

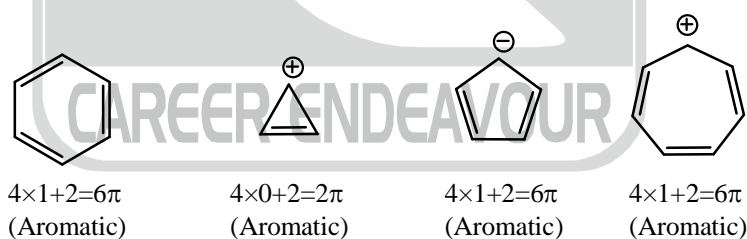
# Aromaticity

## 2.1. Introduction

Aromaticity is a chemical property of organic compound, aromatic compound have following characteristics:

- (i) It has high degree of stability
- (ii) It shows electrophilic substitution reaction rather than electrophilic addition reaction. It means it does not decolourise bromine water solution.
- (iii) Aromatic compound follow Hückel rule. According to which A cyclic planar conjugated species having  $(4n + 2)\pi$  electrons (where  $n = 0, 1, 2, 3, \dots$ ) is aromatic in nature.
- (iv) There is a diamagnetic ring current.
- (v) Each carbon must be  $sp^2$ -hybridized or  $sp$ -hybridized.
- (vi) It has high degree stability due to filled bonding molecular orbital.

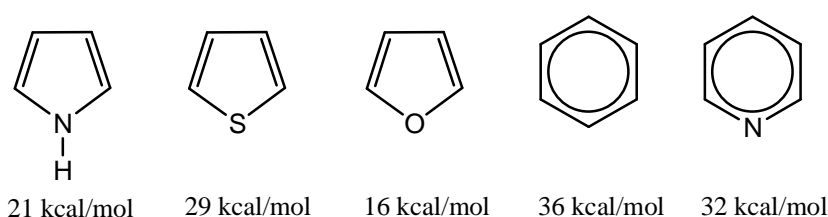
For example:



1. **High Degree of stability:** High degree of stability is associated with resonance energy. The compound which have more resonance energy is more stable. The compound which have more potential energy is least stable.

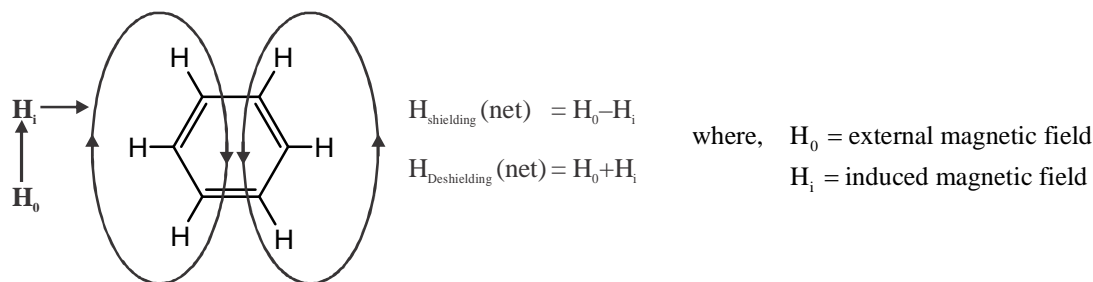
$$\text{Aromaticity} \propto \text{Resonance energy (R.E.)} \propto \text{Stability} \propto \frac{1}{\text{Potential Energy (P.E.)}}$$

2. Greater the resonance energy higher will be the stability of compound. Resonance energy of some aromatic system are given below as

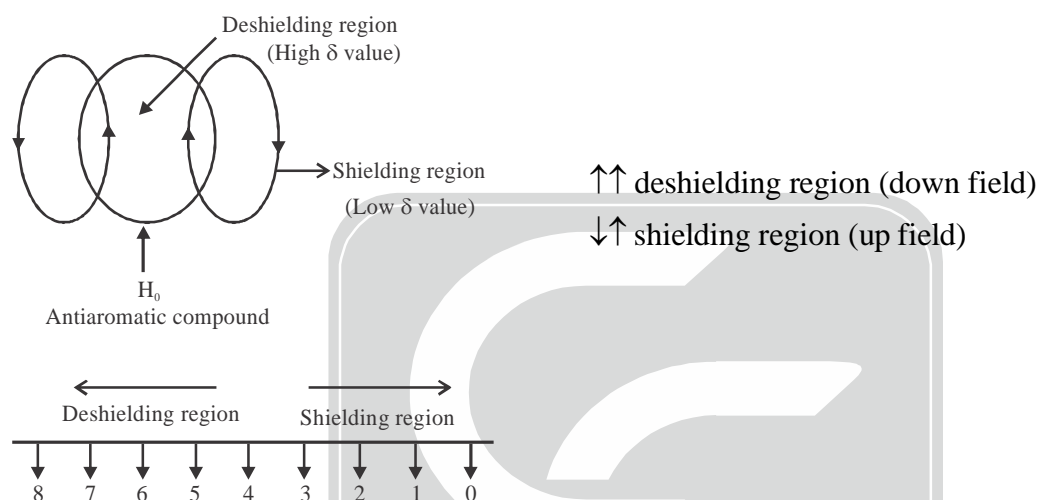


**(3) Presence of diamagnetic ring current:**

Aromatic compounds show diamagnetic ring current due to paired electron.

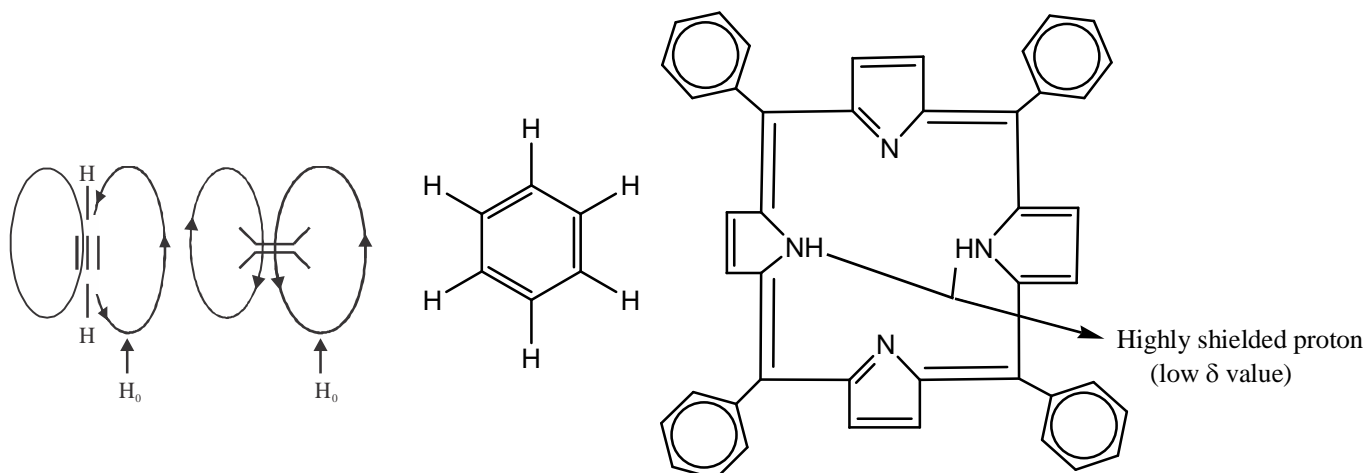


\* Clockwise direction in electron present for aromatic compound.



$\delta$  value –  $sp^2 > sp > sp^3$  (decreasing order) due to anisotropic effect.

- Molecule in which outer protons are deshielded and inner protons are shielded is known as **diatropic** molecule. These type of molecules are always aromatic in nature.
- Similarly, molecule in which inner protons are shielded and outer protons are deshielded are known as **paratropic** molecule. Paratropic molecule is aromatic in nature.
- Antiaromatic compounds show paramagnetic ring current due to unpaired electron.



## 2.2. Hückel Rule:

This is a very popular and useful rule to identify aromaticity in monocyclic conjugated compound. According to which a planar monocyclic conjugated system having  $(4n + 2)\pi$  delocalised (where,  $n = 0, 1, 2, \dots$ ) electrons are known as aromatic compound. For example: Benzene, Naphthalene, Furan, Pyrrole etc.

$n = 0$	$(4 \times 0 + 2)\pi e^- = 2\pi e^-$
$n = 1$	$(4 \times 1 + 2)\pi e^- = 6\pi e^-$
$n = 2$	$(4 \times 2 + 2)\pi e^- = 10\pi e^-$
$n = 3$	$(4 \times 3 + 2)\pi e^- = 14\pi e^-$
$n = 4$	$(4 \times 4 + 2)\pi e^- = 18\pi e^-$

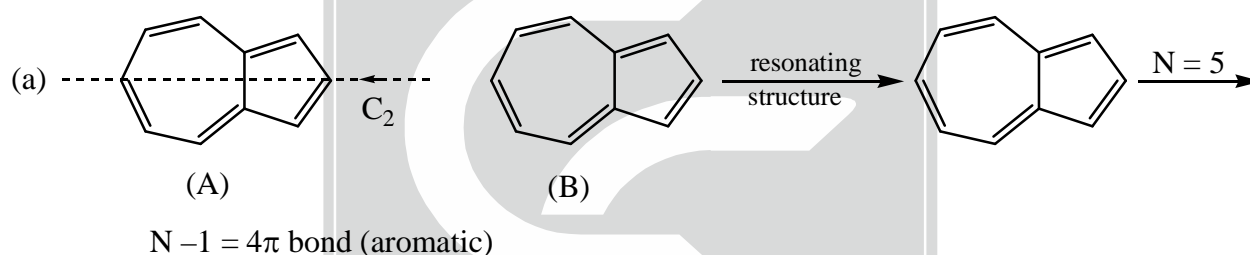
## 2.3. Craig's Rule:

This rule is applicable for polycyclic non-benzenoid compounds. If molecule contain  $C_2$ -axis then count total number of double bonds (N) and calculate value of  $N-1$  which decide aromaticity in compound.

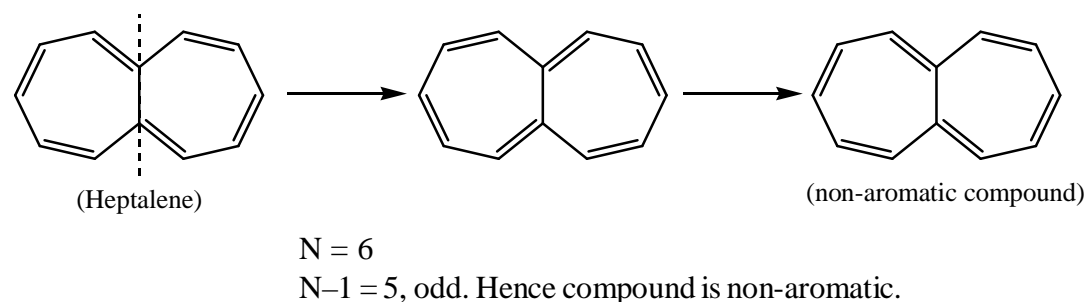
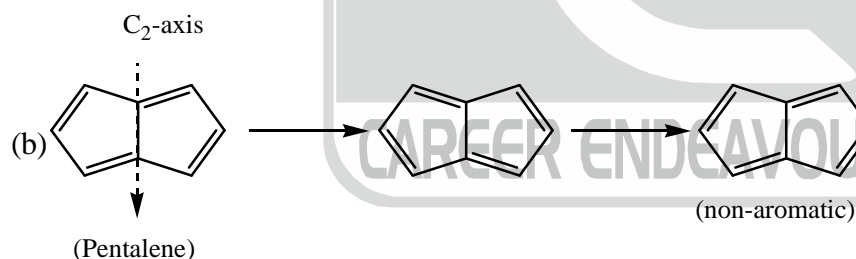
(1) If  $N - 1 = \text{odd}$ , compound is non-aromatic

(2) If  $N - 1 = \text{even}$ , compound is aromatic.

e.g. Azulene




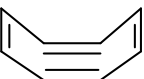

- In system  $C_2$ -axis must be present



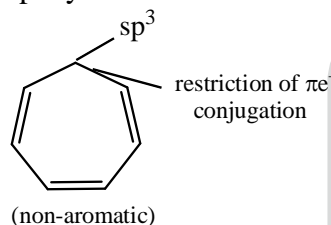
- Pentalene and heptalene is a non-aromatic compound. Since it does not follow Craig's rule.
- The organic compound which show aromaticity are aromatic in nature or diatropic in nature and the protons (outside the rings) signal always exist away from the TMS (these protons are deshielded protons)

## 2.4. Identification of Aromatic, non-aromatic and anti-aromatic compound :

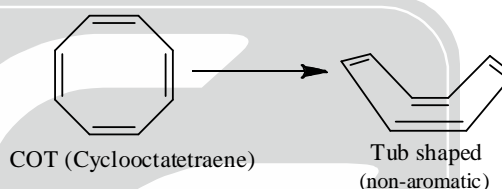
Characteristics of Aromatic,  
Non-Aromatic and Anti-Aromatic Compound

Aromatic	Non-Aromatic	Anti-Aromatic
1. Cyclic	1. Cyclic	1. Cyclic
2. Delocalisation of electron	2. No delocalisation of electron	2. Delocalisation of electron
3. Planar (all atoms must be $sp^2$ or $sp$ hybridised)	3. Non-planar (due to $sp^3$ hybridised atom or due to distorted planarity)	3. Planar (all atoms must be $sp^2$ or $sp$ hybridised)
4. Huckel $(4n + 2)\pi$ electron $n = 0, 1, 2, 3, 4, \dots$	4. Huckel rule not applied	4. $4n \pi$ electron system $n = 1, 2, 3, \dots$
Ex. 	Ex. 	Ex. 

$sp^3$   
 $sp^3$  hybridized carbon atom insert



non-planar structure



### • Order of stability and order of resonance energy :

Aromatic > HOMO-aromatic > Non-aromatic > Anti-aromatic.

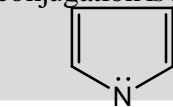
In acyclic compounds: Conjugated > Isolated > Cumulated compound.

**Calculation of  $\pi$ -electrons:** During  $\pi$ -electron count double bond count  $2\pi$  electron and triple bond count  $2\pi$  electron. Also, lone pair in conjugation is also counted.

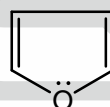
$\Rightarrow 2\pi e^-$

$\equiv \Rightarrow 2\pi e^-$

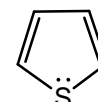
$1 lp \rightarrow 2e$



$6\pi e^- (4\pi e^- + 1 lp)$

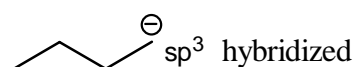
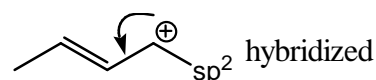
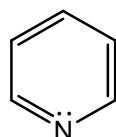
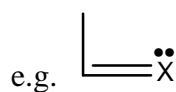


$6\pi e^- (4\pi e^- + 1 lp)$

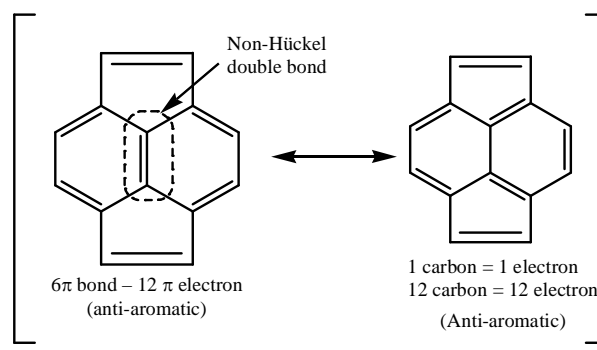
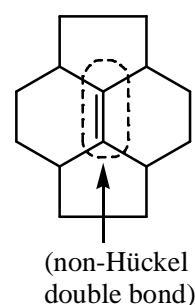
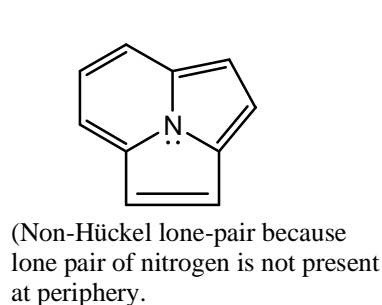


$6\pi e^- (4\pi e^- + 1 lp)$

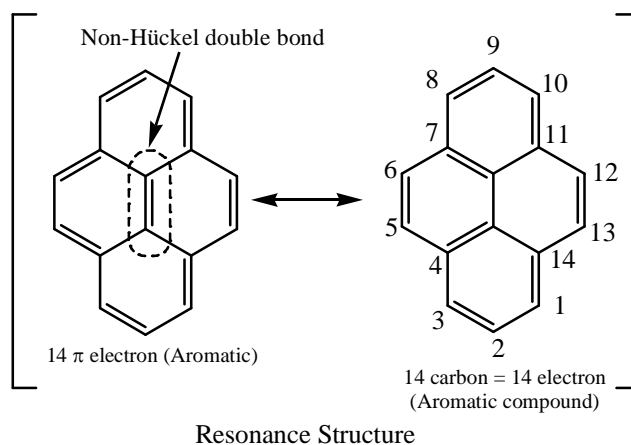
species in which lone pair is not in conjugation can not be counted:



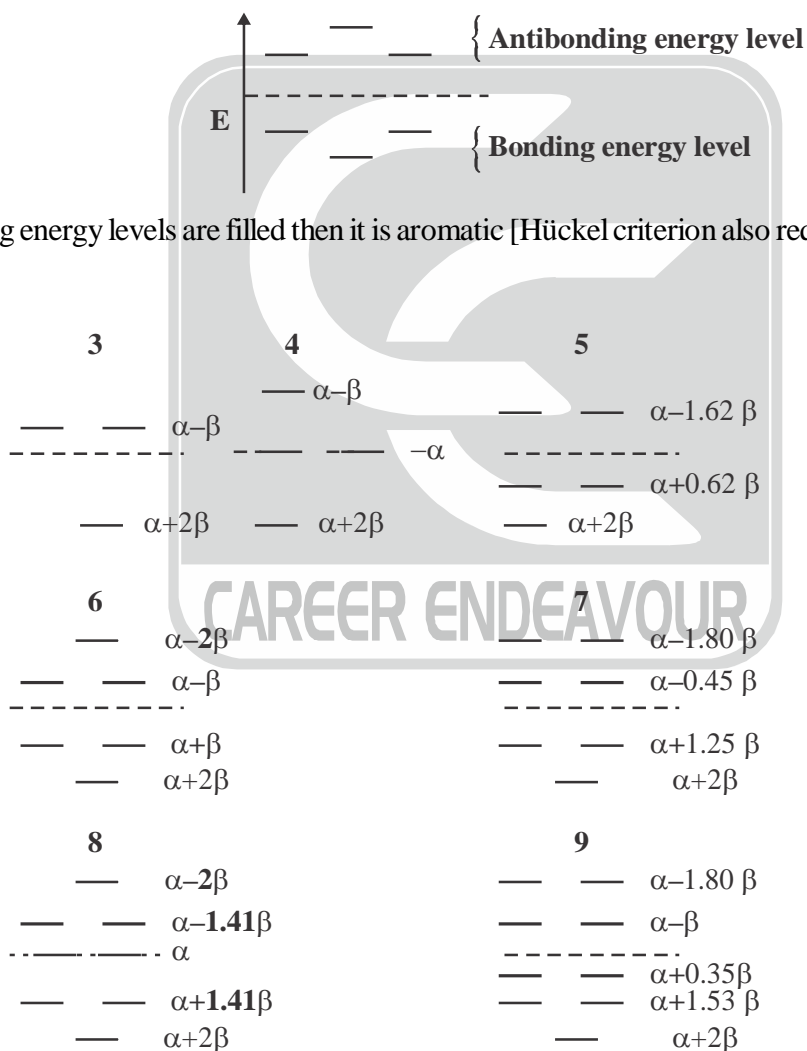
- Lone pair which participate in conjugation system and follow Hückel's rule are called Hückel lone pair while which lone pair does not participate in conjugation are known as non-Hückel lone pair.



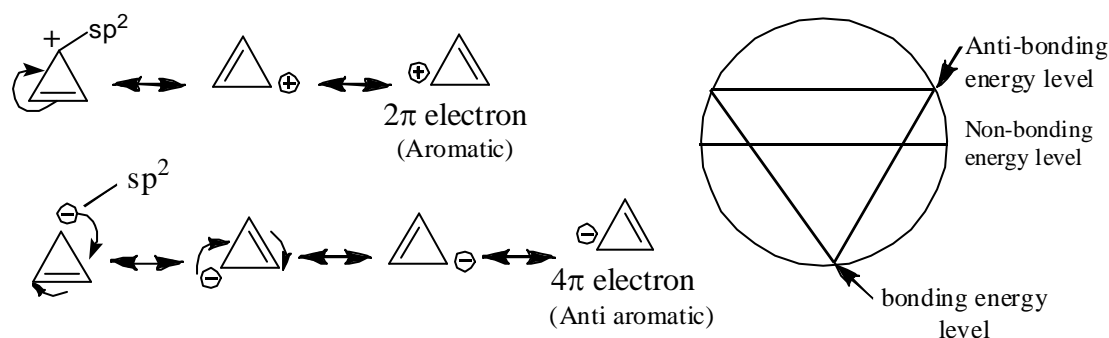
Resonance Structure



- Energy level of aromatic and anti-aromatic compounds can be shown by using **frost circle** or diagram. Energy levels of regular planar polygonic molecules with an even number of atoms form a symmetrical pattern as shown below.



**Figure :** HMO energies for conjugated planar ring systems of three to nine carbon atoms.



Frost Diagram for Cyclopropenyl system

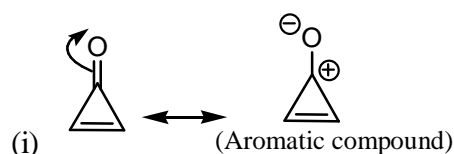
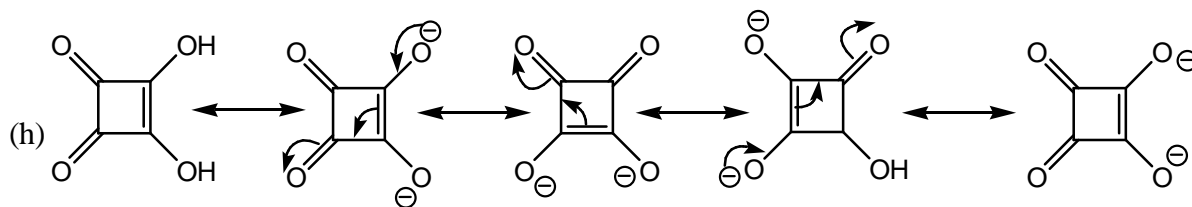
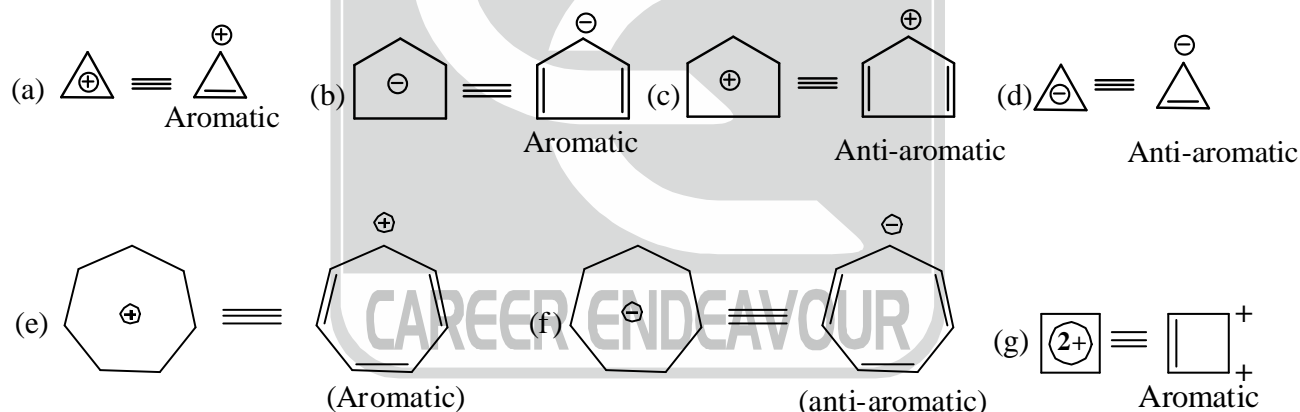
- Anti-aromatic compound behaves as a biradical
- In anti-aromatic compounds two unpaired electron are present which are all paired.
- Oxygen also behave as biradical and triplet state.
- Carbene-triplet state are biradical.

## 2.5. Types of Aromatic Compounds

### (A) $2\pi$ -electron system .

- It follow  $(4n + 2)\pi e^-$  system.
- If electron delocalised then compound is aromatic.
- If electrons not delocalised then compound is non-aromatic
- Compound will never be antiaromatic.

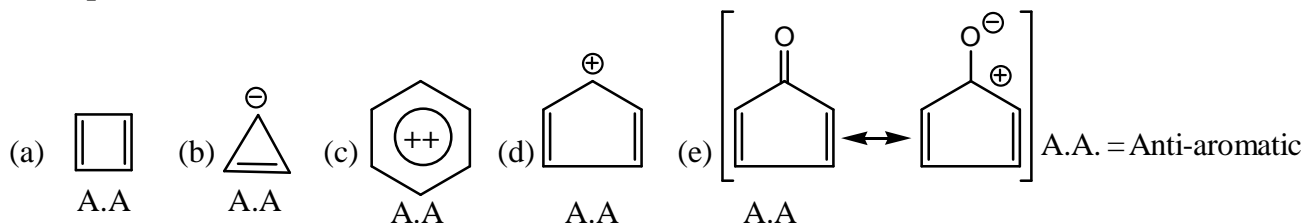
#### Examples:



Displacement of electrons takes place towards higher electronegative atom.

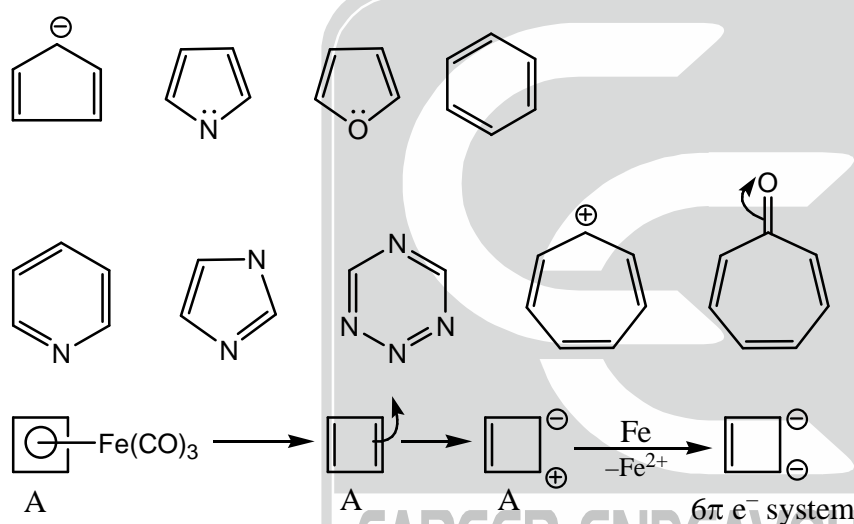
**(B)  $4\pi$ -electronic system:**

- (i) Belongs to  $4n \pi e^-$  system does not follow Hückel rule.
- (ii) If electron is delocalised then compound is antiaromatic.
- (iii) If electron does not delocalise then compound never antiaromatic
- (iv) If electron does not delocalise then compound is non-aromatic.

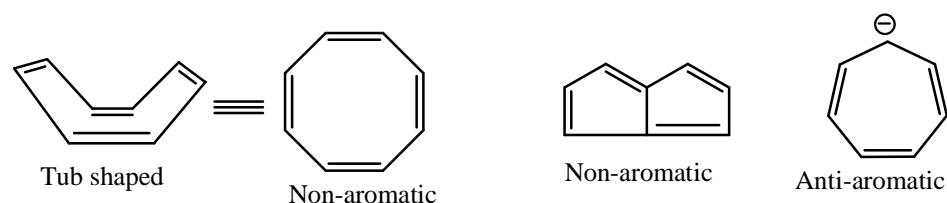
**Examples:****(C)  $6\pi$  electron system:**

- (i) Belongs to  $(4n + 2) \pi e^-$  system.
- (ii) If electron is delocalised then compound will be aromatic.
- (iii) If electron does not delocalise then compound must be non-aromatic

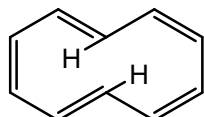
For example

**(D)  $8\pi$  electronic system :**

- (i) Belongs  $(4n) \pi e^-$  rule
- (ii) If electron is delocalised the compound must be anti-aromatic
- (iii) If electron does not delocalise then compound is non-aromatic.

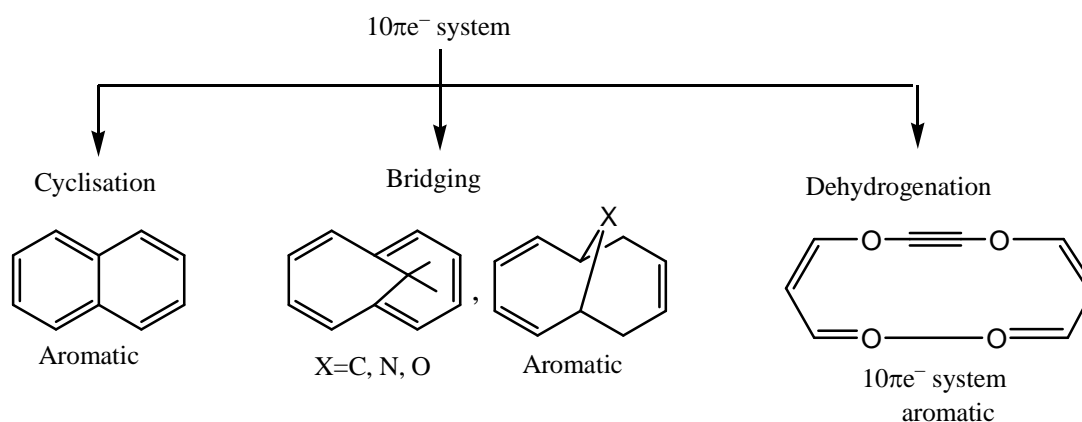
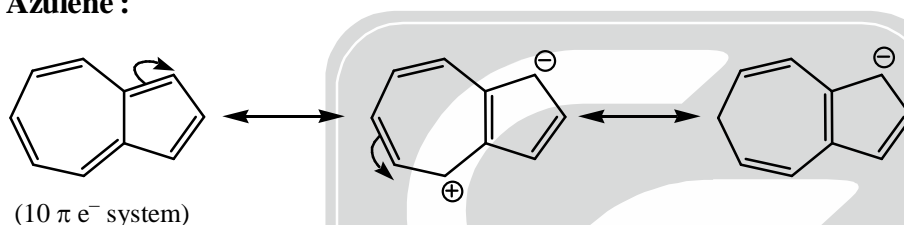
**(E)  $10\pi$  electronic system:**

- (i) Belongs to  $(4n + 2) \pi e^-$  system.
- (ii) If electron delocalised then compound is aromatic in nature.
- (iii) If electron does not delocalise then compound will be non-aromatic
- (iv) Compound will never be anti-aromatic.

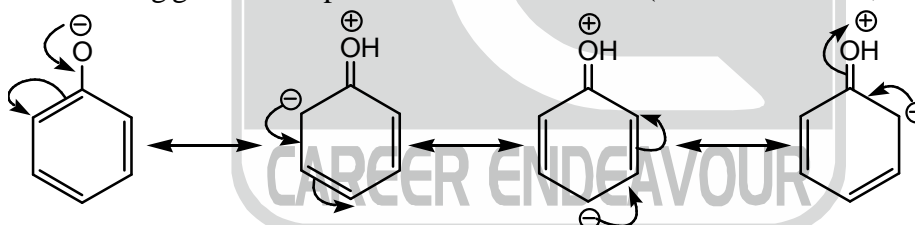


(Non-aromatic)

(Repulsion between H-hydrogen atoms, causes the compound to be non planar. So, compound is non-aromatic)

**Azulene :**

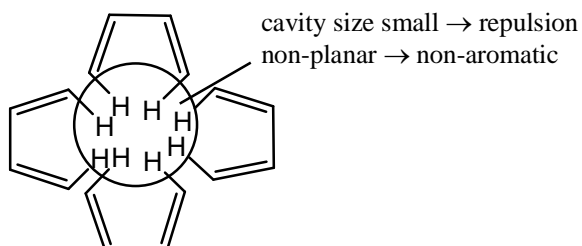
- Azulene is the isomer of Naphthalene
- Azulene is less stable than naphthalene
- Azulene gives electrophilic substitution reaction as well as nucleophilic substitution reaction.
- Five membered ring gives electrophilic substitution reaction (because small size, electronegativity)



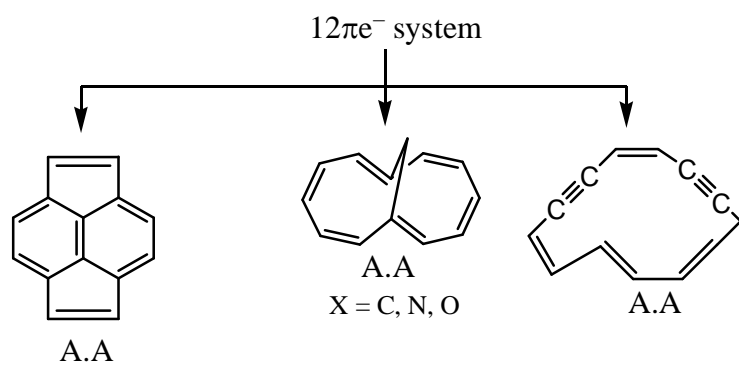
like (same) charge must be at maximum distance and opposite charge must be at minimum distance for stability resonance structure.

**(F)  $12 \pi$  electronic system:**

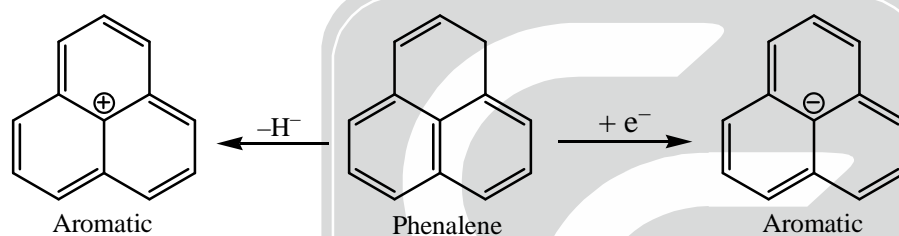
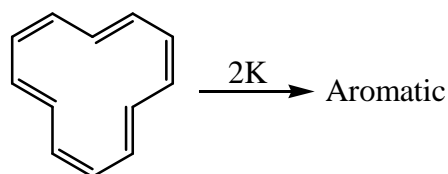
- Belongs to  $(4n)\pi e^-$  system
- If electron is delocalised then compound is anti-aromatic
- If electron does not delocalization then compound will be non-aromatic.
- Compound will delocalised never be aromatic





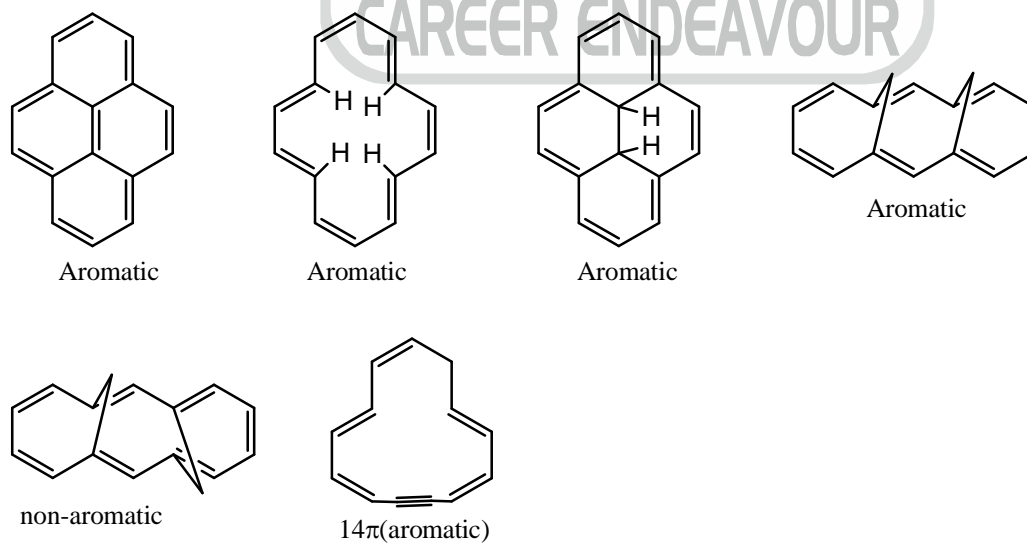


$12\pi e^-$  system-(non-planar)  $\xrightarrow[\text{metal}]{\text{reaction with}}$  aromatic

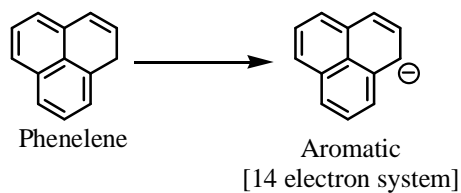


### (G) 14 $\pi$ electronic system:

- (i) Belongs to  $(4n + 2)\pi e^-$  system
- (ii) If delocalize electron then the compound is aromatic.
- (iii) If electron does not delocalised then the compound non-aromatic
- (iv) It never be antiaromatic.

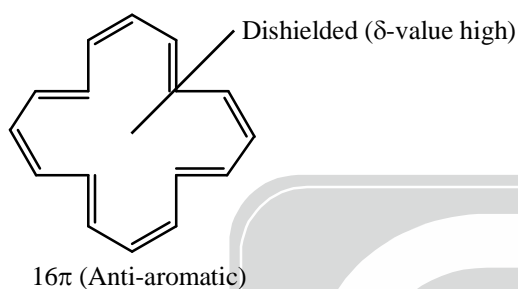


6. Phenylene is acidic in nature why?  
Proton ( $H^+$ ) remove from the phenylene and acidic in nature and system gain aromaticity.

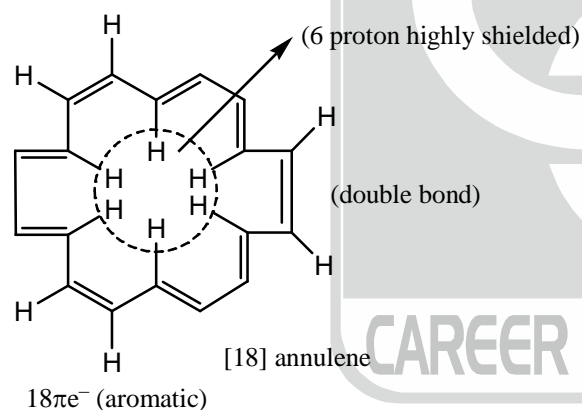


**(H)  $16\pi$  electronic system:**

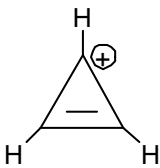
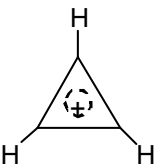
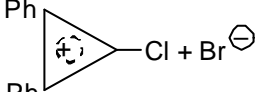

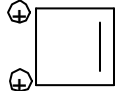

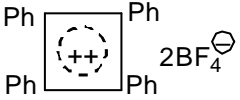



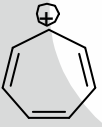

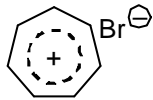
- (i) Belongs to  $4n\pi e^-$  rule.
- (ii) If electron is delocalised then compound is anti-aromatic.
- (iii) If electron does not delocalised then compound will be non-aromatic
- (iv) It never be aromatic.

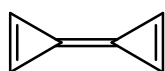


**(I)  $18\pi$  electronic system:**

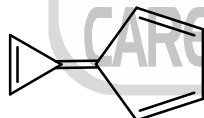


## EXAMPLE OF AROMATIC COMPOUNDS OF IONIC SPECIES

$n$	$p$ -electrons $= (4n + 2)$	Aromatic Compounds	Salts	Examples of Salts
0	2	 Cyclopropenyl cation	 Cyclopropenium salts	 Hydroxydiphenyl Cyclopropenyl bromide  Cyclopropenyl hexachloroantimonate
0	2	 Cyclobutenyl di-cation	 Cyclobutenium salt	 Tetraphenylcyclobutanyl tetrafluoroborate
1	6	 Cyclopentadienyl anion	 Cyclopentadienium salt	 Potassium cyclopentadienide
1	8	 Tropylium cation (Cycloheptatrienyl cation)	 Tropylium salt	 Tropylium Bromide

Other Aromatic System:  
Fused ring aromatic.

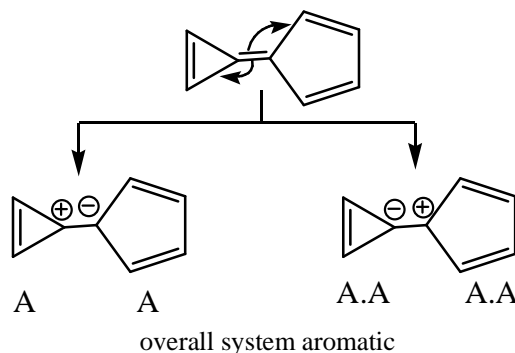
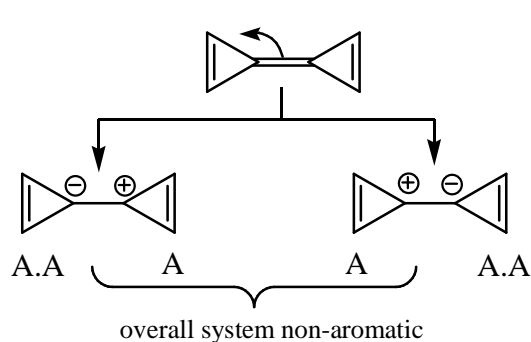
triafulvalene

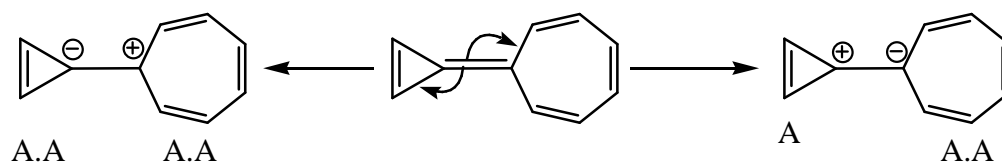


calicene

- Such type of systems is aromatic or non-aromatic but never be anti-aromatic
- If such type of system is aromatic then both ring must be aromatic after displacement of common double bond.

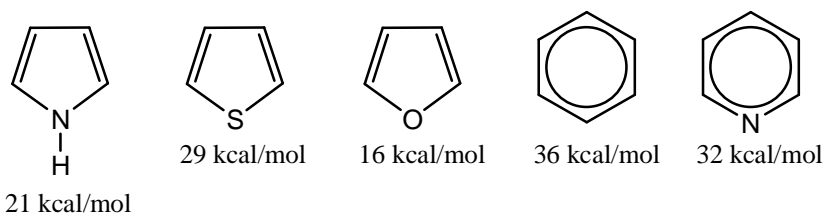
Otherwise both ring will not be aromatic



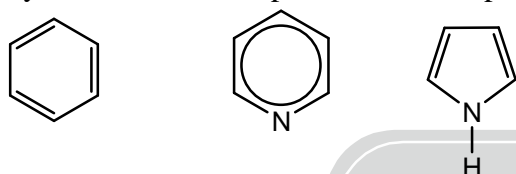


overall system  $\rightarrow$  non-aromatic

### Resonance energy of some aromatic system:



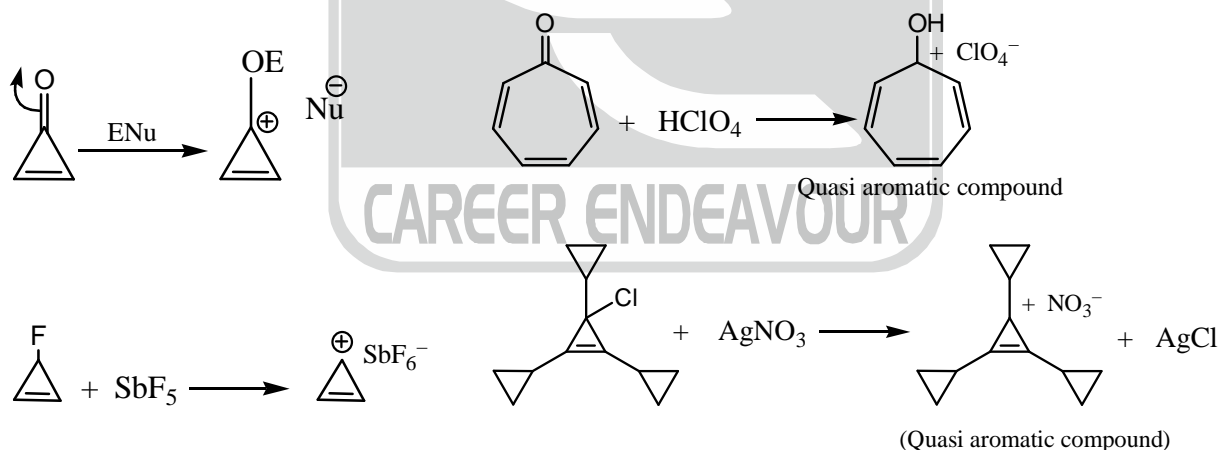
Pyrrole is called as super aromatic compound



$$36 = \frac{6}{6} = 1 \text{ for C-atom energy. } \frac{(\text{total } \pi e^-)}{(\text{total C-atom})} \frac{6}{5} = 1.2 \text{ per C-atom}$$

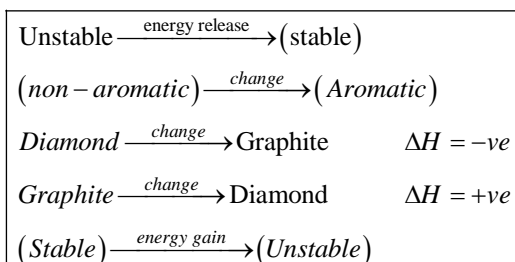
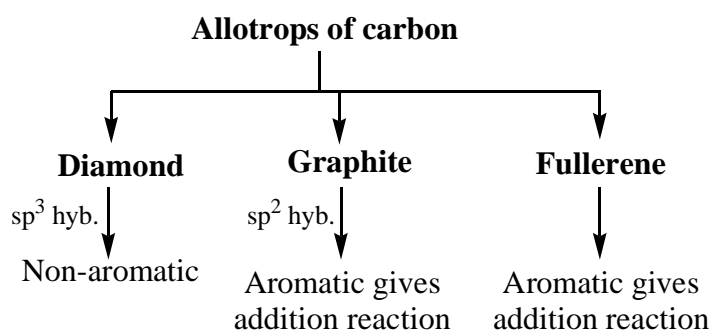
According to electron density at per C-atom, pyrrole is electronically rich. So, pyrrole gives electrophilic substitution reaction more easily than benzene.

**Quasi Aromatic Compound:** These are generally ionic aromatic compound



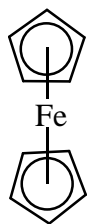
### Allotropes of Carbon:

- (i) Diamond      (ii) Graphite      (iii) Fullerene

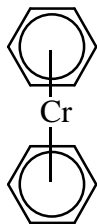


**Organometallic aromatic compound:**

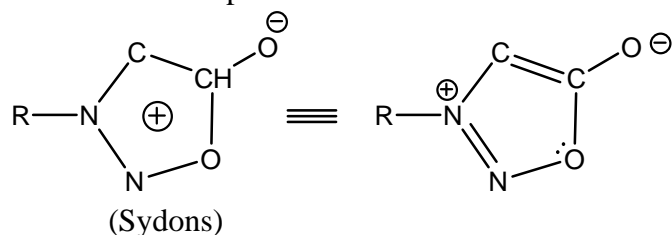
Ferrocene



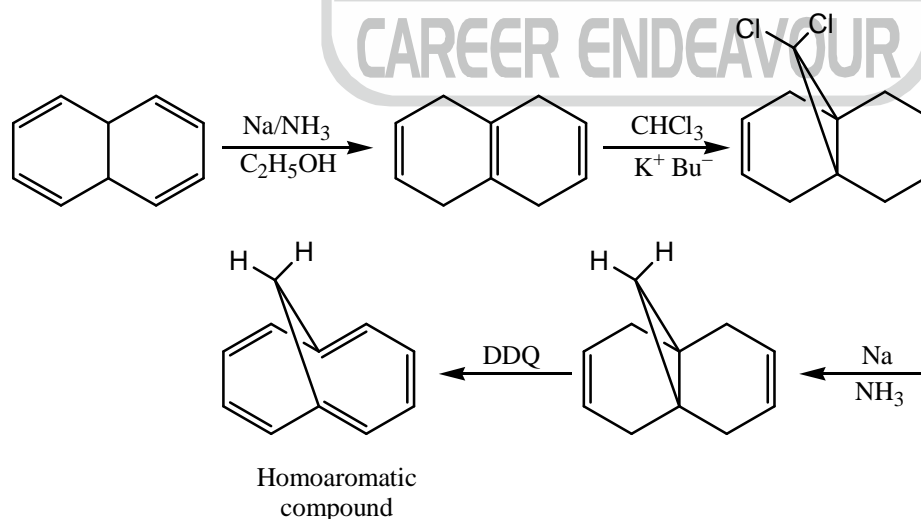
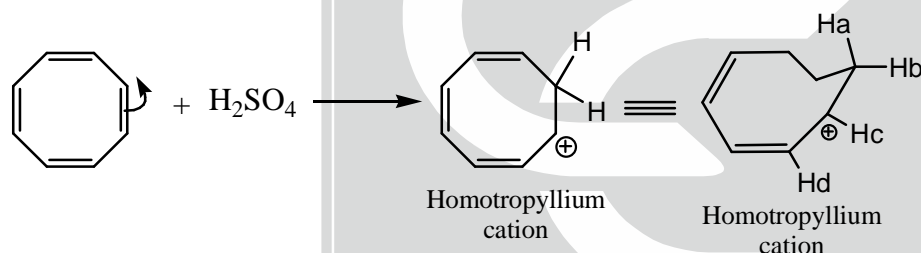
Dibenzene chromium



- Mesoionic Compound: Sydons is the first meso-ionic compound which show aromaticity.
- Meso-ionic compound gives electrophilic substitution reaction
- Meso-ionic compound also known as internal salt.

**2.6. Homo-aromatic compound :**

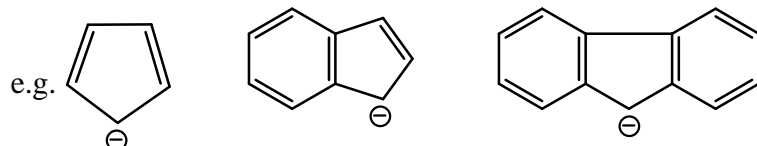
Compound that contain one or more  $sp^3$ -hybridized C-atom in a conjugate cycle but  $sp^3$ -hybridized carbon atom are force to lie almost vertically above the plane of the aromatic system known as homoaromatic compounds.



Stability: Aromatic > Homo-aromatic > non-aromatic > antiaromatic

**Annellation effect :**

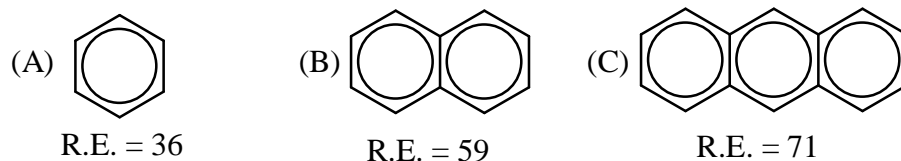
Each ring in fused system give the part of the aromaticity to the adjacent ring called **annellation effect**.



- Number of benzene ring increases
- Aromaticity decreases

**2.7. SOLVED PROBLEMS**

1. Arrange the following compound in correct order of aromaticity?



**Soln.** Resonance energy of each species is written below to structure as we known greater the resonance energy per benzene ring, higher will be the stability of molecule

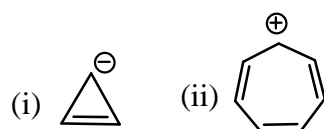
$$\frac{36}{1} = 36$$

$$\frac{59}{2} = 29.5$$

$$\frac{71}{3} = 23.67$$

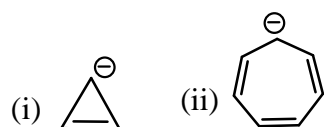
Depending upon the resonance energy per benzene ring the aromaticity of above compound can be arranged as  $A > B > C$ .


2. Which of the following compound is more stable.



**Soln.** (ii)

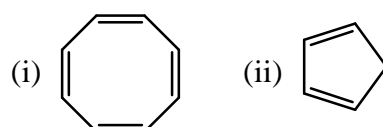
3. Which of the following compound is more anti-aromatic



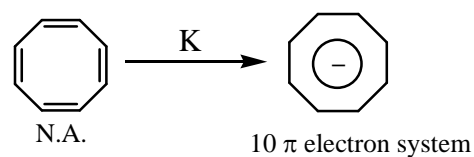
**Soln.** (i)  (More anti-aromatic because more planar)

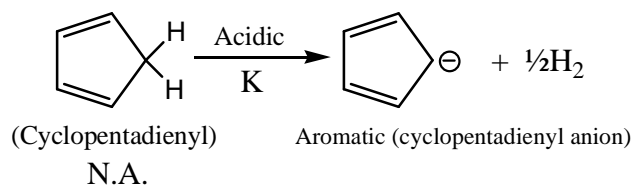
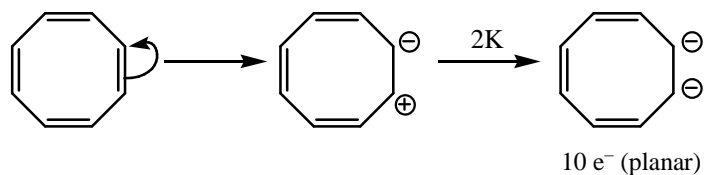
The anti-aromatic compound have tendency to adopt the non-planar structure to maximize its stability.

4. Which of the following compound gives  $H_2$ -gas with metal.



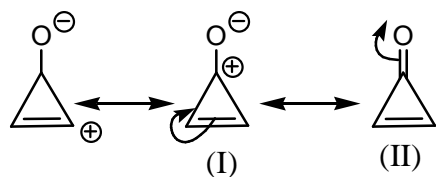
**Soln.** (ii), (i) both.





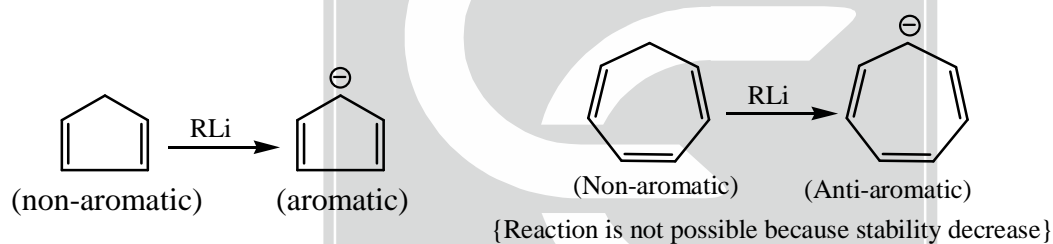
Cyclopentadiene is acidic in nature due to aromatic character of cyclopentadienyl anion.

5. Which of the compound have more dipole moment.



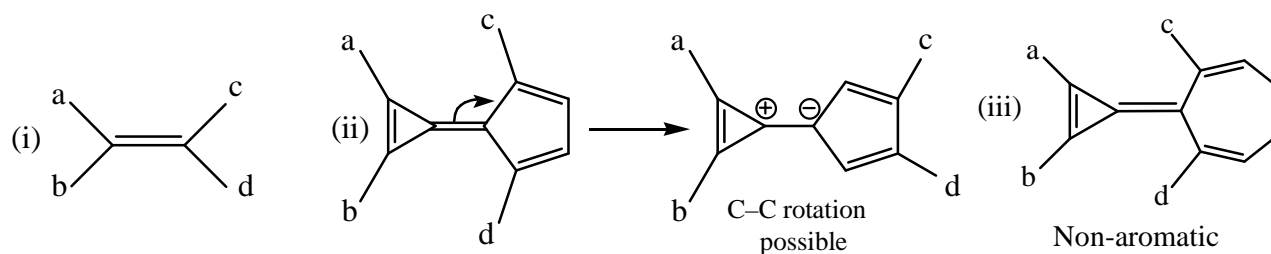
Maximum charge separation  $\rightarrow$  maximum dipole moment  
because  $\mu = q \times d$ , where,  $q$  = amount of charge,  $d$  = distance between two poles.  
(I) have more dipole moment than (II)

6. Which of the following reaction takes place.



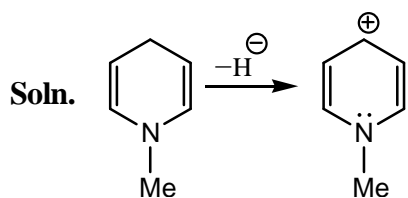
7. Which of the following compound gives geometrical isomerism.

**For geometric isomerism:** At this carbon for both group must be different and C–C bond rotation must be restricted.

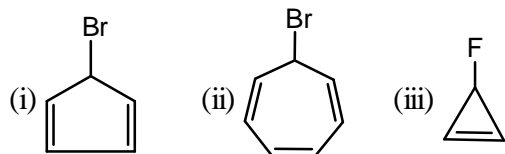


8. Which of the following compound is best hydride donor.

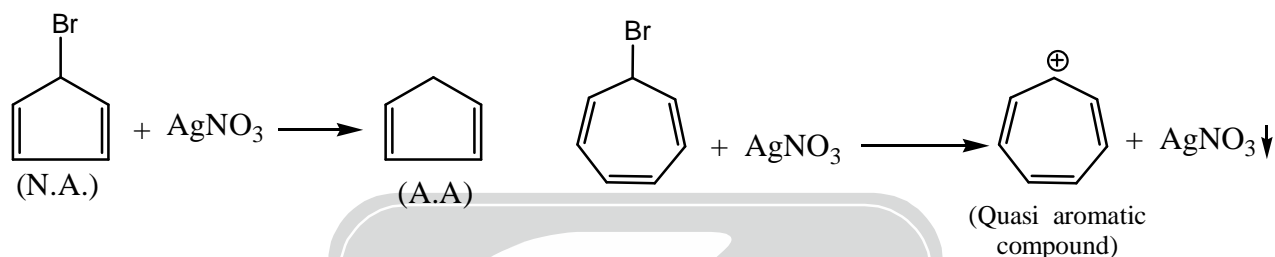




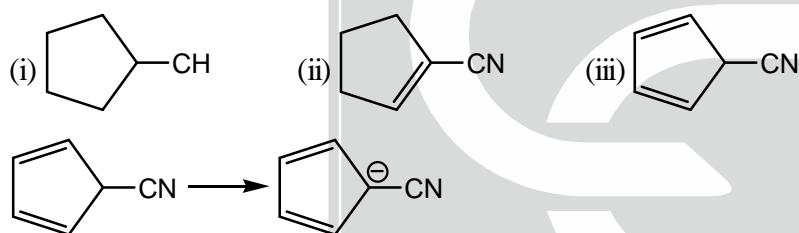
9. Which of the following compound gives ppt. with  $\text{AgNO}_3$ .



**Soln.** (ii) and (iii)

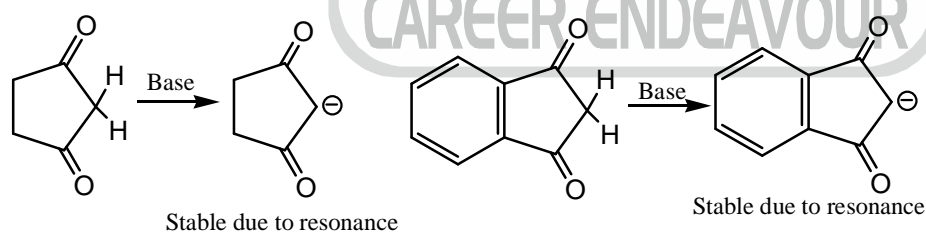


10. Arrange these molecules in correct order of deprotonation.



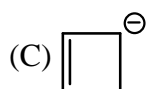
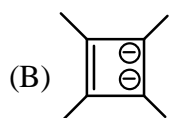
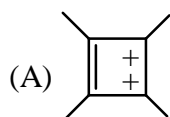
**Soln.** (iii) > (ii) > (i)

**More acidic:**



11. Match the following

**Column-I**



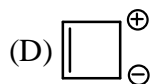
**Column-II**

(i) Aromatic

(ii) Anti-aromatic

(iii) Non-aromatic



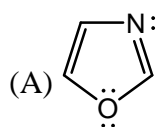


(iv)  $(4n + 2) \pi e^-$

**Soln.** A-(i), (iv); B-(i), (iv), C-(iii), D-(ii)

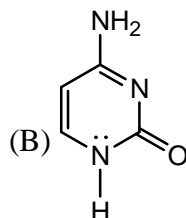
12. Match the following

**Column-I**

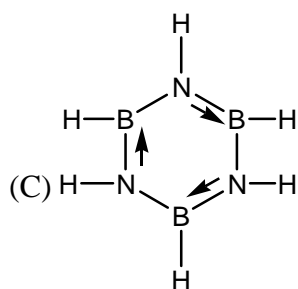


**Column-II**

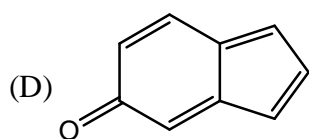
(i) Aromatic



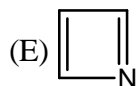
(ii) Non-aromatic



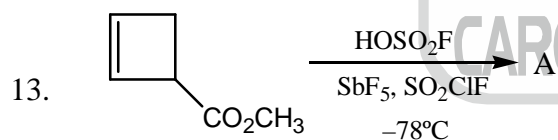
(iii) Anti-aromatic



(iv) Heterocyclic



**Soln.** A-(i), (iv); B-(i), (iv); C-(i), (iv); D-(ii); E-(iii)



In the above reaction, A is

- (a) Antiaromatic      (b) Homoaromatic      (c) Non-aromatic      (d) Antiaromatic

**Soln.** Correct option is (b)

