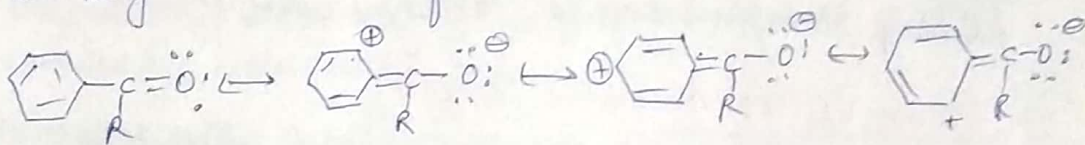


- ⇒ Such an excited state is often called charge-transfer or an electron-transfer excited state.
- ⇒ Acids or bases, pH changes can have very significant effects on primary and secondary bands of aromatic ring  
Also availability of  $n \rightarrow e^-$  T<sub>os</sub>, intensity of primary and secondary band T<sub>os</sub>.

### A Substituents Capable of $\pi$ -conjugation

- ⇒ Substituents that are themselves chromophores usually have  $\pi \rightarrow e^-$ , when  $\pi \rightarrow e^-$  added to it, then interaction of  $\pi \rightarrow e^-$  of benzene ring and the  $\pi \rightarrow e^-$  of substituent can produce a new  $e^-$  transfer band (Intense)
- Notice:- This interaction induces the opposite polarity, the ring becomes  $e^-$  deficient.



### effect of pH on absorption bands :


Substituents	Primary		Secondary	
	$\lambda$ (nm)	$\epsilon$	$\lambda$ (nm)	$\epsilon$
	203.5	7400	257	904
-OH	210.5	6200	270	1450
-O <sup>⊖</sup>	235	9400	287	2600
-NH <sub>2</sub>	230	8000	280	1430
-NH <sub>3</sub> <sup>⊕</sup>	203	7500	254	169
-COOH	230	11600	273	970
-COO <sup>⊖</sup>	224	8400	268	560

⇒ In Benzoic Acid the primary & secondary bands are shifted than Benzene.  
 But magnitude of shifts are smaller in the case of Benzoate.  
 the conjugate Base of Benzoic acid = We expect transfer of  
 solt just shown to be less likely when the functional grp  
 already bears a -ve charge.

c) Electron-releasing & Electron-withdrawing effects

- ⇒ position of maxima differs, depending on the ED & EW nature of attached substituents.
- ⇒ EW grp have no effect on position of secondary bands but they act as chromophore.
- ⇒ ED grp has both wavelength & intensity of secondary bands.
- ⇒ Any substituent, regardless of its influence on the  $e^-$  distribution elsewhere in aromatic molecule, shifts the primary absorption bands to longer wavelength.

UV for various Aromatic compounds:

Substituents	Primary		Secondary	
	$\lambda$ (nm)	E	$\lambda$ (nm)	E
 - H	203.5	7400	254	204
- CH <sub>3</sub>	206.5	7000	261	225
- Cl	209.5	7400	263.5	190
- Br	210	7900	261	192
- OH	210.5	6200	270	1450
- OCH <sub>3</sub>	217	6400	269	1480
- NH <sub>2</sub>	230	8600	280	1430
- CN	224	13000	271	1000
- COOH	230	11600	273	970
- COCH <sub>3</sub>	245.5	9800	-	-
- CHO	249.5	11400	-	-
- NO <sub>2</sub>	268.5	7800	-	-

ER

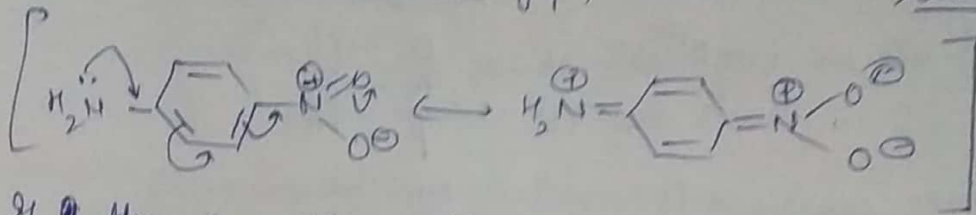
EW

## b) dibstituted benzene derivatives

⇒ for *p*-substituted benzene, 2 possibilities exist. If both are EDG or EWG, they exert effects similar to those observed with monosubstituted benzene.

⇒ The gp with the stronger effect determines the extent of shifting of primary band.

⇒ If one gp is ED while other is EW, the magnitude of shift of primary band is greater than the sum of the shift due to individual gps, this is due to resonance.

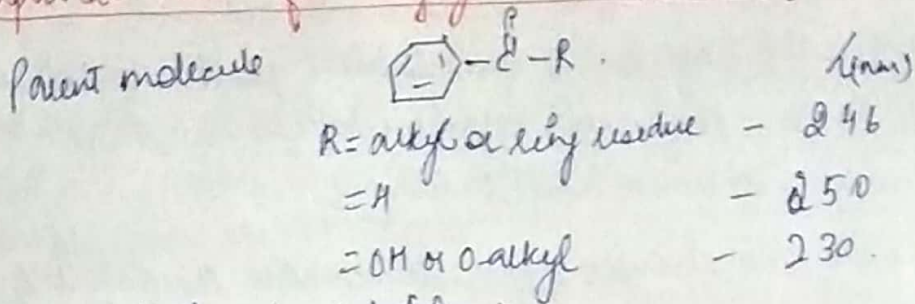


⇒ If they are either ortho or meta to each other, the magnitude of observed shift is equal to sum of shift caused by individual gps.

⇒ In case of ortho substituents, the steric inability of both gps to achieve coplanarity inhibits resonance.

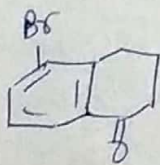
Substituted Benzene derivatives are special case; the  $\nu_r$  values are given below.

Empirical rules for Benzoyl derivatives :-



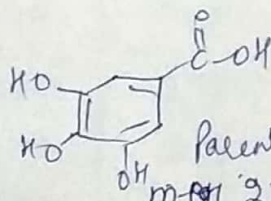
Increment of each substituent

- alkyl or ring residue	$o, m = 3$ $p = 10$
-OH, -OCH <sub>3</sub> or Oalkyl	$o, m = 7$ $p = 25$
-O <sup>⊖</sup>	$o = 11$ $m = 20$ $p = 78$
-Cl	$o, m = 0$ $p = 10$
-Br	$p = 15$ $o, m = 2$
-NH <sub>2</sub>	$o, m = 13$ $p = 58$
-NHCOCH <sub>3</sub>	$o, m = 20$ $p = 45$
-NHCH <sub>3</sub>	$p = 73$
-N(CH <sub>3</sub> ) <sub>2</sub>	$o, m = 20$ $p = 85$



Parent	246
O ring residue	3
m-Br	2
	<hr/> 251nm

observed 253nm



Parent	= 230
m-OH 2x7	= 14
p-OH	= 25
	<hr/> 269nm

observed = 270nm

Poly nuclear Aromatic Hydrocarbon :-  
⇒ Primary and secondary bands are shifted to longer  $\lambda$  nm.  
benzene = 184 nm  
naphthalene = 220 nm

⇒ As conjugation increases, the magnitude of bathochromic shift also increases.

⇒ Poly nuclear Aromatic hydrocarbon give characteristic shapes and fine structure. While substituted one first compared with the UV spectra of poly nuclear aromatic hydrocarbon.

⇒ Nature of chromophore can be identified on the basis of similarity of peak shapes and fine structure.

⇒ Heterocyclic molecule have electronic transitions including  $\pi \rightarrow \pi^*$  &  $n \rightarrow \pi^*$  transitions. UV spectra will be complex & analysis of transition involved will be left to more advanced treatments.