

# ULTRAVIOLET SPECTROSCOPY

SEM-4, CC-8  
PART-5, PPT-6

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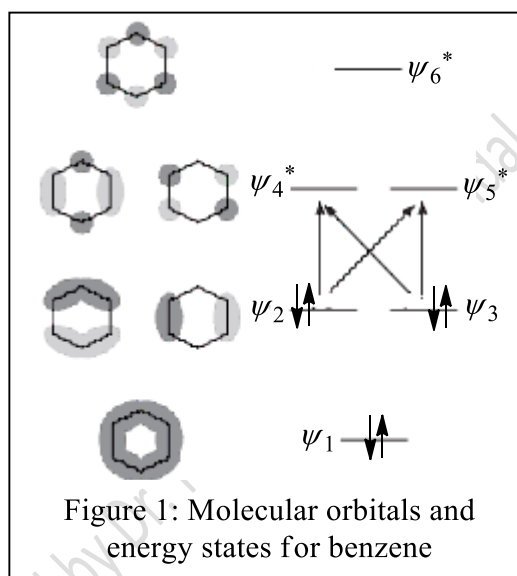
**Kolkata**

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## ULTRAVIOLET SPECTROSCOPY (PART-5, PPT-6)

### Benzenoid Transitions

The absorptions that result from transitions within the benzene chromophore are basically of the  $\pi \rightarrow \pi^*$  type. The UV spectrum of benzene contains three absorption bands. Figure 1 shows the molecular orbitals of benzene. It is expected that four possible electronic transitions of benzene are possible, but each transition has the same energy. Therefore, one can predict that UV spectrum of benzene consists of one absorption band. However, owing to electronic repulsions and symmetry considerations, the actual energy states from which the electronic transitions occur are somewhat modified.

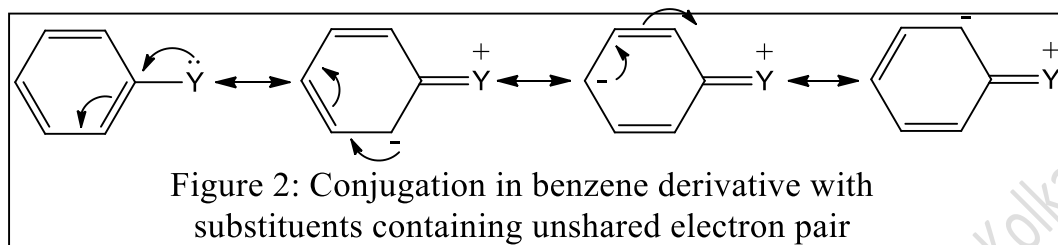


Benzene displays three absorption bands: 184 nm ( $K$  or  $E_1$  band;  $\epsilon_{\max}$  60000), 204 nm ( $E_2$  band;  $\epsilon_{\max}$  7900), 256 nm ( $B$  band;  $\epsilon_{\max}$  200). These bands originate from  $\pi \rightarrow \pi^*$  transitions. The intense band near 180 nm results from an allowed transition, whereas weaker bands near 200 and 260 nm result from forbidden transitions in the highly symmetrical benzene molecule. The transitions at 184 and 204 nm, are the so-called *primary* bands and the transition at 256 nm is considered as *secondary* (fine-structure) band. Of the *primary* bands, the 184 nm band is a highly allowed transition. Nevertheless, this transition is not observed under usual experimental conditions because absorptions at this wavelength are in the *vacuum ultraviolet region* of the spectrum, beyond the range of most commercial instruments.

The 204 nm band is much less intense ( $\epsilon_{\max}$  7900), and it corresponds to a *forbidden* transition. The *secondary* band is the least intense of the benzenoid bands ( $\epsilon_{\max}$  200). It also corresponds to a *symmetry forbidden* electronic transition. The *secondary* band, caused by interaction of the electronic energy levels with vibrational modes, appears with a great deal of fine structure. This fine structure is lost if the spectrum of benzene is determined in a polar solvent or if a single functional group is substituted onto the benzene ring. Substitution on the benzene ring can cause bathochromic and hyperchromic shifts. This is, however, dependent on the nature of the substituents.

## Substituents with Unshared Electrons

Substituents that carry nonbonding electrons ( $n$  electrons) can cause shifts in the *primary* and *secondary* absorption bands. The nonbonding electrons can increase the length of the  $\pi$  system through resonance.

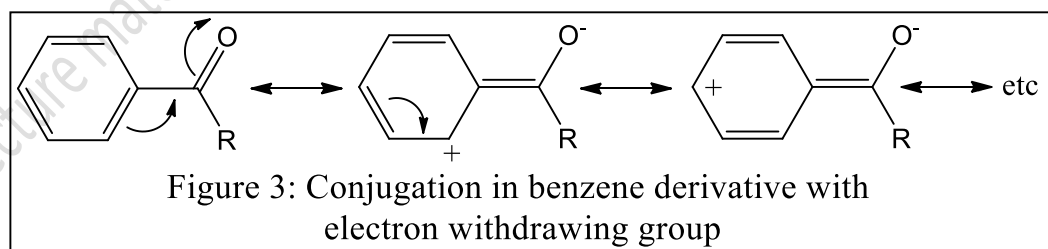


The more available these  $n$  electrons are for interaction with the  $\pi$  system of the aromatic ring, the greater will be the shift. The example of groups with  $n$  electrons are the amino, hydroxyl, methoxy groups, the halogens, etc. Interactions of this type between the  $n$  and  $\pi$  electrons usually cause shifts in the *primary* and *secondary* absorption bands in benzene to longer wavelength (extended conjugation).

In addition, the presence of  $n$  electrons in these compounds gives the possibility of  $n \rightarrow \pi^*$  transitions. If an  $n$  electron is excited into the extended  $\pi^*$  chromophore, the atom from which it was removed becomes electron deficient, while the  $\pi$  system of the aromatic ring acquires an extra electron. This causes a separation of charge in the molecule. However, the extra electron in the ring is actually in a  $\pi^*$  orbital. Such an excited state is often called a charge-transfer or an electron-transfer excited state.

## Substituents Capable of $\pi$ -Conjugation

Substituents that are themselves chromophores usually contain  $\pi$  electrons. Interaction of the benzene-ring electrons and the  $\pi$  electrons of the substituent can produce a new electron transfer band. At times, this new band may be so intense as to obscure the *secondary* band of the benzene system. This interaction, however, induces the opposite polarity; the ring becomes electron deficient.



In the case of benzoic acid, the *primary* and *secondary* bands are shifted substantially from those noted for benzene. However, the magnitudes of the shifts are somewhat smaller in the case of benzoate ion, the conjugate base of benzoic acid. The intensities of the peaks are lower than for benzoic acid as well.

## Electron-Releasing and Electron-Withdrawing Effects

Substituents may have different effects on the positions of absorption maxima, depending on whether they are electron-donating or electron-withdrawing. Any substituent, irrespective of its influence on the electron distribution elsewhere in the aromatic molecule, shifts the *primary* absorption band to longer wavelength.

Electron withdrawing groups have practically no effect on the position of the *secondary* absorption band unless, of course, the electron withdrawing group is also capable of acting as a chromophore. However, electron donating groups increase both the wavelength and the intensity of the *secondary* absorption band. Table 1 summarizes these effects.

## Electron-Releasing and Electron-Withdrawing Effects

Compounds	Primary		Secondary	
	$\lambda_{max}$ (nm)	$\epsilon_{max}$	$\lambda_{max}$ (nm)	$\epsilon_{max}$
Benzene (Ph-H)	204	7400	256	204
Toluene (Ph-CH <sub>3</sub> )	206.5	7000	261	225
Chlorobenzene (Ph-Cl)	209.5	7400	263.5	190
Phenol (Ph-OH)	210.5	6200	270	1450
Anisole (Ph-OMe)	217	6400	269	1480
Aniline (Ph-NH <sub>2</sub> )	230	8600	280	1430
Benzoic acid (Ph-CO <sub>2</sub> H)	230	11600	273	970
Benzaldehyde (Ph-CHO)	249.5	11400		
Acetophenone (Ph-COCH <sub>3</sub> )	245.5	9800		
Nitrobenzene (Ph-NO <sub>2</sub> )	268.5	7800		

## Disubstituted Benzene Derivatives

With disubstituted benzene derivatives, it is necessary to consider the effect of each of the two substituents. For *para*-disubstituted benzenes, two possibilities exist. If both groups are electron-releasing or if they are both electron-withdrawing, they exert effects similar to those observed with monosubstituted benzenes. The group with the stronger effect determines the extent of shifting of the primary absorption band. If one of the groups is electron-releasing while the other is electron-withdrawing, the magnitude of the shift of the *primary* band is greater than the sum of the shifts due to the individual groups. The enhanced shifting is due to resonance interactions as exemplified with *p*-nitroaniline in Figure 4.

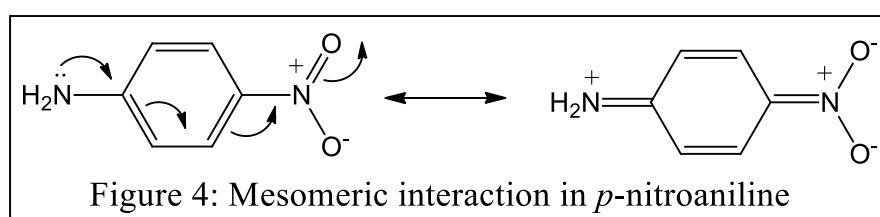
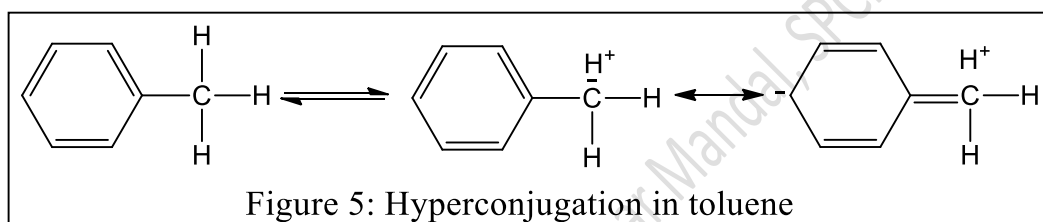


Figure 4: Mesomeric interaction in *p*-nitroaniline

If the two groups of a disubstituted benzene derivative are either *ortho* or *meta* to each other, the magnitude of the observed shift is approximately equal to the sum of the shifts caused by the individual groups. With substitution of these types, there is no opportunity for the kind of direct resonance interaction between substituent groups that is observed with *para* substituents. In the case of *ortho* substituents, the steric inability of both groups to achieve coplanarity inhibits resonance.

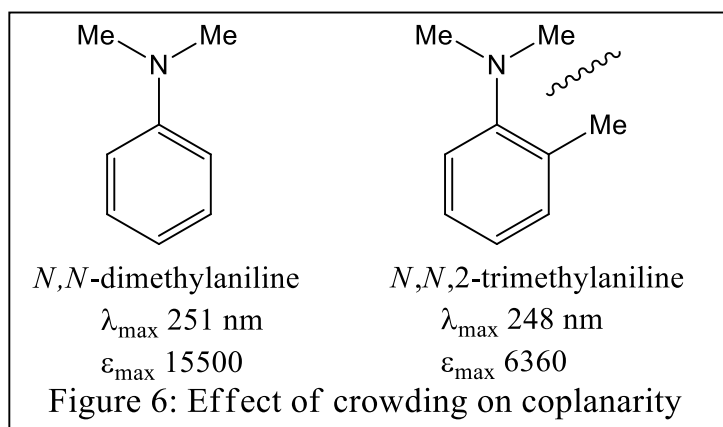
### Benzene Chromophore

Substitution of alkyl groups on the benzene ring produces a bathochromic shift of the *B* band. The bathochromic shift is attributed to hyperconjugation in which the  $\sigma$  electrons of an alkyl C-H bond participate in resonance with the ring. The methyl group is more effective in hyperconjugation than other alkyl groups.



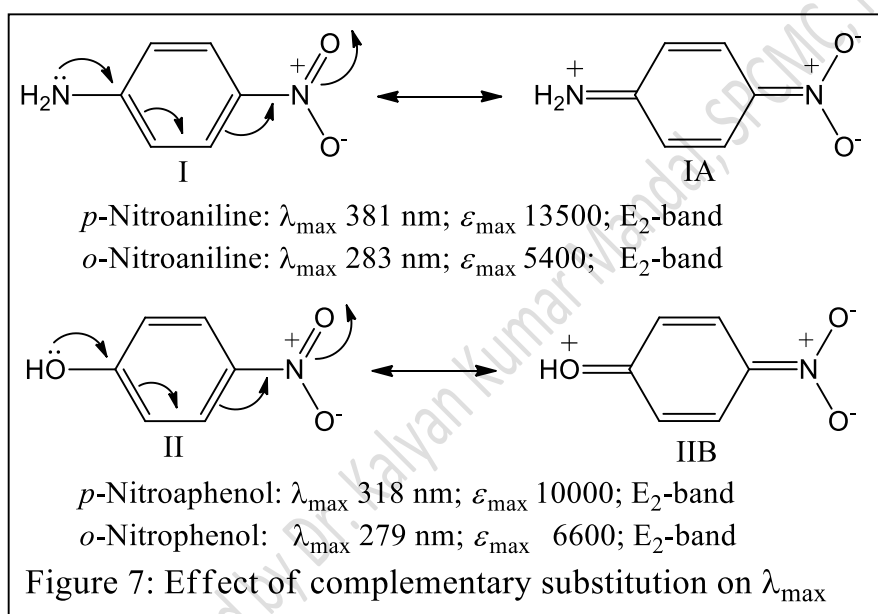
The addition of a second alkyl group to the molecule is more effective in producing a red shift if it is in the *para* position. The *para* isomer absorbs at the longest wavelength with the largest  $\epsilon_{\max}$ . The *ortho* isomer generally absorbs at the shortest wavelength with reduced  $\epsilon_{\max}$ . This effect is attributed to steric interactions between the *ortho* substituents, which effectively reduce hyperconjugation. Substitution on the benzene ring of auxochromic groups (OH, NH<sub>2</sub>, etc.) shifts the *E*- and *B*-bands to longer wavelengths, frequently with intensification of the *B* band because of *n*- $\pi$  conjugation.

Interaction between the nonbonding electron pair(s) of a hetero atom attached to the ring and the  $\pi$  electrons of the ring is most effective when the *p* orbital of the nonbonding electrons is parallel to the  $\pi$  orbitals of the ring. Thus, bulky substitution in the *ortho* position of molecules such as *N,N*-dimethylaniline causes a hypsochromic shift in the *E*<sub>2</sub> band, accompanied by a marked reduction in  $\epsilon_{\max}$ .

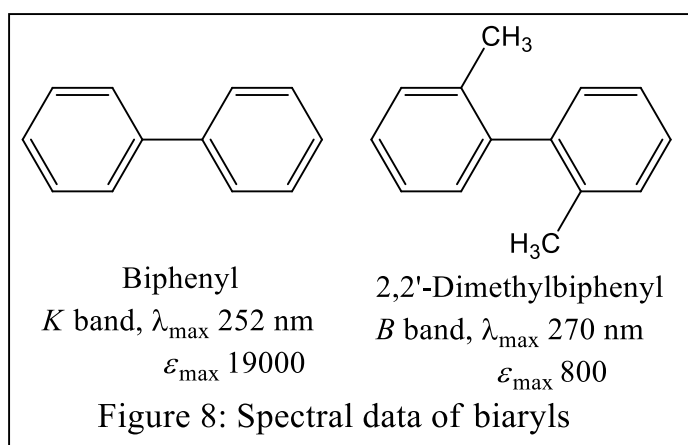


Direct attachment of an unsaturated group (chromophore) to the benzene ring produces a strong bathochromic shift of the *B* band, and the appearance of *K* band (or, *E*<sub>1</sub> band) ( $\epsilon_{\max} > 10000$ ) in the 200-250 nm region (Table 1). When auxochromic groups appear on the same ring as the chromophore, both groups influence the absorption. The influence is most pronounced when an electron-donating group and electron-withdrawing group are *para* to one another (complementary substitution).

The red shift and increase in intensity of the *K* band are related to the cases when an electron donating group, such as -NH<sub>2</sub> group and electron withdrawing group, such as -NO<sub>2</sub> group are *para* to one another (electronically complementary groups) on the benzene ring. The red shift is due to the contributions of the following polar resonance forms (I and II for *p*-nitroaniline and *p*-nitrophenol, respectively) as shown in Figure 7:

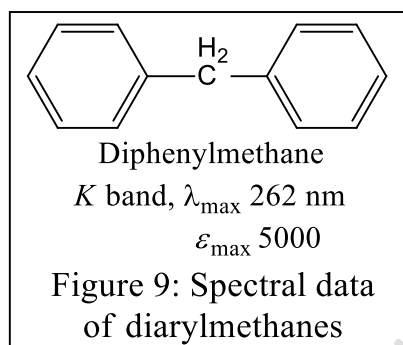


Biphenyl is the parent molecule of a series of compounds in which two aromatic rings are in conjugation. Resonance energy is at a maximum when the rings are coplanar and essentially zero when the rings are at 90° to one another. The effect of forcing the rings out of coplanarity is readily seen from a comparison of the absorption characteristics of biphenyl and its 2,2'-dimethyl homologue (Figure 8) whose absorption characteristics are similar to those of *o*-xylene.



Introduction of a methylene group between two chromophores is capable of disrupting conjugation. Spectral data of diphenylmethane is provided in Figure 9. In some substituted diphenylmethanes, there is an effective overlap of  $\pi$  orbitals of the two rings resulting in homoconjugation. The  $\epsilon_{\max}$  of 4-nitro-4'-methoxydiphenylmethane is not merely the sum of the  $\epsilon_{\max}$  of *p*-nitrotoluene and *p*-methoxytoluene.

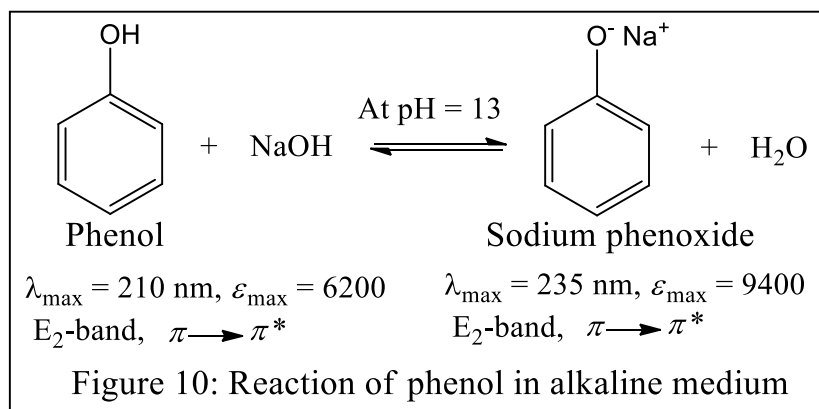
Mono-, di- and triarylbenzenes show almost similar UV spectra. This is because the aryl groups are separated from each other by the intervening methylene or methine group.  $\pi$ - $\pi$  conjugation is similar to that of benzene.



### Effect of pH on $\lambda_{\max}$

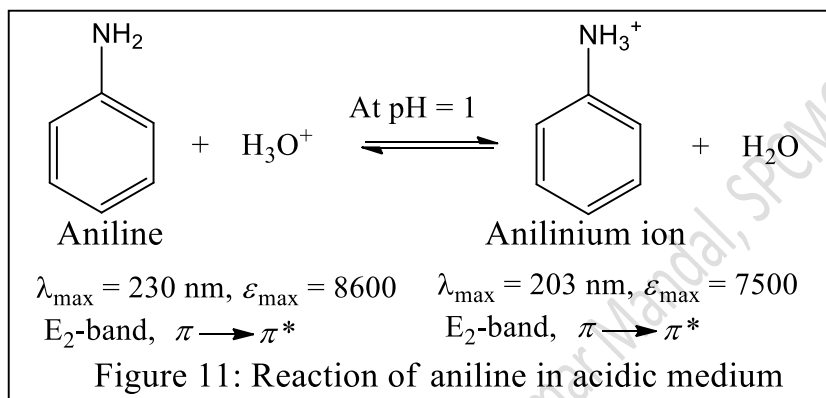
In compounds that are acids or bases, pH changes can have very significant effects on the positions of the *primary* and *secondary* bands. In going from benzene to phenol, the shift from 204 to 210 nm - a 6 nm shift in the *primary* band is noticed. The *secondary* band shifts from 256 to 270 nm - a 14 nm shift. However, in phenoxide ion, the conjugate base of phenol, the *primary* band shifts from 204 to 235 nm (a 31 nm shift), and the *secondary* band shifts from 256 to 287 nm (a 31 nm shift). The intensity of the *secondary* band also increases. In phenoxide ion, there are more *n* electrons, and they are more available for interaction with the aromatic  $\pi$  system than in phenol.

Therefore, substitution on the benzene ring of auxochromic groups (OH, NH<sub>2</sub>, etc) shifts the *E*- and *B*-bands to longer wavelengths because of *n*- $\pi$  conjugation. Conversion of a phenol to the corresponding anion results in a bathochromic shift of the *E*<sub>2</sub>- and *B*-bands and an increase in  $\epsilon_{\max}$  because the *n*-electrons in the anion are available for interaction with the  $\pi$  electron system of the ring.



The comparison of aniline and anilinium ion illustrates a reverse case. Aniline exhibits shift similar to those of phenol. From benzene to aniline, the *primary* band shifts from 204 to 230 nm (a 26 nm shift), and the *secondary* band shifts from 256 to 280 nm (a 24 nm shift). For anilinium ion, the *primary* and *secondary* bands do not shift at all. The quaternary nitrogen of anilinium ion has no unshared pairs of electrons to interact with the benzene  $\pi$  system.

In aqueous acidic medium (pH = 1), aniline is converted to the anilinium cation. The pair of *n*-electrons of aniline is no longer available for interaction with the  $\pi$  electrons of the ring in anilinium cation. Therefore, aniline in aqueous acidic medium shows UV spectrum almost identical to that of benzene.



Compounds	Primary		Secondary	
	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$
Benzene (Ph-H)	204	7400	256	204
Phenol (Ph-OH)	210.5	6200	270	1450
Phenoxide ion (Ph-O <sup>-</sup> )	235	9400	287	2600
Aniline (Ph-NH <sub>2</sub> )	230	8600	280	1430
Anilinium ion (Ph-NH <sub>3</sub> <sup>+</sup> )	203	7500	254	169
Benzoic acid (Ph-CO <sub>2</sub> H)	230	11600	273	970
Benzoate ion (Ph-CO <sub>2</sub> <sup>-</sup> )	224	8700	268	560