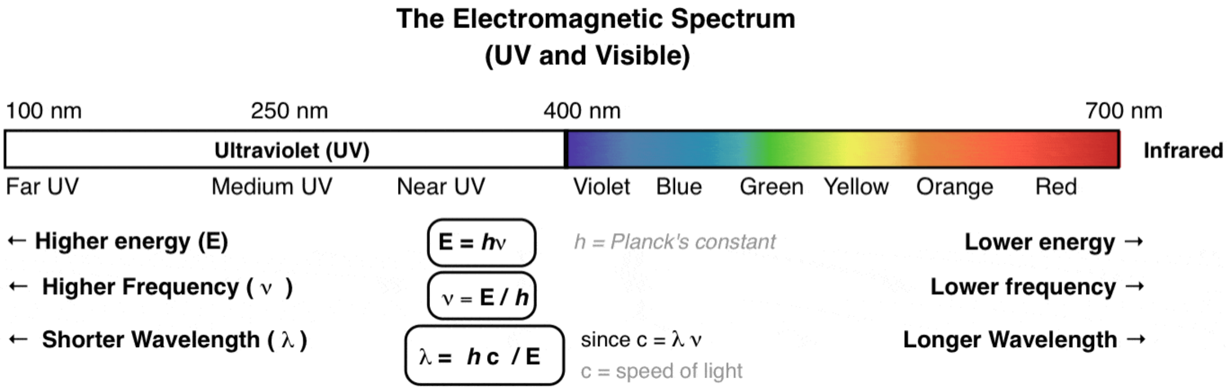
Ultra-violet and visible Spectroscopy

Introduction

Ultraviolet-visible spectroscopy involves the absorption of ultraviolet/visible light by a molecule causing the promotion of an electron (n, **π, σ**) from a ground electronic state to an excited electronic state. So it is also called Electronic Spectroscopy. Substance absorbing in the visible range will appear coloured to the human eye.

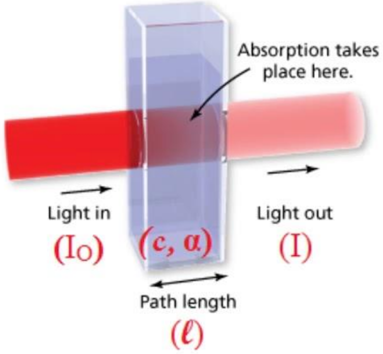


A record of the amount of light absorbed by the sample as a function of the wavelength of light in nm or mμ unit is called absorption spectrum which generally consists of absorption bands.The far ultra-violet region (below 200 mμ) is not much studied due to absorption by oxygen and nitrogen. Moreover, studies in this region require vacuum instruments.

Absorption law

Spectrophotometric analysis often based on Beer -Lambert Law. The Beer-Lambert law states that the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution.

Beer-Lambert Equation



$$A = log_{10}(\frac{I_O}{I}) = \varepsilon cl$$

$$A = \varepsilon cl$$

I_o = Intensity of incident light

I = Intensity of transmitted light

c = concentration of solution in moles per lit.

l = Path length of sample (usually 1cm)

€ = Molar extinction coefficient (or molar absorptivity)

A = Absorbance

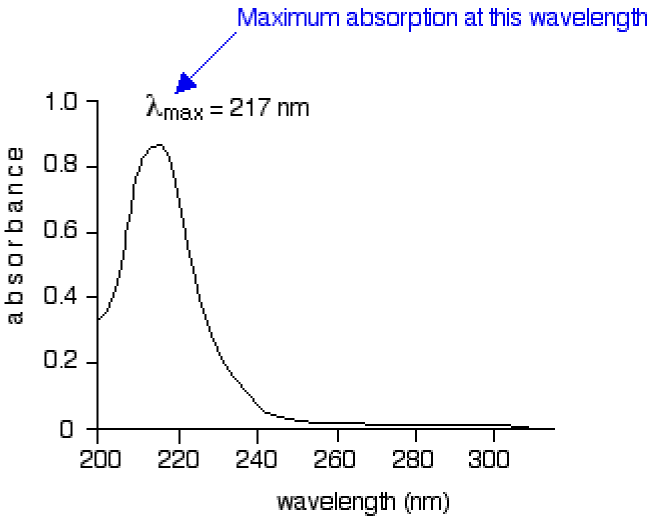
Measurement of Absorption Intensity

The intensity of absorption is directly proportional to the transition probability. Electronic transitions may be as intense or weak according to the magnitude of ε_{max} that corresponds to *allowed* or *forbidden* transition as governed by the selection rules of electronic transition. An allowed transition will have ε_{max} value greater than 1000 while those having low transition probability will have its value less than 1000.

Selection Rules

1. Singlet-Triplet transitions are forbidden. Thus, S→S, T→T, are allowed, but S→T, T→S, are forbidden (where S= Singlet state, T= Triplet state).
2. Transition between orbitals of different symmetry is forbidden. **n → π∗ transition is symmetry forbidden, but π → π∗ transition is symmetry allowed.**

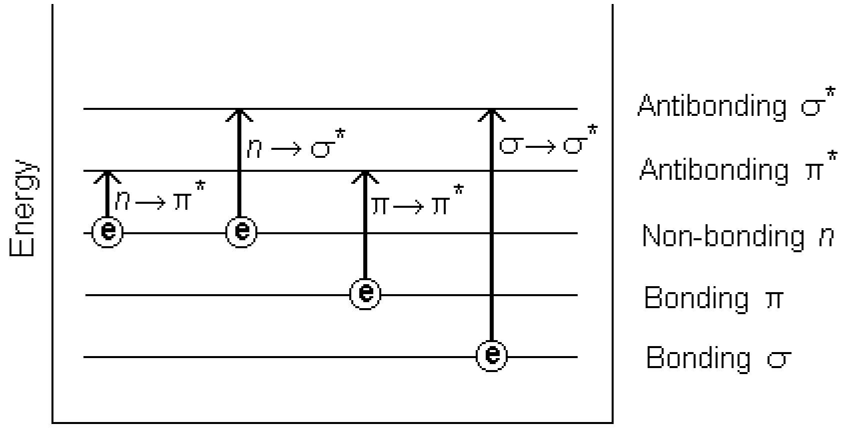
The wavelength of light corresponding to maximum absorption is written as $\lambda_{max.}$ It can be directly read from the horizontal axis as shown in figure. The diagram shown below is simple UV- vis absorption spectrum of 1,3 butadiene with vertical line showing absorbance A which is equal to log I_o/I.



Types of electronic transition

When a molecule is excited by absorption of energy (UV or visible light) its electrons are promoted from bonding to antibonding orbital. The allowed transitions are σ→ σ*, n→ σ*, π→ π* and n→ π*.

The energy required for various transitions obeys the following order: σ→ σ* > n→ σ* > π→ π* > n→ π*.



$\sigma \rightarrow \sigma^*$ Transitions

An electron in a bonding s orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 n

n→ σ^* Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of *n*→ σ^* transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with *n*→ σ^* peaks in the UV region is small.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.

Alkene, alkyne, carbonyl compounds, cyanide, azo compounds having π electrons show $\pi \rightarrow \pi^*$ transitions. Carbonyl compounds having unshared electron pair show both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

Molar absorbtivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to100 L mol^{-1} cm^{-1}. $\pi \rightarrow \pi^*$ transitions normally give molar absorbtivities between 1000 and 10,000 L mol^{-1} cm^{-1}.

High energy transition:

i. $n \rightarrow \sigma^*$ (Intense)
ii. $\pi \rightarrow \pi^*$ (Intense)

Low energy transition:

$n \rightarrow \pi^*$ (Weak)

Transition Probability

It is not always necessary that the excitation of an electron takes place from a bonding orbital or lone pair to antibonding or nonbonding orbital when a compound is exposed to UV or visible light. It can be shown that:

Extinction coefficient $\varepsilon_{max} = 0.87 \times 10^{20}$. P.a [P = Transition probability with values from 0 to 1, a = Target are of the absorbing system, usually called a chromophore]

From the equation it is found that ε_{max} increases with increasing chromore length (a). It have been found that ε_{max} is about 10^5 when chromophore length is in the order of 10Å or 10^{-7} cm. The chromophore with low transition probability will have ε_{max} value below 1000. In addition to that allowed transition have ε_{max} value greater than 10^4 where as forbidden transition have ε_{max} value in between 10-100.

In benzophenone two types of trasitions are observed

1. 252 nm ε_{max} = 20,000 (allowed) (**π to π***)
2. 325 nm ε_{max} = 180 (forbidden) (**n to π*)**

Chromophore

When a molecule absorbs electromagnetic radiation in the ultraviolet/visible range, a transition between different electronic energy levels occurs. Since the wavelength of absorption is a measure of the separation of the energy levels of the orbital concerned. The nucleus holding the electrons together in a bond determine the wavelength of radiation to be absorbed. Thus the nuclei, with which the concerned electrons are bound, affect the energy between the ground and excited states.

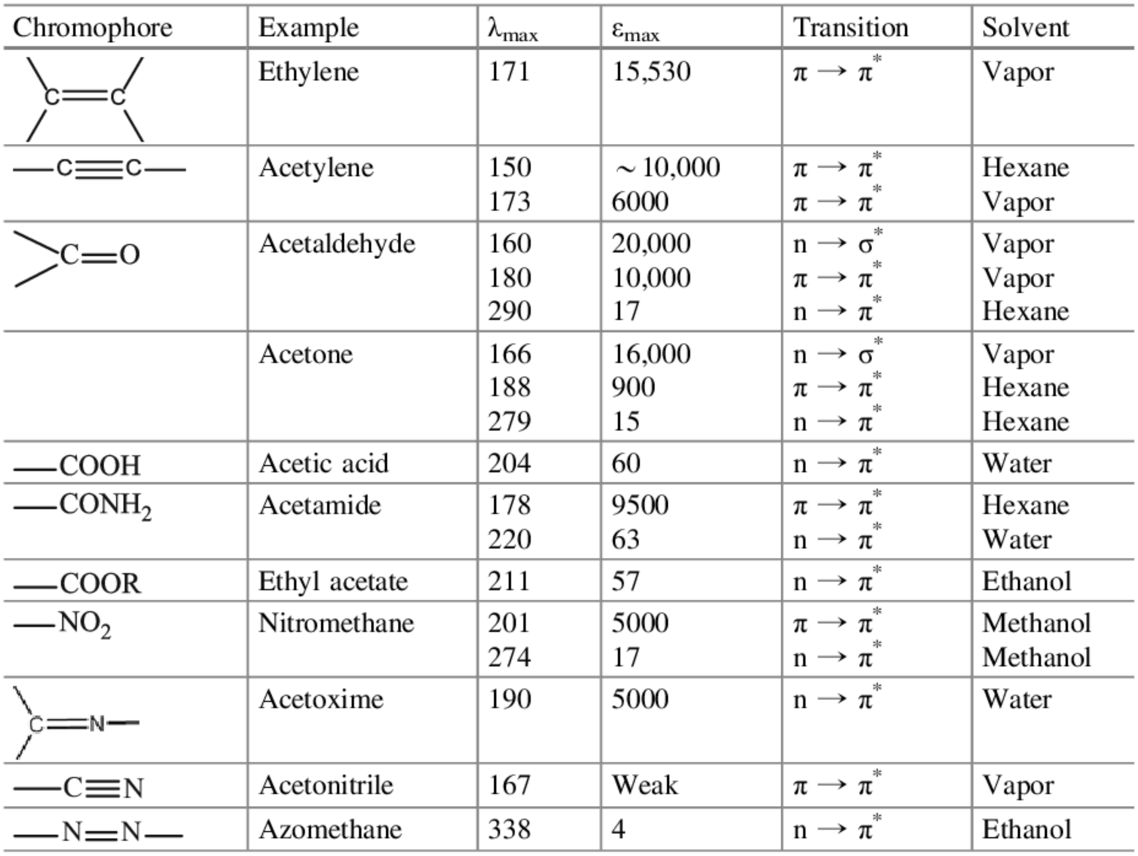
Therefore we can say that the energy of transition and the wavelength of radiation absorbed are properties of atoms not the electron themselves. The group of atoms due to which absorption occurs is called **chromophore**.

A chromophore is defined as an isolated covalently bonded group that shows a characteristic absorption in UV/Visible region. For example C=C, C=C, C=O, C=N, N=N, R-NO2 etc.

If a compound absorbs light in the visible region (400-800 nm), only then it appears coloured to our eyes. Therefore a chromophore may or may not impart colour to a compound depending on whether the chromophore absorbs radiation in the visible or UV region.

All the compounds having the same functional group will absorb at almost the same wavelength if the other factors such as conjugation, substituents etc are absent.

Characteristics of some common unconjugated chromophore



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

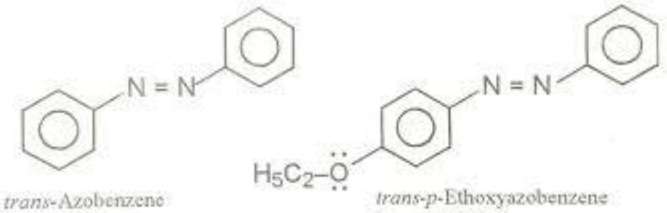
Auxochrome

The substituents covalently attached to a chromophore which themselves do not absorb ultraviolet/ visible radiation, but their presence changes both the intensity as well as wavelength of the absorption maximum are known as auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes. These are also called colour enhancing groups.

The actual effect of an auxochrome on a chromophore depends on the polarity of the auxochrome, e.g. groups like CH_3, CH_3CH_2 and Cl have very little effect, usually a small red shift of 5-10 nm. Other groups such as NH_2 and NO_2 show a strong effect and completely alter the spectrum.

Auxochrome generally increases the value of absorption maxima by extending the conjugation through resonance. The extended conjugation brings the lowest excited state (LUMO) closer to the highest ground state (HOMO) and thus permits a lower energy (longer wavelength) transition. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different value of absorption maxima.

For example benzene shows λ_{max} at 256 nm, whereas aniline shows λ_{max} at 280 nm. Hence the NH_2 group acts as an auxochrome and causes the shifting of λ_{max} to a large value.

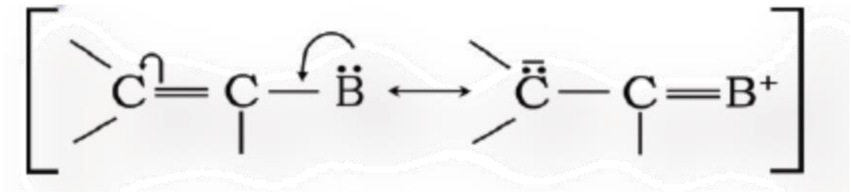


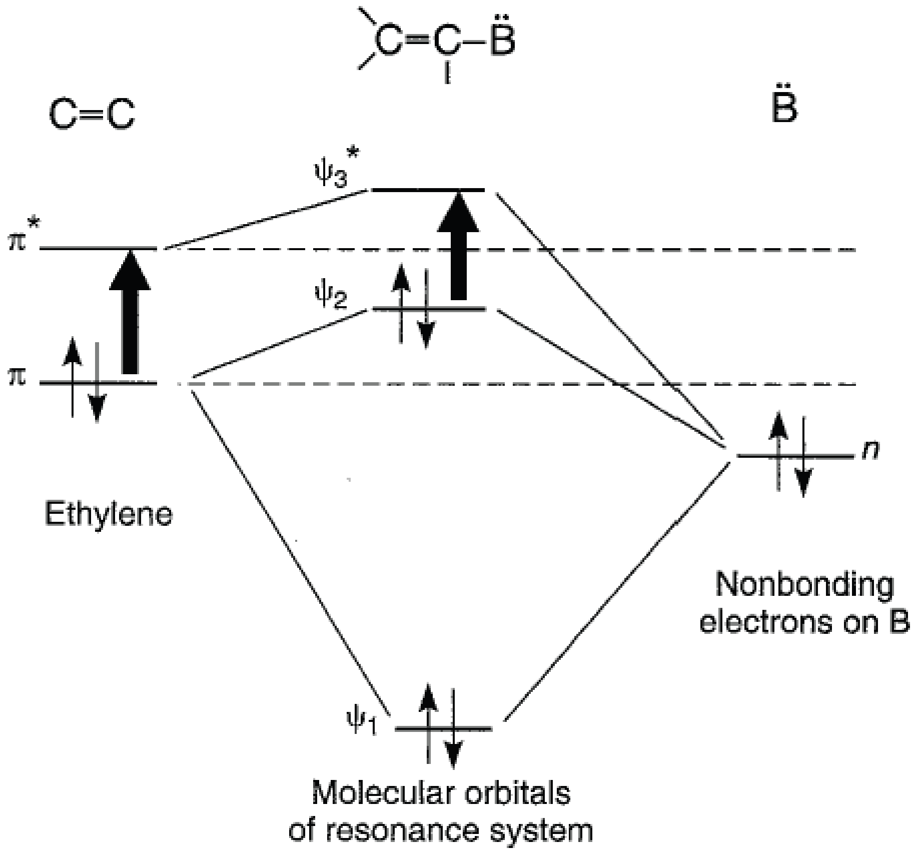
trans-Azobenzene
λ_{max}–320 nm
ϵ_{max} = 21,000

trans-p-Ethoxyazobenzene
λ_{max}–385 nm
ϵ_{max}–42,000

The presence of $–OC_2H_5$ (acting as auxochrome) increases the value of λ_{max} as well as €$_{max.}$

Mechanism: All auochromeic groups contain non bonding electrons. Due to this, There is extension of conjugation of the chromophore by sharing the non bonding electrons.

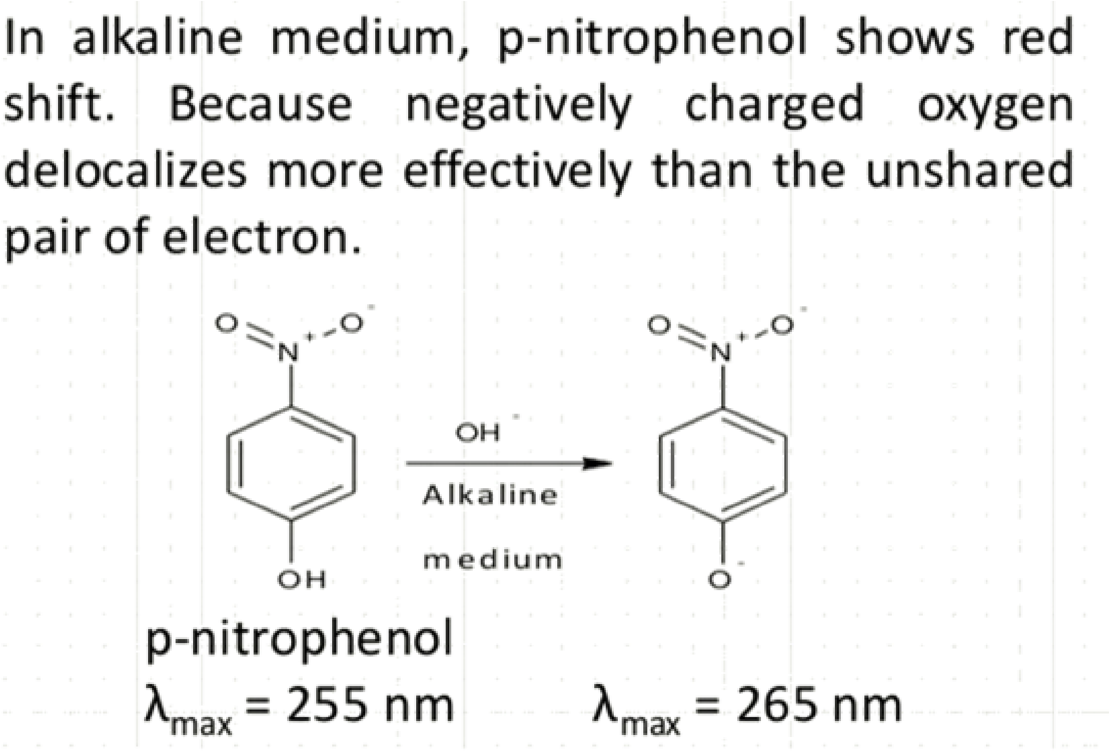




Molecular orbitals of resonance system showing closeness in HOMO and LUMO

Bathochromic Shift or Red shift

The shift of an absorption maximum towards longer wavelength or lower energy is called as bathochromic shift. It may be produced due to presence of an auxochrome or change in solvent polarity. Because the red color has a longer wavelength than the other colors in the visible spectrum, therefore this effect is also known as red shift.



In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.

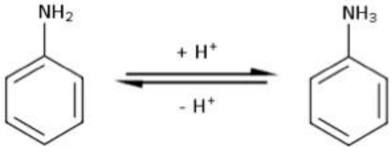
p-nitrophenol

λ_{max} = 255 nm

λ_{max} = 265 nm

Hypsochromic Shift or Blue Shift

The shift of an absorption maximum towards the shorter wavelength or higher energy is called hypsochromic shift. It may be caused due to removal of an conjugation or change in solvent polarity. Because the blue color has a lower wavelength than the other colors in the visible spectrum and hence this effect is also known as blue shift.



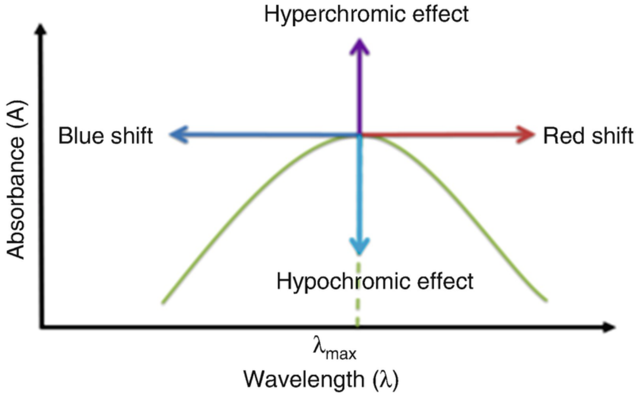
Aniline shows blue shift in acid medium because NH_2 converted to NH_3^+ in acid medium and losses conjugation.

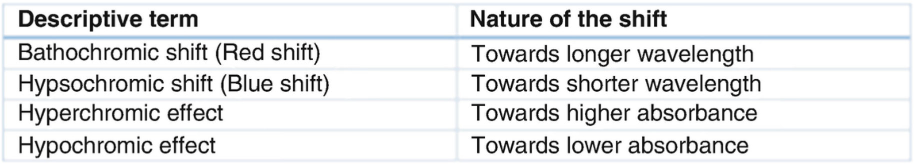
Hyperchromic Effect

It is an effect that results in increased absorption intensity. **The introduction of an auxochrome usually causes hyperchromic shift**. For example benzene shows B band (the secondary band in UV-Vis spectra) at 256 nm and ε_{max} 200, whereas aniline shows B-band at 280 nm and ε_{max} at 1430. The increase in the value of ε_{max} is due to the hyperchromic effect of auxochrome NH_2.

Hypochromic Effect

An effect that results in decreased absorption intensity is called hypochromic effect. This is caused by a group which distorts the geometry of the molecule. For example, biphenyl shows λ_{max} at 250 nm and ε_{max} at 19,000, whereas 2-methyl biphenyl absorbs at λ_{max} 237 nm, ε_{max} 10250. The decrease in the value of absorbance is due to hypochromic effect of methyl group which distorts the chromophore by forcing the rings out of coplanarity resulting in the loss of conjugation.

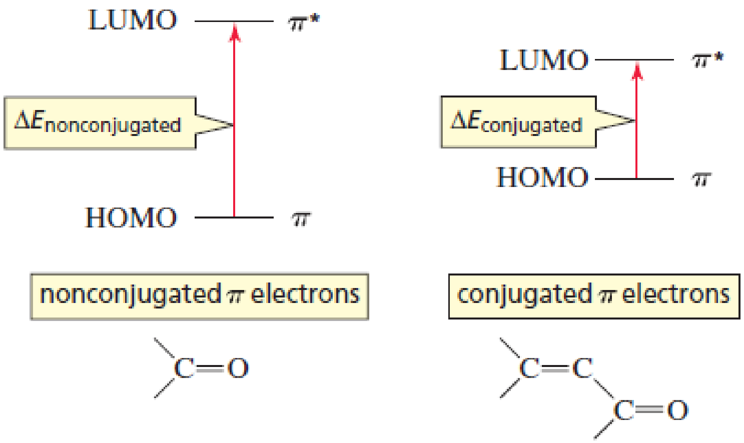




Descriptive term	Nature of the shift
Bathochromic shift (Red shift)	Towards longer wavelength
Hypsochromic shift (Blue shift)	Towards shorter wavelength
Hyperchromic effect	Towards higher absorbance
Hypochromic effect	Towards lower absorbance

Effects of Conjugation

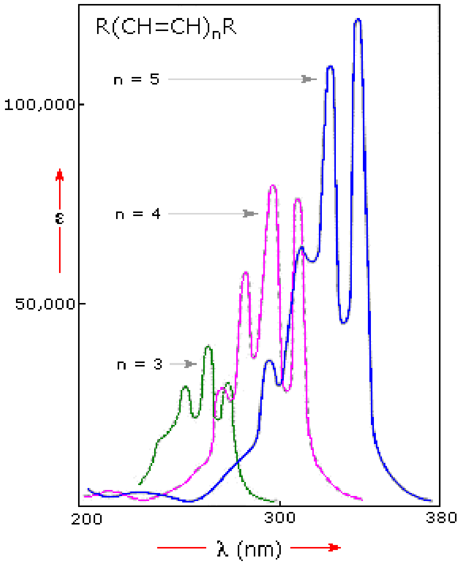
When two or more chromophores are conjugated the absorption maxima is shifted to a larger wavelength or shorter frequency. **Conjugation increases the energy of the HOMO and decreases the energy of LUMO**. As a result less energy is required for an electronic transition in a conjugated system than in a non-conjugated system



Effect of conjugation on electronic transition

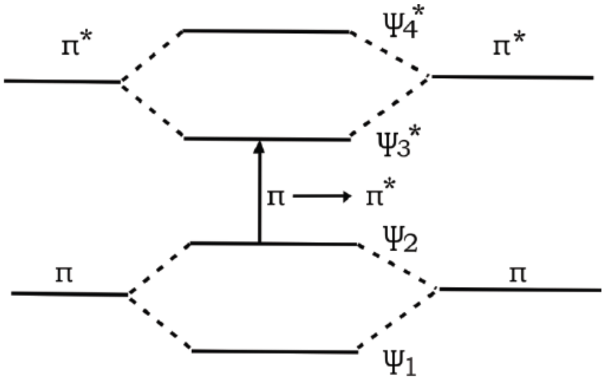
The above figure shows that as the number of conjugated double bonds increases, the value of λ_{max} also increases. The more conjugated double bonds there are in a compound, the less energy is required for the electronic transition, and therefore the longer is the wavelength at which the electronic transition occurs.

It is noteworthy that conjugation of two chromophores not only increases the λ but also increases the intensity (molar absorptivity). This effect of conjugation can be shown by the spectra of the polyenes CH_3-$(CH=CH)_n$-CH_3, where n = 3, 4 and 5.



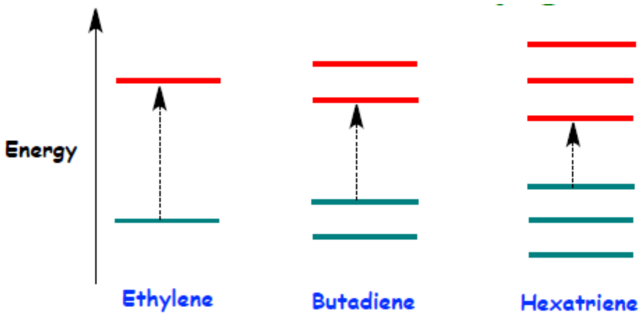
Electronic transitions in conjugated dienes

In case of simple alkene (ethylene) we have only two molecular orbitals, one is ground state π bonding orbital and the other is excited state π* antibonding orbital. The energy gap between these two is 176 kcal/mol. But in case of conjugated dienes, the π molecular orbitals of the two separate C=C groups combine to form two new bonding molecular orbitals designated as ψ_1 and ψ_2, and two new anti-bonding molecular orbitals designated as ψ_3* and ψ_4* .It is clear that the transition of lowest energy π to π* transition in conjugated system is ψ^2 (HOMO) to ψ_4* (LUMO). Hence we can say that the conjugated dienes absorb at relatively longer wavelength than do isolated alkenes.

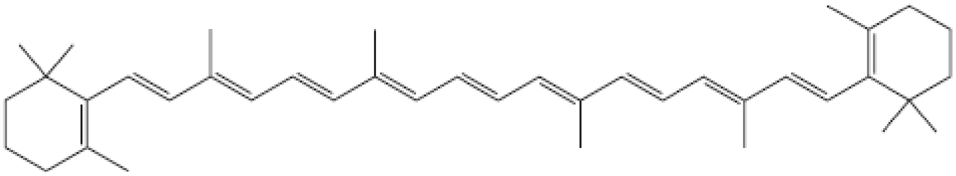


Energy levels of molecular orbitals in conjugated diene system

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 maxima (λ_{max}) to longer wavelength. If a compound has enough conjugated double bonds, it will absorb visible light and the compound will be colored. The β-carotene, a precursor of vitamin A, has eleven conjugated double bonds (Figure 6) and its absorption maximum gets shifted from ultraviolet to the blue region of the visible spectrum giving it an orange colour.

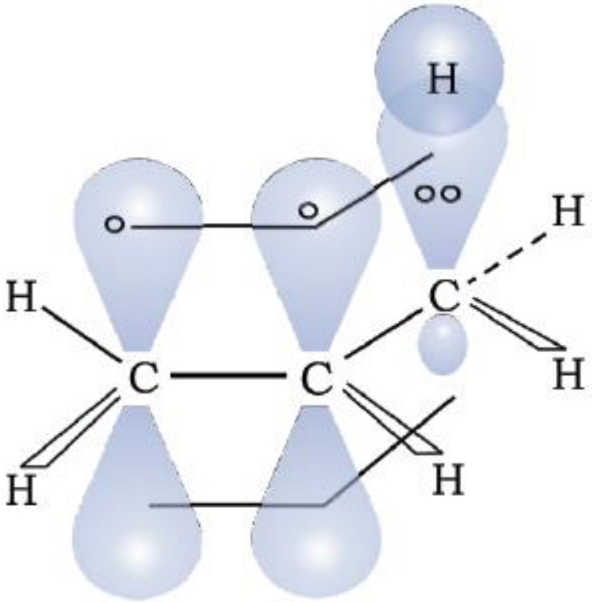


Molecule	λ_{max} (nm)
Ethylene	165
1,3-butadiene	217
1,3,5-hexatriene	258
β-Carotene	470



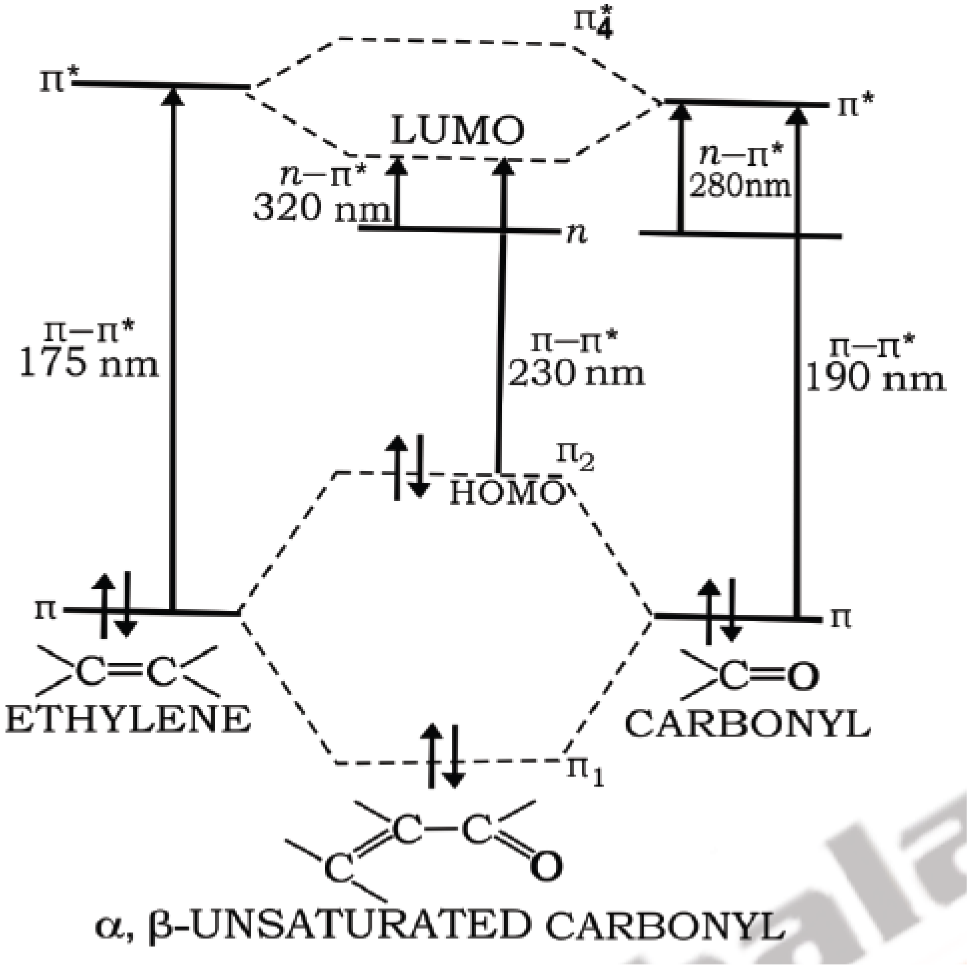
Extended conjugation in β-carotene

In a similar fashion, methyl group also produce bathochromic shift. Although methyl group do not have π electron or unshared electrons yet it is considered that the CH_3 attached with a chromophore interact with the π system through its C-H bonding orbitals that means by hyperconjugation or sigma bond resonance. So conjugation is extended and chromophore length is also increased and bathochromic shift or red shift is occurred.



Extension of π-system by C-H bond through hyperconjugation

If the carbonyl group is conjugated with a C-C double bond i.e. α,β-unsaturated carbonyl compounds, both π to π* and n to π* transitions shift to at longer wavelength compared to the unconjugated carbonyl compounds. However the energy of the n to π* transition does not decrease as rapidly as that of the π to π* band. If the conjugated chain becomes long enough, the n to π* band is buried into the more intense π to π* band system. Figure 8 shows the molecular orbitals of α,β-unsaturated carbonyl system along with the isolated C=C bond and carbonyl group.



Electronic transitions in α,β-unsaturated carbonyl compounds

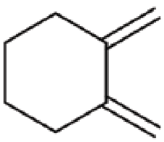
Effect of Steric hindrance

The UV-spectroscopy is very sensitive to the distortion of the chromophores. We know that the position of absorption maximum and its intensity depend on the length and effectiveness of the conjugative system. Electronic conjugation works best when the molecule is planar. If the presence of an auxochrome prevents the molecule from being planar then it may lead to the red or blue shifts depending upon the nature of distortion.

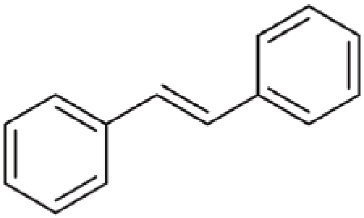
- The diene I shown below is expected to show absorption maximum at 237 nm (As calculated from linear 1,3-diene), but as the structure of the compound is not planar so conjugation is lost and distortion of chromophore causes it to absorb at 220 nm.

Similar trends can also be observed in compounds where geometrical isomerism is possible.

- Generally the trans-isomers show λ_{max} at a longer wavelength and ε_{max} (molar absorptivity or molar extinction coefficient) is higher than for the cis or mixed isomer. For example the *trans*-stilbene (II) absorbs at longer wavelength with greater intensity (λ_{max} = 295 nm, ε = 27000) than the *cis*-stilbene (III, λ_{max} = 280 nm, ε = 13500) due to steric effects. It is due to the fact that *trans*-stilbene (II) has a coplanner structure and delocalization of π electrons occur completely across the molecule while in *cis*-stilbene (III) the delocalization is hindered because it lost coplanarity owing to the overlap of two ortho hydrogen atoms. So in cis stilbine electronic conjugation is reduced and π→ π* transition energy increases and λ_{max} decreases.



I

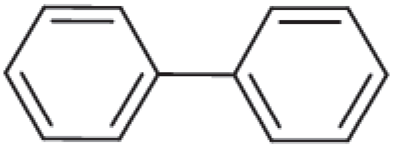


II

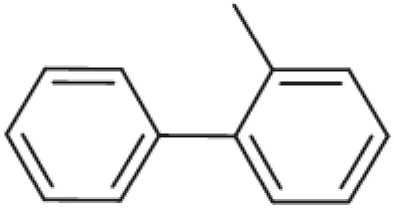
III

- Another example of such cases are biphenyl and its 2-methyl and 2,2'-dimethyl analogues.

Biphenyl system is not completely planar (two ring being at an angle of 450) and in 2-methyl biphenyl the two rings are pushed even further out of co-planarity resulting in the diminished π orbital overlap. As a result, blue shift is observed with less intensity. The biphenyl (IV) has λmax at 250 nm (ε = 19000) and 2-methylbiphenyl (V) has λmax at 237 nm (ε = 10250).



IV



V

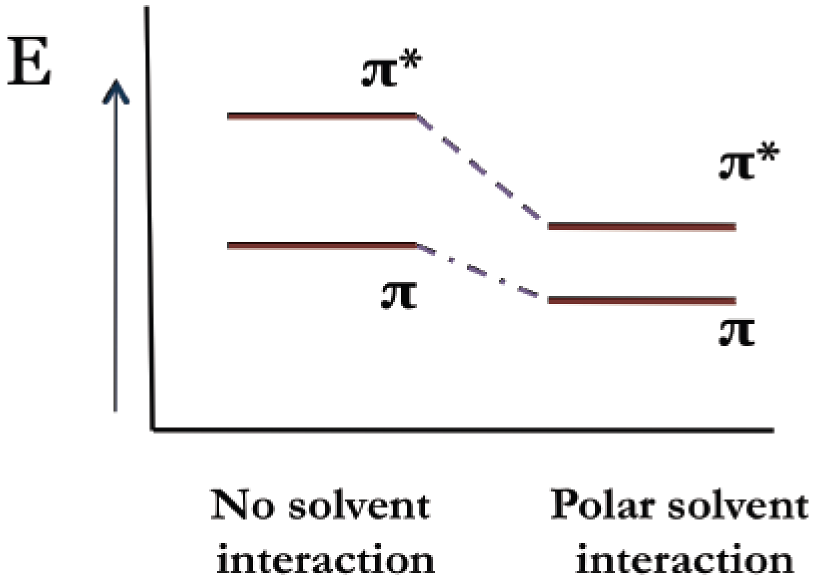
Effect of solvent

The absorption spectrum depends on the solvent in which the absorbing substance is dissolved. The choice of solvent can shift peaks to shorter or longer wavelengths. This depends on the nature of the interaction of the particular solvent with the environment of the chromophore in the molecule under study. It is usually observed that ethanol solutions give absorption maxima at longer wavelength than hexane solutions. Water and alcohols can form hydrogen bonds which results the shifting of the bands of polar substances. Since polarities of the ground and excited state of a chromophore are different, hence a change in the solvent polarity will stabilize the ground and excited states to different extent causing change in the energy gap between these electronic states. 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. Therefore, the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

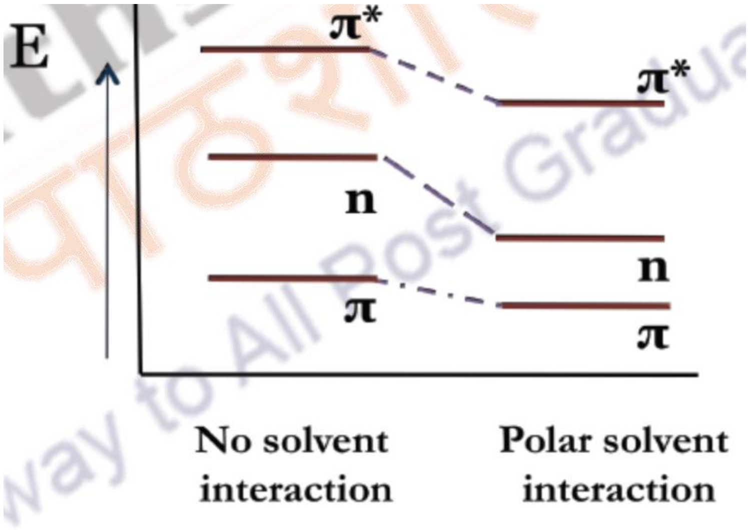
(i) π to π* Transitions

In case of π to π* transitions, the excited states are more polar than the ground state. If a polar solvent is used the dipole–dipole interaction reduces the energy of the excited state more than the ground state. Thus a polar solvent decreases the energy of π to π* transition and hence the absorption in a polar solvent such as ethanol will be at a longer wavelength (red shift) than in a non-polar solvent such as hexane.



(ii) n to π* transitions

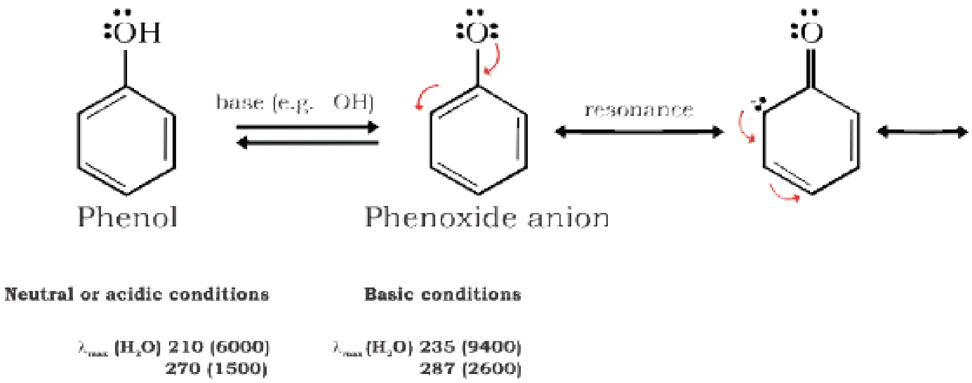
In case of n to π* transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Consequently the energy of ground state is decreased which further causes the increase in energy difference between the ground and excited energy levels. Therefore, absorption maxima resulting from n to π* transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity.



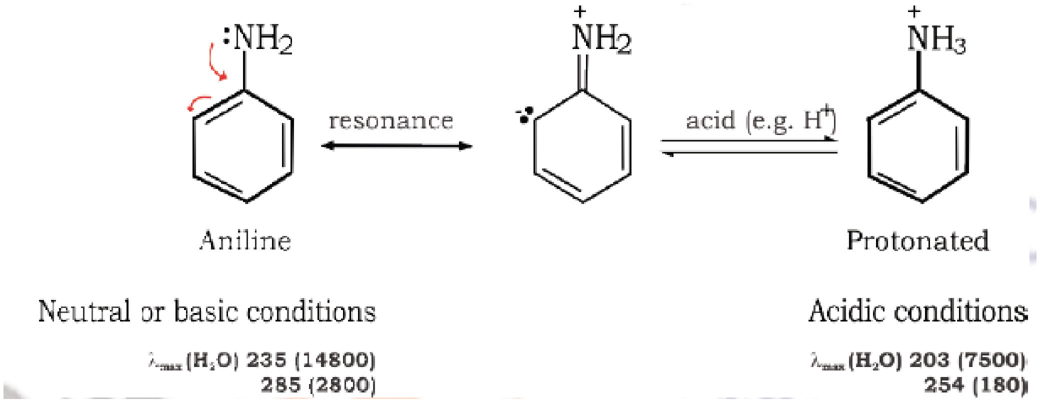
Effect of Sample pH

The pH of the sample solution can also have a significant effect on absorption spectra. The absorption spectra of certain aromatic compounds such as phenols and anilines change on changing the pH of the solution.

Phenols and substituted phenols are acidic and display sudden changes in their absorptions maxima upon the addition of a base. After the removal of the phenolic proton, we get phenoxide ion. In the phenoxide ion lone pairs on the oxygen is delocalized more effetively over the π-sytem of the aromatic ring and increases the conjugation of the same. Extended conjugation leads to a decrease in the energy difference between the HOMO and LUMO orbitals, which results in red or bathochromic shift (to longer wavelength), along with an increase in the intensity of the absorption.



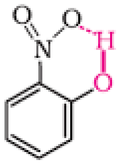
Similarly, an aromatic amine gets protonated in an acidic medium which disturb the conjugation between the lone pair on nitrogen atom and the aromatic π-system. As a result, blue shift or hypsochromic shift (to shorter wavelength) is observed along with a decrease in intensity.



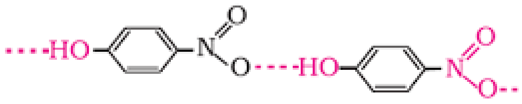
Effect of Hydrogen bonding

Owing to greater polarity, the strength of intramolecular H-bond increases in the excited state relative to ground state. Therefore, the internal or intramolecular H-bonding force increases the stability and thus decreases the energy content of excited state than intermolecular H-bonding. This leads to absorption at longer wavelength, and consequently a bathochromic shift occur with respect to isomer possessing intermolecular H-bond.

So o-nitrophenol with internal H-bond is yellow in colour while its p-isomer is pale yellow coloured substance having intermolecular h-bond.



o-Nitrophenol
(Intramolecular
H-bonding)



p-Nitrophenol
(Intermolecular
H-bonding)

- o-Nitroacetanilide is yellow but para isomer is pale yellow.

Similarly o- isomer posses intramolecular hydrogen bonding but p- isomer posses intermolecular hydrogen bonding. So due to bathochromic shift o-isomer has deeper colour than p- isomer.