

### Module III: Aromatic Hydrocarbons (6 hrs)

Nomenclature and isomerism in substituted benzene. Structure and stability of benzene: Kekule, resonance and molecular orbital description.

Mechanism of aromatic electrophilic substitution: Halogenation, nitration, sulphonation and Friedel-Craft's reactions - Orientation effect of substituents.

Aromaticity and Huckel's rule: Application to benzenoid (benzene, naphthalene and anthracene) and nonbenzenoid (pyrrole, pyridine, indol and tropylium cation) aromatic compounds.

#### Nomenclature and isomerism in substituted benzene

IUPAC names of substituted benzenes follow the rules given below:

Some common substituents, like  $\text{NO}_2$ , Br, and Cl, can be named this way when it is attached to a phenyl group. Long chain carbons attached can also be named this way. The general format for this kind of naming is:

**(positions of substituents (if >1)- + # (di, tri, ...) + substituent)<sub>n</sub> + benzene**

For example, chlorine (Cl) attached to a phenyl group would be named chlorobenzene (chloro + benzene). Since there is only one substituent on the benzene ring, we do not have to indicate its position on the benzene ring (as it can freely rotate around and you would end up getting the same compound.)

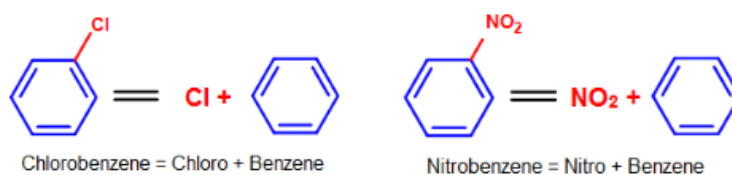
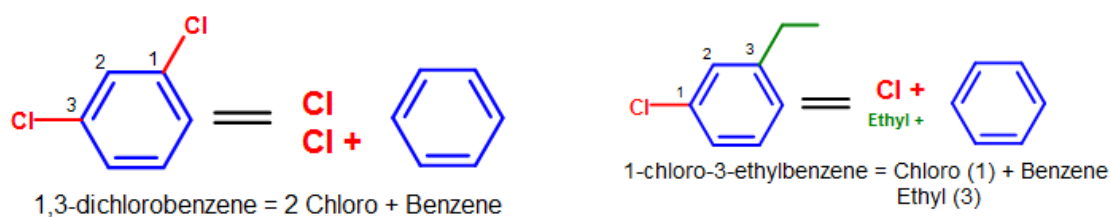
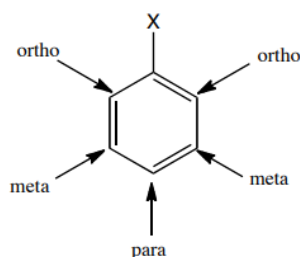
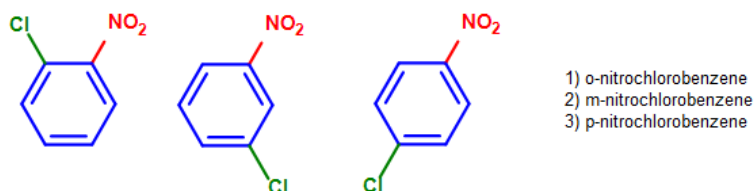
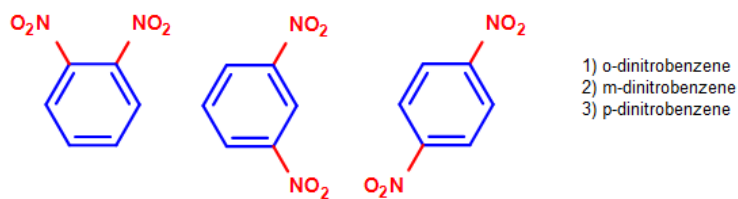


Figure 8. Example of simple benzene naming with chlorine and  $\text{NO}_2$  as substituents.



**If the compound is disubstituted**, the terms *ortho*(*o*-), *meta*(*m*-) and *para*(*p*-) are used to denote 1,2;1,3 and 1,4 relative positions of the substituents. The position of the substituent is assigned such that it receives the lowest numbers.

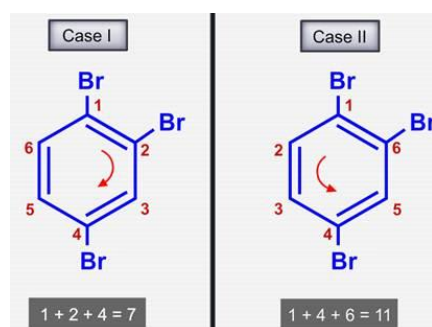




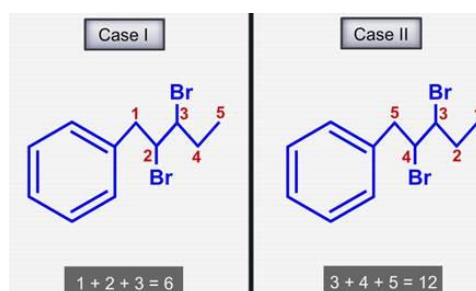
If more than 2 substituents are present,

- Substituents are named alphabetically;
- the positions of the groups are indicated by numbering the carbon atoms according to the **lowest locant rule**.

Case I is preferred among the following.



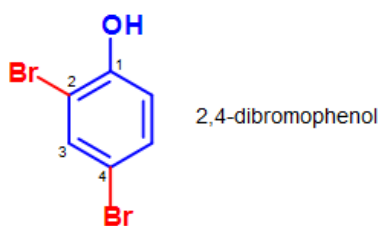
Case I is preferred among the following



- Lowest number is assigned to groups according to the order of **preference of functional groups**

Functional groups listed in decreasing priority order for nomenclature			
Functional group	Prefix*	Suffix	Formula**
Carboxylic Acids	carboxy-	-oic acid -carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$
Acid anhydrides		-oic anhydride -carboxylic anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{array}$
Esters	alkoxycarbonyl	-oate -carboxylate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R}' \end{array}$
Acyl halides	halocarbonyl-	-oyl halide carbonyl halide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{X} \end{array}$
Amides	carbamoyl-	-amide -carboxamide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N} \begin{array}{l} \nearrow \text{R}'' \\ \searrow \text{R}' \end{array} \end{array}$
Nitriles	cyano-	-nitrile -carbonitrile	$\text{R}-\text{C}\equiv\text{N}$
Aldehydes	formyl-	-al -carbaldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$
Thioaldehydes	thioformyl-	-thial	$\begin{array}{c} \text{S} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$
Ketones	oxo-	-one	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$
Thiones	thioxo-	-thione	$\begin{array}{c} \text{S} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$
Alcohols	hydroxy-	-ol	$\text{R}-\text{OH}$
Thiols	mercapto- sulfanyl-	-thiol	$\text{R}-\text{SH}$
Amines	amino-	-amine	$\text{R}-\text{N} \begin{array}{l} \nearrow \text{R}'' \\ \searrow \text{R}' \end{array}$
Ethers	alkoxy- oxa-	-ether -ane	$\text{R}-\text{O}-\text{R}'$
Sulfides	alkylsulfanyl- alkylthio- thia-	sulfide	$\text{R}-\text{S}-\text{R}'$
Alkenes	alkenyl	-ene	$\begin{array}{c} \text{R} \quad \text{R}'' \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}' \quad \text{R}''' \end{array}$
Alkynes	alkynyl	-yne	$\text{R}-\text{C}\equiv\text{C}-\text{R}'$
Alkyl halides	halo-	-ane	$\text{R}-\text{X}$
Nitro	nitro-	-ane	$\text{R}-\text{N}^+ \equiv \text{O}^-$
Alkanes	alkyl-	-ane	$\begin{array}{c} \text{R} \quad \text{R}'' \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{R}' \quad \text{R}''' \end{array}$

\* *alk-* in the prefix, represents the number of carbon atoms in the root carbon chain. See list below.  
 \*\* R, R', R'' and R''' are used to represent generic groups based on C (such as a methyl group) or just H.



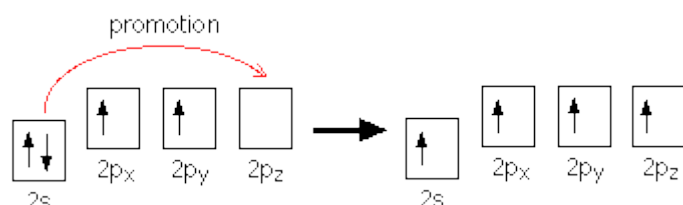
~~6-chlorophenol = Chloro (6) + Phenol~~  
 Oops, this does not give the substituent the lowest number!

2-chlorophenol = Chloro (2) + Phenol  
 This is the correct naming for this compound. It is using the correct base (phenol) and the carbon on the substituent of the base is given priority over the substituent (Cl) on the rest of the ring.

~~1-chlorophenol = Chloro (1) + Phenol~~  
 Sorry, this is not the right answer. Remember that you have to give the carbon on the substituent of the base first priority!

## Structure and stability of benzene

Benzene is built from hydrogen atoms ( $1s^1$ ) and carbon atoms ( $1s^2 2s^2 2p_x^1 2p_y^1$ ). Each carbon atom has to join to three other atoms (one hydrogen and two carbons) and doesn't have enough unpaired electrons to form the required number of bonds, so it needs to promote one of the  $2s^2$  pair into the empty  $2p_z$  orbital.



There is only a small energy gap between the  $2s$  and  $2p$  orbitals, and an electron is promoted from the  $2s$  to the empty  $2p$  to give 4 unpaired electrons. The extra energy released when these electrons are used for bonding more than compensates for the initial input. The carbon atom is now said to be in an excited state.

### Hybridisation

Because each carbon is only joining to three other atoms, when the carbon atoms hybridise their outer orbitals before forming bonds, they only need to hybridise three of the orbitals rather than all four. They use the  $2s$  electron and two of the  $2p$  electrons, but **leave the other  $2p$  electron unchanged**.



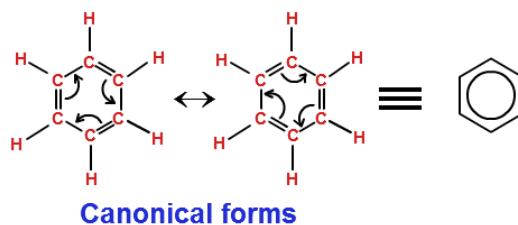
The new orbitals formed are called  **$sp^2$  hybrids**, because they are made by an  $s$  orbital and two  $p$  orbitals reorganising themselves. The three  $sp^2$  hybrid orbitals arrange themselves as far apart as possible - which is at  $120^\circ$  to each other in a plane. The remaining  $p$  orbital is at right angles to them. In benzene is that each carbon atom is joined to two other similar carbon atoms instead of just one (in case of ethane). Each carbon atom uses the  $sp^2$  hybrids to form sigma bonds with two other carbons and one hydrogen atom.

Now  $p$  electron on each carbon atom is overlapping with those on both sides of it. This extensive **sideways overlap** produces a system of pi bonds which are spread out over the whole carbon ring. Because the electrons are no longer held between just two carbon atoms, but are spread over the whole ring, the electrons are said to be delocalised. The six delocalised electrons go into three molecular orbitals - two in each.



Because of the aromaticity of benzene, the resulting molecule is planar in shape with each C-C bond being  $1.39 \text{ \AA}$  in length and each bond angle being  $120^\circ$ . You might ask yourselves how it's possible to

have all of the bonds to be the same length if the ring is conjugated with both single (1.47 Å) and double (1.34 Å), but it is important to note that there are no distinct single or double bonds within the benzene. Rather, the delocalization of the ring makes each count as one and a half bonds between the carbons which makes sense because experimentally we find that the actual bond length is somewhere in between a single and double bond. Finally, there are a total of six p-orbital electrons that form the stabilizing electron clouds above and below the aromatic ring.



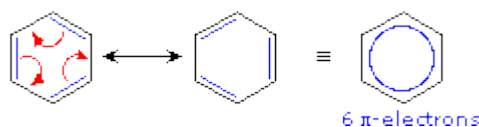
The shape of benzene: Benzene is a planar regular hexagon, with bond angles of  $120^\circ$ . This is easily explained. It is a regular hexagon because all the bonds are identical. The delocalisation of the electrons means that there aren't alternating double and single bonds. It is planar because that is the only way that the p orbitals can overlap sideways to give the delocalised pi system.

The energetic stability of benzene: This is accounted for by the delocalisation. As a general principle, the more you can spread electrons around - in other words, the more they are delocalised - the more stable the molecule becomes. The extra stability of benzene is often referred to as "delocalisation energy".

The reluctance of benzene to undergo addition reactions: With the delocalised electrons in place, benzene is about 150 kJ mol<sup>-1</sup> more stable than it would otherwise be. If you added other atoms to a benzene ring you would have to use some of the delocalised electrons to join the new atoms to the ring. That would disrupt the delocalisation and the system would become less stable. Since about 150 kJ/mole of benzene would have to be supplied to break up the delocalisation, this isn't going to be an easy thing to do.

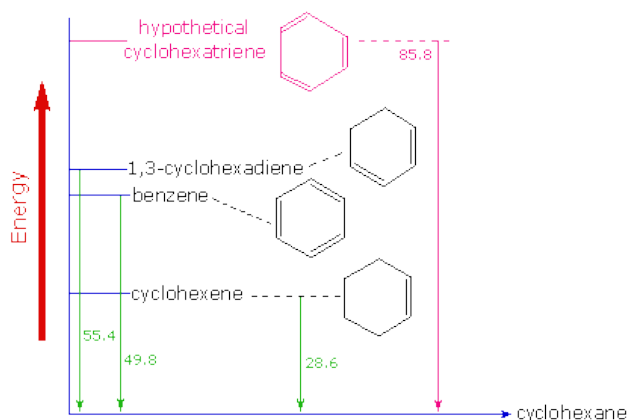
### The High Stability of Benzene

Here, two structurally and energetically equivalent electronic structures for a stable compound are written, but no single structure provides an accurate or even an adequate representation of the true molecule. The six-membered ring in benzene is a perfect hexagon (all carbon-carbon bonds have an identical length of 1.40 Å). The cyclohexatriene contributors would be expected to show alternating bond lengths, the double bonds being shorter (1.34 Å) than the single bonds (1.54 Å). An alternative representation for benzene (circle within a hexagon) emphasizes the pi-electron delocalization in this molecule, and has the advantage of being a single diagram. In cases such as these, the electron delocalization described by resonance enhances the stability of the molecules, and compounds composed of such molecules often show exceptional stability and related properties.

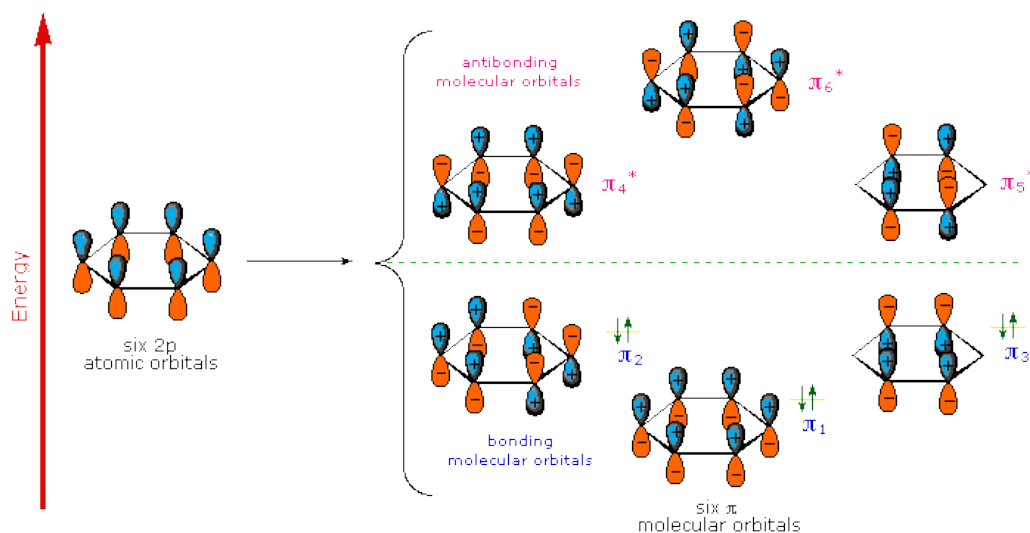


Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product. In the following diagram cyclohexane

represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 28.6 kcal per mole. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 57.2 kcal per mole on complete hydrogenation, and 1,3,5-cyclohexatriene to release 85.8 kcal per mole. These heats of hydrogenation would reflect the relative thermodynamic stability of the compounds. In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 2 kcal, presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 36 kcal/mole more stable than expected. This sort of stability enhancement is now accepted as a characteristic of all aromatic compounds.

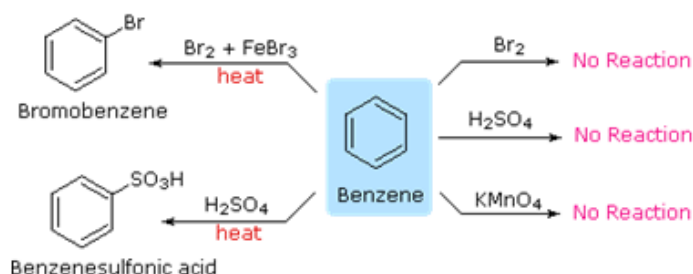


A molecular orbital description of benzene provides a general treatment of "aromaticity". We know that benzene has a planar hexagonal structure in which all the carbon atoms are  $sp^2$  hybridized, and all the carbon-carbon bonds are equal in length. As shown below, the remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding. The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs in the equations that describe these orbitals (in the diagram the phases are also color coded). When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g.  $\pi_1$ ) being lowest in energy. The remaining carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals. It is this completely filled set of bonding orbitals, or closed shell, that gives the benzene ring its thermodynamic and chemical stability, just as a filled valence shell octet confers stability on the inert gases.



## Aromatic electrophilic substitution

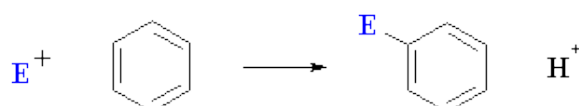
The remarkable stability of the unsaturated hydrocarbon benzene has been discussed in an earlier section. The chemical reactivity of benzene contrasts with that of the alkenes in that substitution reactions occur in preference to addition reactions, as illustrated in the following diagram.



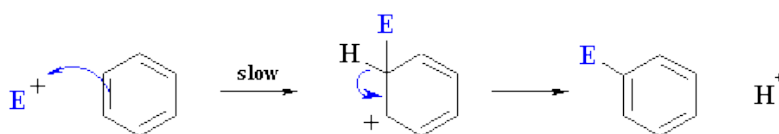
Substitution reactions of benzene are listed below. Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as **Electrophilic Aromatic Substitution**. The catalysts and co-reagents serve to generate the strong electrophilic species needed to effect the initial step of the substitution. The specific electrophile function in each type of reaction is listed in the right hand column.

Reaction Type	Typical Equation	Electrophile E <sup>(+)</sup>
Halogenation:	$C_6H_6 + Cl_2 \xrightarrow[\text{FeCl}_3 \text{ catalyst}]{\text{heat}}$ $C_6H_5Cl + HCl$ Chlorobenzene	Cl <sup>(+)</sup> or Br <sup>(+)</sup>
Nitration:	$C_6H_6 + HNO_3 \xrightarrow[\text{H}_2\text{SO}_4 \text{ catalyst}]{\text{heat}}$ $C_6H_5NO_2 + H_2O$ Nitrobenzene	NO <sub>2</sub> <sup>(+)</sup>
Sulfonation:	$C_6H_6 + H_2SO_4 + SO_3 \xrightarrow[\text{heat}]{} C_6H_5SO_3H + H_2O$ Benzenesulfonic acid	SO <sub>3</sub> H <sup>(+)</sup>
Alkylation: Friedel-Crafts	$C_6H_6 + R-Cl \xrightarrow[\text{AlCl}_3 \text{ catalyst}]{\text{heat}}$ $C_6H_5-R + HCl$ An Arene	R <sup>(+)</sup>
Acylation: Friedel-Crafts	$C_6H_6 + RCOCl \xrightarrow[\text{AlCl}_3 \text{ catalyst}]{\text{heat}}$ $C_6H_5COR + HCl$ An Aryl Ketone	RCO <sup>(+)</sup>

Overall an electrophilic aromatic substitution (EArS) can be represented as follows:

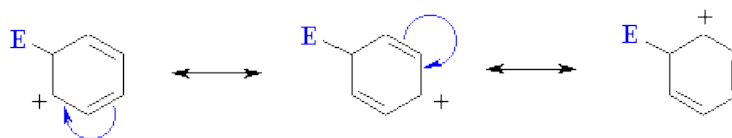


There are three fundamental components to an electrophilic aromatic substitution **mechanism**:



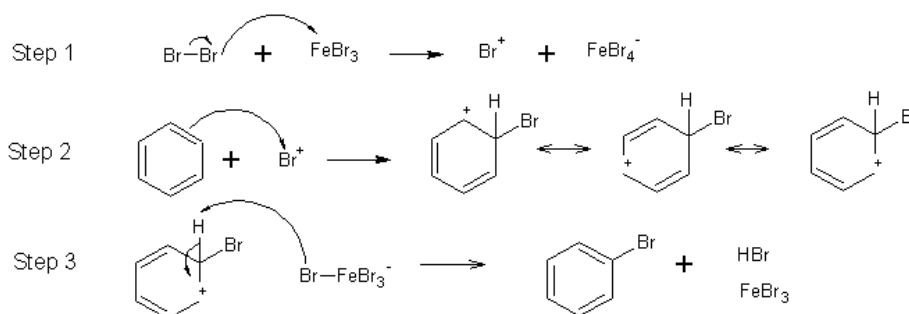
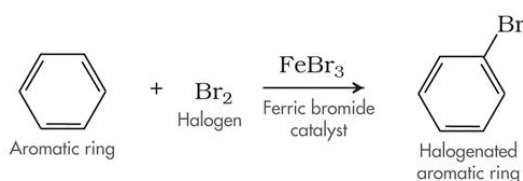
- Step I: Formation of the reactive electrophile, E<sup>+</sup> (not shown here) from the reagents
- Step II: *Slow* reaction of the arene C=C with the E<sup>+</sup> to give a resonance stabilised carbocation

- **Step III:** Loss of  $\text{H}^+$  from the carbocation to restore the  $\text{C}=\text{C}$  and the aromatic system



The reaction of the electrophile  $\text{E}^+$  with the arene is the slow step since it results in the loss of aromaticity even though the resulting cation is still resonance stabilised. This carbocation is also described as the **cyclohexadienyl cation** or **arenium ion** or as a **sigma-complex**.

## 1. Halogenation



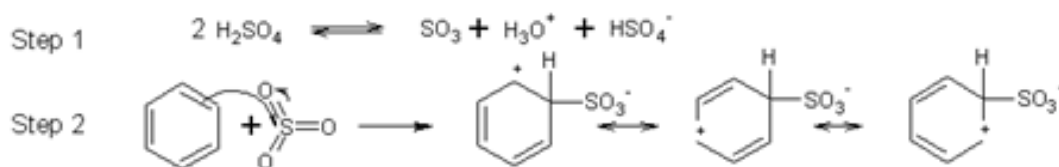
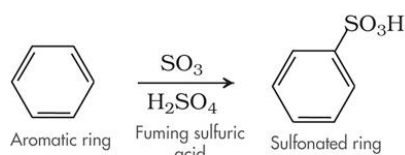

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*Reason why  $\text{FeBr}_3$  necessary for the reaction to occur and not just  $\text{Br}_2$ ?*

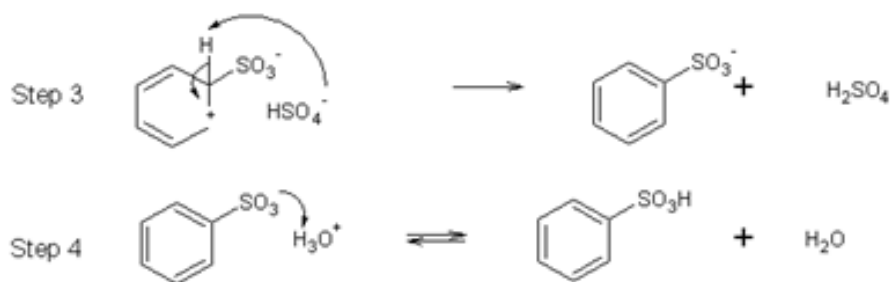
*Disrupting aromaticity is hard to do and requires a strong electrophile-  $\text{Br}_2$  alone has no open octet and no formal positive charge. When it approaches benzene, the electron clouds repel each other creating a brief polarization/ induced dipole due to Van der Waals interactions but this still is not a strong enough electrophile. Using a Lewis acid such as  $\text{FeBr}_3$  or  $\text{AlBr}_3$  increases the polarity of the  $\text{Fe}-\text{Br}$  bond and makes  $\text{Br}$  a better electrophile.*

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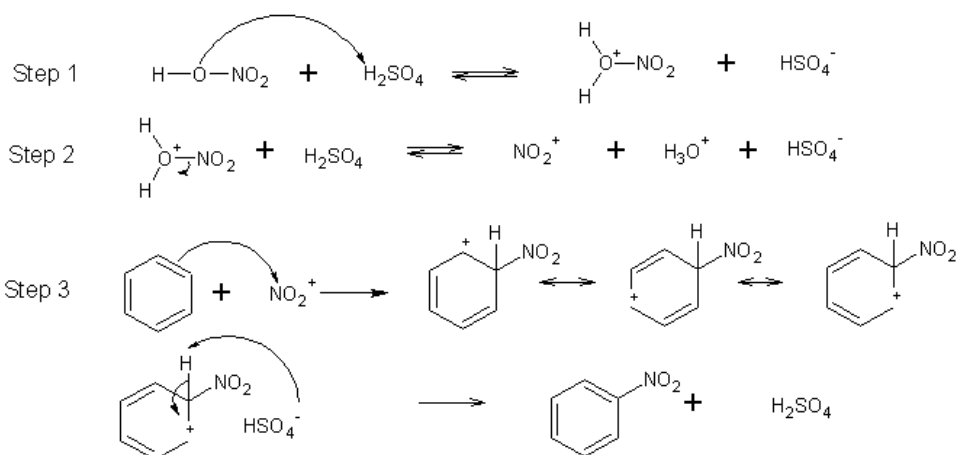
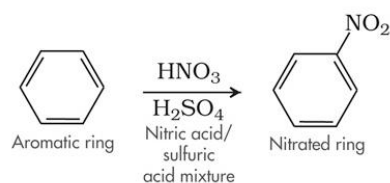
## 2. Sulfonation: This is the only reversible EAS reaction



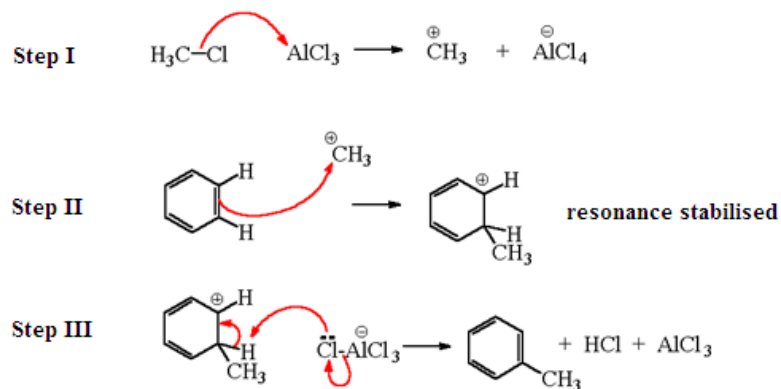
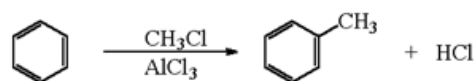




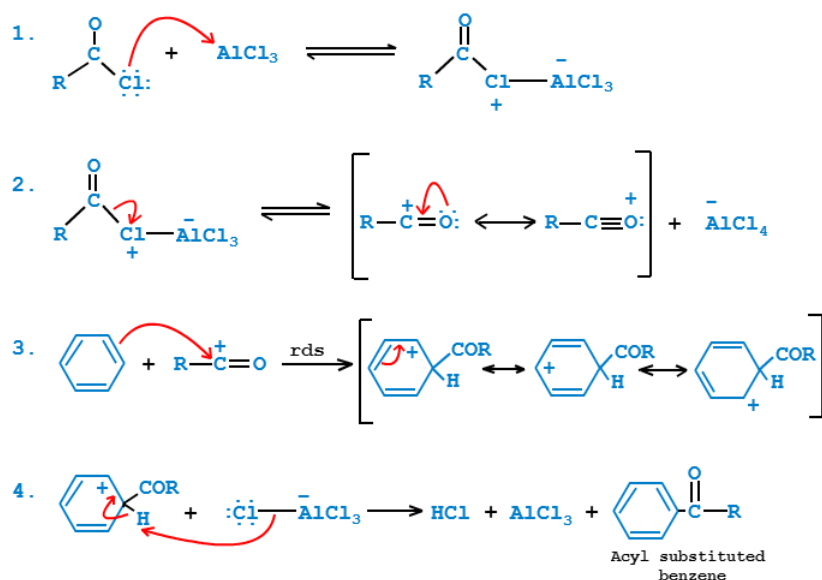
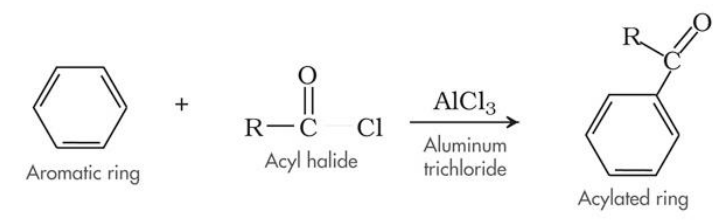
### 3. Nitration



### 4. Friedel-Crafts alkylation



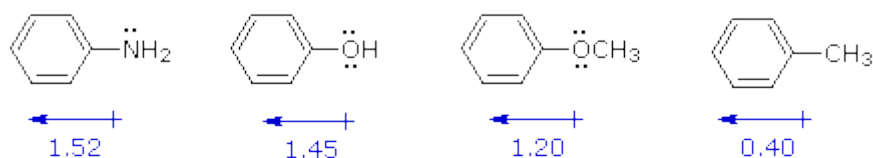
## 5. Friedel-Crafts acylation



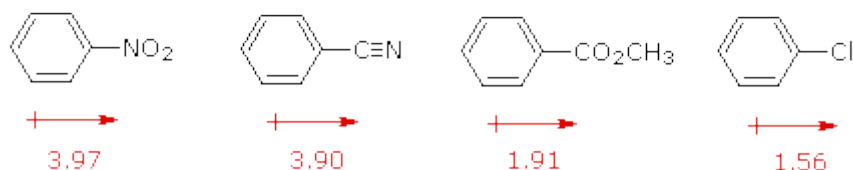
## Substitution Reactions of Benzene Derivatives

Substituents on a benzene ring can influence reactivity in a profound manner. For example, a hydroxy or methoxy substituent increases the rate of electrophilic substitution about ten thousand fold, as illustrated by the case of anisole in the virtual demonstration (above). In contrast, a nitro substituent decreases the ring's reactivity by roughly a million. This activation or deactivation of the benzene ring toward electrophilic substitution may be correlated with the electron donating or electron withdrawing influence of the substituents, as measured by molecular dipole moments. In the following diagram we see that electron donating substituents activate the benzene ring toward electrophilic attack, and electron withdrawing substituents deactivate the ring (make it less reactive to electrophilic attack).

### Activating Substituents



### Deactivating Substituents

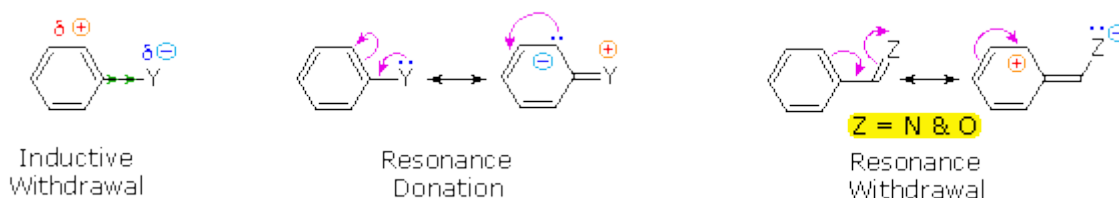


The influence a substituent exerts on the reactivity of a benzene ring may be explained by the interaction of two effects:

The first is the **inductive effect** of the substituent. Most elements other than metals and carbon have a significantly greater electronegativity than hydrogen. Consequently, substituents in which nitrogen, oxygen and halogen atoms form sigma-bonds to the aromatic ring exert an inductive electron withdrawal, which deactivates the ring (left-hand diagram below). The activating effect of alkyl groups can be explained in terms of **hyper conjugation effect** as well.

The second effect is the result of **conjugation of a substituent function with the aromatic ring**. This conjugative interaction facilitates electron pair donation or withdrawal, to or from the benzene ring, in a manner different from the inductive shift. If the atom bonded to the ring has one or more non-bonding valence shell electron pairs, as do nitrogen, oxygen and the halogens, electrons may flow into the aromatic ring by p- $\pi$  conjugation (resonance), as in the middle diagram. Finally, polar double and triple bonds conjugated with the benzene ring may withdraw electrons, as in the right-hand diagram. Note that in the resonance examples all the contributors are not shown. In both cases the charge distribution in the benzene ring is greatest at sites ortho and para to the substituent.

In the case of the nitrogen and oxygen activating groups displayed in the top row of the previous diagram, electron donation by resonance dominates the inductive effect and these compounds show exceptional reactivity in electrophilic substitution reactions. Although halogen atoms have non-bonding valence electron pairs that participate in p- $\pi$  conjugation, their strong inductive effect predominates, and compounds such as chlorobenzene are less reactive than benzene. The three examples on the left of the bottom row (in the same diagram) are examples of electron withdrawal by conjugation to polar double or triple bonds, and in these cases the inductive effect further enhances the deactivation of the benzene ring. Alkyl substituents such as methyl increase the nucleophilicity of aromatic rings in the same fashion as they act on double bonds.



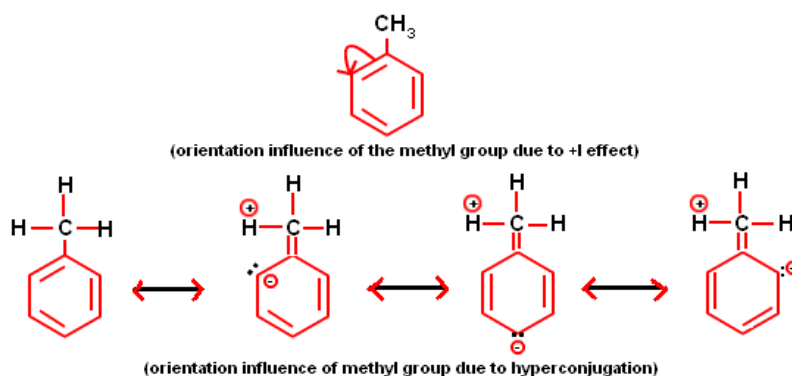
Thus, substituents that activate the benzene ring toward electrophilic attack generally direct substitution to the ortho and para locations. With some exceptions, such as the halogens, deactivating substituents direct substitution to the meta location. The following table summarizes this classification.

#### Orientation and Reactivity Effects of Ring Substituents

Activating Substituents ortho & para-Orientation		Deactivating Substituents meta-Orientation		Deactivating Substituents ortho & para-Orientation	
-O <sup>(-)</sup>	-NH <sub>2</sub>	-NO <sub>2</sub>	-CO <sub>2</sub> H	-F	
-OH	-NR <sub>2</sub>	-NR <sub>3</sub> <sup>(+)</sup>	-CO <sub>2</sub> R	-Cl	
-OR	-NHCOCH <sub>3</sub>	-PR <sub>3</sub> <sup>(+)</sup>	-CONH <sub>2</sub>	-Br	
-OC <sub>6</sub> H <sub>5</sub>	-R	-SR <sub>2</sub> <sup>(+)</sup>	-CHO	-I	
-OCOCH <sub>3</sub>	-C <sub>6</sub> H <sub>5</sub>	-SO <sub>3</sub> H	-COR	-CH <sub>2</sub> Cl	
		-SO <sub>2</sub> R	-CN	-CH=CHNO <sub>2</sub>	

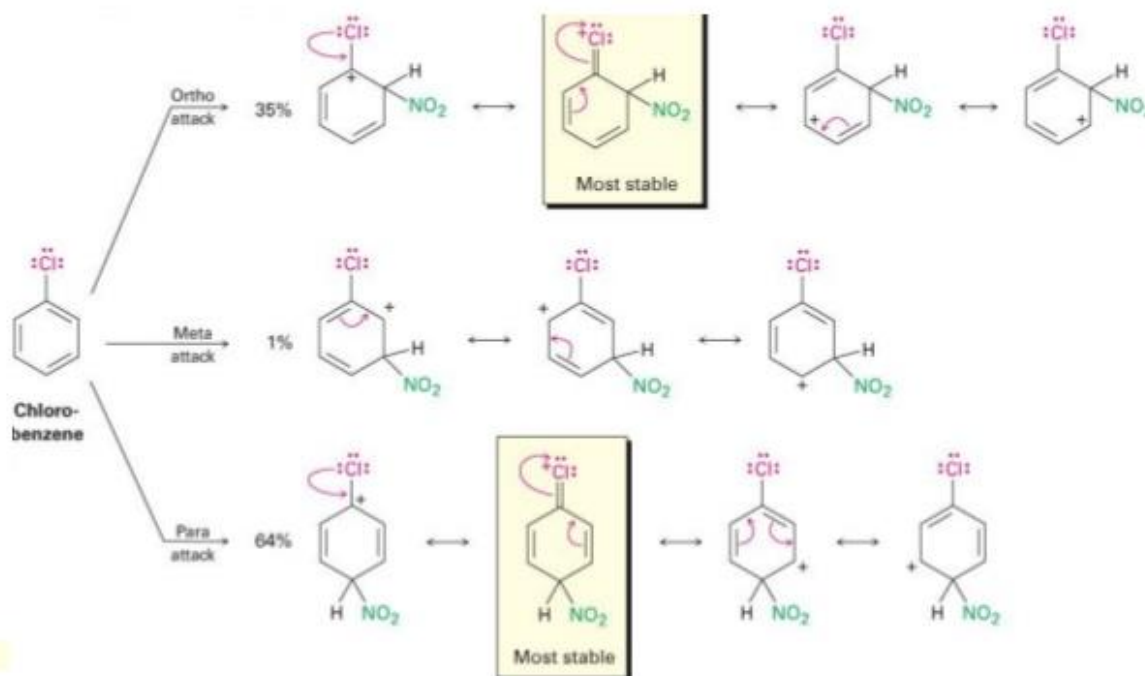
### Why Toluene is *ortho/para* directing?

Resonance arguments are based on the concept of hyperconjugation involving the C–H bonds in the methyl group. The following figure shows some of the possible hyperconjugative resonance structures for toluene. Hyperconjugation explains the mild activating effect of an alkyl group in electrophilic aromatic substitution and its *ortho/para* directing effect.



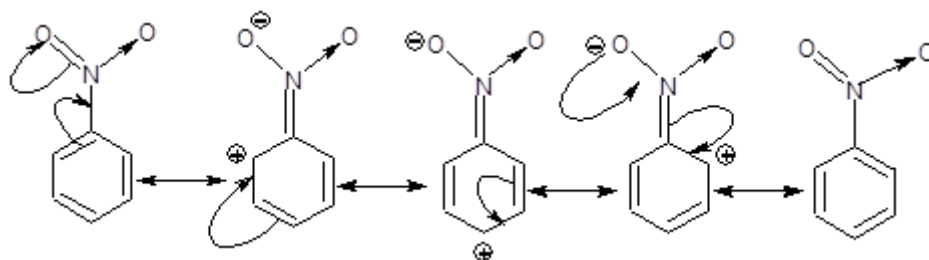
### Why chlorobenzene is *ortho/para* directing even though chlorine is a deactivating group?

When an electrophile attacks chlorobenzene, the carbocation formed is resonance stabilised only at *ortho* and *para* positions while at *meta* position, the resulting complex is highly unstable



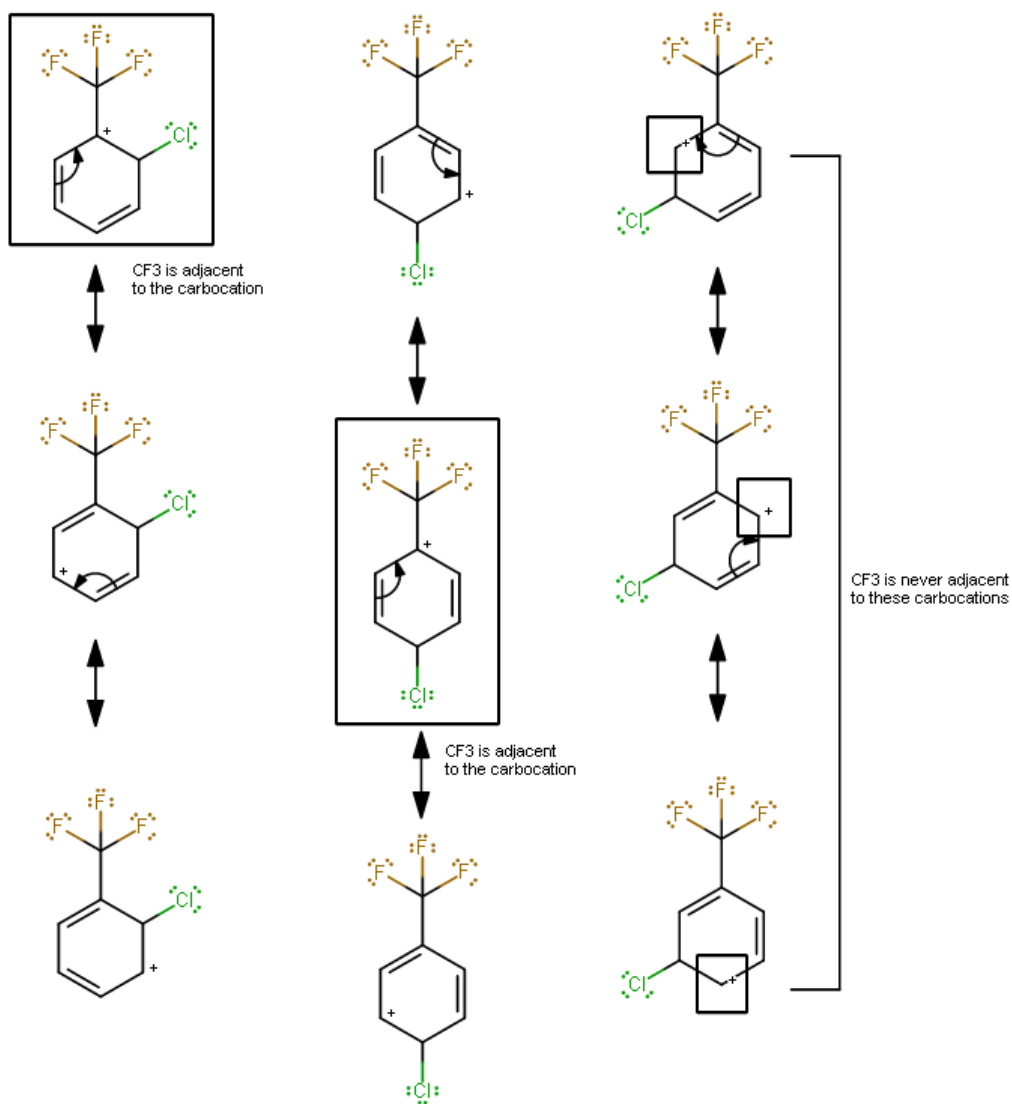
### Why nitrobenzene *meta* directing?

Due to the electron withdrawing effect of nitro group, both *ortho* and *para* positions became very much electron deficient leaving the *meta* position relatively electron rich.



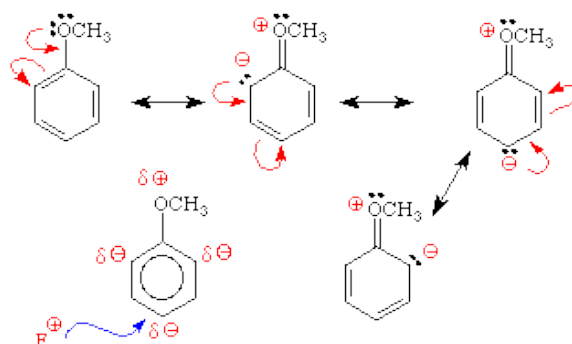
### Why trifluoromethylbenzene *meta* directing?

Draw out the resonance structure for the intermediate that forms after benzene participates as a nucleophile in electrophilic aromatic substitution (EAS). From this we can see that the meta resonance structures, which never have  $\text{CF}_3$  adjacent to a carbocation, though not amazingly stable, are less unstable than the ortho and para resonance structures wherein carbocation directly attaches to  $\text{CF}_3$  moiety.



### Why anisole is *ortho/para* directing?

Groups with unshared pairs of electrons, such as the methoxy group of anisole and the amino group of aniline, are *ortho-para* directing. Through resonance, they donate those unshared electrons to the  $\pi$  system. This puts extra electron density on the *ortho* and *para* carbons and makes them more attractive to an attacking electrophile.



### Aromaticity and Huckel's rule\

In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has  $4n+2$   $\pi$  electrons, it is considered aromatic. This rule is known as Hückel's Rule.

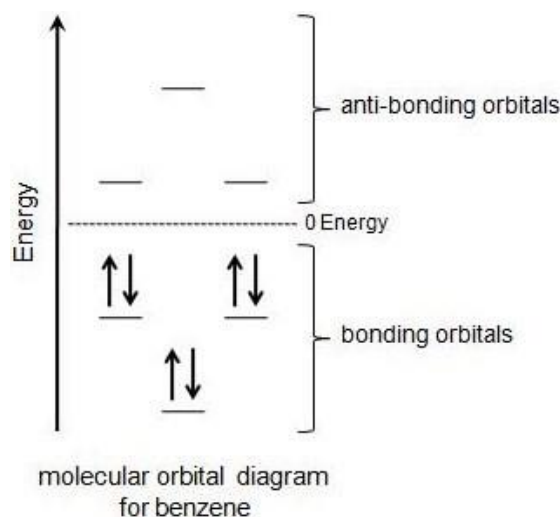
#### Four Criteria for Aromaticity

When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

- The molecule is cyclic (a ring of atoms)
- The molecule is planar (all atoms in the molecule lie in the same plane)
- The molecule is fully conjugated (p orbitals at every atom in the ring)
- The molecule has  $4n+2$   $\pi$  electrons ( $n=0$  or any positive integer)

#### Why $4n+2$ $\pi$ Electrons?

According to Hückel'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. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by  $n$ ), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of  $4n+2$   $\pi$  electrons. You can see how this works with the molecular orbital diagram for the aromatic compound, benzene, below. Benzene has 6  $\pi$  electrons. Its first 2  $\pi$  electrons fill the lowest energy orbital, and it has 4  $\pi$  electrons remaining. These 4 fill in the orbitals of the succeeding energy level. Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.



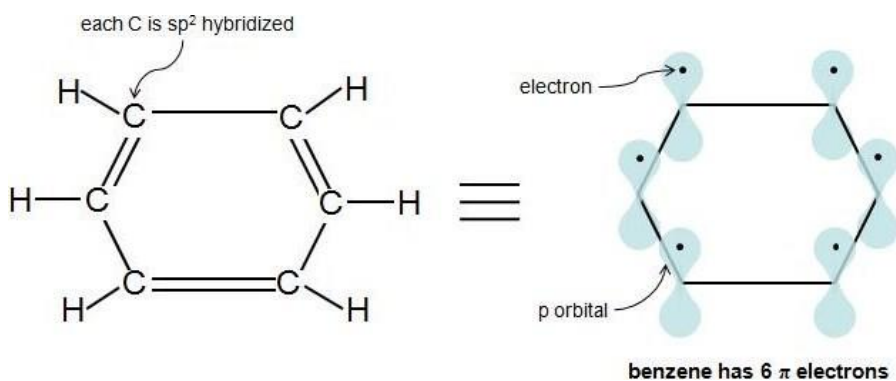
To apply the  $4n+2$  rule, first count the number of  $\pi$  electrons in the molecule. Then, set this number equal to  $4n+2$  and solve for  $n$ . If  $n$  is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six  $\pi$  electrons:

For benzene, we find that  $n=1$ , which is a positive integer, so the rule is met.

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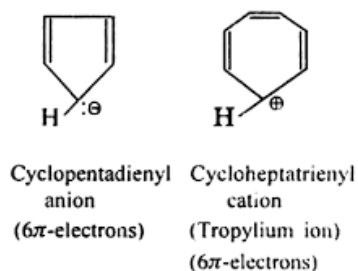
*Perhaps the toughest part of Hückel's Rule is figuring out which electrons in the compound are actually  $\pi$  electrons. Once this is figured out, the rule is quite straightforward.*

$\pi$  electrons lie in  $p$  orbitals and  $sp^2$  hybridized atoms have 1  $p$  orbital each. So if every molecule in the cyclic compound is  $sp^2$  hybridized, this means the molecule is fully conjugated (has 1  $p$  orbital at each atom), and the electrons in these  $p$  orbitals are the  $\pi$  electrons. A simple way to know if an atom is  $sp^2$  hybridized is to see if it has 3 attached atoms and no lone pairs of electrons. This [video](#) provides a very nice tutorial on how to determine an atom's hybridization. In a cyclic hydrocarbon compound with alternating single and double bonds, each carbon is attached to 1 hydrogen and 2 other carbons. Therefore, each carbon is  $sp^2$  hybridized and has a  $p$  orbital. Let's look at our previous example, benzene:

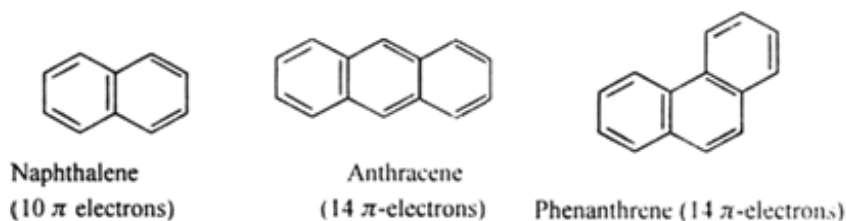



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**Hückel's Rule also applies to ions.** As long as a compound has  $(4n+2)$   $\pi$  electrons, it does not matter if the molecule is neutral or has a charge. For example, cyclopentadienyl anion is an aromatic ion. **Cyclopentadienyl anion** has 6  $\pi$  electrons and fulfills the  $4n+2$  rule. **Tropylium cation** has total pi electron count in the tropylium ion is six, hence aromatic.



Fused ring systems such as naphthalene, anthracene and phenanthrene are aromatic and obey Huckel's rule. Naphthalene has two rings and is thus a bicyclic compound. It is conjugated around the perimeter of the rings and there are a total of 5 pi bonds and zero lone pairs, giving us 10 pi electrons total. 10 is a Huckel number (satisfying  $4n+2$  for  $n=2$ ) and naphthalene is an aromatic molecule. Similarly in case of, anthracene and phenanthrene, the number of  $\pi$  electrons is 14 and  $n = 3$ .

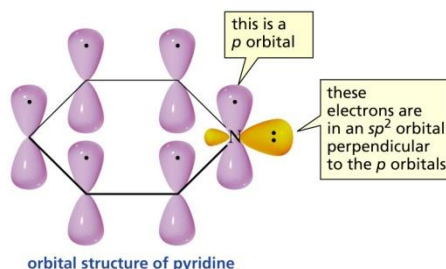


**Pyrrrole** is cyclic and conjugated (that lone pair on nitrogen can contribute to the pi-system). There are two pi bonds and one lone pair of electrons that contribute to the pi system. This gives us 6 total pi electrons, which is a Huckel number (i.e. satisfies  $4n+2$ ). Therefore it's aromatic.

**Pyridine** is cyclic, conjugated, and has three pi bonds. The lone pair on nitrogen does not take part in delocalisation and hence is not considered when counting the number of  $\pi$  electrons. Therefore we can ignore the lone pair for the purposes of aromaticity and there are a total of six pi electrons, which is a Huckel number and the molecule is aromatic.

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*In Pyridine, nitrogen's perpendicular  $sp^2$  orbital contains a localized electron pair. It does not participate in the  $\pi$  orbital system, and therefore does not count towards the  $4n+2$  rule.*

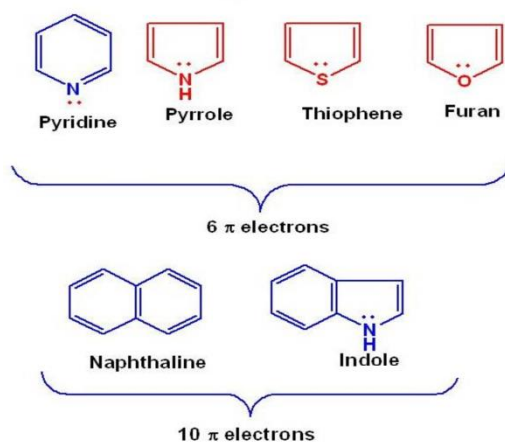



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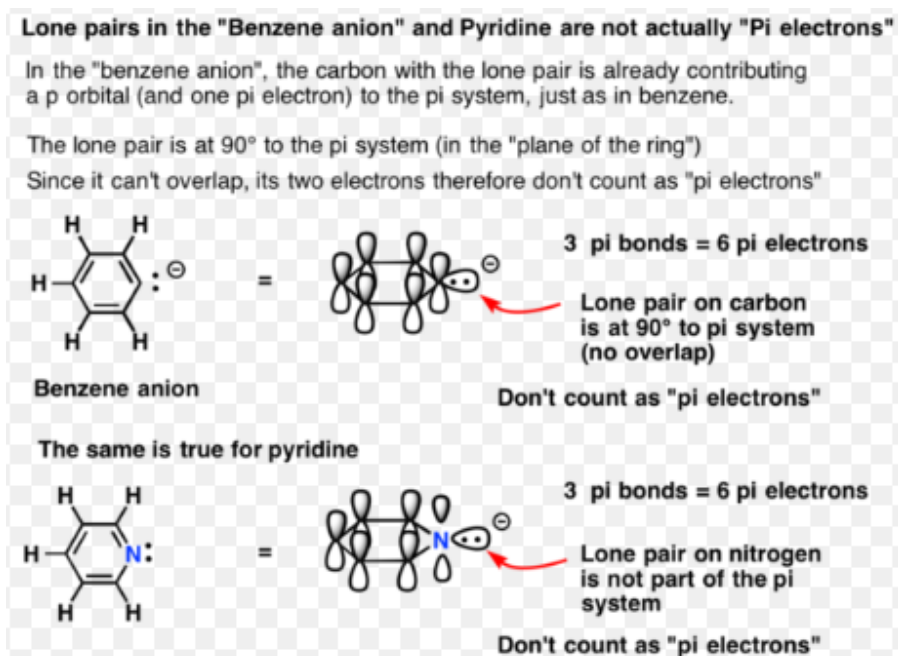
**Indole** is a bicyclic molecule that looks like a molecule of benzene fused to a molecule of pyrrole. It is conjugated; every atom around the perimeter of the two rings participates in the pi system. It has 4 pi bonds and a single pair of electrons on the nitrogen that participates in the pi system, giving 10 pi electrons in total. This is a Huckel number and indole is in fact aromatic.



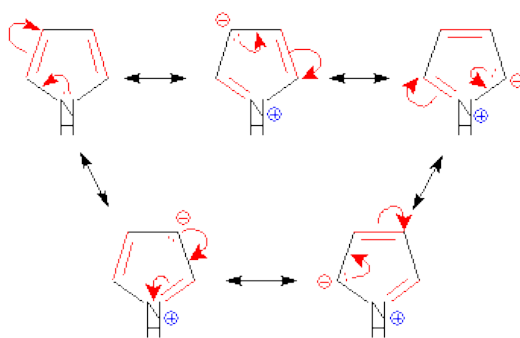
**Thiophene**, the sulfur analog of **furan**, is cyclic and conjugated all the way around the ring. It has two pi bonds. What's interesting about thiophene (and furan) is that although there is an atom bearing two lone pairs in the ring, we can only count one of those lone pairs toward the pi-system. [Each atom can contribute a maximum of one orbital and two electrons towards aromaticity]. The other lone pair is in the plane of the ring, much like the lone pair on the nitrogen of pyridine, above. Therefore thiophene has six pi electrons total, which is a Huckel number, and thiophene is aromatic.



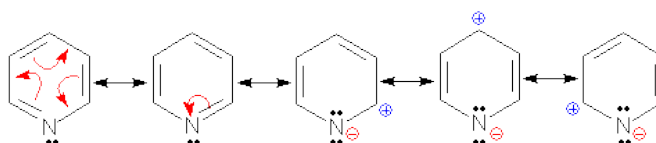
If you remove a proton from benzene, you get the **benzene anion**. Like benzene, it's cyclic, conjugated, had 3 pi bonds and those pi bonds are all in the pi system. It's tempting to look at that lone pair and to think that it might contribute to the pi system as well, giving 8 pi electrons total. However, that lone pair is in the plane of the molecule (along with the other C-H bonds) and thus can't overlap with the p-orbitals. Therefore, for the purposes of determining aromaticity, we can ignore the lone pair and it is aromatic.



### Why is pyridine more basic than pyrrole?



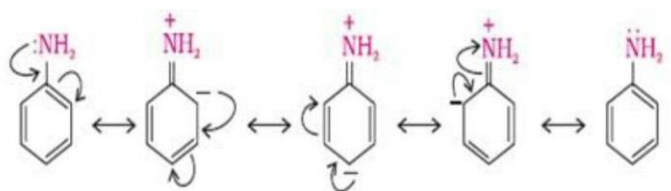
The lone pair of N in pyrrole is in resonance so this lone pair can't be donated.



The lone pair of N in pyridine is localized and hence ready for donation. So, Pyridine is more basic than Pyrrole.

### Why is pyridine more basic than aniline?

In case of aniline, lone pair on nitrogen is involved in resonance hence it is not readily available for donation. Thus aniline is weakly basic. In pyridine, electron density at nitrogen seems to get increased due to resonance. Hence it can donate pair of electrons comparatively easily. Thus pyridine is more basic than aniline.



### Which one is more basic? Aniline or 4-bromoaniline? Why?

Aniline is more basic. Consider 4-bromoaniline. There is an electron-withdrawing -Br substituent para to the -NH<sub>2</sub> substituent, which puts it in a good position to withdraw electron density from the N atom. This reduces the availability of the lone pair.

### What is basicity order of thiophene pyrrole and furan?

Thiophene, pyrrole and Furan are all five membered heterocyclic aromatic compounds, with the hetero atom being sulfur (S), nitrogen (N) and oxygen (O) respectively. They are aromatic as they are planar ring systems, and resonance is possible due to delocalization of the two pi bonds and the lone pair of electrons of the heteroatom. However, if we compare the electronegativity of the heteroatoms, we will see that O is more electronegative as compared to N, S being the least electronegative. Hence, O will have the least tendency, among the three, to donate its lone pair of electrons for resonance, and will rather draw the electronic density of the ring towards itself. The concentration of electron density on the heteroatom makes it a good electron donor (Lewis base). Thus the order of basicity will be

## Furan > Pyrrole > Thiophene

### **Why is pyrrole less basic than aniline?**

The lone pair of electrons of N in pyrrole is delocalized. It is part of the pi system, thus involved in aromatization. This lone pair is no longer available for a proton hence it is a weak base.

On the other hand, aniline is already aromatic. Though the lone pair of electrons of -NH<sub>2</sub> group of aniline is delocalized over the benzene ring; it is not involved in aromatization. This lone pair is still available for a proton; hence aniline is stronger base than pyrrole.

### **Why does furan have less aromatic character than pyrrole?**

Furan is less aromatic than pyrrole because oxygen is more electronegative than nitrogen. Aromaticity in 5-membered heterocyclic rings requires delocalization of a lone pair on the heteroatom. A more electronegative atom will be less able to "turn loose" its lone pair, and so furan's oxygen is less able to participate in the cyclic delocalization that aromaticity requires.

### **Why aniline is less basic than methylamine?**

Answer 1: Aniline or Phenylamine is a amine group attached to a phenyl group, or C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>. The ring structure possesses resonance. Electrons are delocalised from individual atoms and their position varies around the structure. The source of the basicity of the amine group is the lone pair on the nitrogen atom. This lone pair can form a dative covalent bond with a H<sup>+</sup> ion. But in Aniline, the lone pair on the nitrogen is also delocalised. It loses the lone pair to resonance, and so cannot donate an electron to a proton, and therefore loses a lot of its basicity. Methylamine, CH<sub>3</sub>NH<sub>2</sub>, on the other hand does not possess resonance, and the lone pair on the nitrogen is in place, so it can accept protons, making it basic.

Answer 2: The benzene ring in aniline is electron withdrawing in nature. It withdraws the lone pair of electrons of the nitrogen and hence, is less basic. The basic strength (of some compounds) is determined by the capacity of the compound to donate the electron pair. In methylamine, the methyl group attached is an electron donating group. It increases the electron density on the nitrogen atom. This makes the nitrogen to donate the electron more easily in methyl amine than in aniline.

Hence, aniline is less basic than methyl amine.