Student Corner

Aromaticity and Reactions of Aromatic Molecules/Ions

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Fully conjugated (**FC**) and unsaturated ring systems are known as aromatic compounds. Aromaticity is a chemical property that determines the stability of **cyclic** molecules. Basically, there are three structural features that determine the aromaticity of a compound.

1. *The ring system should be **fully planar**.*

Fully planar (**FP**) cyclic compounds are those, in which all the atoms are *sp*^{2} hybridized and exhibit trigonal planar geometry around each atom.

2. *Ring system should be **fully conjugated**.*

A conjugated cyclic structure possesses a **delocalized** electron cloud formed due to the overlap of *p*-orbitals on each carbon atom in the carbocycle, which are perpendicular to the ring.

3. *Ring system should obey the **Hűckel rule**.*

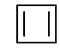
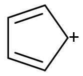
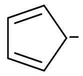
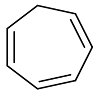
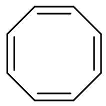
When a cyclic planar molecule has (**4n+2**) number of π-electrons, where n is an integer that compound is known to be aromatic. According to this rule, cyclic unsaturated planar systems with **2**, **6**, **10**, **14** or **18** π electrons are said to be aromatic.

Aromatic, anti-aromatic and non-aromatic molecules

A molecule is said to be **aromatic** (**A**) if it satisfies all three rules. An **anti-aromatic** (**AA**) molecule is a cyclic planar conjugated molecule that does not satisfy the Hűckel rule. Molecules which do not satisfy any of the three rules are called **non-aromatic** (**NA**).

Some examples for (**A**), (**AA**), and (**NA**) compounds are given below.

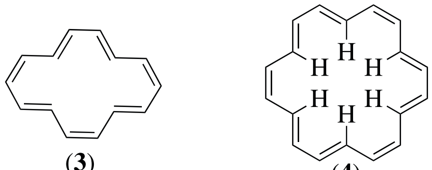
NP = Non-planar, **NC** = Non-conjugated

Compound		**Property**
	$(C_3H_3)^+$	FP, FC, A (2e)
	(C_4H_4)	FP, FC, AA (4e)
	$(C_5H_5)^+$	FP, FC, AA (4e)
	$(C_5H_5)^-$	FP, FC, A (6e)
Benzene	(C_6H_6)	FP, FC, A (6e)
Naphthalene	$(C_{10}H_8)$	FP, FC, A (10e)
Anthracene	$(C_{14}H_{10})$	FP, FC, A (14e)
	(C_7H_8)	NP, NC, NA (6e)
	(C_8H_8)	NP, FC, NA (8e)

Completely conjugated monocyclic hydrocarbons are known as annulenes. The criteria to determine the aromaticity of higher **annulenes** are as same as mentioned above.

(**1**)
[10] annulene
NP, FC, NA(10e)

(**2**)
[12] annulene
FP, FC, AA(12e)



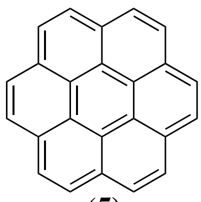
(**3**)
[14] annulene
FP, FC, A(14e)

(**4**)
[18] annulene
FP, FC, A(18e)

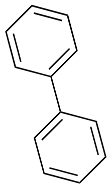
Fig.1 Some higher annulenes

As the number of carbons in annulenes increases the hydrogens placed outside and inside of the ring increase. [10]-Annulene tends to deviate from its planar geometry due to the steric influence of the inner hydrogens. Though [14]-annulene fulfills all features for aromaticity, the aromatic stability is only found at lower temperatures (30 °C). [18]-Annulene is the most stable higher aromatic annulene.

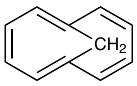
Exercise: *Determine the aromaticity of the following hydrocarbons: coronene (**5**), biphenyl (**6**) and bicyclo[4.4.1] undeca-1,3,5,7,9-pentaene (**7**).*



(5)



(6)

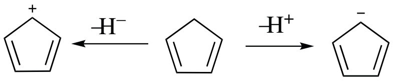


(7)

Electron filling of aromatic compounds

In an aromatic molecule, all bonding π orbitals are **filled** with paired electrons, while the presence of unpaired electrons in bonding, non-bonding or anti-bonding orbitals makes the molecule anti-aromatic.

Cyclopentadiene (Cp) (**9**) is not aromatic as it has a sp^3-hybridized carbon in the ring. Though its anion (**10**) and the cation (**8**) have planar structures and a similar number of π orbitals, their aromaticity differs as the numbers of delocalized π-electrons in the ring are 6e and 4e, respectively.

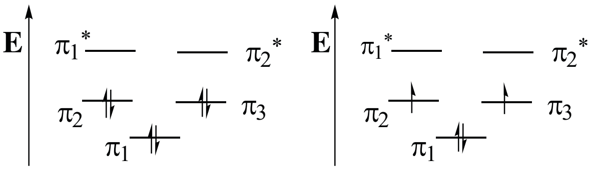


(8) **(9)** **(10)**

Fig. 2 Cation (**8**) and anion (**10**) derived from cyclopentadiene (**9**)

The anion (**10**) has (4n+2) π-electrons which are found as three sets of paired electrons in bonding π-orbitals (Fig. 3A), while the cation (**8**) has two unpaired electrons (Fig. 3B).

The aromaticity of a cyclic molecule gives extra stability to itself. The anti-aromatic state is less stable than the aromatic and non-aromatic states since anti-aromatic systems have the freedom to undergo conformational changes.



(A) **(B)**

Fig. 3 Filling of π-orbitals of Cp^- and Cp^+

Spherical aromaticity

Recently, scientists have discovered how to state the aromaticity of spherical structures, since the validity of the Hűckel rule limits only to planar structures.

A spherical structure such as a fullerene is said to be aromatic once its π-electron count satisfies $2(n+1)^2$ where n becomes an integer. The famous Buckminsterfullerene, C_{60} is nonaromatic as $n^2 = 29$.

Aromatic electrophilic substitution (AES)

Benzene ([6]-annulene) is the simplest aromatic annulene. Due to its high stability, it does not undergo typical reactions of alkenes. In an AES, ring hydrogen is substituted by an electrophilic reagent (E^+).

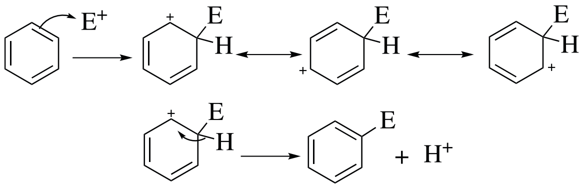
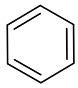


Fig. 4 Mechanism for AES reaction

Here the aromatic molecule acts as a nucleophile and the reaction mechanism involves three carbocations.

Halogenation, nitration, Friedel-Crafts alkylation and acylation, Gattermann-Koch formylation and sulfonation are some ES reactions of benzene (Table 1).

Table 1 Electrophilic substitution reactions of benzene (PhH); (X = Cl, Br)

Reactant	Conditions	Product(s)
	X_2/AlX_3	PhX
	conc. $HNO_3 + H_2SO_4$	$PhNO_2$
	RX/$AlCl_3$	PhR
	RCOX, $AlCl_3$	PhCOR
	SO_3, H_2SO_4	$PhSO_3H$
	CO+HCl/CuCl/$AlCl_3$	PhCHO

Ortho, meta and *para* directors

A mono-substituted benzene may undergo a substitution of a second hydrogen/group more easily than the benzene itself whilst some other substituted benzenes undergo reactions less easily due to deactivation of benzene ring. For example, aniline undergoes electrophilic substitution a million times faster than benzene does. On the other hand, at room temperature, nitrobenzene does not undergo electrophilic substitution.

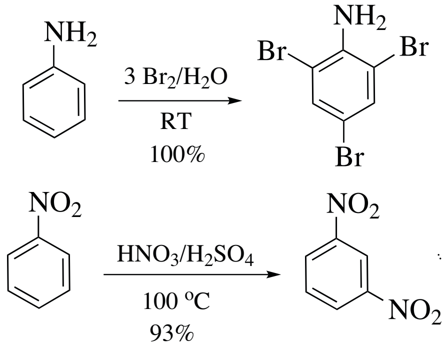
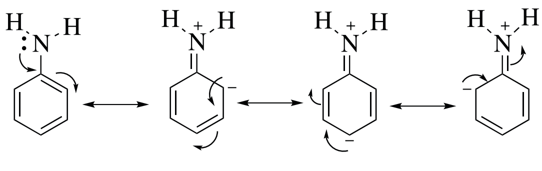
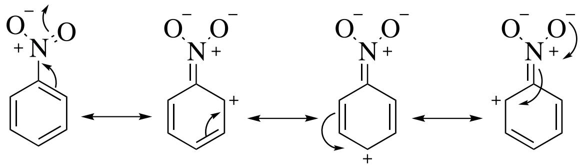


Fig. 5 AES reactions of $PhNH_2$ and $PhNO_2$

The NH_2 group of aniline is an **activating** group and its presence causes the ring to be more susceptible to further substitution. It is an ***ortho*** and ***para*** director and **resonance structures** of aniline are shown below.



The NO_2 group of nitrobenzene **deactivates** the benzene ring by withdrawing the electron density towards itself. Thus, it is a *meta* director (*meta*-carbons have more electron density); its resonance structures are shown below.



The following diagram gives the effect of the first substituent on the second substitution.

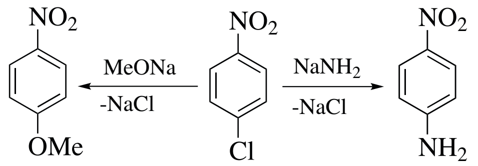
Increasing Activation

ortho, para- Directors	*meta-* Directors
$-NR_2$, R = H, alkyl	-COR
-OH	-COOR
-OR	$-SO_3H$
-NHCOR	-CHO
$-C_6H_5$ /aryl	-COOH
-R	-CN
-X (deactivating)	$-NO_2$
	$-NR_3^+$

Increasing Deactivation

Aromatic nucleophilic substitution (ANS)

Benzene, itself cannot undergo NS reactions easily. Benzene derivatives with electron withdrawing groups (EWGs) and benzylic halides can undergo ANS reactions. The chlorine in (**11**) can be replaced by nucleophiles such as MeO^- and H_2N^- to give (**12**) and (**13**).



(**12**) (**11**) (**13**)

Fig. 6 Examples for ANS reactions

ANS reaction needs a leaving group (LG) on the benzene ring and EWG/s at *meta* or/and *para* position/s to the LG. This is a two-step process with **addition** (nucleophile) and **elimination** (LG) reactions, thus it is called a $\mathbf{S_N(Ar)}$ reaction.

Note that ANS of chlorobenzene with $NaNH_2$ in liquid NH_3 proceeds *via* **benzyne mechanism**.

Addition reactions

Aromatic molecules can undergo some addition reactions: *e.g.* chlorination, catalytic hydrogenation, and Birch reduction.

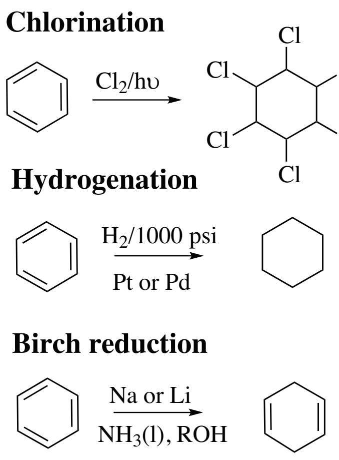


Fig. 7 Addition reactions of benzene

Complexes of aromatic molecules/ions

Aromatic molecules and ions can donate their π electron cloud to a metal centre to form **transitional metal complexes** such as $[(C_6H_6)Cr(CO)_3]$, $[(C_6H_6)_2Cr]$, $[FeCp_2]$ and $[(C_6H_6)FeCp]^+$.

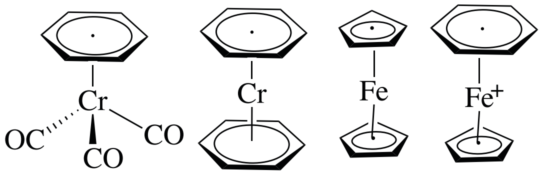


Fig. 8 Metal complexes of benzene & Cp^-

These arene and Cp complexes can be made easily by reacting benzene or CpH with metal salts. Upon coordination to a metal, benzene and Cp ligands become more susceptible towards **nucleophilic substitutions**.

NMR spectroscopy

NMR Spectroscopy serves as a useful tool in determining the aromaticity of a compound. The proton **chemical shift** (δ_H) of nonaromatic cyclooctatetraene (C_8H_8) appears around 5.78 ppm. In aromatic molecules, the protons attached to peripheral carbons are more **deshielded** or downfield shifted, and proton resonances appear above 7 ppm. In benzene, the six ring protons are chemically and magnetically equivalent and δ_H appear around 7.26 ppm in $CDCl_3$ due to **ring current**. Protons located inside the ring are **shielded** due to the induced magnetic field.

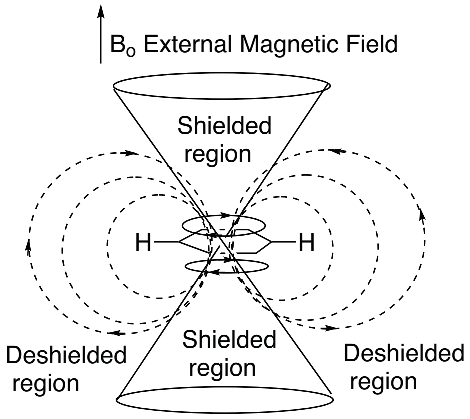


Fig. 9 Ring current of benzene in an applied magnetic field

[18]-Annulene (**4**) is an aromatic molecule and its six inner protons are **highly shielded** with a proton resonance at -**1.8** ppm. The twelve outer ring protons are highly **deshielded** with a proton resonance at **8.9** ppm. The δ_H of coronene (**5**) is also 8.9 ppm.

However, when one of the ring protons is substituted, the ring protons become magnetically inequivalent and show absorptions as a multiplet around the same areas. The carbon-13 resonances of aromatic carbons appear around 120-170 ppm.

Problems

1. Determine the aromaticity of the following: (i) pyrene, (ii) pyridine, (iii) thiophene and (iv) $C_7H_7^+$.
2. Write the major product/s formed during the following reactions.
    - (i) $PhH + {}^{n}PrCl/AlCl_3 \rightarrow$
    - (ii) $PhOH + Br_2/FeBr_3 \rightarrow$
    - (iii) $PhCMe_3 + EtCl/AlCl_3 \rightarrow$
    - (iv) 2-Bromoanisole + $NaNH_2/NH_3 \rightarrow$
    - (v) 4-Chloronitrobenzene + $NaOH/\Delta \rightarrow$
    - (vi) 2-Bromonitrobenzene + NaOMe →
3. Write the mechanism for the conversion of benzene into the following products.

(i) 4-Nitroaniline

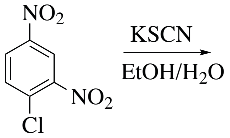
(ii) 3-Iodosulphonic acid

(iii) 4-Nitrocarboxylic acid

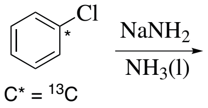
(iv) 3-Chloroaniline

4. Compare the proton chemical shifts of $[(C_6H_6)FeCp]^+$ with that of benzene.
5. Predict the number of peaks and their δ_H values for aza[18]annulene ($C_{17}H_{17}N$).
6. Determine the product(s) of the following substitution reactions.

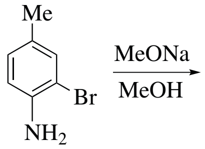
(a)



(b)



(c)



Student Corner

Monsanto and Cativa processes of acetic acid synthesis

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

In 1960, chemists at BASF developed the carbonylation of methanol into acetic acid.

$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3COOH$$

Monsanto process

Monsanto Company introduced a new catalytic system in 1966. It is now known as the Monsanto acetic acid process, which operates at about 180 °C, under CO pressure of about 40 atm, using **rhodium catalyst**. Over six million tonnes of acetic acid are produced annually.

Catalyst

The catalyst system contains a **rhodium source** (*e.g.* $RhCl_3$, or $[RhCl(CO)(PPh_3)_2]$) and **iodide ions** (HI). The **active catalyst** is *cis*-$[Rh(CO)_2I_2]^-$.

Monsanto process consists of three coupled reactions/cycles. The cycles (i) and (iii) are **non-metallic** and (ii) is **organometallic**.

(i) Conversion of MeOH to MeI by HI.

$$MeOH + HI \longrightarrow MeI + H_2O \text{ -- (1)}$$

(ii) Catalytic carbonylation of MeI to MeCOI by the catalyst $[Rh(CO)_2I_2]^-$.

$$MeI + CO \longrightarrow MeCOI \text{ ------ (2)}$$

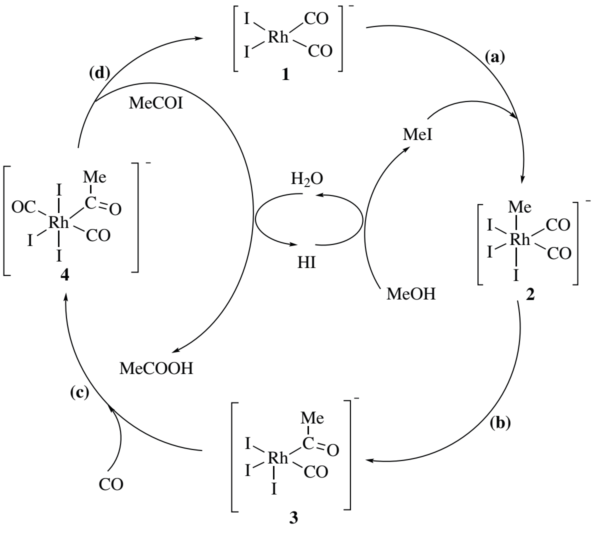
(iii) Hydrolysis of MeCOI to produce $MeCO_2H$ and HI.

$$MeCOI + H_2O \longrightarrow MeCO_2H + HI \text{ -- (3)}$$

The **overall reaction** is obtained by adding equations (1), (2) and (3), which gives

$$MeOH + CO \longrightarrow MeCO_2H$$

Let us look at the complete catalytic carbonylation process involving the active catalyst *cis*-$[Rh(CO)_2I_2]^-$. The proposed full catalytic cycle is given in scheme 1.



Scheme 1 Combined catalytic cycle for the Monsanto Process