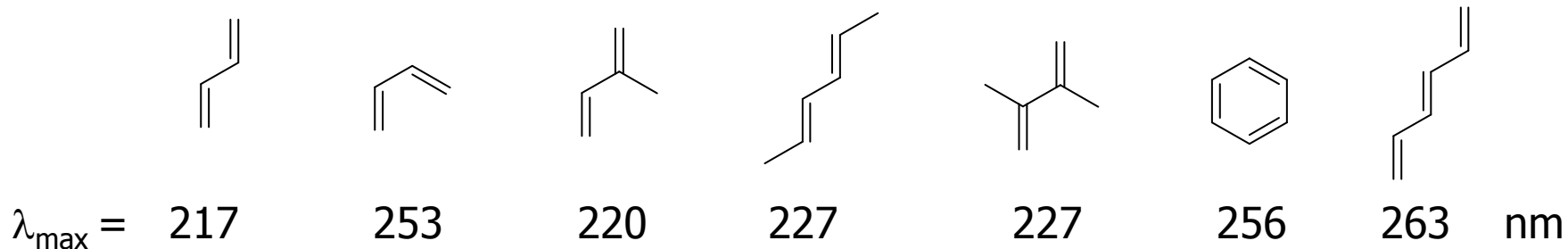
A. Dienes

1. General Features

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption ($\epsilon = 20,000+$) based at 217 nm within the observed region of the UV

While this band is insensitive to solvent (as would be expected) it is subject to the bathochromic and hyperchromic effects of alkyl substituents as well as further conjugation

Consider:



Structure Determination

A. Dienes

2. Woodward-Fieser Rules

Woodward and the Fiesers performed extensive studies of terpene and steroidal alkenes and noted similar substituents and structural features would predictably lead to an empirical prediction of the wavelength for the lowest energy $\pi \rightarrow \pi^*$ electronic transition

This work was distilled by Scott in 1964 into an extensive treatise on the Woodward-Fieser rules in combination with comprehensive tables and examples – (A.I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon, NY, 1964)

A more modern interpretation was compiled by Rao in 1975 – (C.N.R. Rao, *Ultraviolet and Visible Spectroscopy*, 3rd Ed., Butterworths, London, 1975)

Dienes

2. Woodward-Fieser Rules - Dienes

The rules begin with a base value for λ_{\max} of the chromophore being observed:



acyclic butadiene = 214 nm

The incremental contribution of substituents is added to this base value from the group tables:

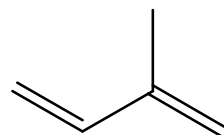
Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
-OCOCH ₃	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
-NR ₂	+60

Structure Determination

A. Dienes

2. Woodward-Fieser Rules - Dienes

For example:



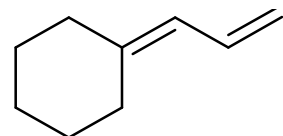
Isoprene - acyclic butadiene =
one alkyl subs.

214 nm
+ 5 nm

219 nm

Experimental value

220 nm



Allylidencyclohexane

- acyclic butadiene =
one exocyclic C=C
2 alkyl subs.

214 nm
+ 5 nm

+10 nm

229 nm

Experimental value

237 nm

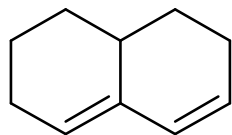
Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

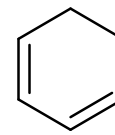
There are two major types of cyclic dienes, with two different base values

Heteroannular (transoid):



$$\varepsilon = 5,000 - 15,000$$
$$\text{base } \lambda_{\text{max}} = 214$$

Homoannular (cisoid):



$$\varepsilon = 12,000 - 28,000$$
$$\text{base } \lambda_{\text{max}} = 253$$

The increment table is the same as for acyclic butadienes with a couple additions:

Group	Increment
Additional homoannular	+39

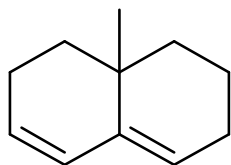
Where both types of diene are present, the one with the longer λ becomes the base

Structure Determination

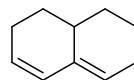
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

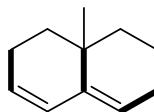
For example:



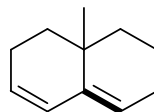
1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene
heteroannular diene = 214 nm



3 alkyl subs. (3 x 5) +15 nm



1 exo C=C + 5 nm
234 nm

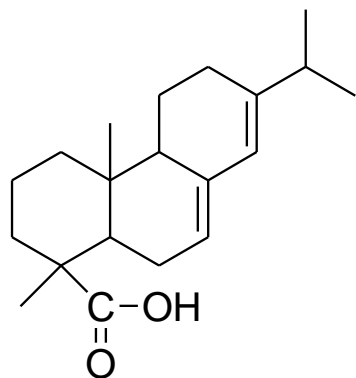


Experimental value 235 nm

IV. Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

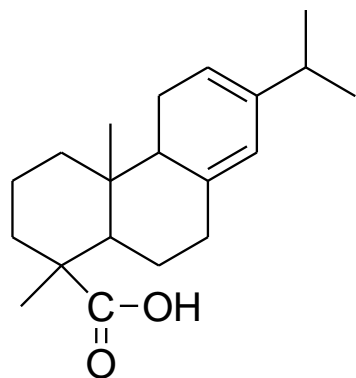


heteroannular diene = 214 nm

4 alkyl subs. (4 x 5) +20 nm

1 exo C=C + 5 nm

239 nm



homoannular diene = 253 nm

4 alkyl subs. (4 x 5) +20 nm

1 exo C=C + 5 nm

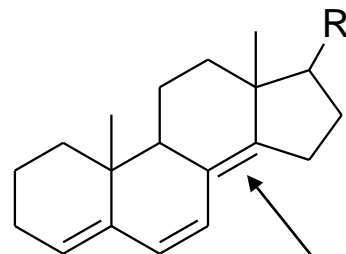
278 nm

Structure Determination

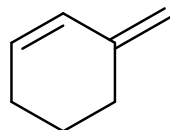
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

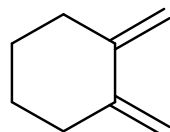
Be careful with your assignments – three common errors:



This compound has three exocyclic double bonds; the indicated bond is exocyclic to **two** rings



This is **not** a heteroannular diene; you would use the base value for an acyclic diene



Likewise, this is **not** a homoannular diene; you would use the base value for an acyclic diene



Base value = 214

Exocyclic double bond = 5, Ring residue $2 \times 5 = 10$

$\lambda_{max} = 229 \text{ nm}$.

5.



Base value = 253 nm

D.B. Ex long = 30 "

Exocyclic D.B = 5 "

Ring residue = 15 (5×3) "

Polar gr = 6 "

$\lambda_{max} = \underline{\underline{309 \text{ nm}}}$

6.



Base value = 253 nm

2 D.B.E. = 60 "

Ring residue (5) = 25 "

Exocyclic double bond = 5 "

$\lambda_{max} = \underline{\underline{343 \text{ nm}}}$

7.



$$\begin{aligned} \text{Base value} &= 253 \text{ nm} \\ \text{Ex. D.B. (2x5)} &= 10 \text{ " } \\ \text{D.B. Ex Long} &= 30 \text{ " } \\ \text{Ring Residue} &= 20 \text{ " } \end{aligned}$$

$$\lambda_{\text{max}} \underline{\underline{313 \text{ "}}}$$

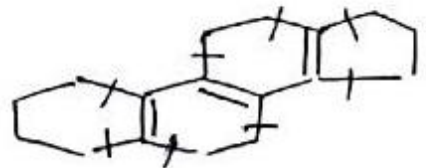
8.



$$\begin{aligned} \text{B.V} &= 214 \text{ " } \\ \text{Ring Residue} &= 25 \text{ " } \\ \text{D.B. E. Long} &= 30 \text{ " } \\ \text{Exocyclic D.B. (3)} &= 15 \text{ " } \end{aligned}$$

$$\lambda_{\text{max}} \underline{\underline{284 \text{ "}}}$$

9.



$$\text{B.V} = 253 \text{ nm}$$

$$\text{D.B. Ex.} = 30 \text{ "}$$

$$\text{Ring Residue (8)} = 40 \text{ "}$$

$$\lambda_{\text{max}} \underline{\underline{323 \text{ "}}}$$

10.



$$253 \text{ nm B. value}$$

$$\underline{20 \text{ " R. Residue}}$$

$$\underline{\underline{273 \text{ "}}}$$

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

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

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

where

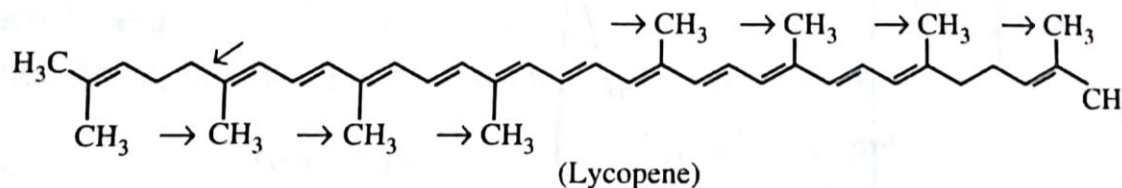
n = no. of conjugated double bonds.

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.

Consider the case of Lycopene :



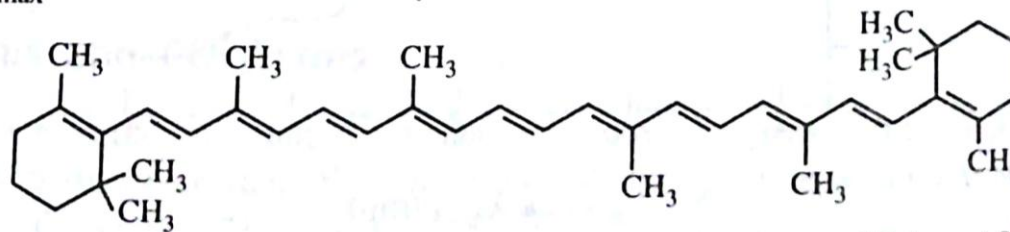
In this compound, only eleven double bonds are in conjugation. Thus, $n = 11$. In addition to this, there are eight substituents (methyl groups and chain residues). Thus, $M = 8$. As there is no ring system, there are neither exo nor endocyclic double bonds in this conjugated system. λ_{max} can be calculated as under :

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

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

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

Similarly, λ_{max} can be calculated for β -carotene.



The calculated value of λ_{max} is found to be 453.3 nm and $\epsilon_{max} = 19.1 \times 10^4$.

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

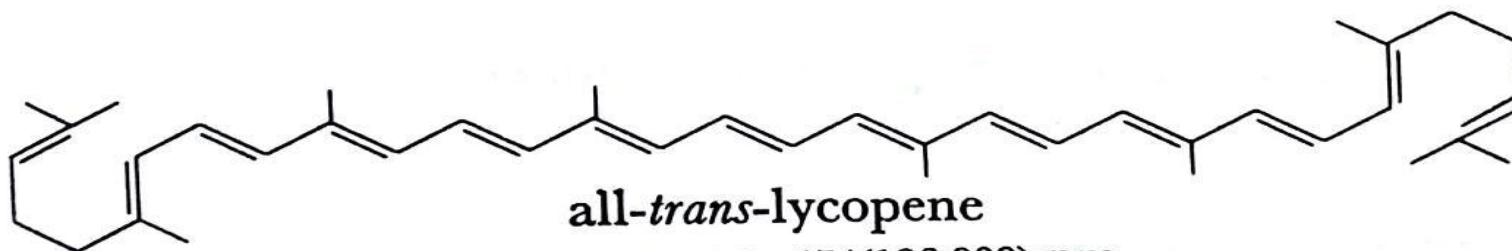
$$\epsilon_{\max} = (1.74 \times 10^4)n \quad \text{where}$$

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



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

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

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

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

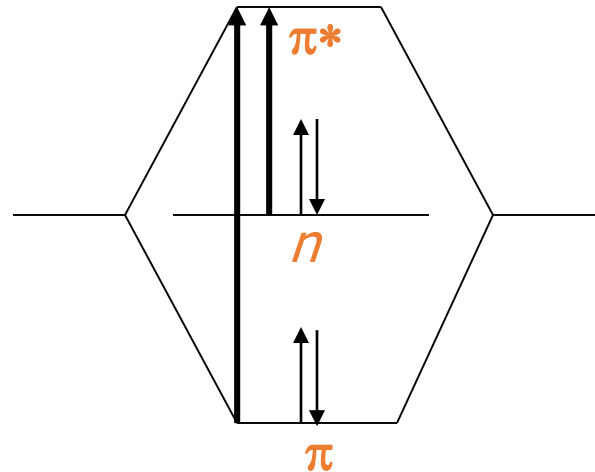
$$\epsilon_{\max}^{\text{obs}}(\text{hexane}) = 18.6 \times 10^4 \quad \text{UV-Vis spec-2}$$

Structure Determination

B. Enones

1. General Features

Carbonyls, as we have discussed have two primary electronic transitions:



Remember, the $\pi \rightarrow \pi^*$ transition is allowed and gives a high ϵ , but lies outside the routine range of UV observation

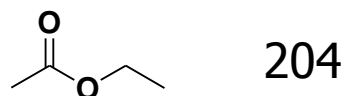
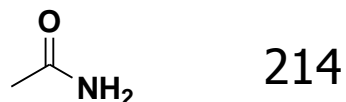
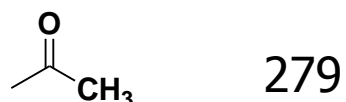
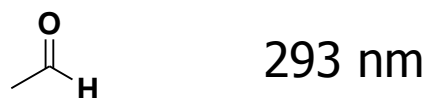
The $n \rightarrow \pi^*$ transition is forbidden and gives a very low ϵ , but can routinely be observed

IV. Structure Determination

B. Enones

1. General Features

For auxochromic substitution on the carbonyl, pronounced hypsochromic shifts are observed for the $n \rightarrow \pi^*$ transition (λ_{\max}):



This is explained by the inductive withdrawal of electrons by O, N or halogen from the carbonyl carbon – this causes the n -electrons on the carbonyl oxygen to be held more firmly

It is important to note this is different from the auxochromic effect on $\pi \rightarrow \pi^*$ which extends conjugation and causes a bathochromic shift

In most cases, this bathochromic shift is not enough to bring the $\pi \rightarrow \pi^*$ transition into the observed range

IV. Structure Determination

B. Enones

1. General Features

Conversely, if the C=O system is conjugated both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are bathochromically shifted

Here, several effects must be noted:

- i. the effect is more pronounced for $\pi \rightarrow \pi^*$
- ii. if the conjugated chain is long enough, the much higher intensity $\pi \rightarrow \pi^*$ band will overlap and drown out the $n \rightarrow \pi^*$ band
- iii. the shift of the $n \rightarrow \pi^*$ transition is not as predictable

For these reasons, empirical Woodward-Fieser rules for conjugated enones are for the higher intensity, allowed $\pi \rightarrow \pi^*$ transition

IV. Structure Determination

B. Enones

1. General Features

These effects are apparent from the MO diagram for a conjugated enone:

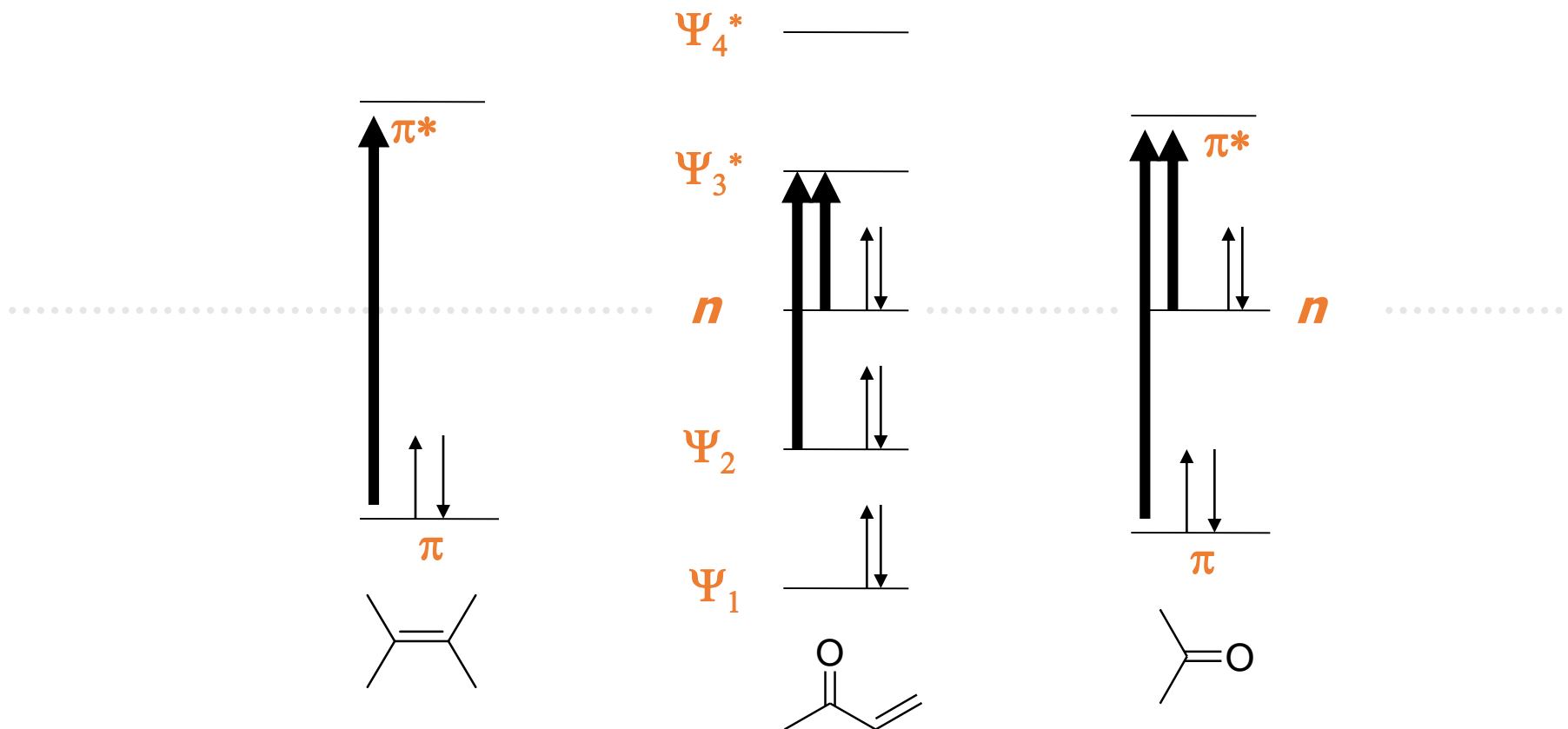


Table 2.6 : Rules for α , β -Unsaturated Aldehydes and Ketones

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

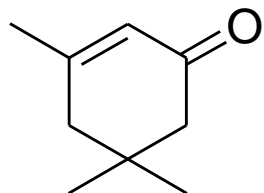
Value assigned to				
ketones	$\begin{array}{c} \beta \\ \\ -\text{C}=\text{C}-\text{CO}- \\ \\ \alpha \end{array}$	acyclic or 6-ring cyclic	215 nm	
		5-ring cyclic	202 nm	
aldehydes	$\begin{array}{c} \\ -\text{C}=\text{C}-\text{CHO} \\ \end{array}$		207 nm	
acids and esters	$\begin{array}{c} \\ -\text{C}=\text{C}-\text{CO}_2 \text{H(R)} \\ \end{array}$		197 nm	
extended conjugation				
	$\begin{array}{c} \delta \\ \\ -\text{C}=\text{C}-\text{C}=\text{C}-\text{CO}- \text{ etc.} \\ \quad \quad \quad \\ \gamma \quad \beta \quad \alpha \end{array}$		add 30 nm	
homodiene component			add 39 nm	
Increments for				
	α	β	γ	δ
—R alkyl (including part of a carbocyclic ring)	10 nm	12 nm	γ and higher	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	

Unlike conjugated alkenes, solvent does have an effect on λ_{\max}

These effects are also described by the Woodward-Fieser rules

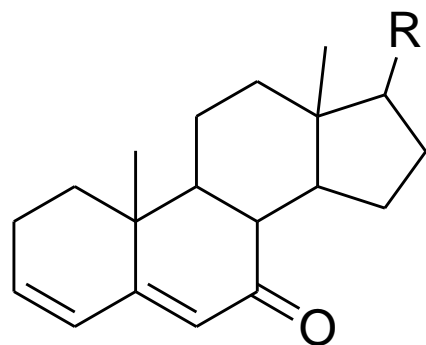
Solvent correction	Increment
Water	+8
Ethanol, methanol	0
Chloroform	-1
Dioxane	-5
Ether	-7
Hydrocarbon	-11

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



cyclic enone =	215 nm
2 x β - alkyl subs. (2 x 12)	<u>+24 nm</u>
	239 nm

Experimental value	238 nm
--------------------	--------



cyclic enone =	215 nm
extended conj.	+30 nm
b-ring residue	+12 nm
d-ring residue	+18 nm
exocyclic double bond	<u>+ 5 nm</u>
	280 nm

Experimental	280 nm
--------------	--------

Dicarbonyl Compounds-

α -Diketones: Acyclic α -diketones such as biacetyl exist in the *s-trans* conformation with the dihedral angle of 180° .

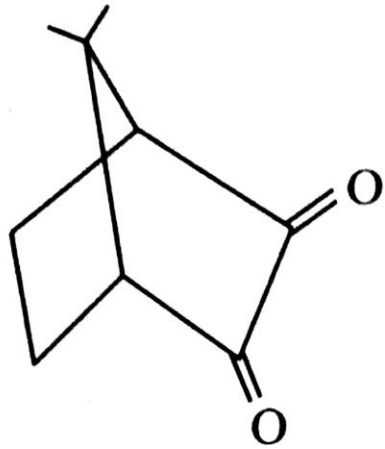


$$\phi = 180^\circ$$

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

$$\epsilon_{\text{max}} = 10.$$

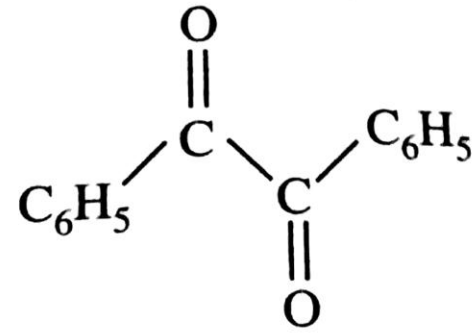
Normal weak band (ϵ) at 275 nm \rightarrow ($n \rightarrow \pi^*$) and a weak band near 450 nm , the latter results from the interaction of the carbonyl groups.



Camphoquinone
(I)
Dihedral angle 0-10°

$$\lambda_{max} = 488 \text{ nm}$$

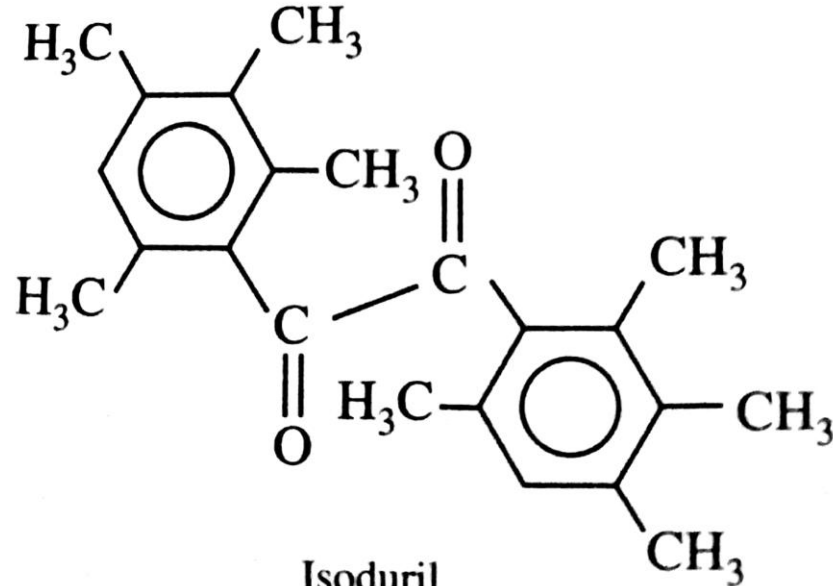
$$\epsilon_{max} = 17$$



Benzil
(II)
Dihedral angle = 90°

$$\lambda_{max} = 370 \text{ nm}$$

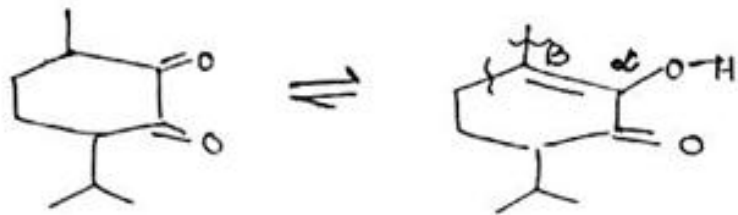
$$\epsilon_{max} = 40$$



Isoduril
(III)
Dihedral angle = 180°

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

In cyclic diketones: The endic forms are more stable, thus the absorption is related to that of an α, β unsaturated system carbonyl system. Six membered cyclic α -diketones rarely exist in solution as endic forms. In strong alkaline solution λ_{max} shifts to about 50 nm towards longer wave lengths, due to the formation of enolate ion.



Base value — 215 nm
 2 β substituents — 24 "
 α OH group — 35 "

$$\lambda_{max}^{EtOH} = \underline{\underline{274 \text{ nm}}}$$

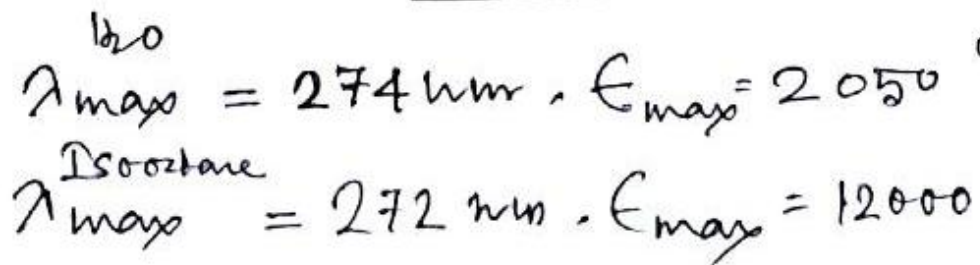
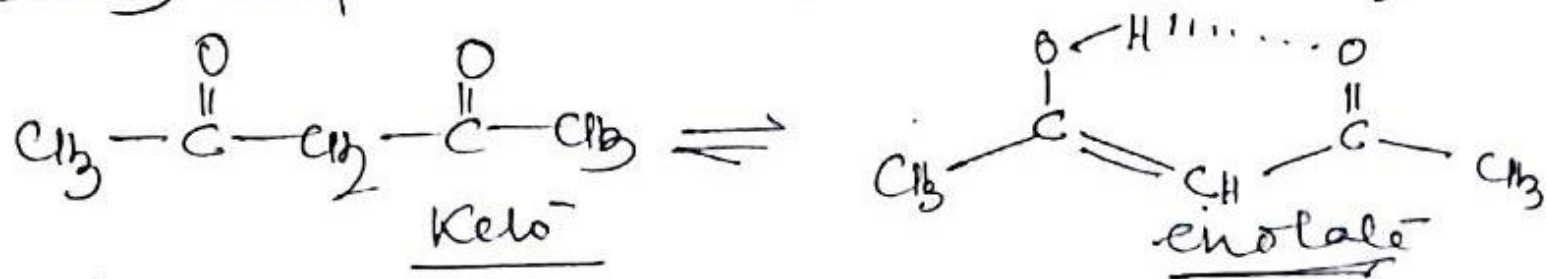
B - Diketones.

The UV spectra of β -B-diketones depend on degree of enolisation. The possibility of intramolecular hydrogen bonding stabilise the enolic form in acetyl acetone.

The enolic species exists $\sim 15\%$ in aqueous solution.

In vapour phase, or in solutions of non polar solvents enolic form exists $\sim 91-92\%$. The absorption is

directly dependant on the concentration of the enol form.



} Thus intensity of absorption increases drastically on changing solvent from polar to nonpolar.

Cyclic β -diketones such as cyclohexane 1,3-dione exists almost exclusively in endic form even in polar solvent. The enolic structures show strong absorption in 230-260 nm region due to $\pi-\pi^*$ transition in the s-trans-enone system.

1,3-cyclohexanedione in (EtOH) absorbs at 253 nm (ϵ_{max} 22,000). The formation of enolate ion, in alkaline solution, shifts the strong absorption band into the 270-300 nm region.



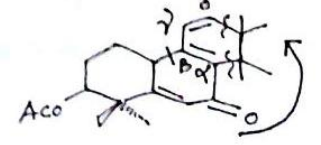
λ_{max} calculation for endic form

Base value	= 215
1 β subs	= +12
β -OH	= 30

$$\lambda_{max}^{EtOH} = 257 \text{ nm}$$

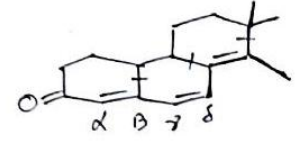
Observed value $\approx 253 \text{ nm}$

9.



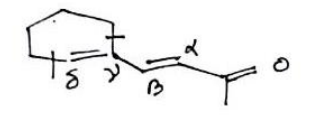
Base value + 215 nm
 Homoannular diene + 39 nm
 One double bond extended conjugation + 30
 1 α ring residue + 10
 1 β " " + 12
 1 δ " " + 18
 λ_{max} 324

10.



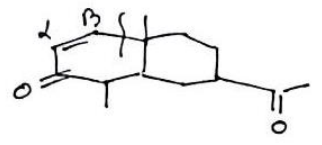
Base value 215 nm
 2 double bond ext. conj 60 "
 2 exocyclic double bond 10 "
 1 β -ring residue 12 "
 1 (δ +1) " " 18
 2 (δ +2) " " 36
 $\lambda_{max} = 351$ nm

11.



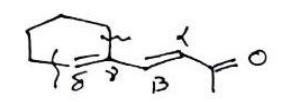
Base value 215 nm
 Double bond ext 30
 1 δ ring residue 18
 1 δ " " 18
281 "

12.



Base value 215 nm
 1 β ring residue 12 "
227 "

13.



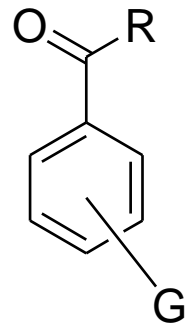
UV-Vis spec-2
 $215 + 30 + 18 + 18 = 281$

Aromatic System

Substituent Effects

d. Di-substituted and multiple group effects

Parent Chromophore	λ_{\max}
R = alkyl or ring residue	246
R = H	250
R = OH or O-Alkyl	230



G	Substituent increment		
	<i>o</i>	<i>m</i>	<i>p</i>
Alkyl or ring residue	3	3	10
-O-Alkyl, -OH, -O-Ring	7	7	25
-O-	11	20	78
-Cl	0	0	10
-Br	2	2	15
-NH ₂	13	13	58
-NHC(O)CH ₃	20	20	45
-NHCH ₃			73
-N(CH ₃) ₂	20	20	85

Aromatic system or Benzene Chromophore

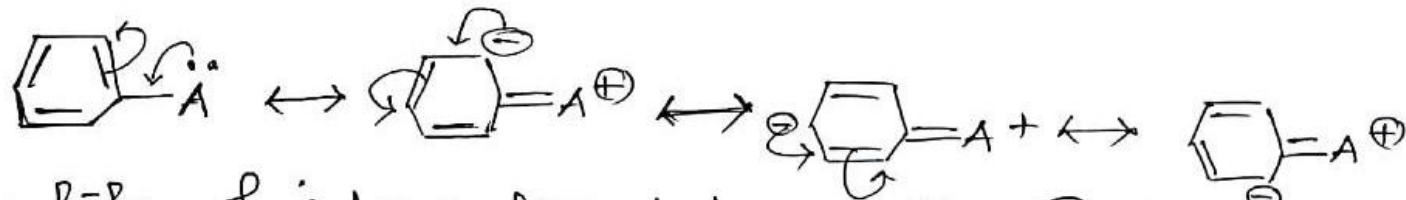
The electronic transition in benzene is mainly due to $\pi-\pi^*$ transition. In benzene three electronic transitions take place leading to three bands. Primary band at $\sim 184 \text{ nm}$ (ϵ_{max} : 48,000 or 60,000?) and 202 nm (ϵ_{max} : 7900) and a secondary band at 254 nm (ϵ_{max} : 200). The first one i.e. at 184 nm is the allowed transition.

Effect of substituents on λ_{max} of Benzene:

Substituents in benzene ring can cause bathochromic and hyperchromic shifts.

A. Substituents with unshared electron pairs. \Rightarrow

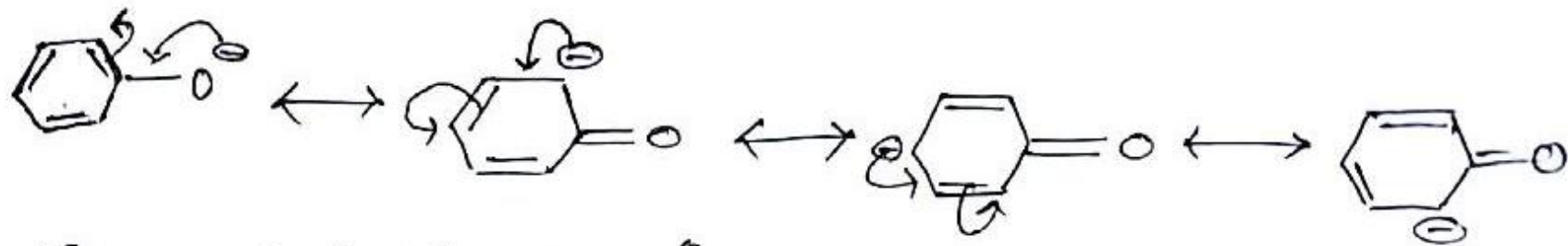
Substituents with unshared pair of electrons can shift the primary and secondary absorption bands. The non bonding electrons can increase the length of the π system through resonance.



This type of interaction between n and π electrons usually shifts the primary and secondary absorption bands of benzene to longer wave lengths.

On moving from benzene to phenol the primary band shifts by 7 nm towards longer wave lengths, while the secondary band by 16 nm.

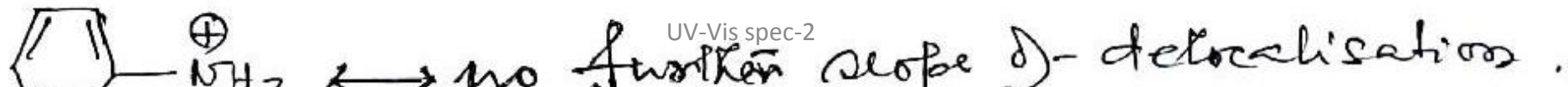
⑦ Phenol vs phenoxide ion: Conversion of phenol to phenoxide ion results in bathochromic shift of the secondary band and the ϵ_{max} also increases, because the non bonding electron pair on oxygen becomes more available for delocalisation with π electron system of the ring than in phenol.



Aniline vs Anilinium ion

On going from benzene to aniline the primary as well as the secondary band shift towards longer wave lengths (204 \rightarrow 230; 254 \rightarrow 280 nm).

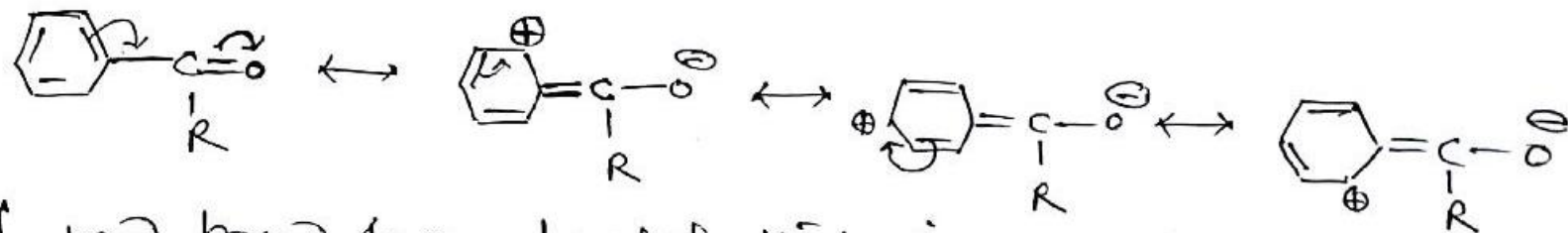
But when aniline is protonated these band shifts are not observed i.e. it is found to behave almost same as benzene does. Because the lone pair of electrons on nitrogen becomes protonated and remains no longer available for delocalisation with π electron system of benzene ring.



Alkyl substitution in benzene ring produces a bathochromic shift δ - secondary band (from 255 nm to 261 nm) with almost no report of primary band shift. This is due to the hyperconjugation δ - the σ electrons of alkyl C-H bond with π electron cloud δ - Benzene ring.

The *ortho*, ^{di}alkyl benzene absorbs at shorter wavelength (with lower ϵ_{max}) than that δ - the para isomer (with even higher ϵ_{max}). This can be explained on the basis δ - steric interaction in *ortho* substituents, which hinders the hyperconjugation.

π Conjugating substituents:



A new band may develop that is so intense that it may obscure (difficult to understand/view) the secondary band δ benzene.

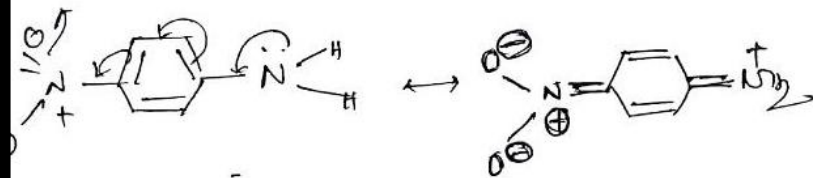
In this case the ring becomes electron deficient

Disubstituted Benzene:

Two cases may arise for para isomers.

Case - I — Both the groups are of same type (i.e. either both of them are electron releasing or both are electron withdrawing) the effect is same as that of mono substituted benzenes. The group having stronger effect controls the extent of shift.

Case - II If one is electron withdrawing, but the other is electron releasing, there is a pronounced red shift in the main absorption band. This is due to the extension of conjugation between the substituents through benzene ring.



But in case of ortho or para, such extension is not possible.

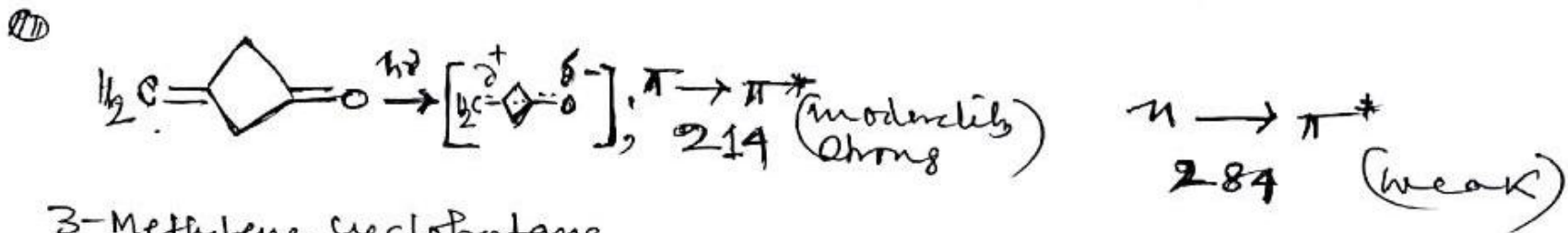
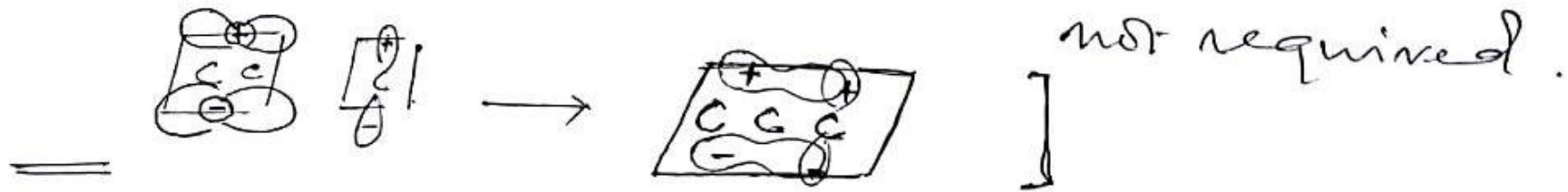
TRANS ANNULAR EFFECT

It is clear that conjugation between $C=O$ and $C=C$ in ~~trans~~ ~~trans~~ sense results in bathochromic shift of the absorption bands of $C=O$ or ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$)

But some cases are found where these two groups are not conjugated to each other in CLASSICAL sense. These are generally cyclic systems, where the geometry / shape of the molecule enables them to involve in π overlap. This causes shift of the UV absorption band.

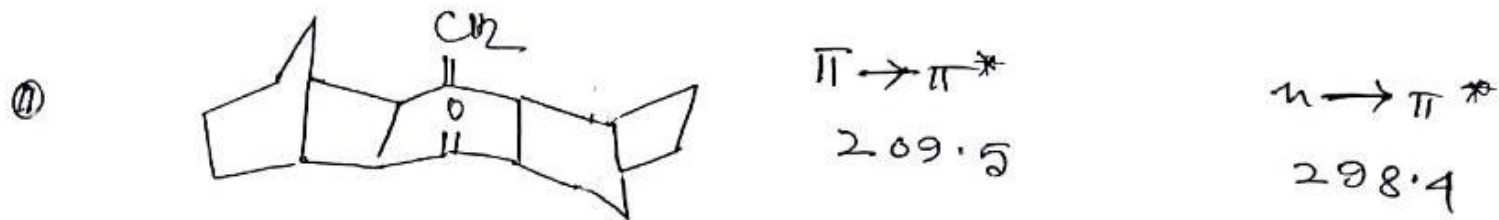
These type of interactions that apparently found to be ~~no~~ non-existent are known as TRANS ANNULAR conjugation.

Example: [The orbital overlap may occur in two ways.
In π type overlap, the molecular orbitals (m-o) and
 atomic orbitals (a.o) overlap so as to retain the
 π bond nodal plane,

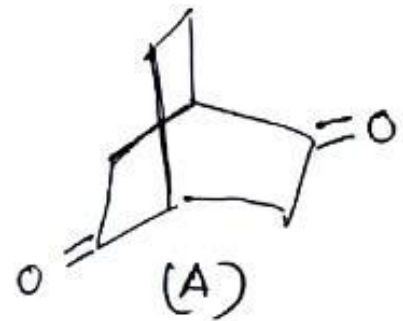


3-Methylene cyclopentane

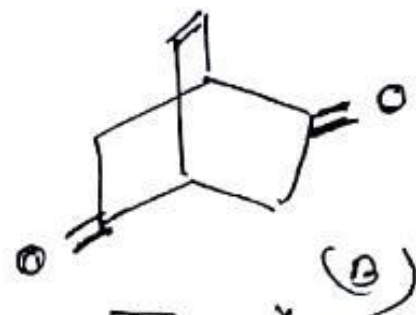
The UV-spectra closely matches with α, β unsaturated ketones.



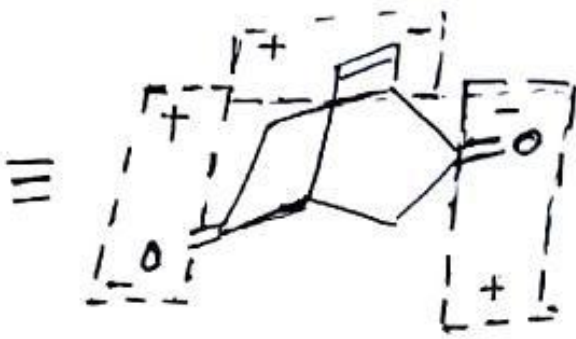
Here σ type overlap of π -orbitals takes place



$n \rightarrow \pi^*$
 $\lambda_{max} \rightarrow \underline{296 \text{ nm}}$

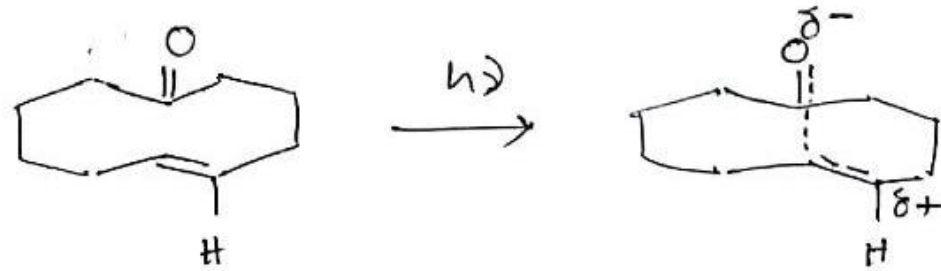


$\pi \rightarrow \pi^*$ 223 nm
 $n \rightarrow \pi^*$ 307, 296 nm

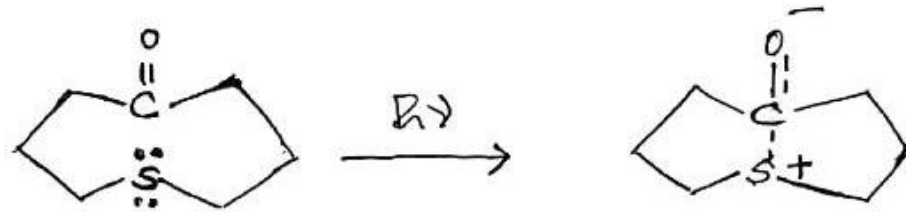


Compound (A) saturated bicyclic ketone shows normal absorption of carbonyl group. But the unsaturated analogue (B) shows absorption pattern closely similar to α - β unsaturated ketones. Here actually the C=C part takes part in σ type overlap of π orbitals of carbonyl group.

It has been shown by Weinstein that - while cyclodecenone and cis-cyclodec-5-enone show a normal $n \rightarrow \pi^*$ absorption (289.9 nm), the trans analogue has an additional band. This third band is due to the weak bond in the excited state, and the band so formed is known as PHOTO DESMOTIC BAND.

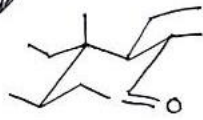


Similarly :-



λ_{max} 238 nm

Here the π orbital of $C=O$ group and the p orbital of S overlaps.



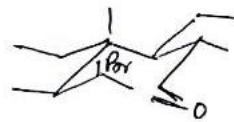
(A)

$$\lambda_{\max} = 283 \text{ nm}$$



(B)

$$\lambda_{\max} = 279 \text{ nm}$$



(C)

$$\lambda_{\max} = 309 \text{ nm}$$

Introduction δ - α Poromine atom axial @ lowers the $n \rightarrow \pi^*$ transition by $\sim 4-10 \text{ nm}$ and increases by $10-30 \text{ nm}$ when it is added equatorially (C) in comparison with the parent compound (A).



(D)

$$\lambda_{\max} 282 \text{ nm}$$



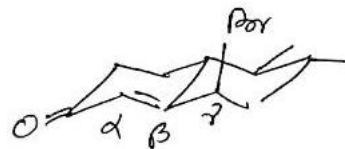
(E)

$$\lambda_{\max} 279 \text{ nm}$$



(F)

$$\lambda_{\max} \sim 293 \text{ nm}$$



Here also the axial substituent causes shift of $n \rightarrow \pi^*$ towards longer wavelengths and equatorial to shorter (comparison with unsubstituted one).

UV Spectroscopy

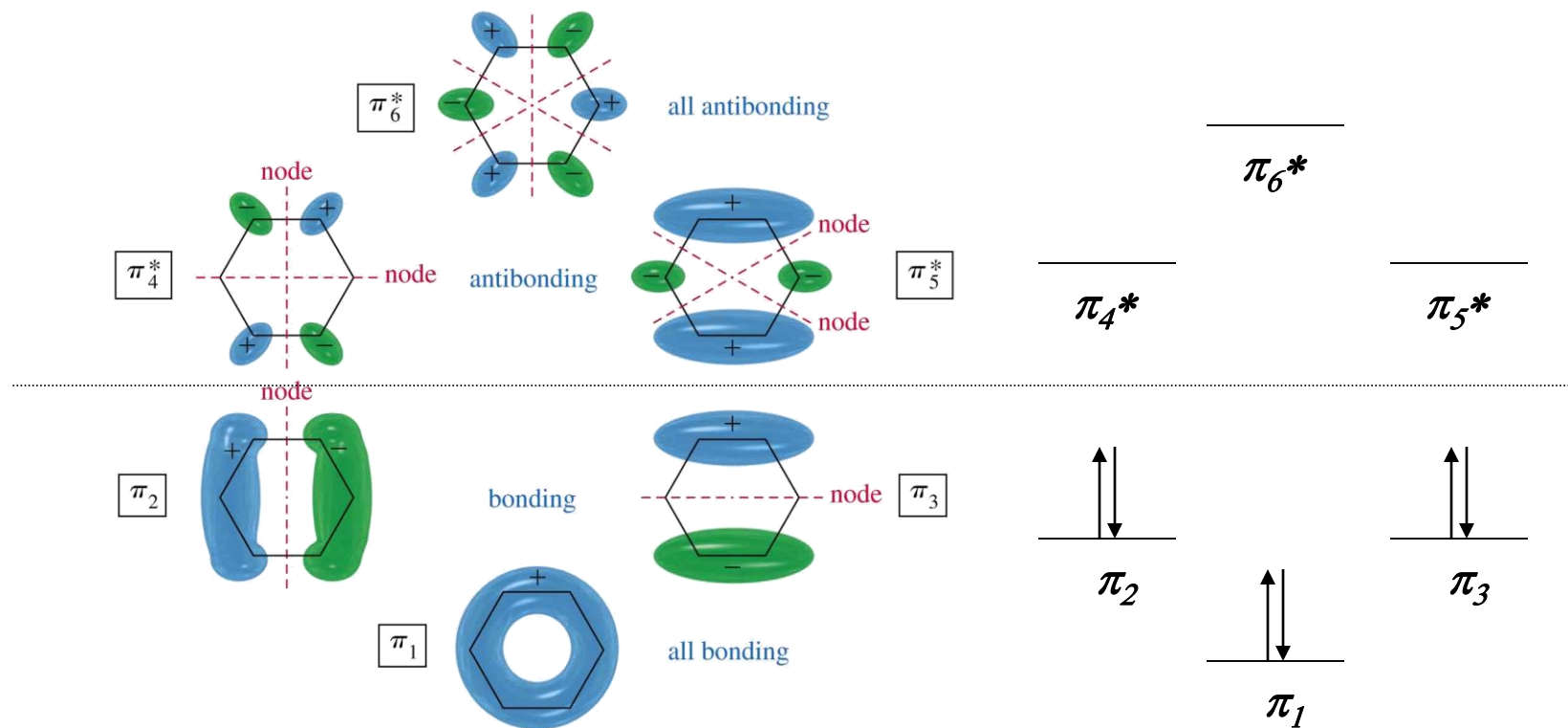
Structure Determination

C. Aromatic Compounds

1. General Features

Although aromatic rings are among the most widely studied and observed chromophores, the absorptions that arise from the various electronic transitions are complex

On first inspection, benzene has six π -MOs, 3 filled π , 3 unfilled π^*



UV Spectroscopy

Visible Spectroscopy

A. Color

1. General

- The portion of the EM spectrum from 400-800 is observable to humans- we (and some other mammals) have the adaptation of seeing color at the expense of greater detail



	λ , nm
Violet	400-420
Indigo	420-440
Blue	440-490
Green	490-570
Yellow	570-585
Orange	585-620
Red	620-780

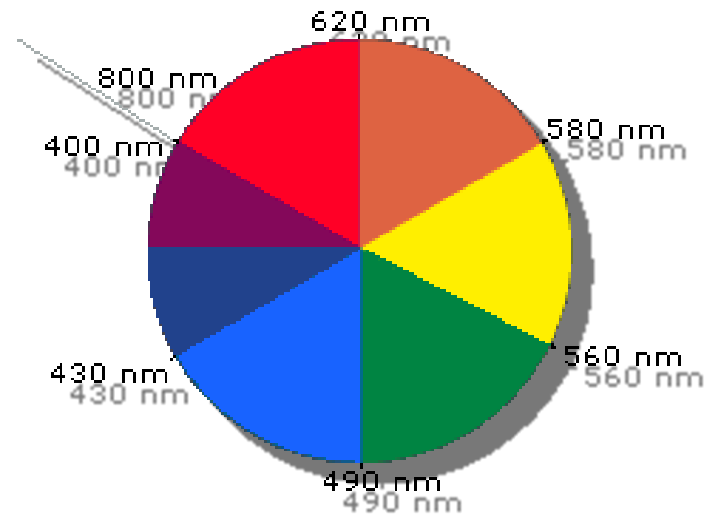
UV Spectroscopy

Visible Spectroscopy

A. Color

1. General

- When white (continuum of λ) light passes through, or is reflected by a surface, those λ s that are absorbed are removed from the transmitted or reflected light respectively
- What is “seen” is the complimentary colors (those that are not absorbed)
- This is the origin of the “color wheel”



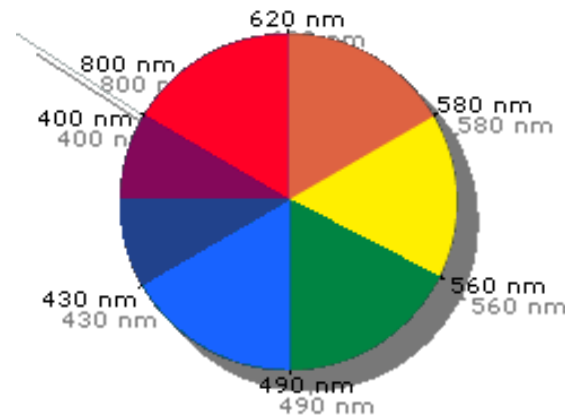
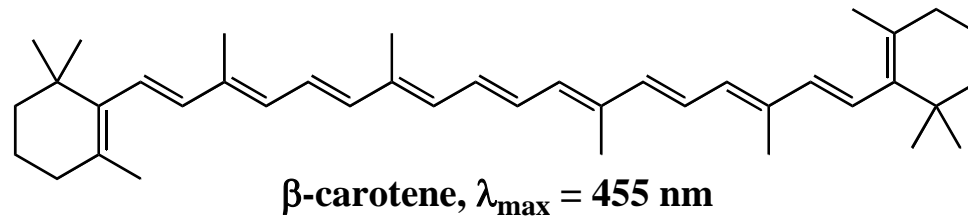
UV Spectroscopy

V. Visible Spectroscopy

A. Color

1. General

- Organic compounds that are “colored” are typically those with extensively conjugated systems (typically more than five)
- Consider β -carotene



λ_{\max} is at 455 – in the far blue region of the spectrum – this is absorbed

The remaining light has the complementary color of orange

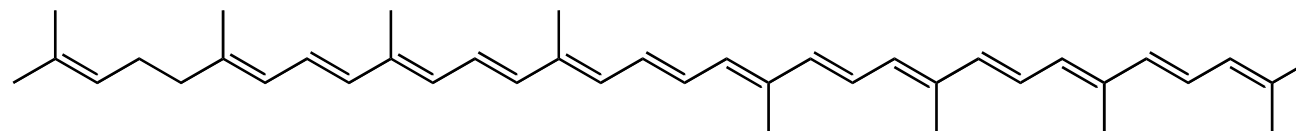
UV Spectroscopy

V. Visible Spectroscopy

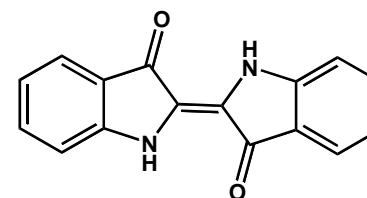
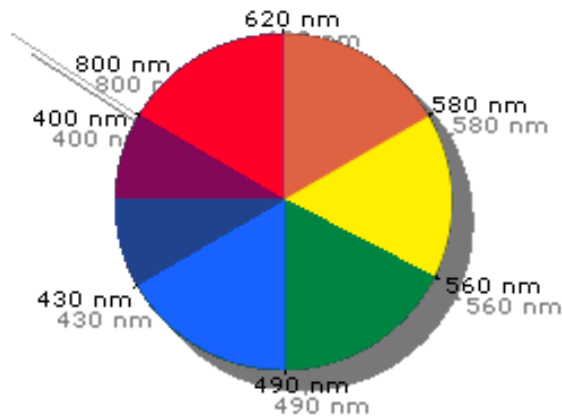
A. Color

1. General

- Likewise:



lycopene, $\lambda_{\max} = 474 \text{ nm}$



indigo

λ_{\max} for lycopene is at 474 – in the near blue region of the spectrum – this is absorbed, the compliment is now red

λ_{\max} for indigo is at 602 – in the orange region of the spectrum – this is absorbed, the compliment is now indigo!

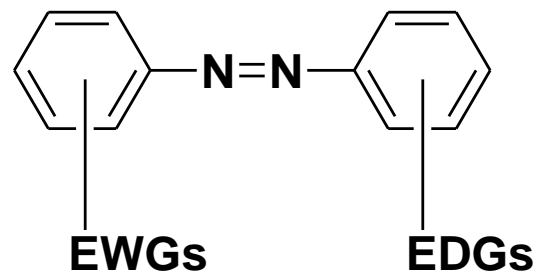
UV Spectroscopy

V. Visible Spectroscopy

A. Color

1. General

- One of the most common class of colored organic molecules are the azo dyes:



From our discussion of di-substituted aromatic chromophores, the effect of opposite groups is greater than the sum of the individual effects – more so on this heavily conjugated system

Coincidentally, it is necessary for these to be opposite for the original synthetic preparation!

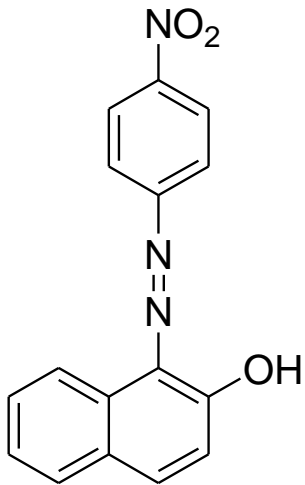
UV Spectroscopy

V. Visible Spectroscopy

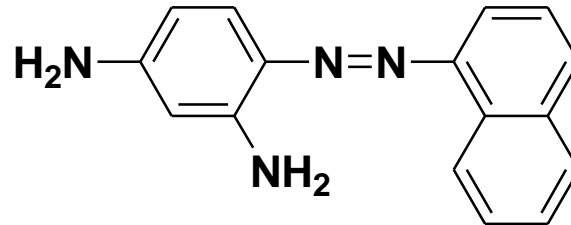
A. Color

1. General

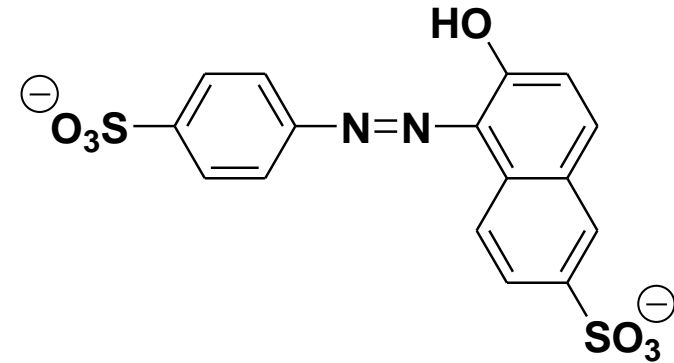
- These materials are some of the more familiar colors of our “environment”



Para Red



Fast Brown



Sunset Yellow (Food Yellow 3)

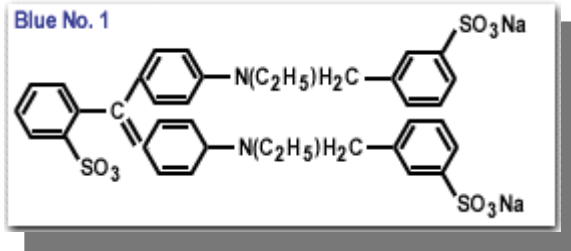


The colors of M&M's

Bright Blue

Common Food Uses

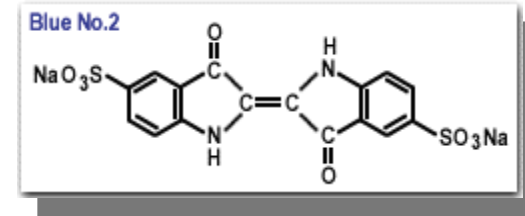
Beverages, dairy products, powders, jellies, confections, condiments, icing.



Royal Blue

Common Food Uses

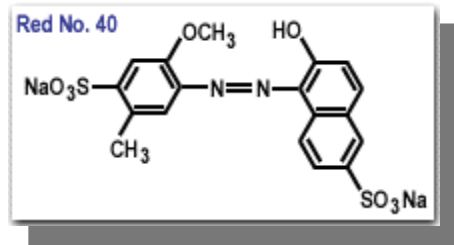
Baked goods, cereals, snack foods, ice-cream, confections, cherries.



Orange-red

Common Food Uses

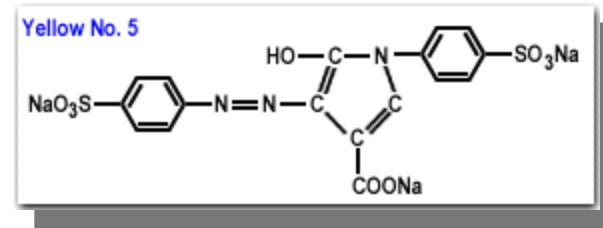
Gelatins, puddings, dairy products, confections, beverages, condiments.



Lemon-yellow

Common Food Uses

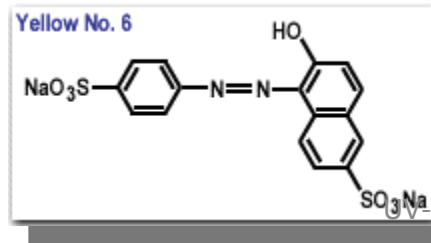
Custards, beverages, ice-cream, confections, preserves, cereals.



Orange

Common Food Uses

Cereals, baked goods, snack foods, ice-cream, beverages, dessert powders, confections



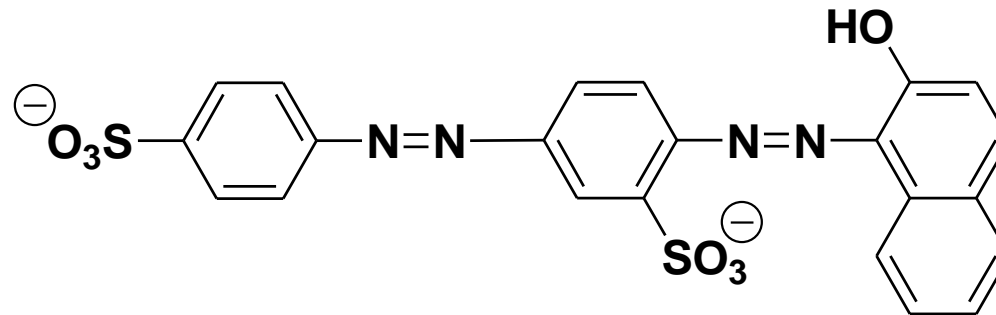
UV Spectroscopy

V. Visible Spectroscopy

A. Color

1. General

- In the biological sciences these compounds are used as dyes to selectively stain different tissues or cell structures
- Biebrich Scarlet - Used with picric acid/aniline blue for staining collagen, reticulum, muscle, and plasma. Luna's method for erythrocytes & eosinophil granules. Guard's method for sex chromatin and nuclear chromatin.



UV Spectroscopy

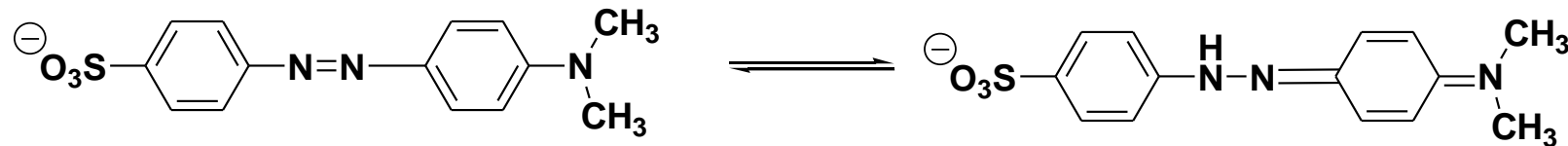
V. Visible Spectroscopy

A. Color

1. General

- In the chemical sciences these are the acid-base indicators used for the various pH ranges:
- Remember the effects of pH on aromatic substituents

Methyl Orange



Yellow, pH > 4.4

Red, pH < 3.2

