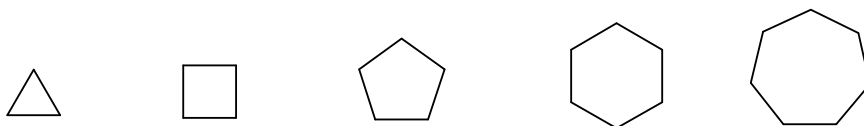


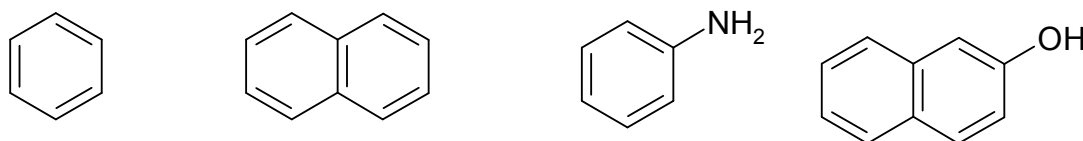
## Aromaticity:

'Aroma' means fragrant smell. The previously isolated compounds with aroma were named as Aromatic compounds. Michael Faraday isolated benzene in 1825. Aromatic compounds are seen to have special stability rather than aroma. For the sake of classification, the cyclic compounds are studied for their structure,  $\pi$  electron number and  $\pi$  electron energy (stability). The different classes of compounds are as follows:

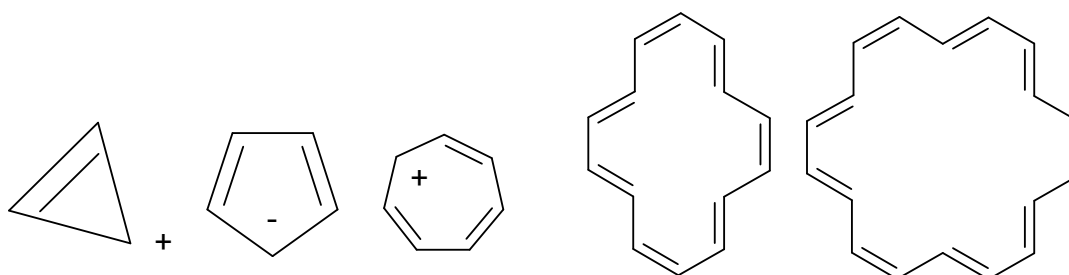
1. Alicyclic compounds: Cyclic compounds resembling aliphatic compounds.



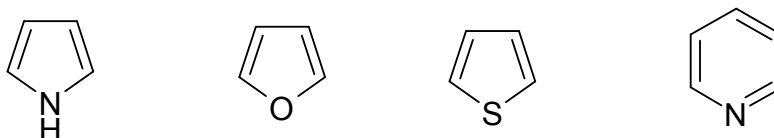
2. Aromatic compounds: Cyclic compounds with maximum unsaturation, conjugated system, planar structure with  $4n+2$   $\pi$  electrons having  $\pi$  -electron energy **less** than their corresponding acyclic analogues are called aromatic compounds.. These are further classified into benzenoid, nonbenzenoid and heterocyclic compounds.



benzenoid aromatics

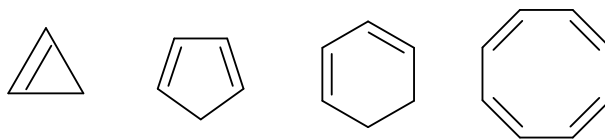


nonbenzenoid aromatics



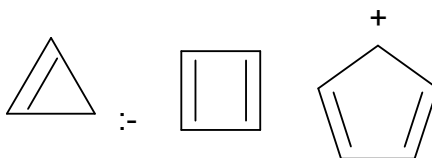
heterocyclic aromatics

3. Nonaromatic compounds: Cyclic compounds with maximum unsaturation, conjugated system, planar structure with  $4n \pi$  electrons having  $\pi$ -electron energy **equal to** their corresponding acyclic analogues are Nonaromatic compounds. They have planar structure.



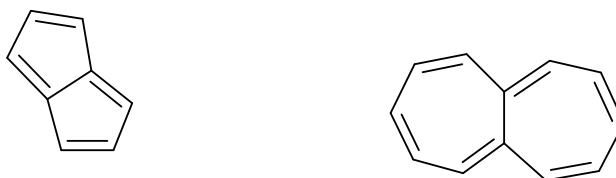
Nonaromatics

4. Antiaromatic compounds: Cyclic compounds with maximum unsaturation, conjugated system, planar structure with  $4n \pi$  electrons having  $\pi$ -electron energy **greater than** their corresponding acyclic analogues are Anti-aromatic compounds.



Anti-aromatics

5. Pseudo Aromatic compounds: Cyclic compounds with maximum unsaturation, conjugated system, but **nonplanar** structure are Pseudo-aromatic compounds.



pseudo aromatics

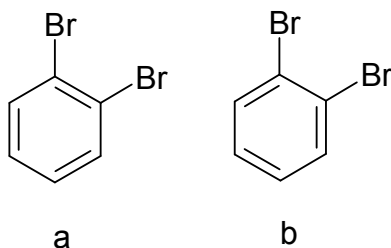
### Concepts around benzene:

1. Kekule's structure of benzene: Kekule proposed planar, hexagonal ring structure with alternate double bonds for benzene.

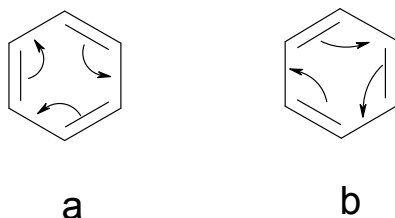


Kekule's structures

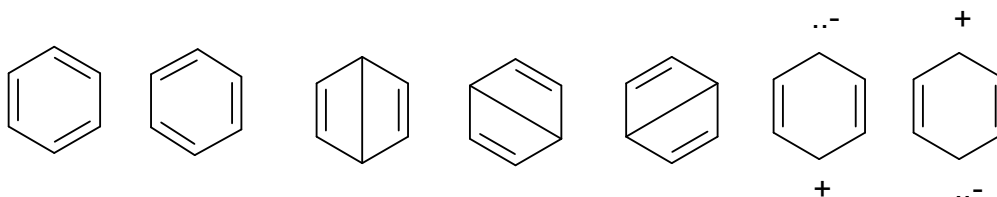
These structures show that there are two kinds of bonds in benzene and hence 1,2 dibromobenzene must be having two different structures as



But in benzene all bonds are equal and dibromobenzene is having only one structure. To explain this Kekule proposed delocalization of the double bonds within ring.

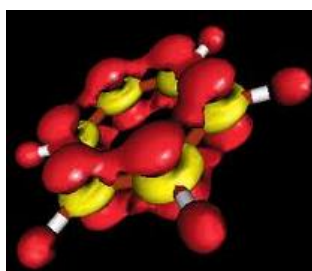
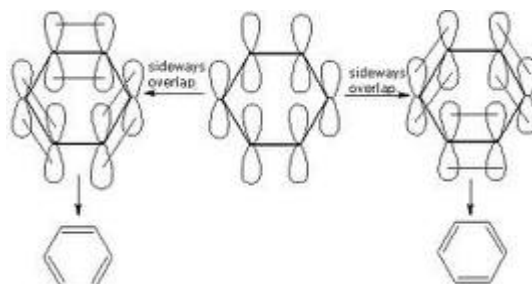
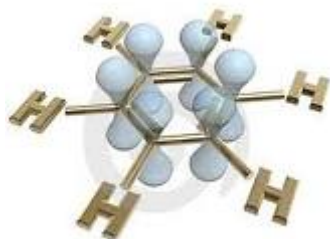


2. Resonance structure of benzene: benzene is believed to be a resonance hybrid of all the resonating structures as

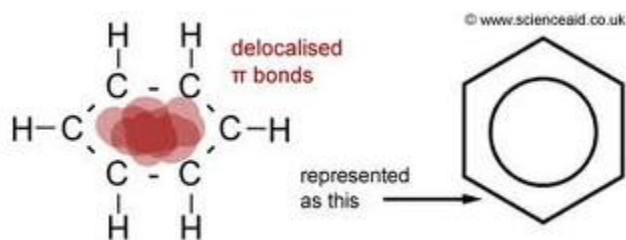


All these structures are canonical forms of the real structure of benzene and actual benzene is a resonance hybrid of all these.

3. Molecular orbital picture of benzene: It assumes that the six carbon atoms have  $sp^2$  hybridization and one un-hybridized  $P_z$  orbital each which overlaps sidewise to form electron cloud one above and below the ring of the six carbons as shown in following structures.



4. Representation of benzene ring: The real structure of benzene is represented by hexagon with a ring inside.



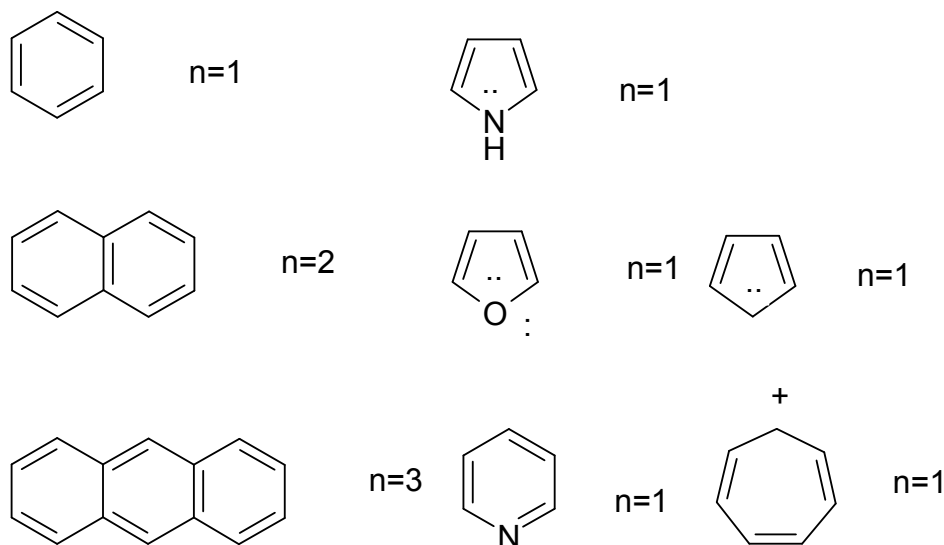
Modern theory of aromaticity: Benzene is different from other polyene compounds as

1. It is stable towards oxidizing reagents.
2. It undergoes substitution reactions rather than addition reactions.

3. All six C-C bonds are of equal length  $1.39 \text{ \AA}$ , which is in between  $1.34 \text{ \AA}$  and  $1.54 \text{ \AA}$  for C=C and C-C bonds respectively.

This different behavior is named as aromaticity. Eric Huckel proposed his theory of aromaticity as follows: A compound having planar, cyclic, conjugated system is aromatic if the number of delocalized  $\pi$  electrons is  $(4n+2)$  where, n is an integer as 0,1,2,3 etc. i.e the rings with 2,6,10,14,18  $\pi$  electrons are aromatic.

Application of Huckel's rule to different rings:



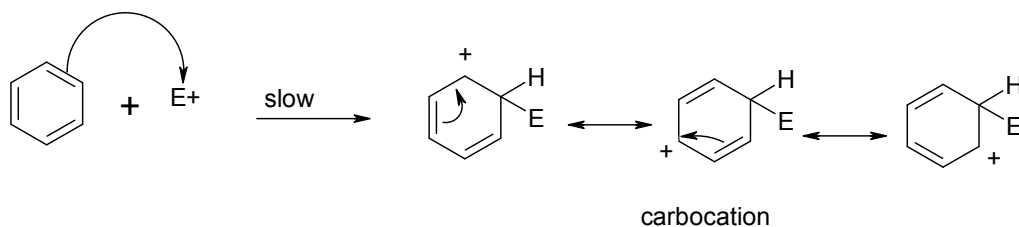
### MECHANISM OF ELECTROPHILIC SUBSTITUTION REACTIONS:

The reactions involving replacement of Hydrogen from benzene by any electrophile are called electrophilic substitution reactions.

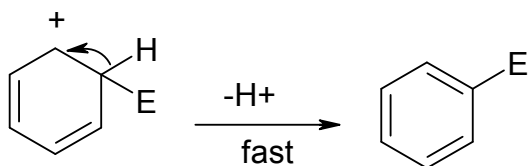
Examples: Nitration, Sulphonation, Halogenation, Friedel Craft Alkylation/Acylation

General mechanism: in electrophilic substitution reactions, first step is slow step in which, the attack of electrophile on benzene ring results in the formation of the carbocation. The positive charge on the ring is delocalized over the ring by delocalization, which is shown by resonating structures.

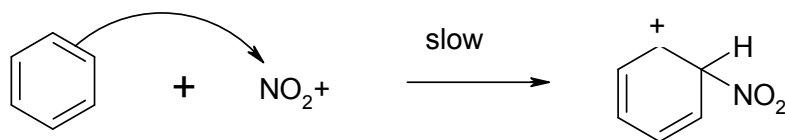
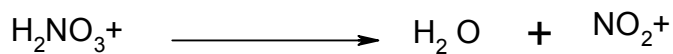
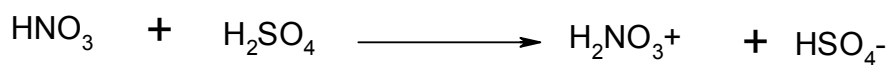
step I



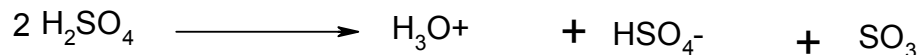
Step II is deprotonation. The carbocation loses one proton (instead of adding nucleophile as it would result in the loss of aromaticity) to get the substituted benzene as product.



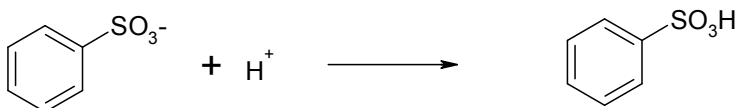
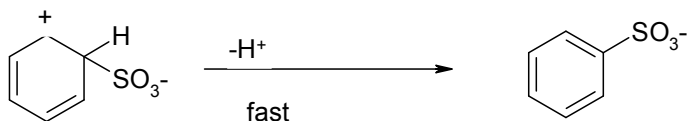
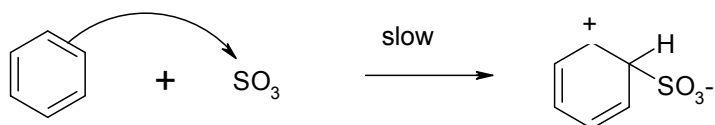
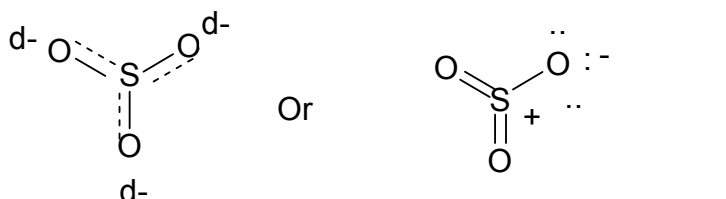
1. Nitration: replacement of H by  $\text{NO}_2$  is called nitration.



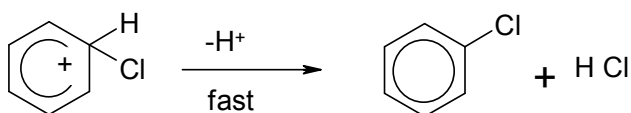
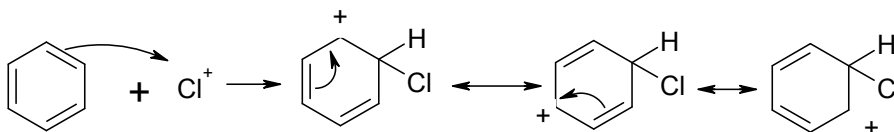
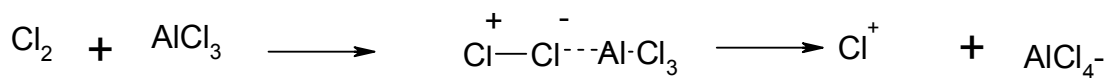
2. Sulphonation:



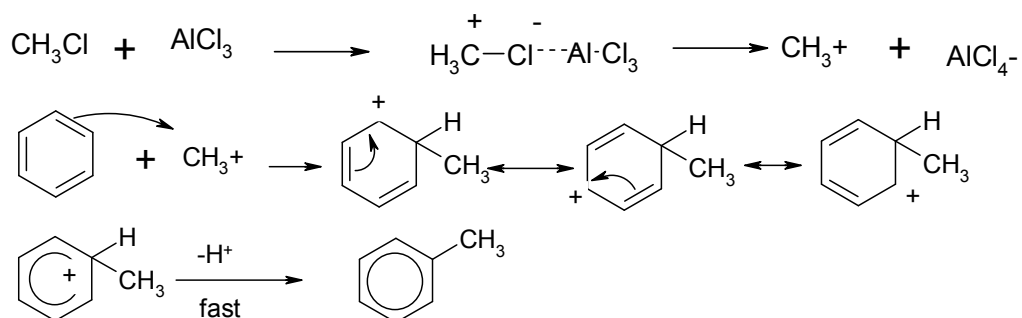
Although  $\text{SO}_3$  is neutral molecule, it acts as electrophile because of the structure of  $\text{SO}_3$



3. Halogenation: substitution of Hydrogen by halogen atom in presence of metal halides as  $\text{FeBr}_3$ ,  $\text{AlCl}_3$  and  $\text{ZnCl}_2$  is electrophilic substitution reaction.



4. Friedel Craft's Alkylation reaction:



5. Friedel Craft's Acylation reaction:

