UNIT-V: Orientation of aromatic substitution (9 h)

Concept of aromaticity, Huckel's rule - application to Benzenoid (Benzene, Naphthalene) and Non - Benzenoid compounds (cyclo propenyl cation, cyclopentadienyl anion and tropylium cation) Orientation of aromatic substitution - ortho, para and meta directing groups. Ring activating and deactivating groups with examples (Electronic interpretation of various groups like NO2 and Phenolic). Orientation of (i) Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, Carbonyl and sulphonic acid groups (iii) Halogens

Concept of aromaticity: Aromatic compounds are those which resembles benzene like chemical behaviour and are extremely stable cyclic molecules due to their unique electron delocalization

Characteristics.

(1) Although their molecular formulae suggest a high degree of unsaturation, yet they fail to give to characteristic tests of unsaturated compounds (Bayer's test).

(ii) They undergo readily certain electrophilic substitution reactions such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation, and acylation, etc.

(iii) Their molecules are flat or nearly flat as shown by physical methods such as X-ray and electron diffraction methods

Huckel's rule:

According to Huckle a compound is said to be aromatic if it satisfies the following conditions:

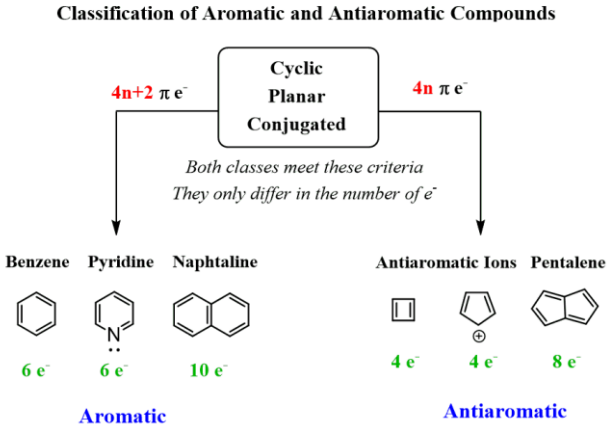
1. Planar (all atoms lie in one plane).
2. Cyclic conjugation (continuous overlap of p-orbitals).
3. Complete delocalization of π-electrons.
4. Huckel's rule: it must contain (4n + 2) π electrons (n = 0, 1, 2, …).

If a ring has 4n π electrons, it is antiaromatic (unstable). If it does not have continuous conjugation, it is non-aromatic

Why 4n+2 Electrons?

According to Huckel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable

Examples :



Benzenoid and Non-Benzenoids:

Aromatic compounds can be broadly divided into two categories: benzenoids (those containing a benzene ring) and non-benzenoids (those not containing a benzene ring)

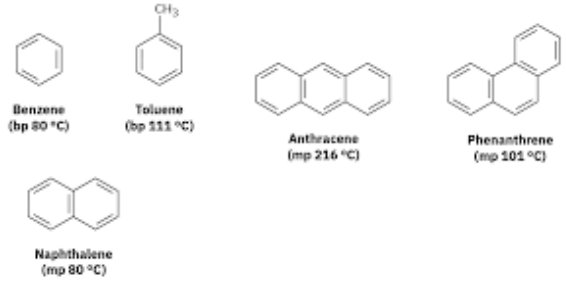
Benzenoid Compounds"

Definition: Compounds containing at least one benzene ring (C6H6) with aromatic character.

Characteristics:

- Planar, cyclic, conjugated π-system.
- Follow Huckel's rule (4n+2 π electrons).
- Highly stable due to resonance.
- Undergo electrophilic aromatic substitution (EAS).

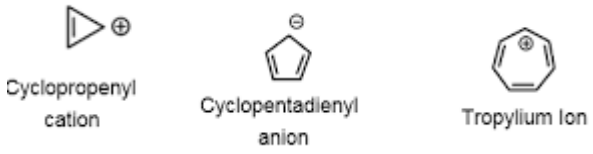
Examples: Benzene, Toluene, Naphthalene, Anthracene, Phenanthrene.



Non-Benzenoid Compounds

Definition: Compounds that do not contain a benzene ring but obeys Huckel's rule and aromatic are called Non-benzenoid

Cyclopropenyl cation (C_3H_3+), Tropylium ion (C_7H_7+), Cyclopentadienyl anion ($C_5H_5^-$).all follows Huckel's rule (4n+2 π e-).



Benzenoid	Non-Benzenoids
Contain benzene ring	No benzene ring
Always aromatic	May be aromatic, non-aromatic, or anti-aromatic
Stable (4n+2 π electrons)	Stability varies
Examples: Benzene, Naphthalene	Examples: Tropylium ion, Cyclobutadiene, Cyclooctatetraene

Orientation of aromatic substitution:

The substituents already attached to the benzene ring not only govern the orientation of further substitution but also affect the reactivity of the benzene ring.

the nature of the group already attached to benzene ring determines the position of the incoming group. In general, groups have been classified into two categories:

(a) Ortho-para directing groups. The groups which direct the incoming group towards ortho, and para positions are called ortho-para directing groups. Groups such as -R, $-C_6H_5$-OH, -SH, -OR, $-NH_2$, NHR, NR_2, Cl, Br, I, etc. are all ortho-para directing groups.

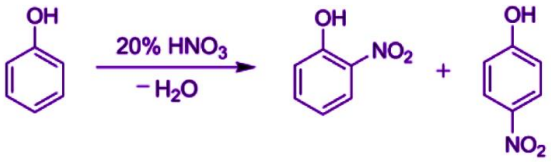
(b) Meta directing groups. The groups which direct the incoming groups towards meta position are called meta directing groups. Groups such as -COOH, -CHO, CN, $-NO_2$, COR, $-SO_3H$, etc., are all meta directing groups.

It may be mentioned that groups which contain double or triple bond are usually meta directing while those which do not contain multiple bonds are ortho-para directing.

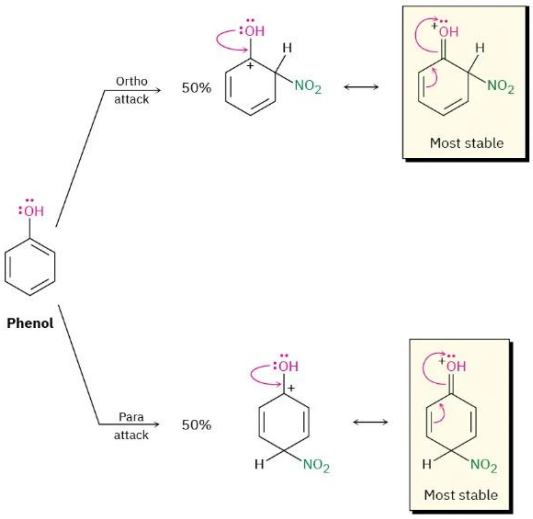
Ring activating and Ring deactivating :

Reactivity of the benzene ring in electrophilic substitution reactions depends upon the tendency of the substituent group already present in the benzene ring to release or withdraw electrons. A group that releases electrons activates benzene ring while the one which draws electrons deactivates the benzene ring. It is found that except halogens all ortho-para directing groups activate the ring and all meta directing groups deactivate the ring towards further electrophilic substitution.

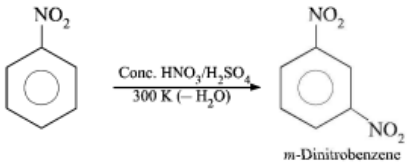
Thus, nitration of Phenol (ring activating) can be carried out at room temperature



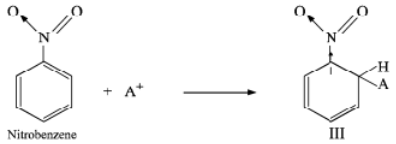
Phenolic OH has a strong, electron-donating resonance effect(+M effect) that outweighs a weaker electron-withdrawing inductive effect(-I effect) and tend to decrease the positive charge on the carbocation and thus stabilize the ion. As a result, the rate of the reaction increases.



the nitration of nitrobenzene requires more drastic conditions.



The NO_2 group destabilize the carbocation through high electronegativity and -I effect by intensifying the positive charge on it. Consequently, the rate of further electrophilic substitution reaction decreases

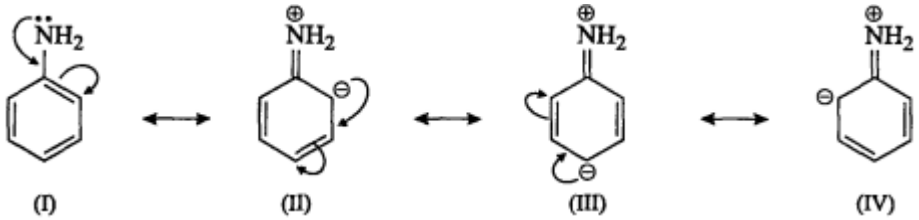


It may be mentioned that release or withdrawal of electrons may occur due to Inductive effect or Resonance effect or Hyperconjugation or Mesomeric effect

Orientation of (i) Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, Carbonyl and sulphonic acid groups (iii) Halogens**:**

Amino NH_2 Group:

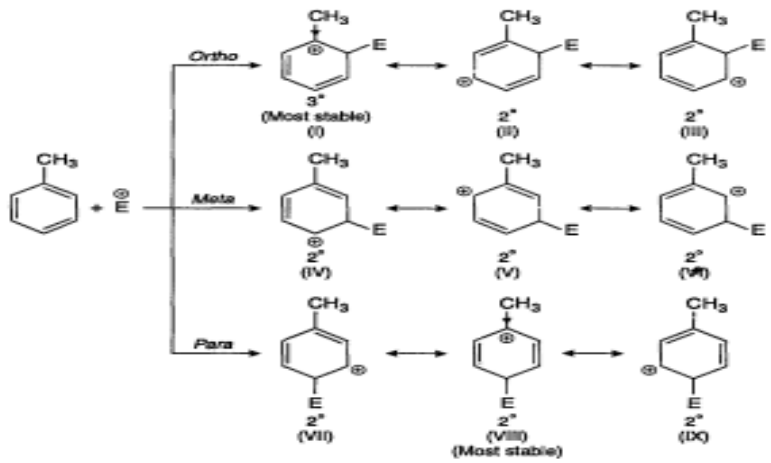
The lone pair of electrons present on oxygen atom is in conjugation with the pi electrons of the ring and exhibits a strong + R effect, thus increasing the overall electron density on the benzene ring. Although the -I effect opposes the + R effect but latter predominates because resonance effect is primary where inductive effect is secondary in nature. Also, the relative increase of electron density is greater at 0- and p-positions due to nature of conjugation .hence the substitution occurs at ortho and para positions.



Methyl CH_3 Group:

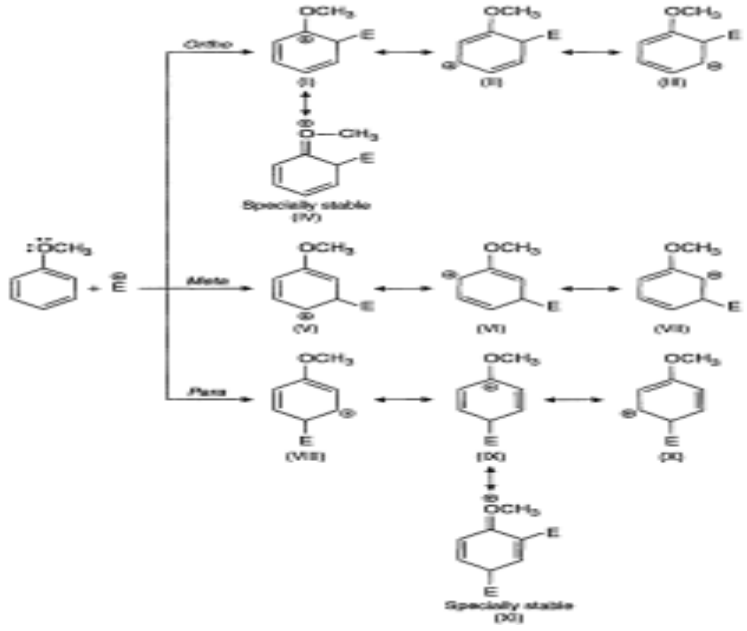
When a substituted benzene undergoes an electrophilic substitution reaction, one is formed depends on the relative stabilities of the carbocations. In the case of ortho and para substitution of toluene, however, the positive charge is spread over two secondary (2°)carbons and one tertiary (3°) Methyl carbon donates electrons by inductive effect, the indicated resonance contributors, (I) and (VIII) are most stable This is because the substituent is attached directly to the positively charged carbon, which

it can stabilize by inductive electron donation. Therefore, the most stable carbocation is obtained by directing the incoming group to the ortho and para position



Methoxy OCH_3 Group:

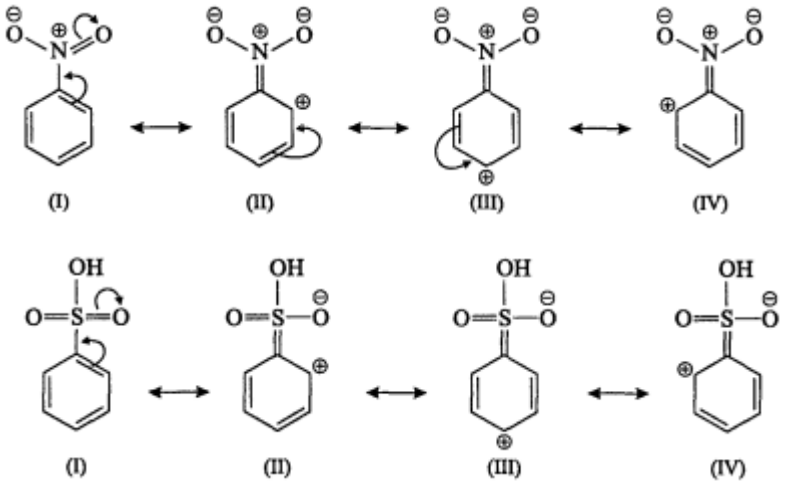
If a substituent donates electrons by resonance, the carbocation formed by putting the incoming electrophile on the ortho and para positions have a fourth resonating structure as a result of resonance electron donation by the substituent . This is a specially stable resonance contributor because it is the only one whose all atoms have complete octets. Therefore, all groups that donate electrons by resonance are ortho/para directors.



Nitro NO_2 Group:

The groups like -N02, -CHO, -CN, -COOH, etc. have a pi bond conjugated to the benzene ring and strongly electron attracting atom linked to the key atom through this multiple bond. Due to conjugation electron attracting atom causes withdrawal of electrons away from the ring and towards the group by a - R effect, this deactivates the nucleus. However, the effect is more pronounced at 0-

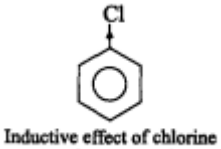
and p- positions leaving m- position as point of relatively high electron density. The - I effect assists the - R effect As the molecule is' a resonance hybrid of various contributing structures, there is small positive charge at the ortho and para position (structures II-IV). The meta positions remain the position of relatively high electron density and attract electrophiles resulting in m- substitution.



Halogen Groups:

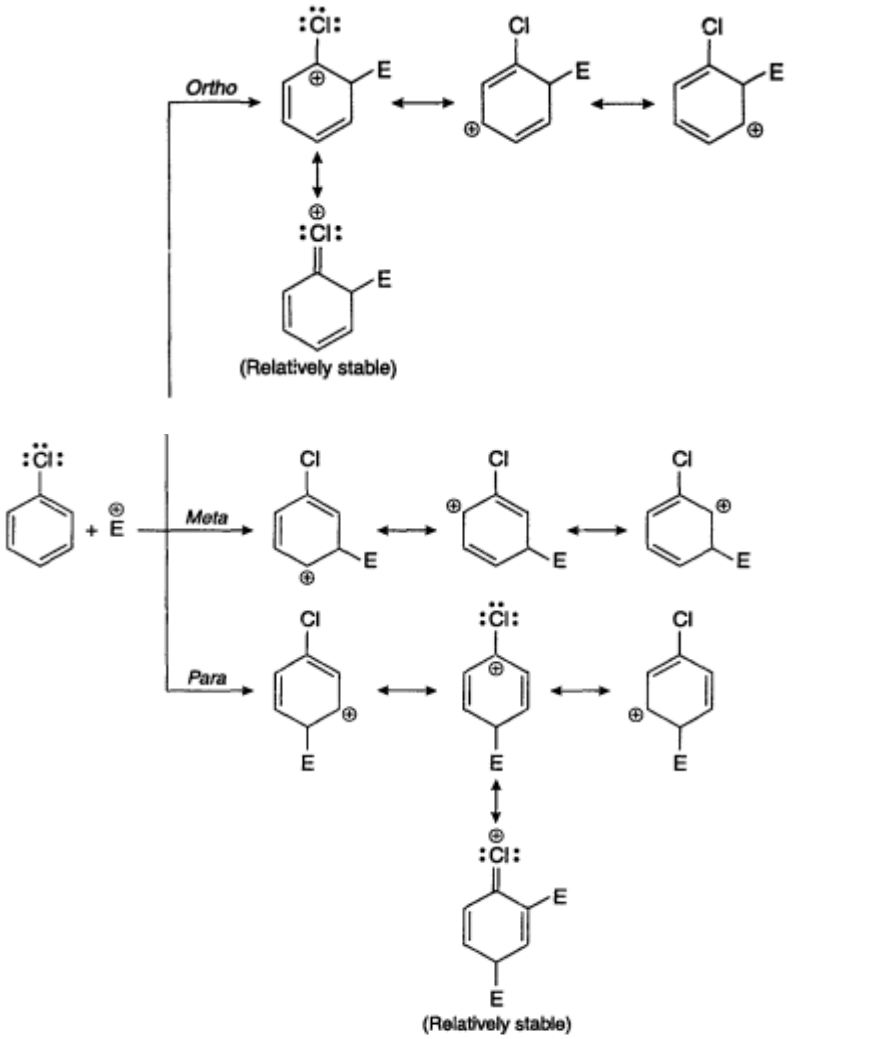
Halogens are ortho/para directing groups but are deactivating groups

(1) The halogens are strongly electronegative and withdraw electron from a carbon atom through the sigma bond (- I effect).
(2) The halogens have non-bonding electrons that can donate electrons through pi bonding (+ R effect)
their electron withdrawing inductive effect influences reactivity and their electron donating resonance effect governs orientation.
Thus, we would expect a chlorine atom to withdraw electrons from the benzene ring and thereby deactivate it.



Inductive effect of chlorine atom deactivates ring

when electrophilic attack does take place, the chlorine atom stabilizes the carbocation (arenium cation) resulting from ortho and para-attack relative to that from meta-attack. The chlorine atom does this by donating an unshared pair of electrons. These electrons give rise to relatively stable resonance structures (with octet)



Unit 5: Orientation of Aromatic Substitution

Long Answer Questions (10 Marks)

1. Explain the concept of aromaticity and Huckel's rule with examples from benzenoid and non-benzenoid compounds.
2. Discuss the orientation of aromatic substitution in terms of electron-donating and electron-withdrawing groups.
3. Describe the effect of activating and deactivating groups on the orientation of aromatic substitution.
4. Discuss the electronic interpretation of groups like NO2 and phenolic on aromatic substitution.
5. Explain the effects of amino, methoxy, and methyl groups on the orientation of aromatic substitution.

Short Answer Questions (5 Marks)

1. What is Huckel's rule? Explain its application to benzene.
2. Discuss the effect of halogen groups on aromatic substitution.
3. Explain the concept of ortho-para and meta-directing groups in aromatic substitution.
4. What are activating and deactivating groups in the context of aromatic substitution?
5. Discuss the role of methyl and methoxy groups in the orientation of aromatic substitution