

TYPES OF ORGANIC CHEMISTRY REACTIONS

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Organic reactions are the chemical reactions that are undergone by organic compounds (the chemical compounds containing carbon). A few important types of organic reactions are illustrated below.



Substitution



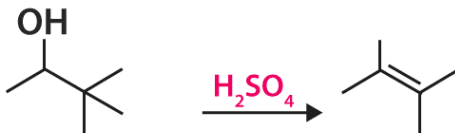
Addition



Elimination



Rearrangement



Chapter 3. Electronic Displacements

Permanent Effect	Temporary Effect
1. Inductive Effect (IE)	4. Inductomeric Effect
2. Mesomeric Effect (ME)	5. Electromeric Effect
3. Hyperconjugation (hc)	

3. 1. Inductive effect (IE) or polarization effect

Partial polarization of e⁻s forming 'σ' bond towards more electronegative atom.

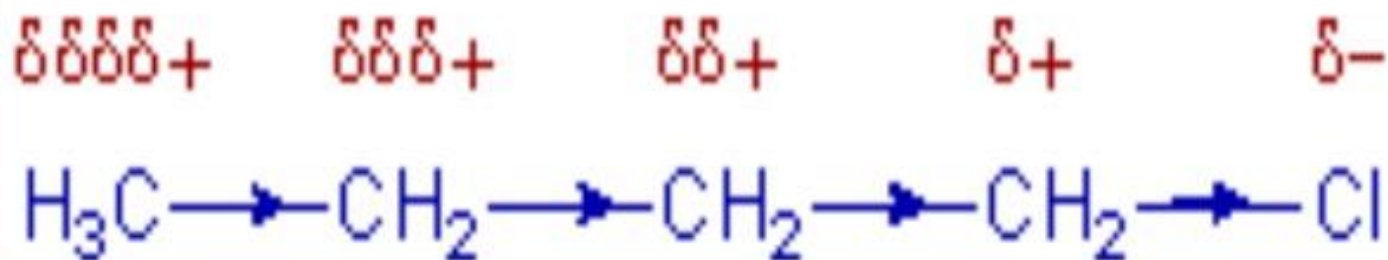


Characteristics of inductive effect:

- It is a permanent effect.
- It is operated only in sigma (σ) bonds.
- Only σ electrons are involved.
- In inductive effect electrons are partially displaced.
- IE is transmitted along the chain.
- As length of the chain increases the IE decreases.

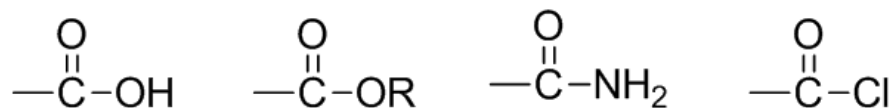
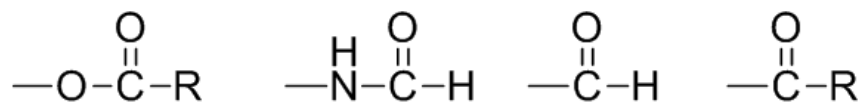
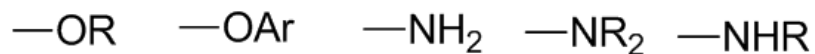
INDUCTIVE EFFECT

The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect.

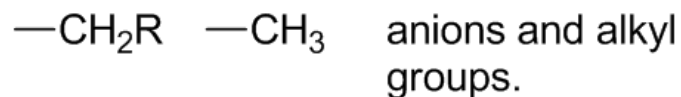
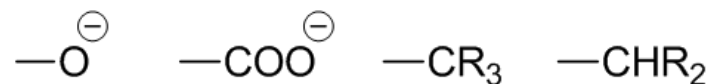


+I and -I Inductive effecting groups

-ve Inductive effect group (-IE)

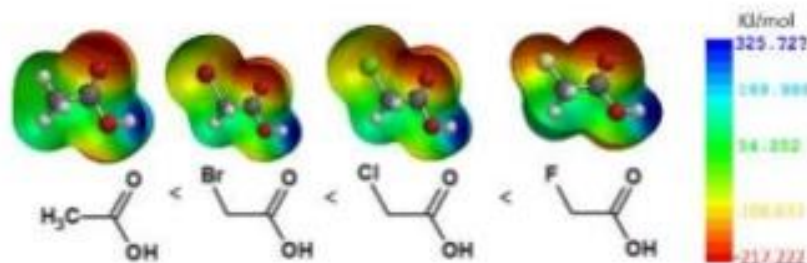


+ve Inductive effect group (+IE)



Inductive Effects on Acidity

The increased acidity of carboxylic acids can be attributed to electrostatic effects, such as induction. More electronegative groups will greatly change the distribution of electron density in the molecule by withdrawing electrons. This effect will make the proton more acidic.



Acidity increases as more electronegative substituents are added to the molecule and withdraw electron density from the acidic proton

The relative distance of the electronegative group also affects the acidity of carboxylic acids. The closer the electron withdrawing substituent is to the reactive proton, the more acidic the molecule becomes.

Compound	pKa
CH ₃ CO ₂ H	4.74
BrCH ₂ CO ₂ H	2.9
ClCH ₂ CO ₂ H	2.85
FCH ₂ CO ₂ H	2.65
CH ₃ CH ₂ ClCO ₂ H	2.89
CH ₃ ClCH ₂ CO ₂ H	4.05
ClCH ₂ CH ₂ CO ₂ H	4.53

Reusch, W. *Carboxylic Acids*. <https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/crbacid1.htm> (Accessed October 2015).

Inductive Effects

pKa Values

$\text{H}-\text{COOH}$	3.75	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{COOH}$	4.8
CH_3-COOH	4.75	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2-\text{COOH} \\ \\ \text{Cl} \end{array}$	4.5
$\text{CH}_3\text{CH}_2-\text{COOH}$	4.87	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{COOH} \\ \\ \text{Cl} \end{array}$	4.0
$\text{CH}_3\text{CH}_2\text{CH}_2-\text{COOH}$	4.81	$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CH}-\text{COOH} \\ \\ \text{Cl} \end{array}$	2.9
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{COOH} \\ \\ \text{CH}_3 \end{array}$	5.02		

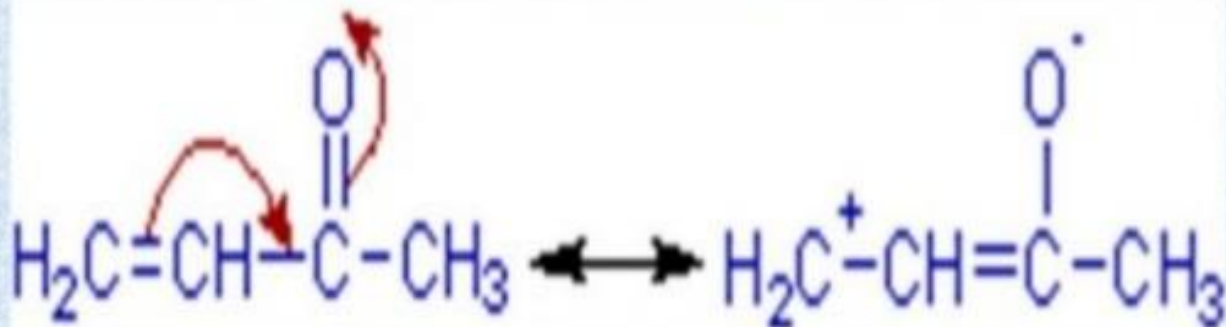
Alkyl groups release electrons.
This decreases acidity

When the chlorine atom is moved further away from the carboxyl group, acidity decreases

distance

RESONANCE EFFECT OR MESOMERIC EFFECT :

The mesomeric effect is defined as the polarity produced in the molecule by the interaction of two π bonds or between a π bond and lone pair of electrons present on an adjacent atom. It is symbolized by M or R.



Positive resonance or mesomeric effect (+M or +R):

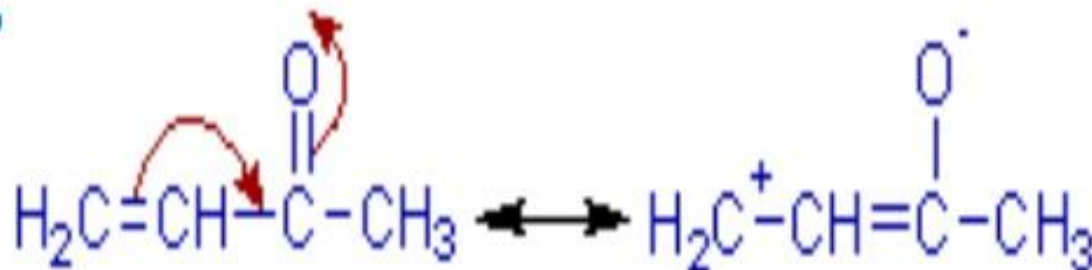
- The -NH_2 group in aniline also exhibits +R effect. It releases electrons towards benzene ring through delocalization.



Negative mesomeric effect (-M or -R):

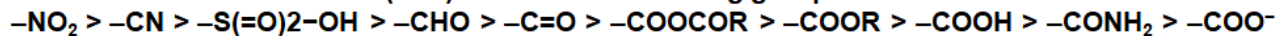
- Example:

- 1) The negative resonance effect (-R or -M) of carbonyl group is shown below. It withdraws electrons by delocalization of π electrons and reduces the electron density particularly on 3rd carbon.

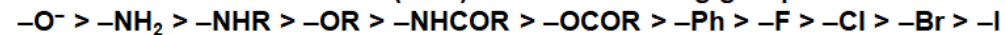


- Mesomeric Effect (-ME) π electrons are involved	+ Mesomeric Effect (+ME) non-bonding 'n' electrons are involved
<div style="text-align: center;"> $\text{H}_2\text{C}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}=\overset{\ominus}{\text{O}} \longleftrightarrow \text{H}_2\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{C}}=\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{O}}$ </div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \\ \text{aldehyde} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{R} \\ \text{ketone} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \\ \text{acid} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR} \\ \text{ester} \end{array}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{Cl} \\ \text{acylchloride} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \\ \text{amide} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}-\text{R} \\ \text{anhydride} \end{array}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $-\text{C}\equiv\text{N}$ nitriles </div> <div> $-\text{NO}_2$ nitro </div> <div> $-\text{SO}_3\text{H}$ sulfonic acid </div> </div>	<div style="text-align: center;"> $\text{H}_2\text{C}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{Cl}}: \longleftrightarrow \text{H}_2\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{C}}=\overset{\oplus}{\text{Cl}}:$ </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $-\overset{\cdot\cdot}{\text{Cl}}:$ </div> <div> $-\overset{\cdot\cdot}{\text{Br}}:$ </div> <div> $-\overset{\cdot\cdot}{\text{I}}:$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{H}$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{R}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \parallel \\ -\overset{\cdot\cdot}{\text{N}}-\text{C}-\text{R} \\ \text{acetamide} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\overset{\cdot\cdot}{\text{O}}-\text{C}-\text{R} \\ \text{acetate} \end{array}$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{Ar}$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{Ph}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $-\overset{\cdot\cdot}{\text{S}}\text{H}$ </div> <div> $-\overset{\cdot\cdot}{\text{S}}\text{R}$ </div> <div> $-\overset{\cdot\cdot}{\text{N}}\text{H}_2$ </div> <div> $-\overset{\cdot\cdot}{\text{N}}\text{HR}$ </div> <div> $-\overset{\cdot\cdot}{\text{N}}\text{HR}_2$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div>thiols</div> <div>thioether</div> <div>amines</div> </div>

Order of - Mesomeric Effect (-ME) electron withdrawing groups:

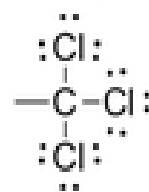
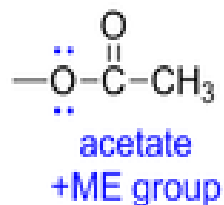


Order of + Mesomeric Effect (+ME) electron donating groups:

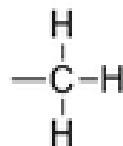


In **-ME** group there will be **no lone pair** electrons.

For example:



neither +ME nor -ve



neither +ME nor -ve

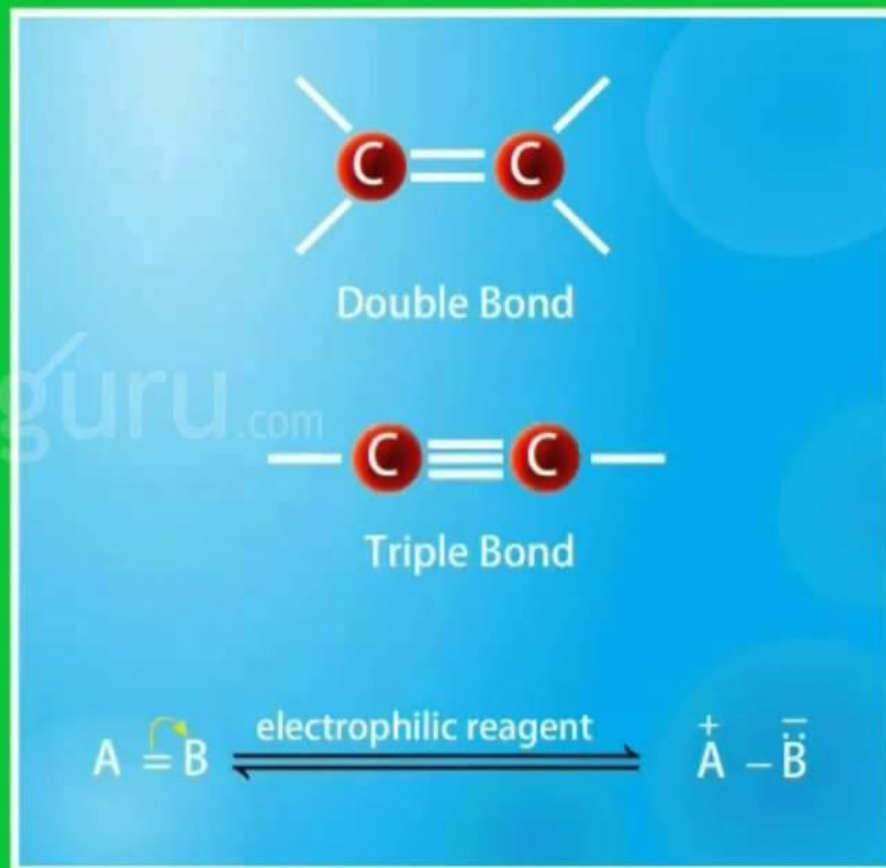
Applications of Mesomeric Effect

- i. Stability of allyl and benzyl carbocations
- ii. Stability of allyl and benzyl free radicals
- iii. Acidity of carboxylic acids
- iv. Basicity of amines

Electromeric Effect (E effect)

When a compound containing double or triple bond is exposed to attack by an electrophilic reagent, electron pair is transferred completely from one atom to another.

The atom to which the electron pair is transferred becomes negatively charged and the other atoms become positively charged.



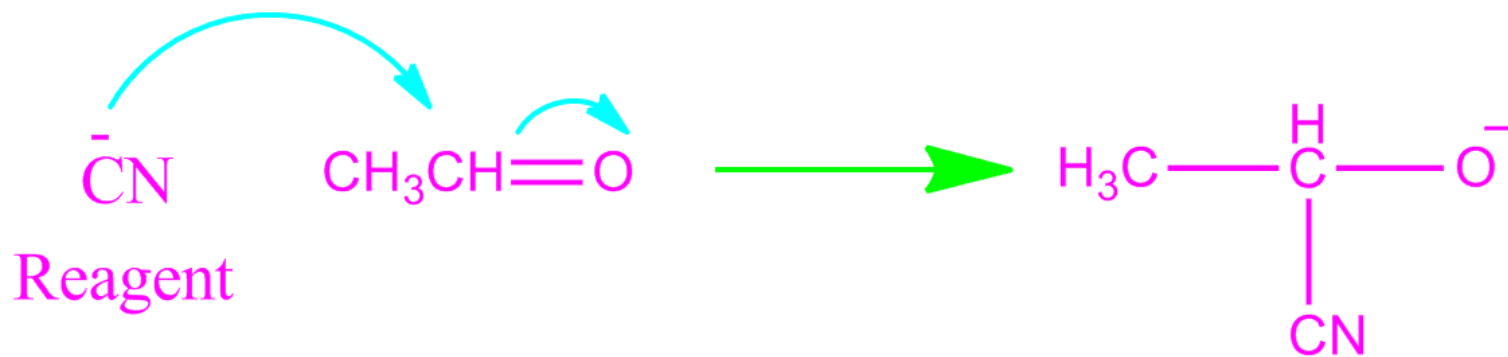
Types of Electromeric Effect

- +E effect : When displacement of electrons is away from the atom or group.
- e.g : addition of H^+ to alkene.
- -E effect : When displacement of electrons is towards the atom or group.
- e.g : addition of cyanide ion(CN^-) to the carbonyl group.

+ E effect :

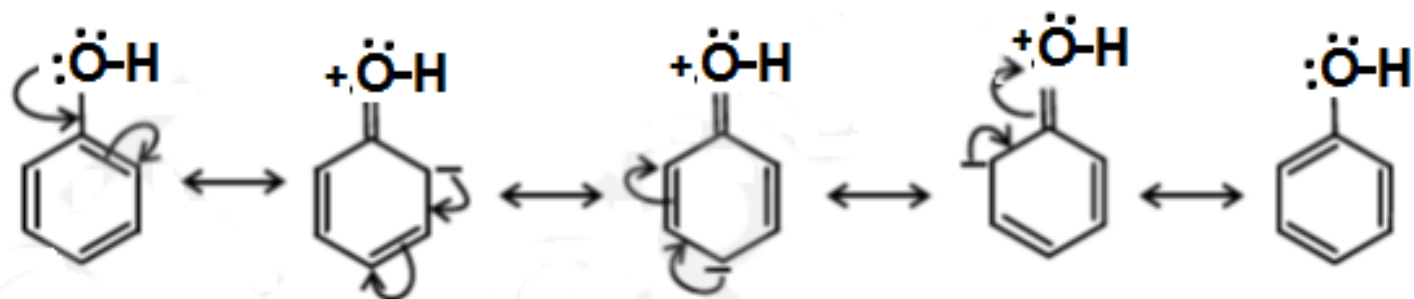


- E effect :

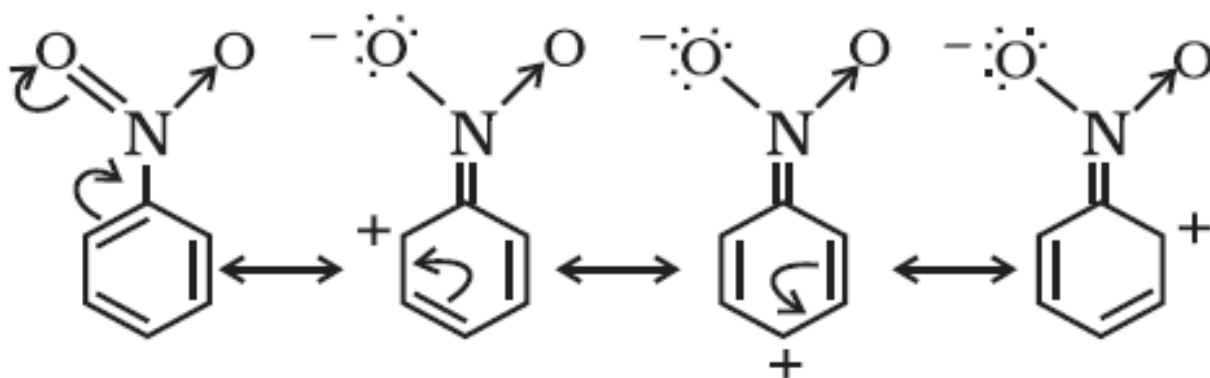


Positive resonance effect (+R effect)

Phenol

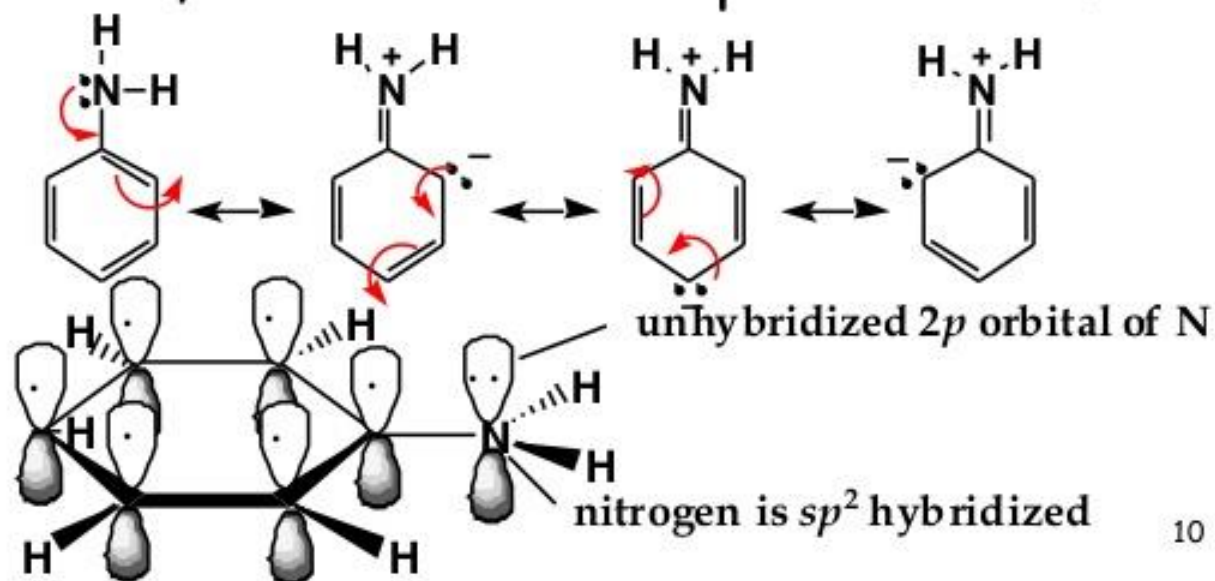


Negative resonance effect (-R effect) in nitrobenzene



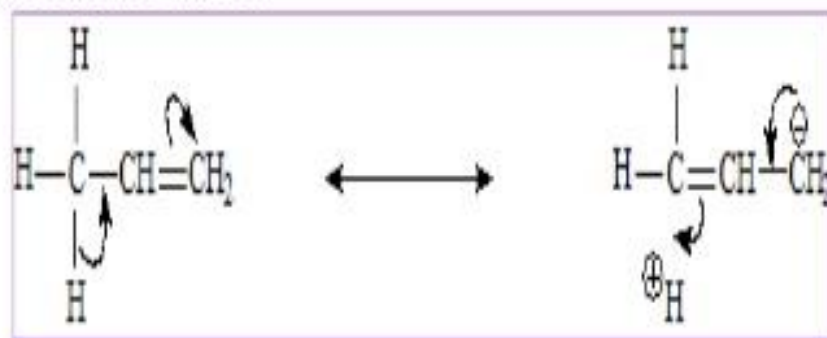
Basicity-Aromatic Amines

- Aromatic amines are weaker bases than aliphatic amines because of two factors:
 - Resonance stabilization of the free base, which is lost on protonation.



Hyperconjugation: No bond resonance

- ▶ The electrons of the sigma bond between C and H are involved in delocalization.
- ▶ In structure to the right: No bond between C and H due to migration of the sigma bond. Hence Hyperconjugation is also called as 'NO BOND RESONANCE'.
- ▶ This does not indicate that hydrogen is completely detached from the structure, but some degree of ionic character in the C – H bond and some single bond character between carbon – carbon double bond.



HYPERCONJUGATION

V E R S U S

RESONANCE

Hyperconjugation is the stabilization effect on a molecule due to the interaction between a sigma bond and a pi bond

Involves sigma bond orbitals and p orbitals or pi bond orbitals

Causes the sigma bond length to be shortened

Resonance is the stabilizing of a molecule through delocalization of bonding electrons in the pi orbital

Involves only pi bond orbitals

Has no effect on sigma bonds

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