

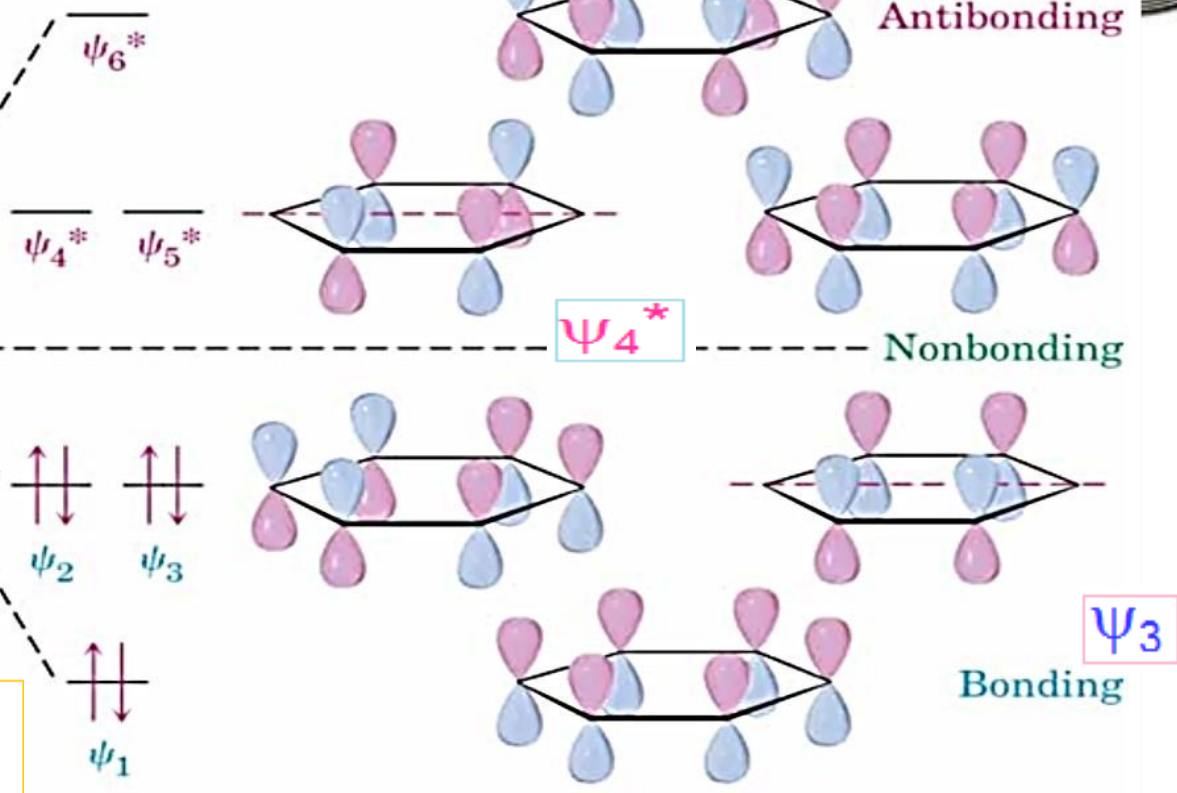
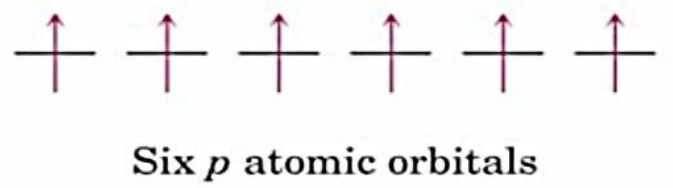
# Aromatic Compounds



## 1. General Features

benzene has six  $\pi$ -MOs, 3 filled  $\pi$ , 3 unfilled  $\pi^*$

- 3 bonding, low-energy MO:  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$
- 3 antibonding high-energy MO:  $\psi_4^*$ ,  $\psi_5^*$ , and  $\psi_6^*$



Six benzene molecular orbitals

Orbitals with the same energy are degenerate:

- 2 bonding orbitals,  $\psi_2$  and  $\psi_3$
- 2 antibonding orbitals,  $\psi_4^*$  and  $\psi_5^*$

$\psi_3$  and  $\psi_4^*$  have no  $\pi$  electron density on 2 carbons because of a node passing through these atoms



## Benzene chromophore

*Benzene displays three absorption*

Bands	$\lambda$ max. nm	$E_{max}$ .	Type of bands
E1(allowed )	180-184	60000	Primary band
E2(forbidden )	200-204	7900	Primary band
B(forbidden )	254-257	200	Secondary band(benzoid band ) fine str.

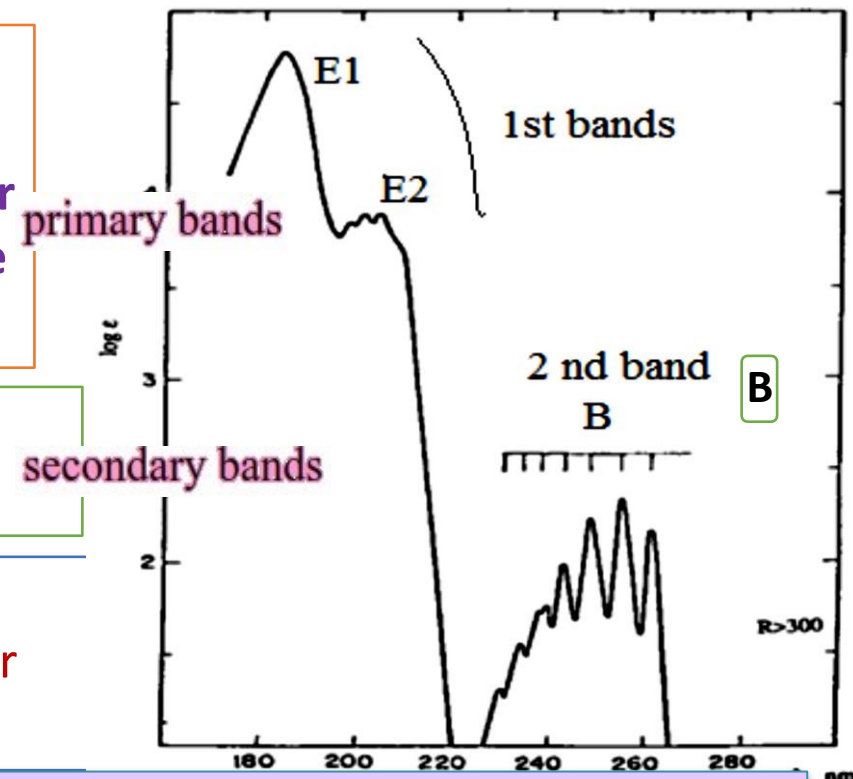
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These bands arise from transition  $\pi \rightarrow \pi^*$

- ✓ Allowed transition == intense band near 180nm
- ✓ Forbidden transition == weaker bands near 200&260nm (230-260) ,In highly symmetrical benzene molecule

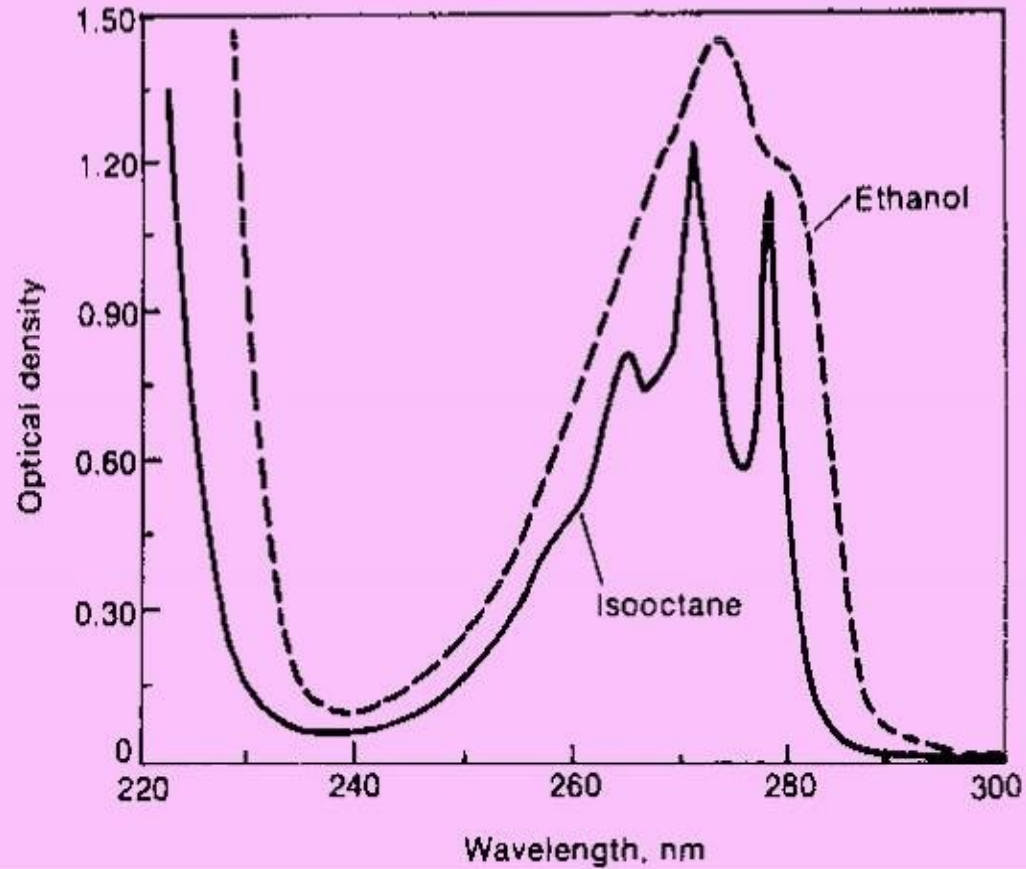
Increase  $\lambda_{max}$  → E1 (not appear )E2 (shorter to appear ) & B with increase  $E_{max}$ . Or stable and loss its fine structure

❖ The B-band of benzene & many of its homologs is characterize by considerable fine structure (in case of vapor phase or in nonpolar solvent



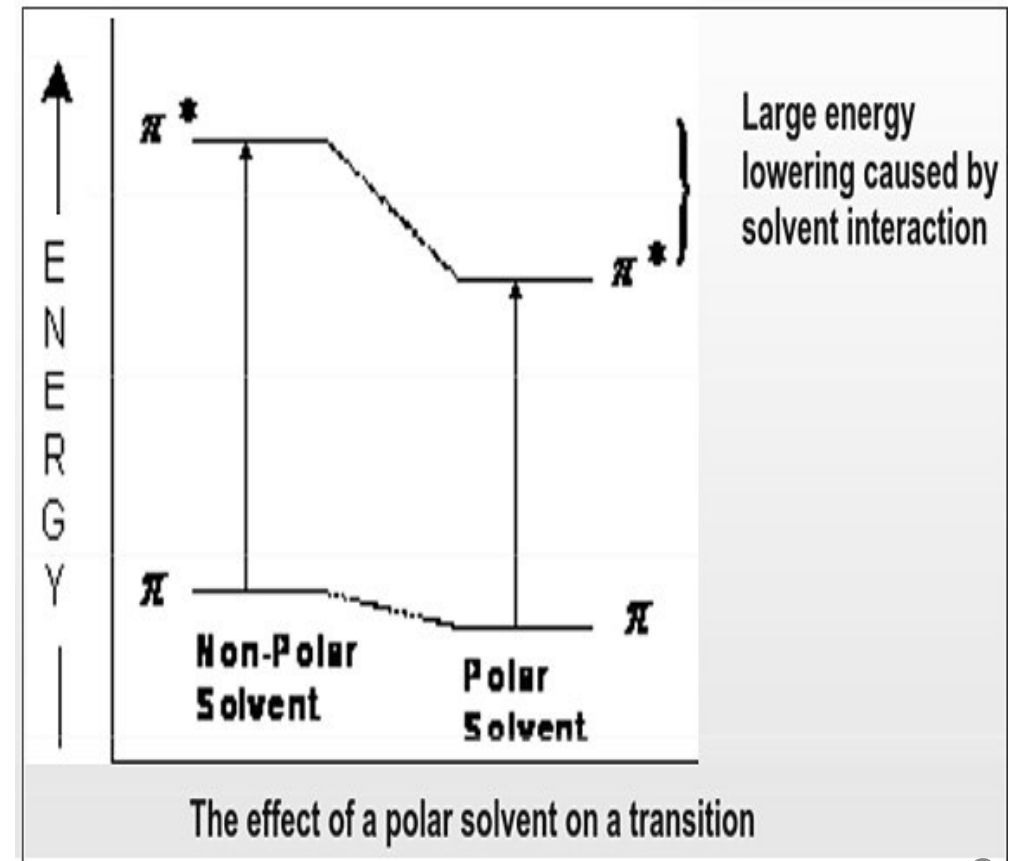
In polar solvent  
solvent interaction

large energy lowering caused by  
decrease fine structure



Ultraviolet Spectra of Phenol in Ethanol and in Isooctane

- Non-polar solvents do not form H-bond with solute, so "fine structure" is often observed.
- Polar solvents form solute-solvent complexes through H-bonding, hence, "fine structure" may disappear.



**Substation of alkyl group on the benzene ring**

**B-band**



Bathochromic shift (red shift)

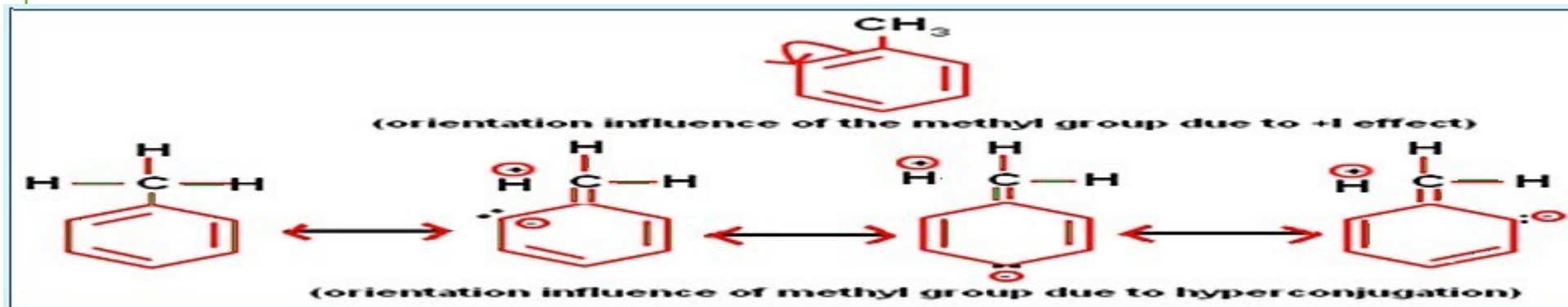
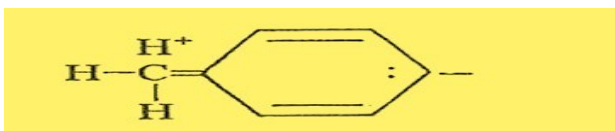
➤ But the effect of alkyl substitution upon the E-band is not clear defined

Q) Why this substitution

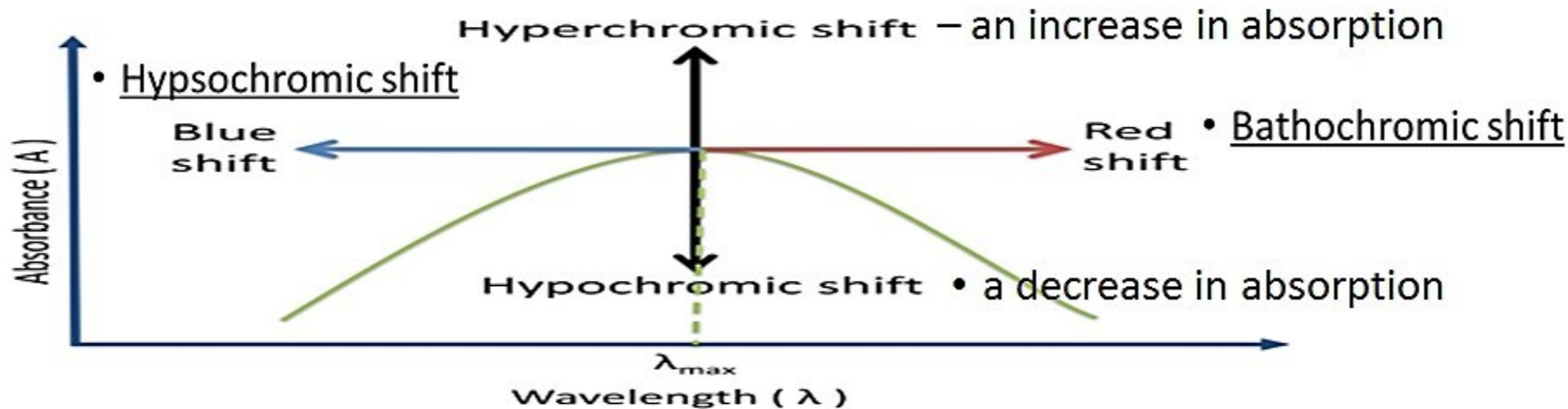
Bathochromic shift (red shift)

Ans.) that due to hyperconjugation in which the  $\sigma$  electrons of alkyl C-H bond participate in resonance with the ring.

Note :- the CH<sub>3</sub> group is more effective in hyperconjugation than other alkyl group



# Shifts and Effects



Q) The ortho isomer generally absorbs at the shortest wavelength with reduce E max. Why?

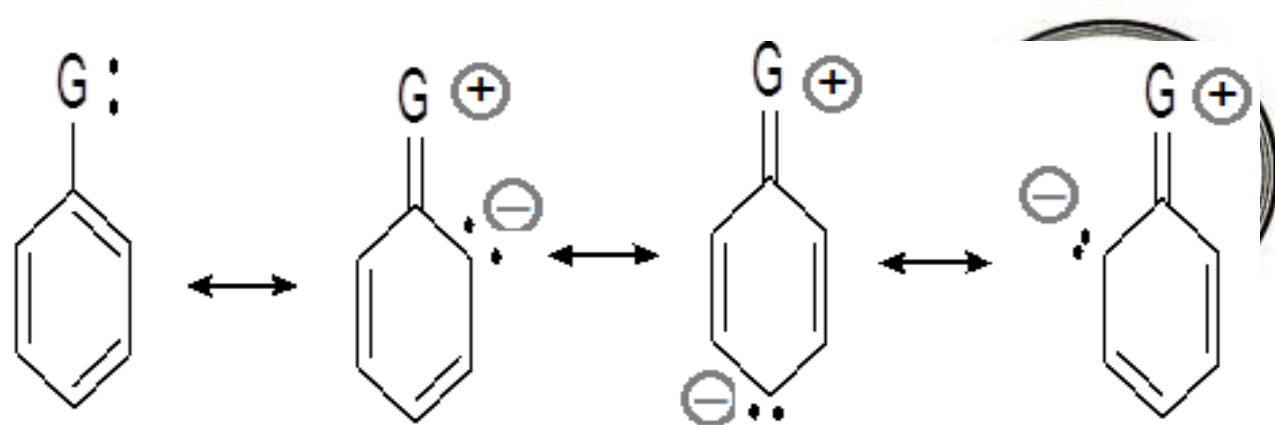
Ans.) because of steric interact is between the ortho substituents decrease the hyperconjugation and **decrease the E max. &  $\lambda_{max}$ .**

Compounds	$\lambda_{max}$ .	E max.
Benzene	256	200
Toluene	261	300
M-xylene	262.5	300
3,5-tri methyl benzene	266	305
Hexamethyl benzene	272	300

$$P > m > O$$

Absorption data for alkyl benzene (B-band )  
 $\lambda_{max}$ . Of the most intense peak in band with fine structure

Compound	E2-band		B-band	
	$\lambda_{\text{max}}$	E max.	$\lambda_{\text{max}}$	E max.
Benzene	204	7,900	256	200
Phenol	210.5	8200	270	1450
Phenolode anion	235	9400	287	2600
Aniline	230	8600	280	1430
Anilinium cation	203	7500	254	160



**Q) The nonbonding electrons resonance with  $\pi$  bonds of the ring to increase E max. &  $\lambda_{\text{max}}$ . Why?**

**Ans.)** as the nonbonding electrons are more available for interaction with the  $\pi$  system to greater the shift will be

- Non-bonding electrons extend the  $\pi$ -system through resonance – lowering the energy of transition  $\pi \rightarrow \pi^*$
- More available  $n$ -pairs of electrons give greater shifts
- The presence of  $n$ -electrons gives the possibility of  $n \rightarrow \pi^*$  transitions

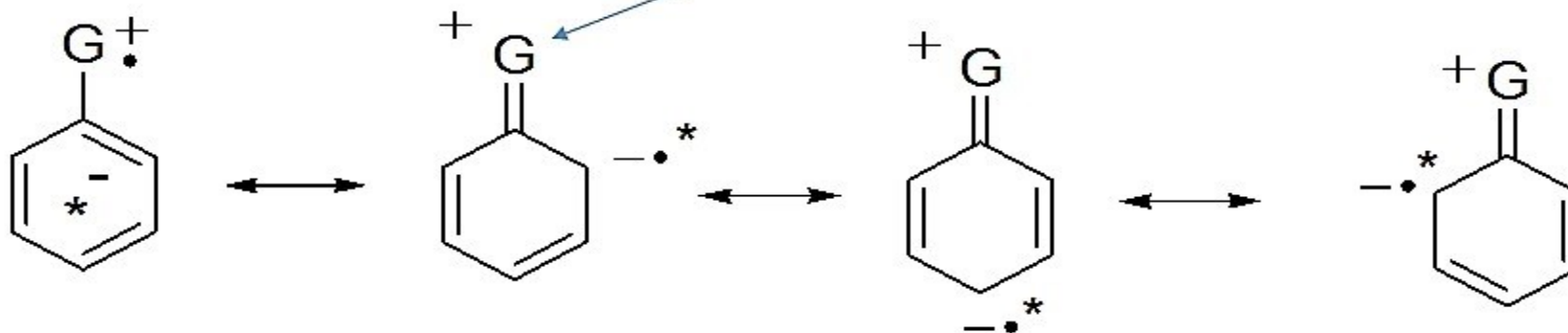
o EWG has little effect on B band o EDG shifts B band to longer  $\lambda$

- Because the unshared of electrons activating the ring by the resonance
- Decrease of excited state to **decreases** required energy for transition (red shift )

By resonance

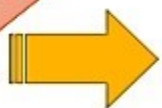
- If this occurs, the electron now removed from G, becomes an extra electron in the anti-bonding  $\pi^*$  orbital of the ring

This state is referred to as a *charge-transfer excited state*



In the case the effect of the  $n \rightarrow \pi^*$  on the compound is, if an *n-electron is excited to the extended  $\pi^*$  chromophore*, the atom from which it was removed become electron deficient while the  *$\pi$  system of the aromatic ring acquire an extra electron this cause a separation of charge in the molecules*

Note :-



- ✓ *extra electron in the ring acutally in a  $\pi^*$  orbital*
- ✓ *Charge transfer or electron transfer excited state*

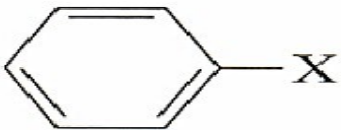
## The effect of PH :- i.e.

### 1) Aniline

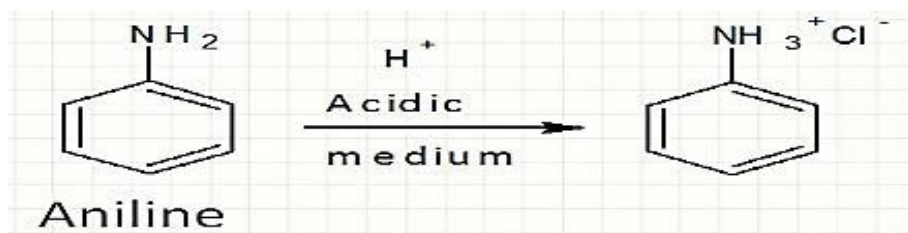
### 2) phenol



- ❑ In arylamines the interaction of the nitrogen lone pair with the  $\pi$ -electron system of the ring shifts the ring's absorptions to longer wavelengths.
- ❑ Tying up the lone pair by protonation causes the UV-Vis spectrum of anilinium to resemble benzene.

	X	$\lambda_{max}$ (nm)	$\epsilon_{max}$	
	Benzene	H	204, 256	7,900, 200
	Aniline	NH <sub>2</sub>	230, 280	8,600, 1,430
	Anilinium ion (resemble benzene)	NH <sub>3</sub> <sup>+</sup>	203, 254	7,500, 160

protonation of nitrogen eliminates the *n*-pair, raising transition energy



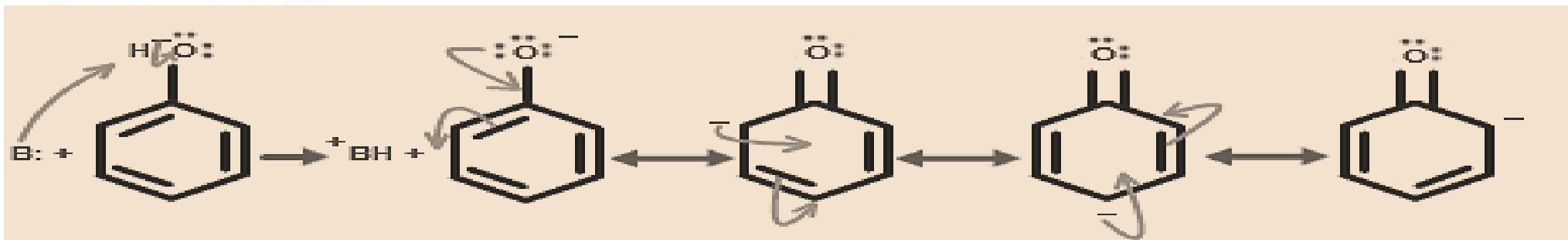
⚡ Aniline shows blue shift in acidic medium, it loses conjugation.

the pair of nonbonding electron of aniline is no longer available for interaction with  $\pi$ -electron system of the ring . Its spectrum almost identical to that of benzene result .

Q/ it was found that trimethyl amine in acidic media don't show absorption due to  $n \rightarrow \sigma^*$ ?



- When absorption maxima ( $\lambda_{max}$ ) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an auxochrome or by the change of solvent.
- e.g. An auxochrome group like  $-OH$ ,  $-OCH_3$  causes absorption of compound at longer wavelength.



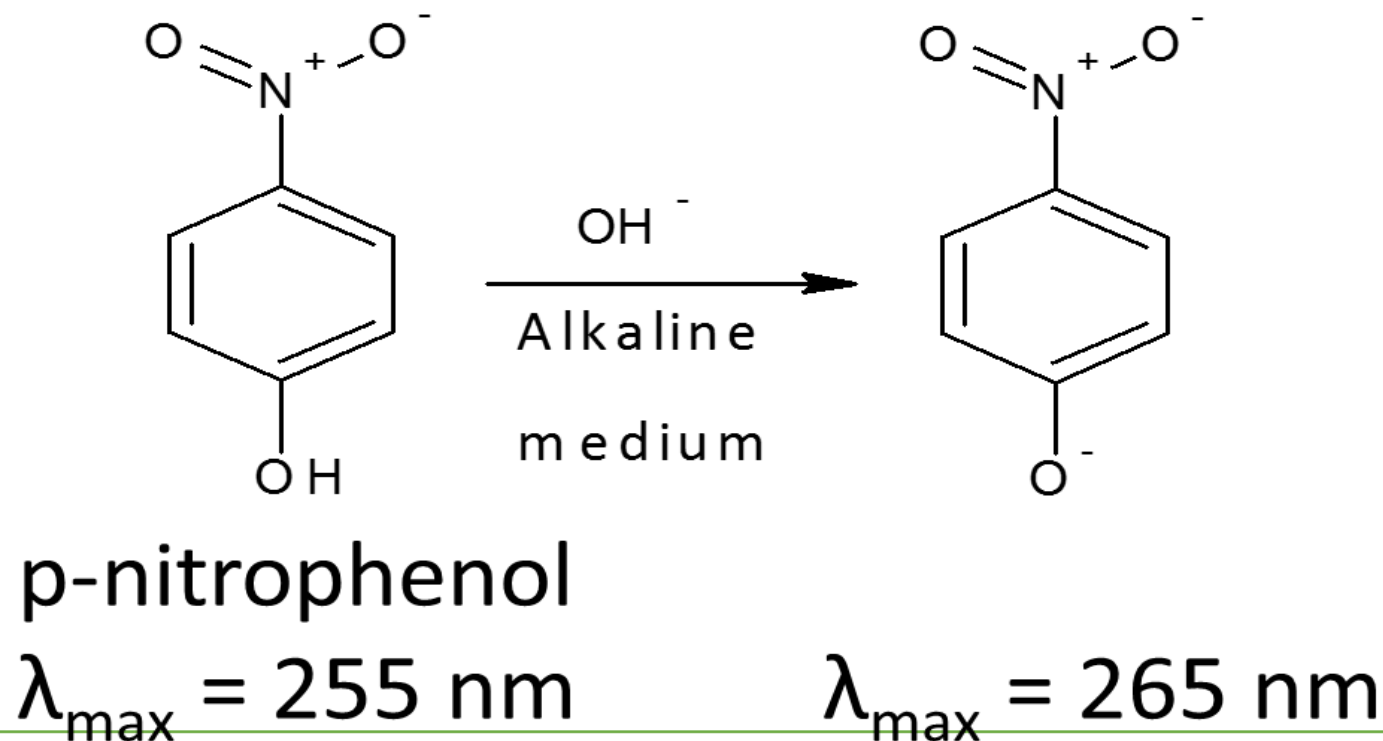
bathochromic shift of the E2 and B-bands and increase in  $\epsilon_{max}$ .

Compound	E2-band		B-band	
	$\lambda_{max}$ .	E max.	$\lambda_{max}$ .	E max.
Benzene	204	7,900	256	200
Phenol	210.5	8200	270	1450
Phenolode anion	235	9400	287	2600

The negative charge of oxygen delocalizes more effectively than the unshared pair of electron

deprotonation of oxygen gives more available *n*-pairs, lowering transition energy

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

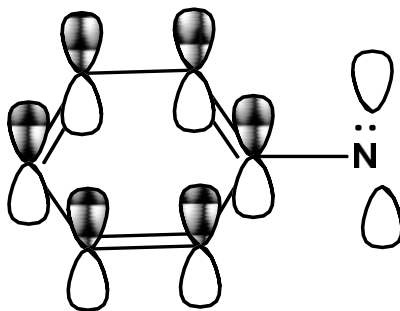


If an unk. sample of benzene derv.( aniline or phenol ),how to diff. between them by uv only ?

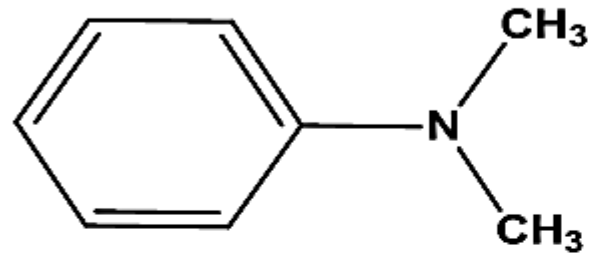
To one of them :( you can do it to each one):

- 1 - take the uv at neutral pH ----- uv spectra I .
- 2 - take the uv at acidic pH( i.e.=1) ----- uv spectra II .
- 3 - take the uv at basic pH ( i.e.-13) ----- uv spectra III .

Interaction between the nonbonding electron pair of heteroatom attached to the ring & and the  $\pi$  electrons of the ring is most effective when the p orbital of the nonbonding electron is parallel to the  $\pi$  orbital of the ring



Thus, bulky substitution in the ortho position of molecules such as N,N-dimethyl aniline cause a hypsochromic (Blue shift) shift in the E2 band & accompanied by a marked reduction E max

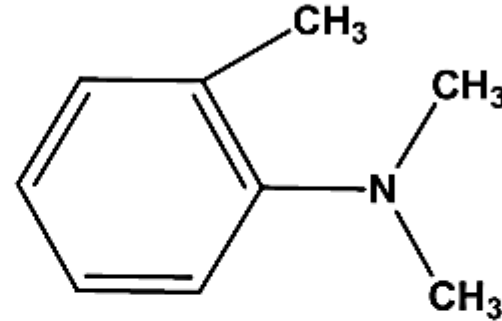


N,N-dimethyl aniline

$\lambda_{max}$  251  
 $\epsilon_{max}$  15.500



ortho



2-methyl-N,N-dimethyl aniline

248  $\rightarrow$   $\lambda$   
 6360  $\rightarrow$   $\epsilon_{max}$

$\downarrow$  (the) nonbonding e pair of N not effectively interaction w(with) the  $\pi$ .es of  $\wedge$  ring . ( not completely parallel)

\* This effect in case of O > m >>> P  $\leftarrow$  very very  $\downarrow$

# Disubstituted benzene Derivatives

( 2 nd. law )



- When auxochromic gr.s appear on the same ring as the chromophore, both groups (gr.s) influence the absorption.
- For predicting  $\lambda_{\max}$  of the primary band of substituted benzene the following rules are used. ( in case of disubstituted benzene)

- Table XXV:

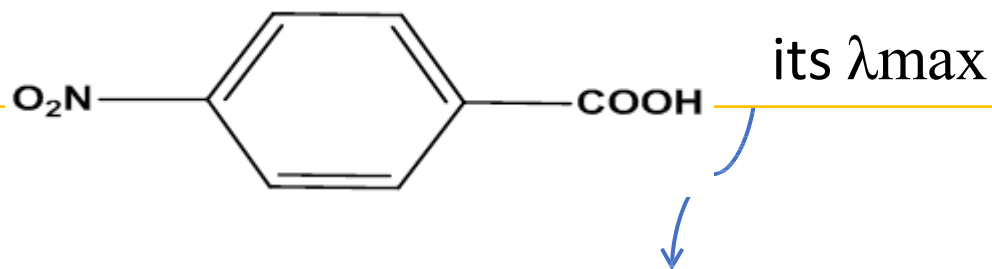
<u>substituent</u>	<u>shift</u>	:	<u>substiotuent</u>	<u>shift</u>
- CH <sub>3</sub>	3		-NH <sub>2</sub>	26.5
- CHO	46		- OH	7.0
- COCH <sub>3</sub>	42		- OCH <sub>3</sub>	13.5
- CO <sub>2</sub> H	25.5		- NO <sub>2</sub>	65.0

Base value is (203.5 nm) for 1° band (  $\pi \rightarrow \pi^*$  interact)

## A- For Para substitution

1- Both groups are e. donating EDG or e withdrawing EWG: only the effect of the group causing the larger shift is used ( so it is similar to monosubstituted benzene)

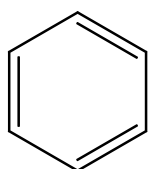
i.e P- nitrobenzenic acid



Would be expected to be the same as that of nitro-benzene

Why ? because  $\lambda_{\max}$  parent cpd. = 203.5 nm

- CO <sub>2</sub> H	25.5	- NO <sub>2</sub>	65.0
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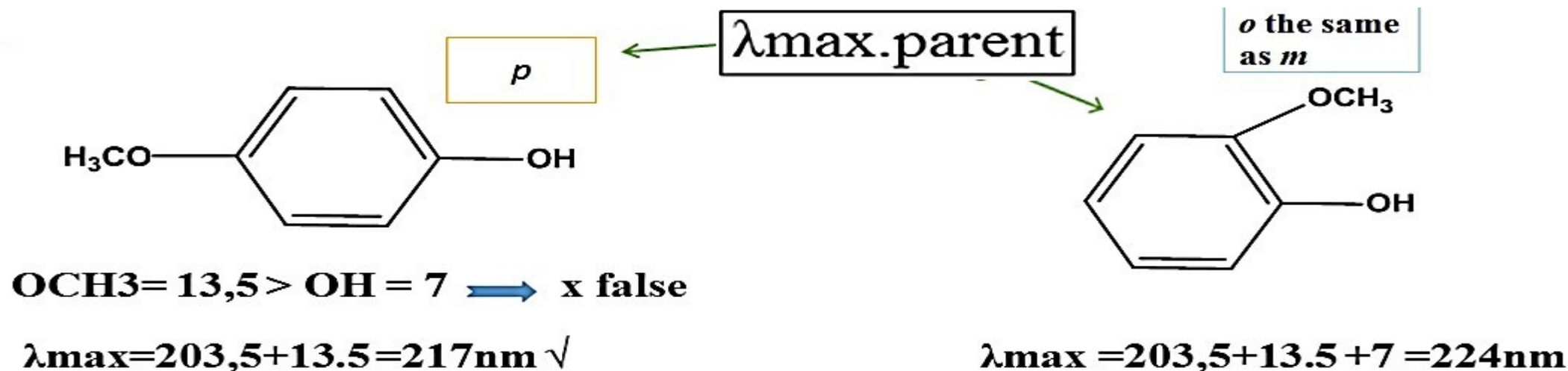
$$\begin{array}{r}
 + 65 \\
 \hline
 268.5 \text{ nm}
 \end{array}
 \leftarrow
 \begin{array}{r}
 \text{NO}_2 > \text{CO}_2\text{H} \\
 65 \quad 25.5
 \end{array}$$

So if both the groups are electron-donating then the observed spectrum is closer to monosubstituted benzene. The group with stronger effect determines the extent of shifting of primary band.

B/Meta and ortho: if the two gr.s are *o*- or *m*- to one another the effect is usually the sum of the two individual effects (the shift effect are additive (meta : no resonance ....ortho steric effect)

So: by Uv: we can diff. between *p* & (-*o*, -*m*) derivetave..... no resonance

Note: -*o*, -*m* can not diff. between them by Uv

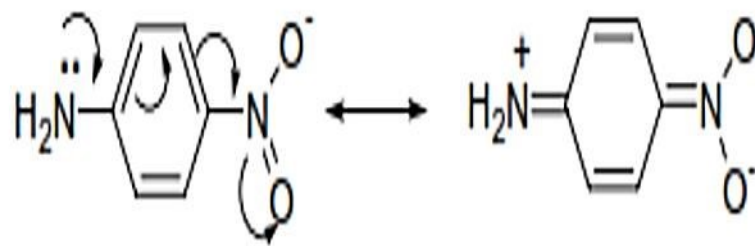
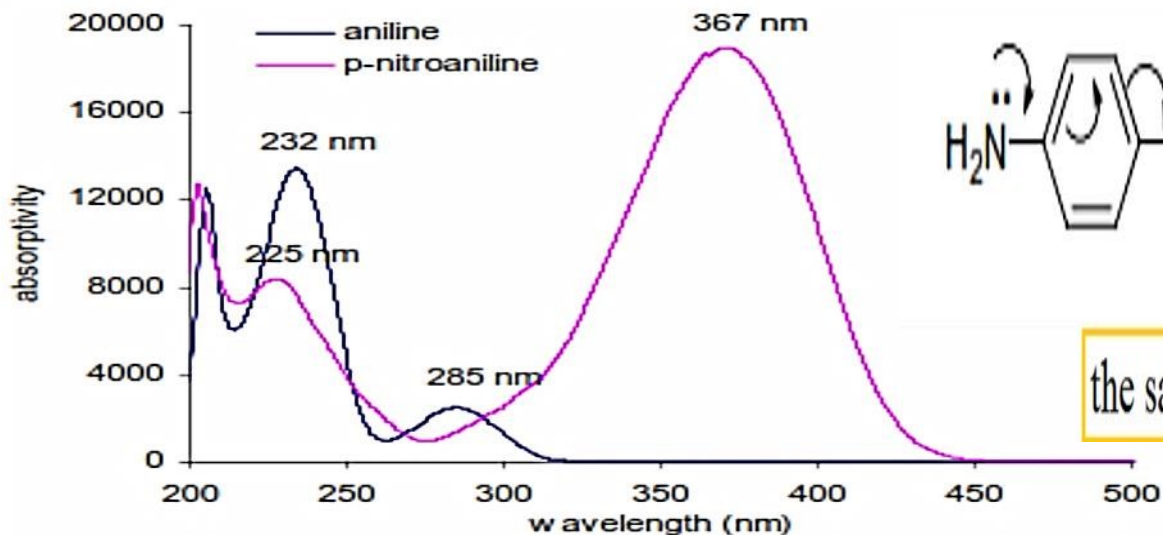


2. One gr. Is EDG and other one is EWG : The calculated  $\lambda_{max}$  is usually **much lower then the observed**  $\lambda_{max}$  (the same reasons) given for p-nitrophenal (resonance)



Calc. ≠ obs  
Resonance effect {  $\odot$  With  $\pi$  ring }  
↓  
(greater extension of conjugat) → ↑  $\lambda_{max}$

So if one group is electron-releasing and other is electron-withdrawing, the magnitude of red shift is grater compared to the effect of single substituent individually. This is attributed to the increased electron drift from electron-donating group to the electron-withdrawing group through  $\pi$ -bond of benzene ring. For example, aniline shows secondary band at 285 nm which due to presence of electron-withdrawing p-nitro substituent is shifted to 367 nm with a significant increase in absorptivit .



the same in case p-nitrophenol

Aniline secondary band at 285 nm



p-nitro aniline secondary band at 367 nm

UV-spectra of aniline and p-nitroaniline in methanol

\* The red shift & ↑ in intensity of the k-band



\* The influence is most pronounced when an electron donating gr EDG & e attracting gr. are para to the another (complementary substitut)