

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

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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.

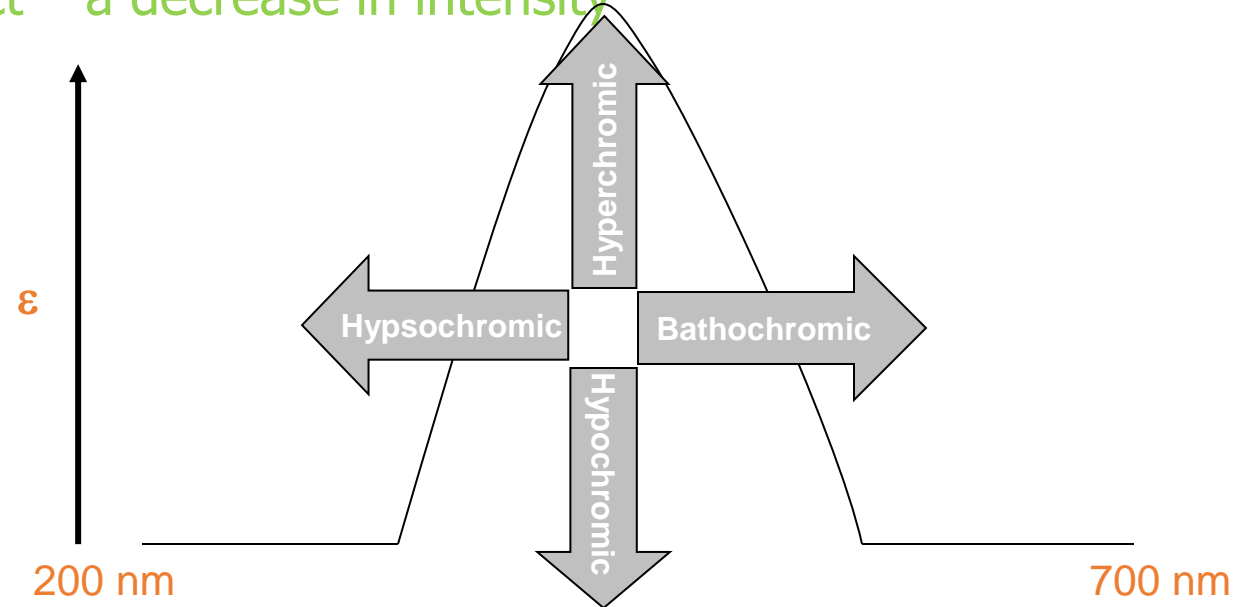
Certain substituents that do not absorb in the UV-Vis region but when attached to a chromophore bring about a shift of the absorption band towards the red end of the spectrum (longer wave length) are called *auxochromes*.

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

Substituent Effects

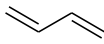
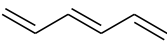
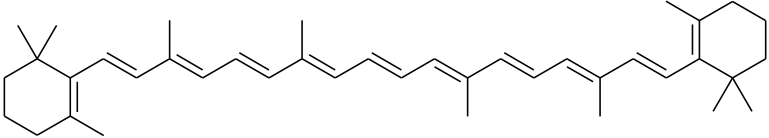

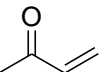
General – Substituents may have any of four effects on a chromophore

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

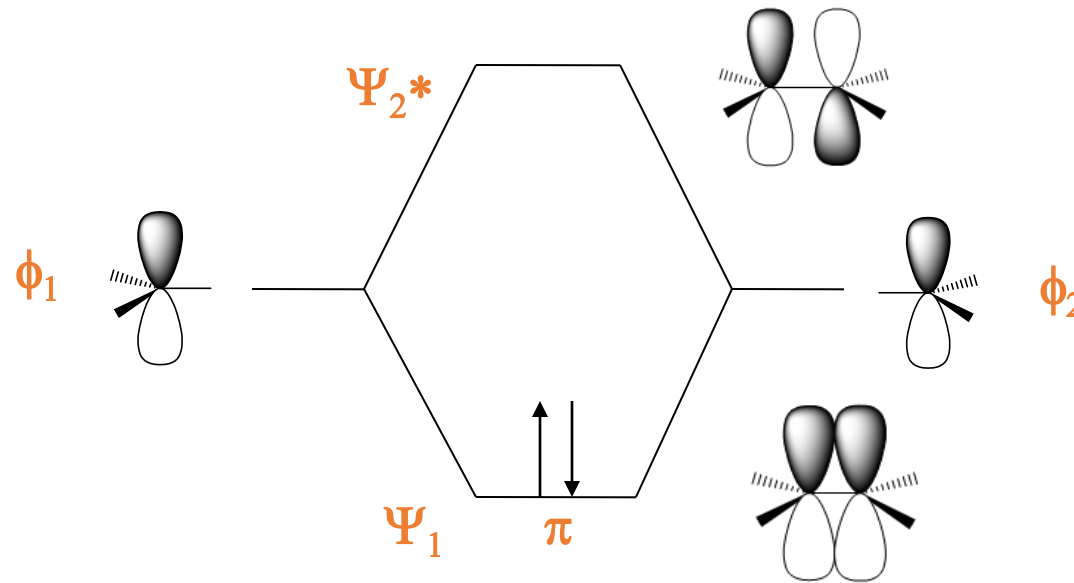
Conjugation - most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore

	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
	$n \rightarrow \pi^*$ 330 $\pi \rightarrow \pi^*$ 213	27 7,100

Conjugation of Alkenes

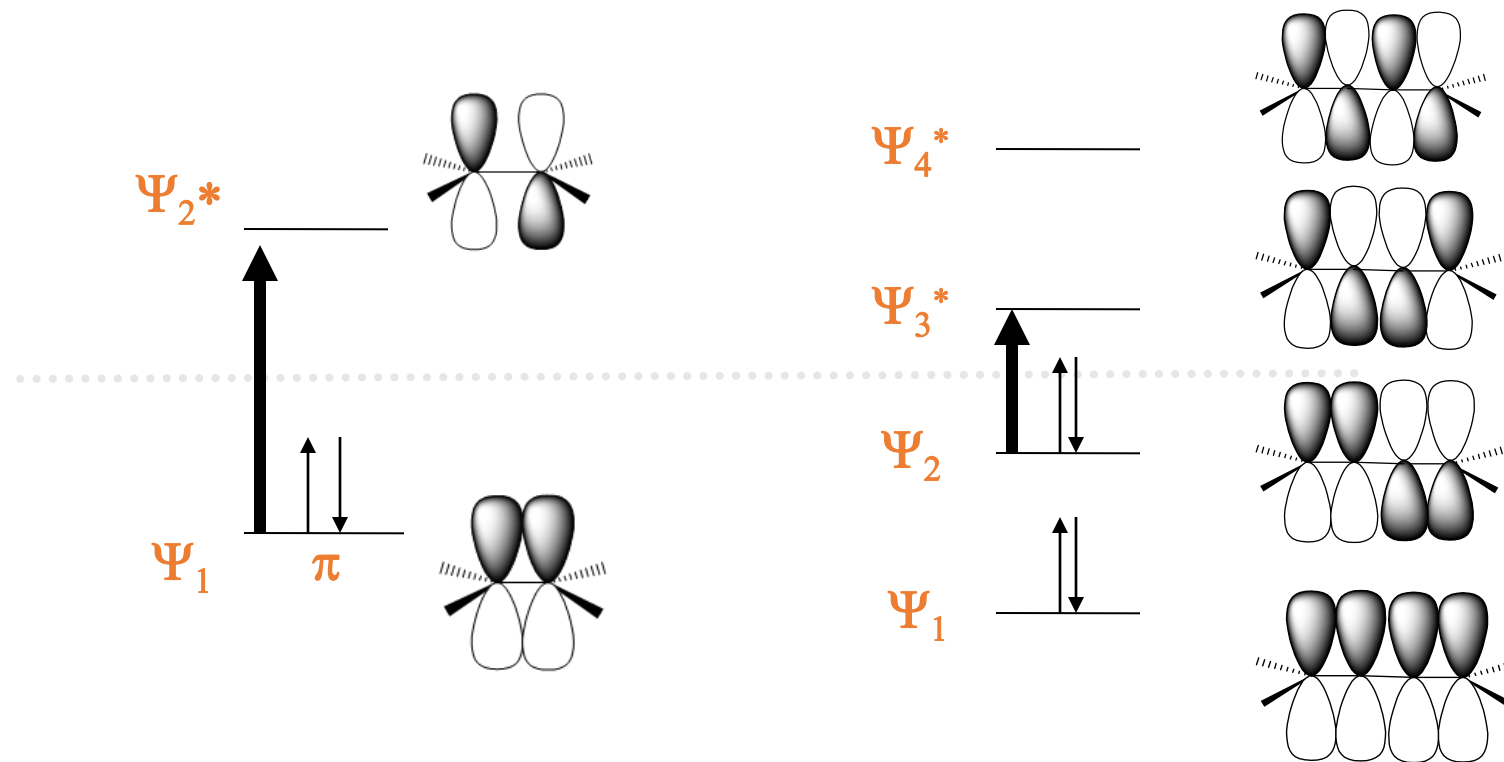
The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation

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

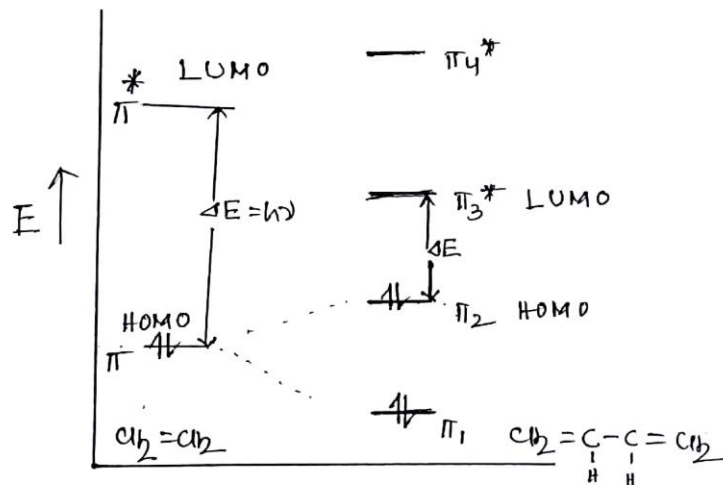


ΔE for the HOMO \rightarrow LUMO transition is **reduced**

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)

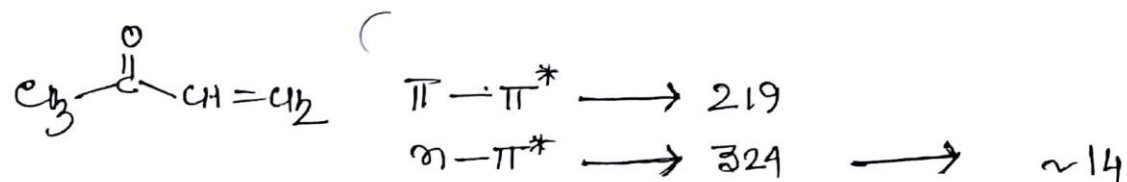
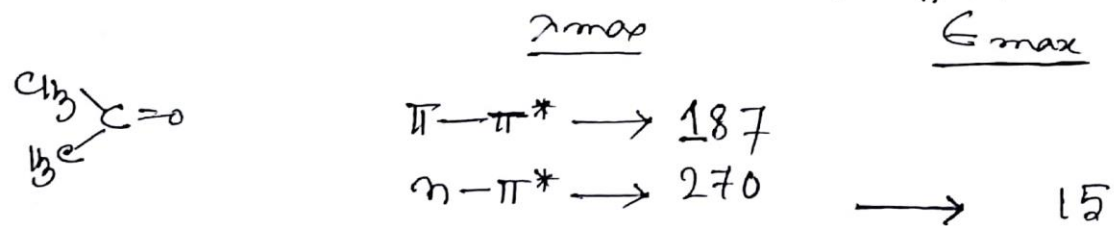


As the no of conjugation increases the length of conjugated system increase, which further decrease the energy gap between HOMO and LUMO. So with the increasing no of conjugation the system will move towards higher and higher λ_{max} values.

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.

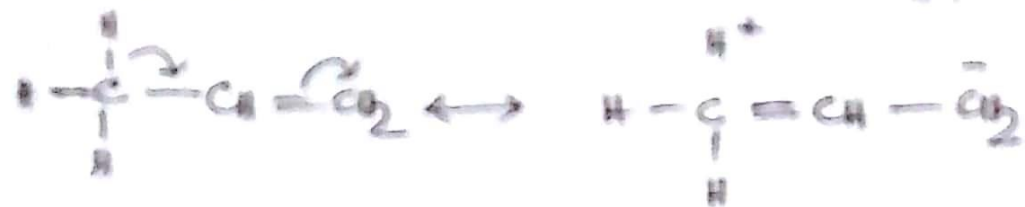


1. $\pi \rightarrow p$ Conjugation The conjugation of a lone pair of electrons from a heteroatom with an unsaturated π electron system results a $\pi \rightarrow p$ conjugation. This increases λ_{max} but ϵ_{max} remains almost-unchanged.

<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)

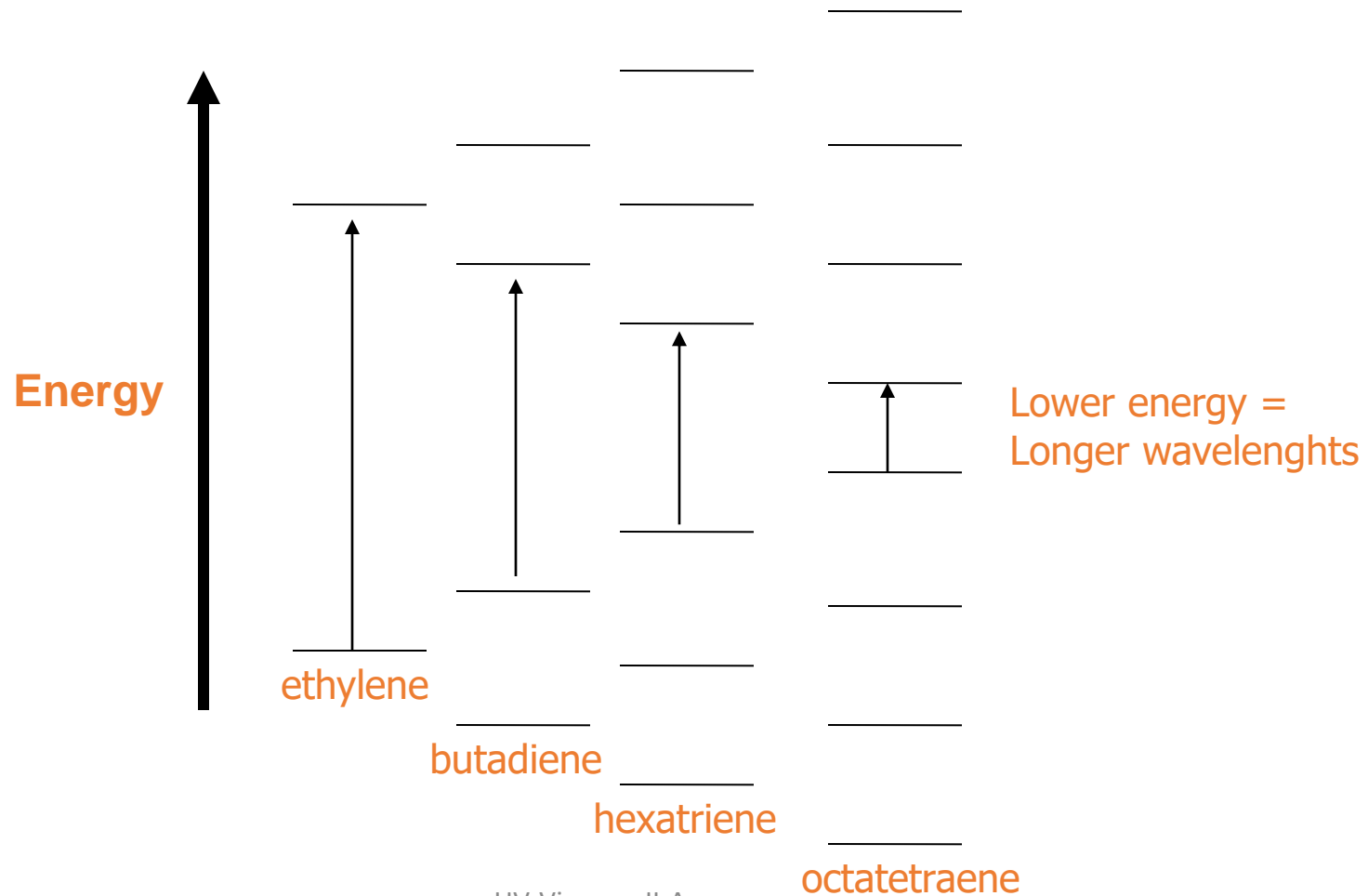
Alkyl substituents when attached to the unsaturated system results very small shift towards longer wave length. This is attributed to hyperconjugation.



$\text{H}_2\text{C}=\text{CH}=\text{CH}=\text{CH}_2$	$\frac{\lambda_{\text{max}}}{217}$	$\frac{\epsilon_{\text{max}}}{\sim 2.1 \times 10^3}$
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	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

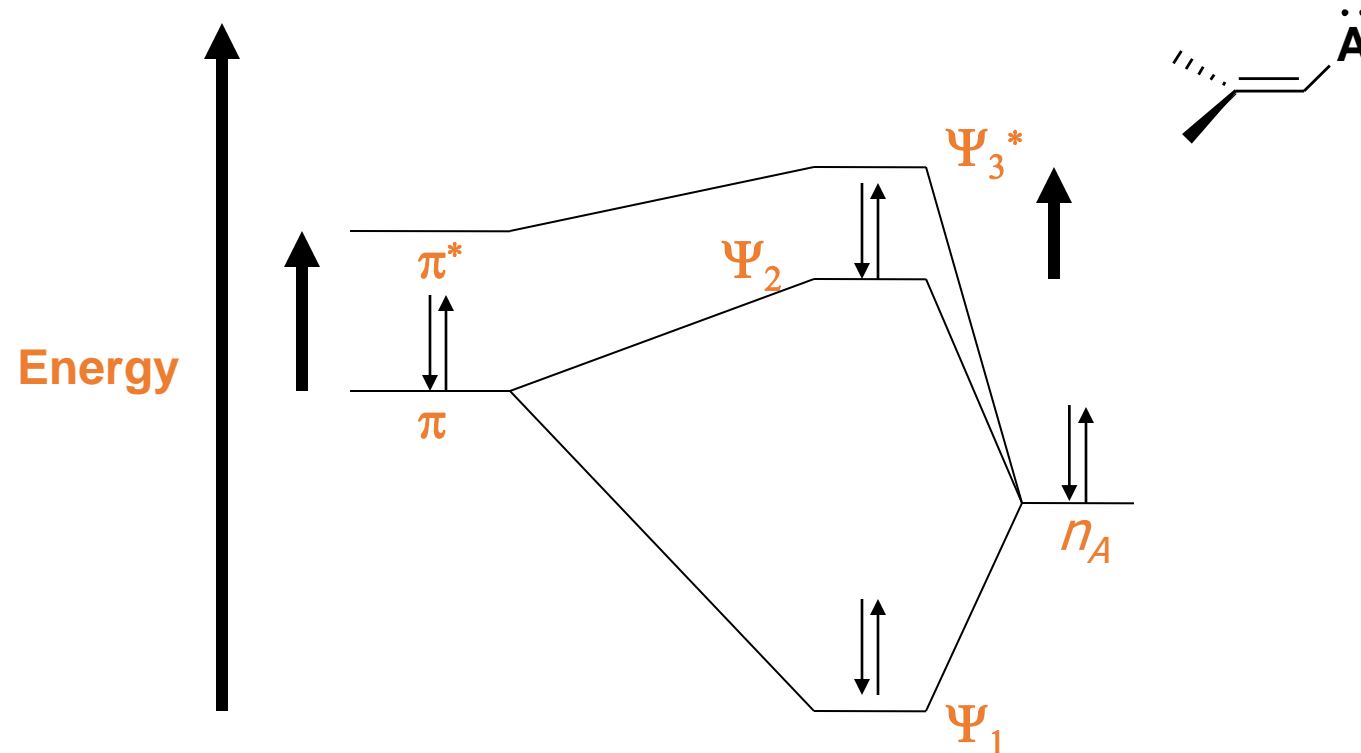
Extending this effect to longer conjugated systems the energy gap becomes progressively smaller thereby making it absorb at higher wavelengths.



Conjugation of Alkenes

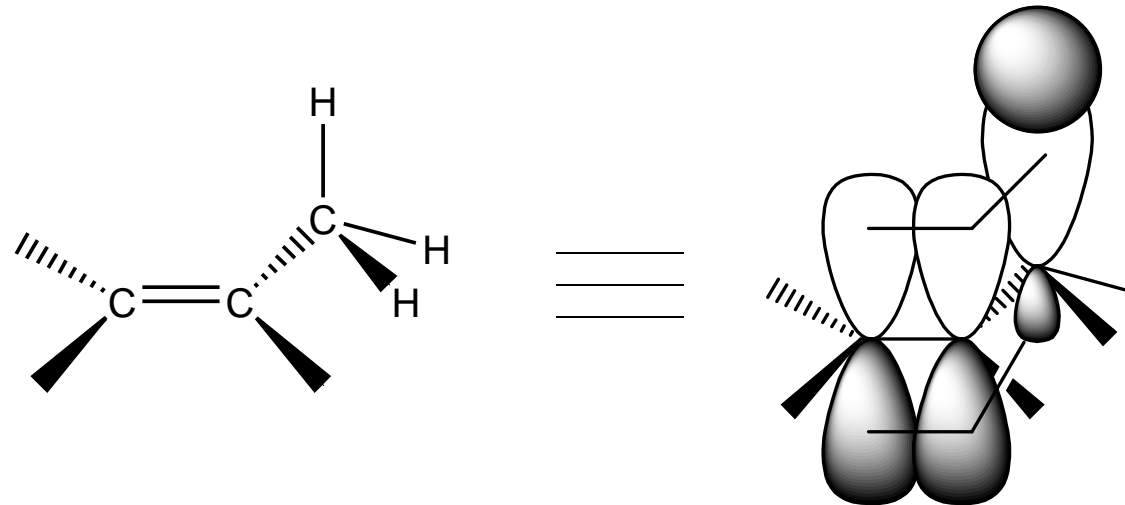
Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems - auxochromes

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



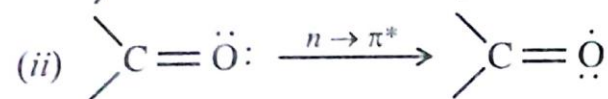
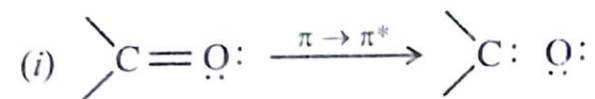
Conjugation of Alkenes

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

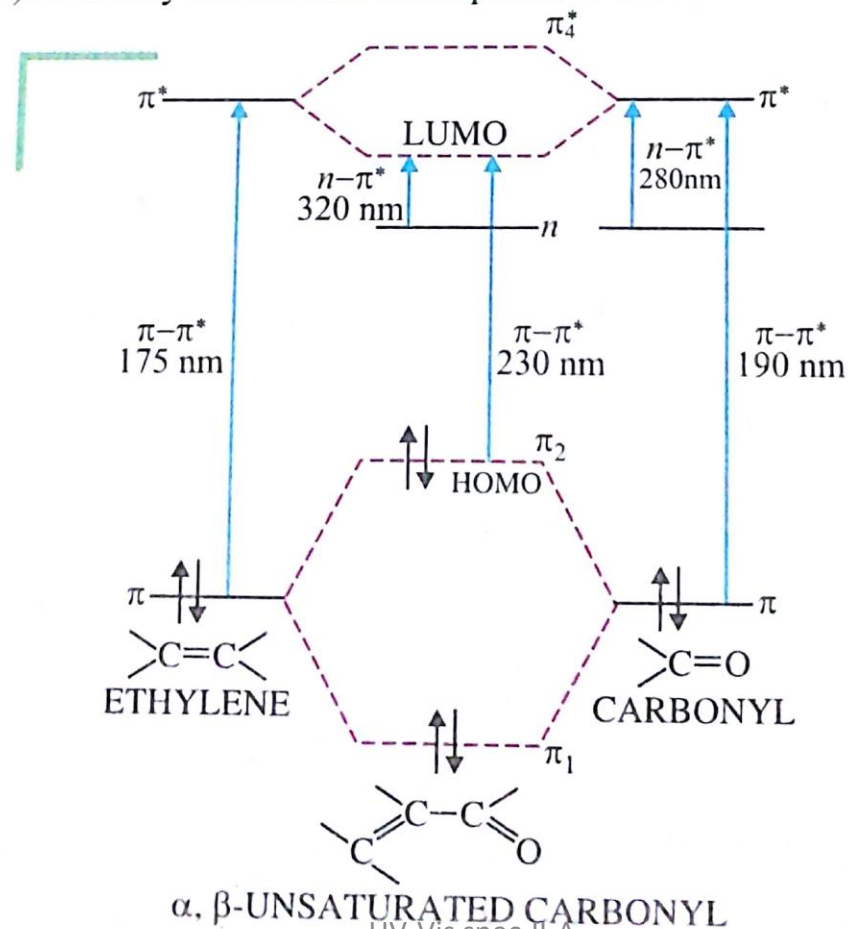


Fig. 2.23. UV transitions in α, β -unsaturated carbonyl compounds.

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.

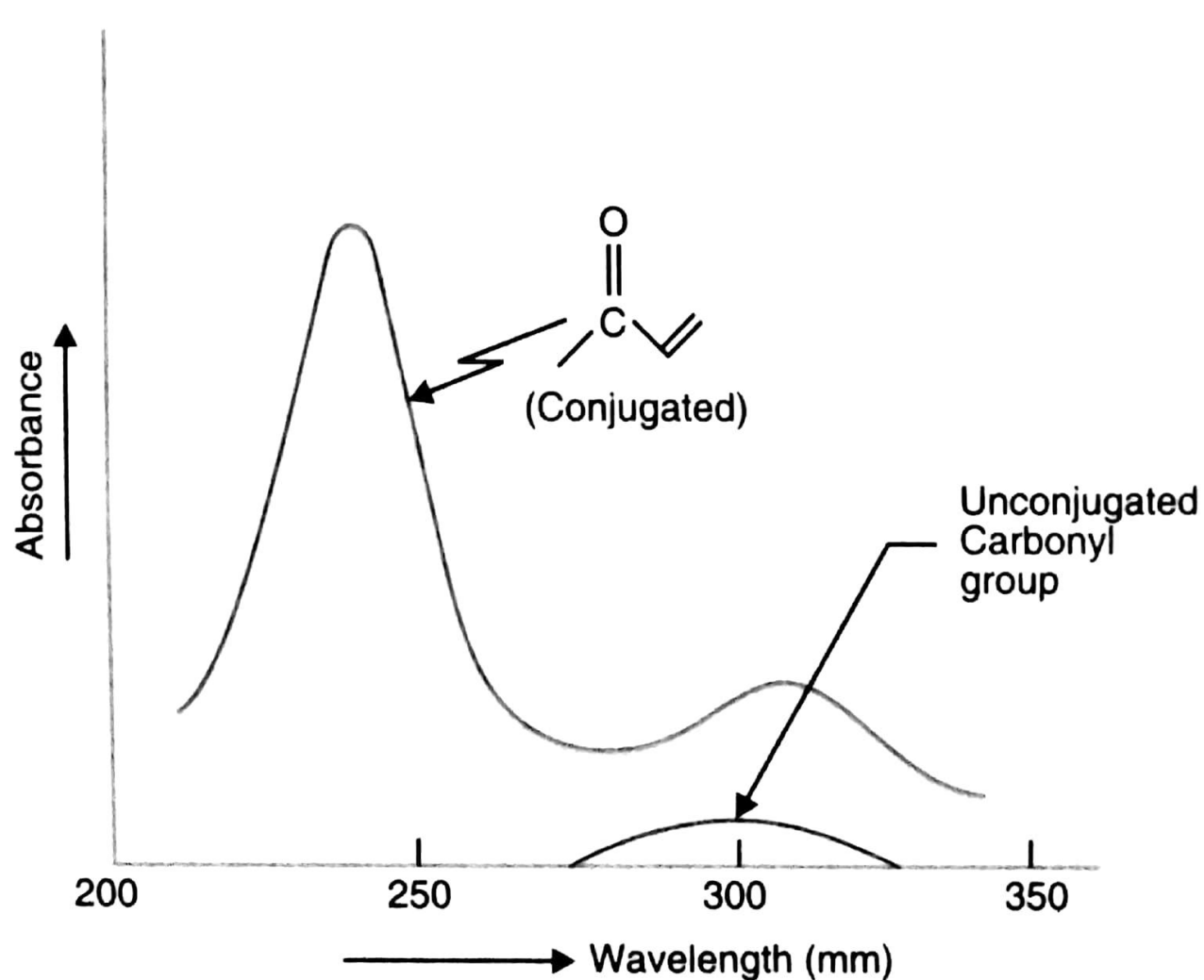


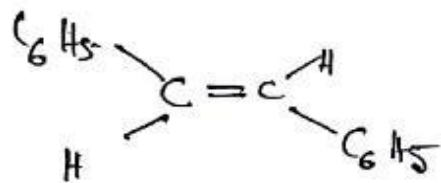
Fig. 2.25. UV Absorption spectra for conjugated and unconjugated carbonyl compounds.

twist to conformation

①

Effect of geometrical isomerism and steric effect -

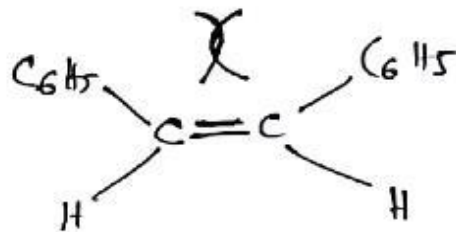
cis-Stilbene vs trans-Stilbene



Trans Stilbene

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

$$\epsilon \approx 27,000$$



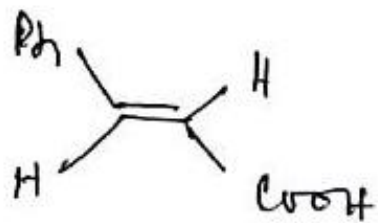
cis Stilbene

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

$$\epsilon \approx 13,500$$

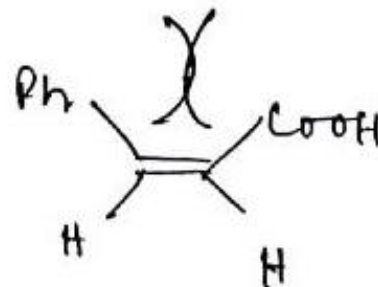
In cis isomer, the two phenyl rings are very close to each other and due to repulsion the two Ph rings are slightly out of plane from the C=C. Thus effective overlap/conjugation is reduced. Thus λ_{max} for cis < λ_{max} of trans ($\pi \rightarrow \pi^*$ overlap is much more effective)

Similar to:



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

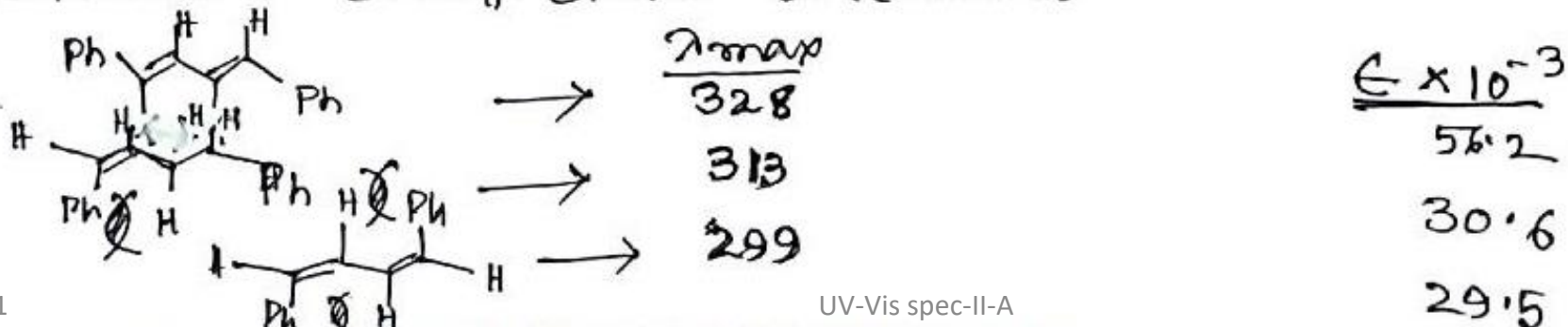
$$(\epsilon_{max} = 16000)$$



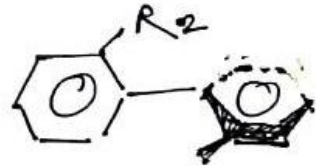
$$\lambda_{max} = 268 \text{ nm}$$

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

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.



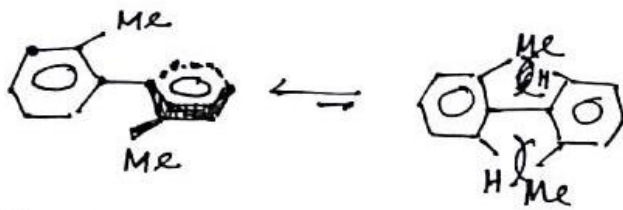
$$\left. \begin{array}{l} R_1 = H \\ R_2 = H \end{array} \right\} \lambda_{max} = 249$$

Twist conformation

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

When $R_1 = R_2 = Me$ or larger groups.

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



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.

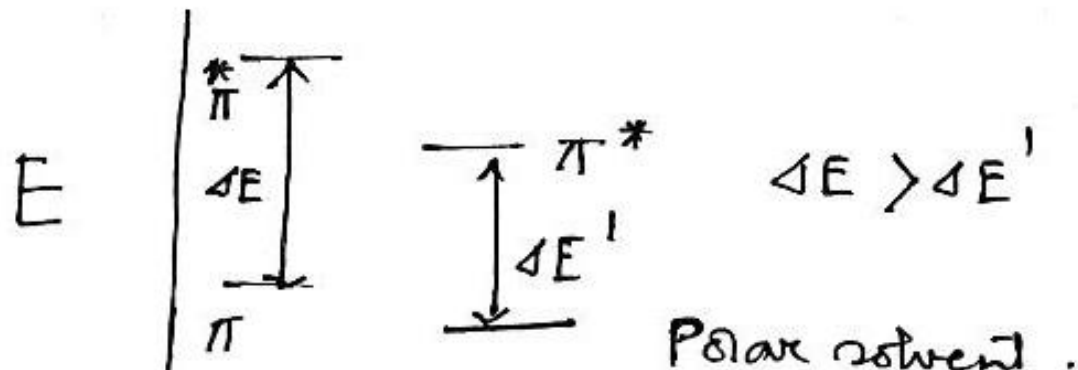
(i) $\pi \rightarrow \pi^*$ Transitions

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 -

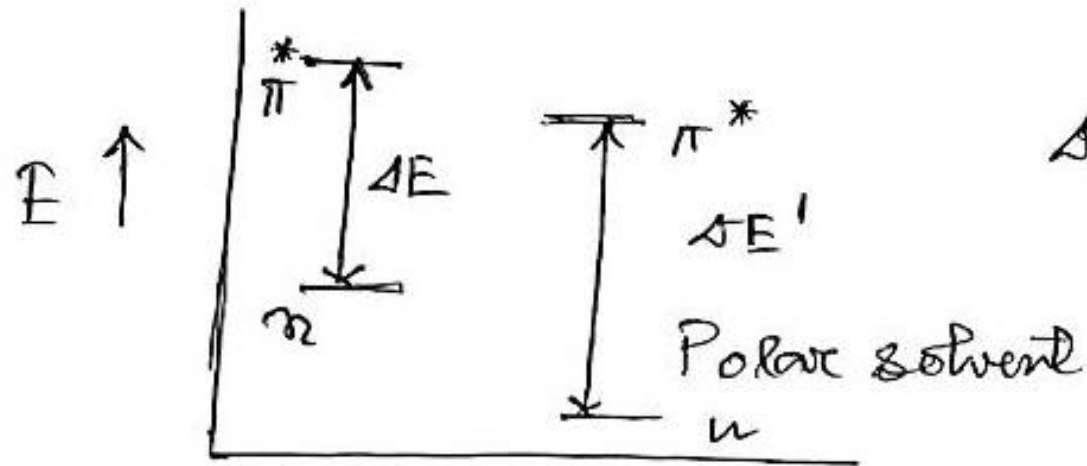
$\pi \rightarrow \pi^*$ transition.

Here the excited state is often 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)

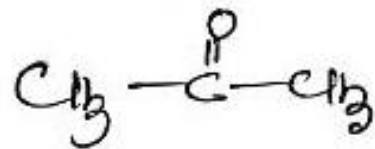


$n \rightarrow \pi^*$ transition

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)



$$\Delta E < \Delta E'$$



$\lambda_{max} =$

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.

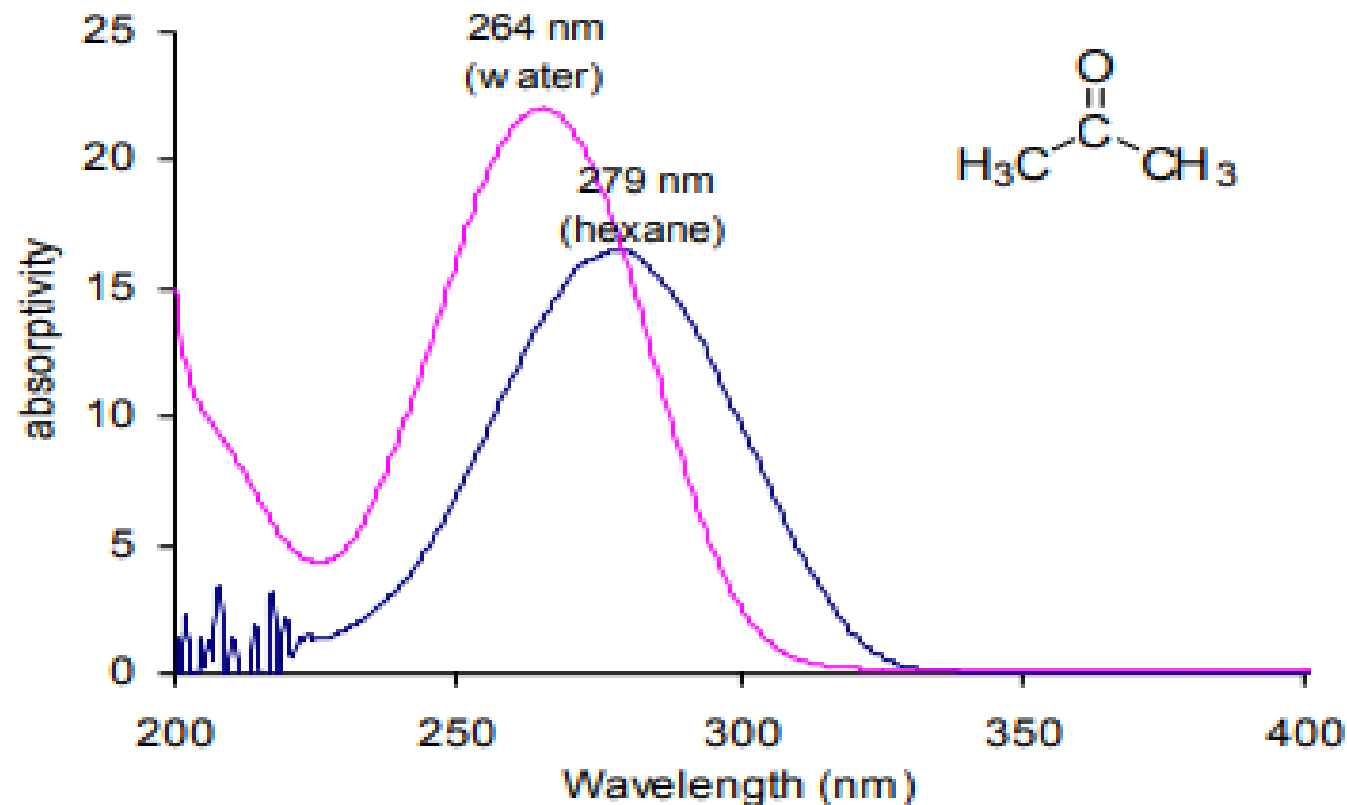


Figure 5 : UV-spectra of acetone in hexane and in water