

<b>Subject</b>	<b>Chemistry</b>
<b>Paper No. and Title</b>	<b>Paper 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)</b>
<b>Module No. and Title</b>	<b>Module 8: Aromaticity of fused rings</b>
<b>Module Tag</b>	<b>CHE_P1_M8</b>

<b>Principal Investigator</b>		<b>Co- Principal Investigator and Technical Coordinator</b>
<b>Prof. A.K.Bakhshi</b> Sir Shankar Lal Professor, Department of Chemistry, University of Delhi		<b>Dr. Vimal Rarh</b> Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi  <i>Specialised in : e-Learning and            Educational Technologies</i>
<b>Paper Coordinator</b>	<b>Content Writer</b>	<b>Reviewer</b>
<b>Prof. J M Khurana</b> Professor, Department of Chemistry, University of Delhi	<b>Dr. Vimal Rarh</b> Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi  <b>Dr. Geetu Gambhir</b> Asst Professor, Department of Chemistry, Acharya Narendra Dev College, University of Delhi	<b>Dr. V K Sharma</b> Asst Professor Department of Chemistry, Hindu College, University of Delhi
<b>Anchor Institute : SGTB Khalsa College, University of Delhi</b>		

<b>CHEMISTRY</b>	<b>PAPER 1: ORGANIC CHEMISTRY- I(Nature of Bonding and Stereochemistry)</b>
	<b>MODULE 8: Aromaticity of fused rings</b>

## TABLE OF CONTENT

1. Learning Outcomes
2. Introduction
3. Classification of fused ring systems
4. Aromaticity in fused ring systems
  - 4.1. Aromaticity of some benzenoid fused systems
    - 4.1.1. Naphthalene
    - 4.1.2. Anthracene
    - 4.1.3. Phenanthrene
    - 4.1.4. Resonance energy of fused ring systems
  - 4.2. Aromaticity of some non-benzenoid fused systems
    - 4.2.1. Azulenes
    - 4.2.2. Oxaazulenaones
5. Other fused ring systems
  - 5.1. Phenalene
  - 5.2. Benzo cyclobutadiene
  - 5.3. Ferrocene
6. Summary

**CHEMISTRY**

**PAPER 1: ORGANIC CHEMISTRY- I(Nature of Bonding and Stereochemistry)**

**MODULE 8: Aromaticity of fused rings**

## 1. Learning Outcomes

After studying this module, you shall be able to:

- Learn about the fused rings
- Understand that how fused rings are classified
- Learn about the aromaticity of the fused rings
- Understand aromaticity in the benzenoid and non-benzenoid fused ring systems
- Learn about some other special cases

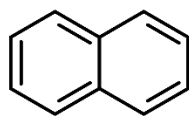
## 2. Introduction

As you are already aware that the aromatic compounds apparently contain alternate double and single bonds in a cyclic structure and resemble benzene in chemical behavior. Up till now we have discussed the aromaticity in monocyclic rings. In this module, we shall discuss about the aromaticity of fused rings.

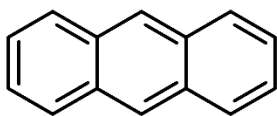
So, before starting with the aromaticity of fused rings first we should know what fused rings are.

A fused aromatic ring is one which shares one side of the ring. These are monocyclic rings that shares their connecting bond. Such type of molecules which contain these kind of fused rings (e.g. phenanthrene or anthracene) are generally referred to as linear or angular polyacenes. For example: acenes are a class of organic compounds and polycyclic aromatic hydrocarbons made up of linearly fused benzene rings.

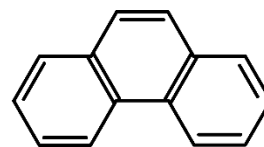
Some of the examples are given below:



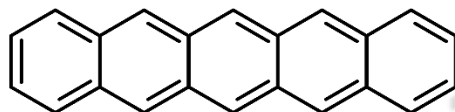
**Naphthalene**



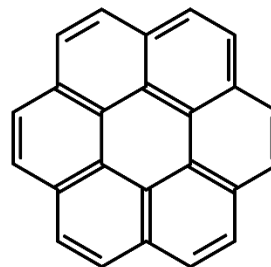
**Anthracene**



**Phenanthrene**



**Pentacene**

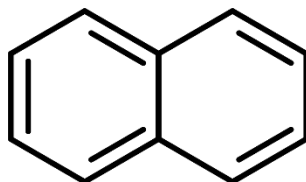


**Coronene**

### 3. Classification of fused ring systems

Fused ring systems are classified into two categories depending on the number of atoms and bonds shared by the rings. These are as follows:

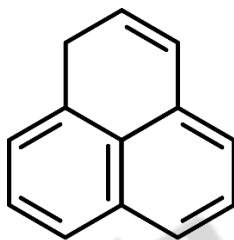
- i. **Ortho-fused rings** –If the two rings of the fused system that have only two atoms and one bond is common between the rings then it is said to be *ortho-fused rings* as in case of naphthalene.



**Naphthalene**

As shown in the figure of naphthalene two rings are *ortho-fused*.

- ii. **Ortho and peri fused rings** – If three atoms are common between the first ring and the other two rings then it is said to be *ortho and peri fused rings*. This type of fused rings is generally present in the polycyclic rings where the ring is *ortho fused* with two different sides of two rings which themselves are *ortho fused*. For Example, in case of phenalene.



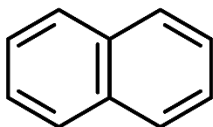
**Phenalene**

#### 4. Aromaticity in fused ring system

As we have discussed in the previous module, a molecule is said to be aromatic if all the following conditions are fulfilled:

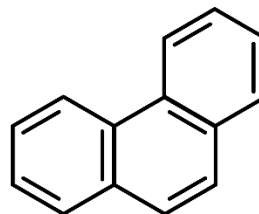
1. It is *cyclic, planar* and has *continuous delocalization* of  $\pi$  electrons (electrons in p orbitals) with or without the participation of lone pair(s)/- charge/ + charge (*i.e.*, having electrons or vacant p orbital).
2. The delocalized  $\pi$ -electron cloud must contain a total of  $(4n+2)\pi$  electrons, where n is a whole number (*i.e.*, n =0,1,2,3 and so on). Putting n= 0 in  $(4n+2)\pi$  we get  $2\pi$  electrons, similarly putting n=1, we get  $6\pi$  electrons; n= 2 gives  $10\pi$  electrons; n= 3 gives  $14\pi$  electrons and so on.

The criteria for the aromaticity in the fused rings also follows the same rule as applied to the monocyclic systems. If the above two conditions are followed, then only, the compound is aromatic. For example, the aromaticity of naphthalene and phenanthrene are shown below:



**Naphthalene**

1. ✓
2.  $10 \pi e^-$



**phenanthrene**

1. ✓
2.  $14 \pi e^-$

Aromaticity in above benzenoid structures is well accounted for, but few non benzenoid structures also tend to show aromatic stabilization.

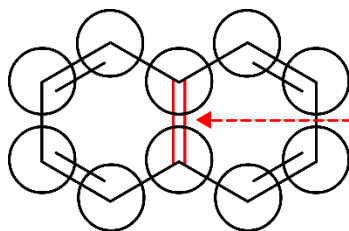
**Note:**

- a. The p-orbitals in which the electrons are delocalizing must be parallel to each other so that a continuous overlap of electrons is possible along the ring.
- b. The selection of closed loop should be such that all the p-orbitals which are parallel to each other are present in that loop.

**4.1 Aromaticity of some benzenoid fused rings**

**4.1.1 Naphthalene**

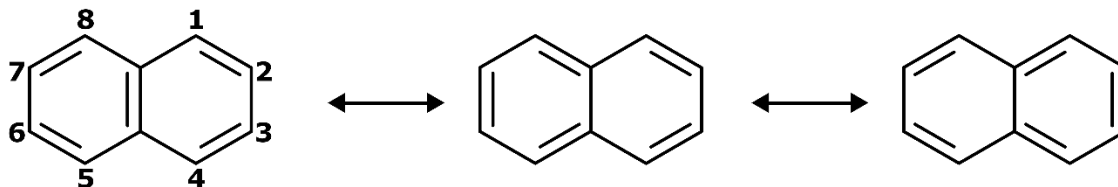
It is the simplest polycyclic aromatic compound which contain two benzene rings fused together at the *ortho* bond.



*This pi bond count toward Hückel's rule*

It is easily seen to have a closed loop of p orbitals hosted on a set of coplanar carbon atoms. Naphthalene contains 5 C=C bonds in the closed loop. Naphthalene contain  $10 \pi$  electrons. So, according to *Hückel's Rule* ( $n=2$ ) naphthalene obeys  $(4n+2)\pi$  electron rule. It shows that

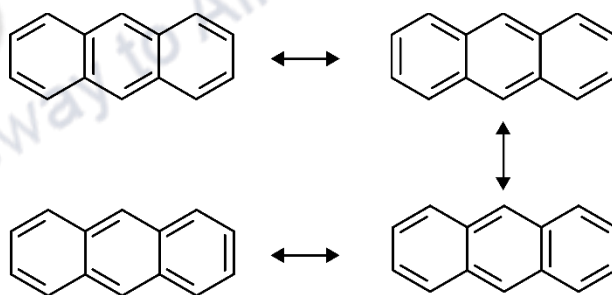
naphthalene is aromatic. As in this case it contains a central double bond which makes it different from the other two canonical forms which are equivalent to each other.



In naphthalene, the reactivity of the ring system is greater than that of the benzene. This has been explained by considering one of the naphthalene rings as aromatic and the other as a butadiene. As in naphthalene if one ring is to have six electrons other must have four electrons. So, the reactivity of the fused rings is generally more than benzene.

#### 4.1.2. Anthracene

Anthracene is another example of aromatic fused system which contain three *ortho* fused benzene rings. It is colorless solid which shows blue fluorescence in ultraviolet light. It is the component of coal tar. Anthracene contains 7 C=C bonds in the closed loop Anthracene contain 14  $\pi$  electrons. So, according to Hückel's Rule ( $n=3$ ) Anthracene obeys  $(4n+2)\pi$  electron rule. Anthracene shows four canonical forms.

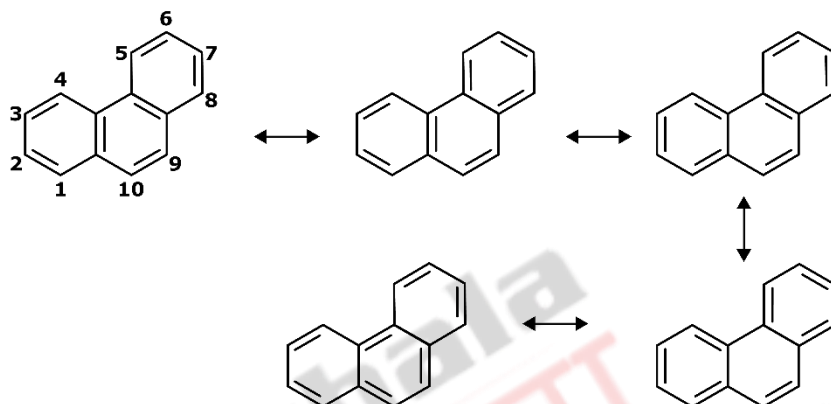


#### 4.1.3. Phenanthrene

Phenanthrene are the polycyclic aromatic hydrocarbons containing three aromatic rings. As discussed earlier it is an *ortho and peri fused ring*. It is composed of one phenyl and one anthracene ring.



Phenanthrene contain 7 C=C bonds in the closed loop. Phenanthrene also contain 14  $\pi$  electrons. So, according to Hückel's Rule ( $n=3$ ) phenanthrene obeys  $(4n+2)\pi$  electrons rule. It shows that phenanthrene is aromatic. The resonance structures of phenanthrene are shown below:



#### ***Resonance energy of fused benzenoid rings***

The resonance energies of these systems increase as the principal canonical form increases. For benzene, naphthalene, anthracene and phenanthrene the principal canonical form formed are two, three, four and five respectively having resonance energy 36,61,84 and 92 kcalmol<sup>-1</sup>. This can be explained by taking the example of naphthalene which contain two benzene rings fused together. So,

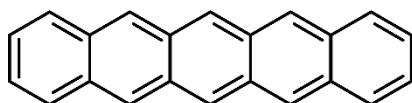
Expected resonance energy of naphthalene =  $2 \times 36 = 72$  kcalmol<sup>-1</sup>

Observed resonance energy of naphthalene = 61 kcalmol<sup>-1</sup>

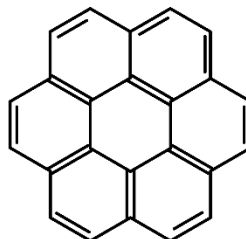
In this case the total number of  $\pi$  electrons are 10 not 12 which indicates that two benzene rings share a pair of electrons and therefore delocalization energy per ring is decreased. This decrease in resonance energy reduces the aromaticity. Due to this reason in general condensed polycyclic hydrocarbons have relatively less aromatic character which result in higher reactivity.



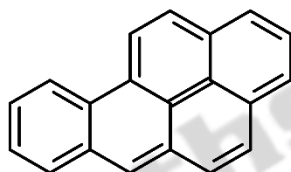
Some other examples of benzenoid fused ring systems



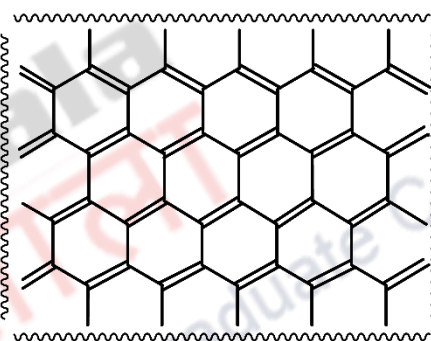
**Pentacene**



**Coronene**

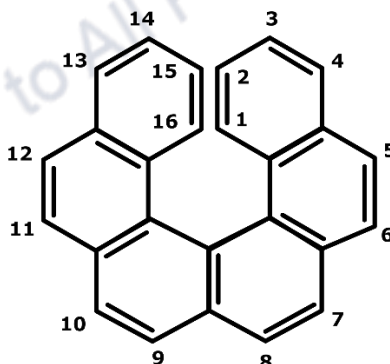


**Benzo[a]pyrene**



**Graphene**

*Essentially an infinite sheet of fused benzene rings*

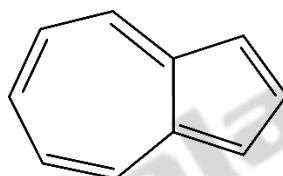


**hexahelicene**

## 4.2. Aromaticity of some non-benzenoid fused rings

### 4.2.1. Azulenes ( $C_{10}H_8$ ). Bicyclo[5.3.0] decapentaene

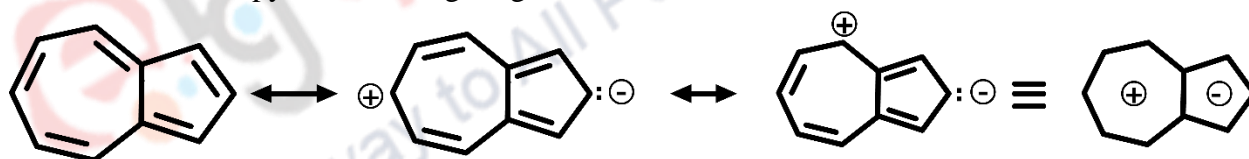
Azulenes is an isomer of naphthalene and one of the few benzenoid structure which show significant aromatic stabilization. It is a deep blue compound with the structure as shown and the name is derived from the Spanish word 'Qzul' meaning Blue. It is a fused cyclo-heptatriene and cyclopentadiene system.



**Azulene**

The compound shows the dipole moment of 0.80. In contrast to the fact that cyclopentadiene and cycloheptatriene independently possess antiaromatic characteristics which are responsible for their instability. But, this fused compound is aromatic and is stable.

Charged resonating structures shows the -ve charge on the five-membered ring, making it equivalent to  $6\pi e^-$  cyclopentadienyl anion and seven membered ring bearing +ve charge is similar to  $6\pi e^-$  tropylium cation, giving it an aromatic character.

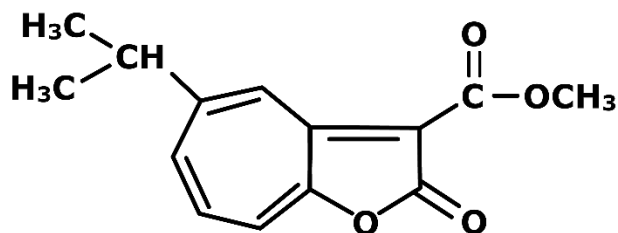


In order to achieve the aromatic stabilization one electron from the seven-membered ring is transferred to the five-membered ring. The main contributing structures to the hybrid show a charge separation which is responsible for the observed dipole moment.

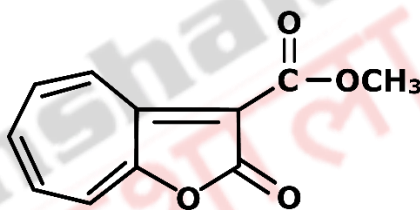
### 4.2.2. Oxaazulanones

Just like azulene oxaazulanones are also made up of one seven membered ring fused with a furan ring. These are also the non-benzenoid compounds aromatic compounds. 5-Isopropyl-3-(methoxycarbonyl)-2H-cyclohepta[b]furan-2-one and 3-(Methoxycarbonyl)-2H-cyclohepta[b]furan-2-one are the examples of oxaazulanones shown below:

a) 5-Isopropyl-3-(methoxycarbonyl)-2H-cyclohepta[b]furan-2-one



b) 3-(Methoxycarbonyl)-2H-cyclohepta[b]furan-2-one



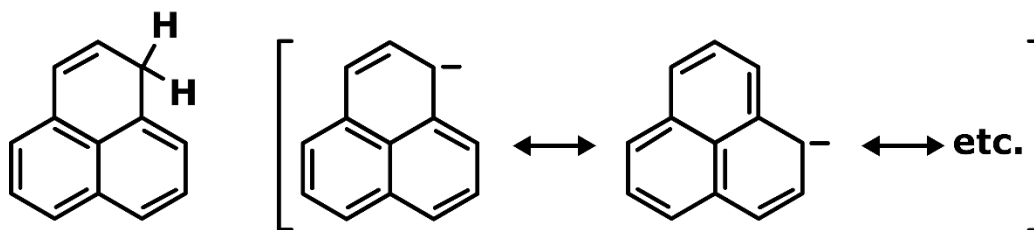
In case of oxazulones, these are aromatic rings but does not contain benzenoid structure. Oxygen in the cyclic structure is  $sp^2$  hybridized because one of the two lone pairs occupies a  $p_z$  orbital, allowing oxygen to contribute to the continuous loop of  $p_z$  orbitals and ultimately completes the closed loop for electron delocalization.

## 5. Other special cases

Not all fused systems can be fully aromatic. This can be completely explained by taking some examples:

### 5.1. Phenalene

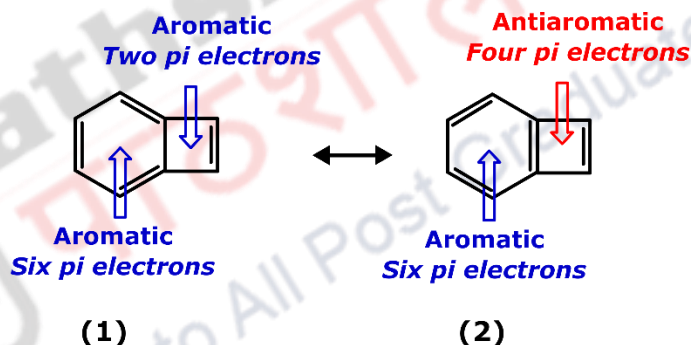
In case of phenalene the double bond cannot be distributed in such a way so that each carbon has one single and one double bond so it is not aromatic. But it is acidic in nature so reacts rapidly with potassium methoxide to give the corresponding anion as shown. The anionic form of phenalene is completely aromatic.



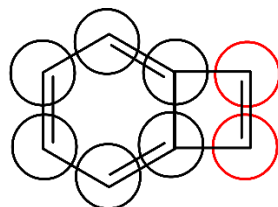
**Phenalene**

### 5.2. Benzo cyclobutadiene

Benzo cyclobutadiene is a fused ring which is composed of one benzene ring and the other is cyclobutadiene. The two structures of benzo cyclobutadiene are shown below



If we consider the two rings of Benzo cyclobutadiene separately as shown in the diagram. In structure (1) benzene ring portion contain six  $\pi$  electron and cyclobutadiene portion contain two  $\pi$  electrons. So, both the rings are aromatic whereas in structure (2) benzene ring portion is aromatic as it contains  $6\pi$  electrons and cyclobutadiene is antiaromatic as it contains  $4\pi$  electrons.

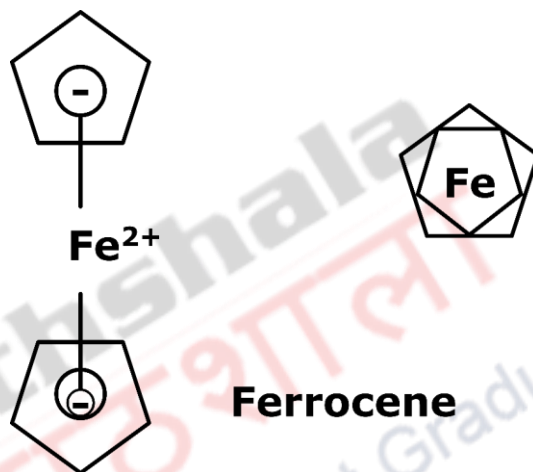


**Benzo cyclobutadiene**

But If we consider a closed loop in Benzo cyclobutadiene it contains total of  $8\pi$  electrons so it does not obey the Hückel's Rule of  $(4n+2)\pi$  electrons. So, it is not aromatic rather it is antiaromatic.

### 5.3. Ferrocene (bis $\eta^5$ - cyclopentadienyl) ions

Molecular formula  $\text{Fe}(\text{C}_5\text{H}_5)_2$  is a metallocene an organometallic compound containing of  $\text{Fe}^{2+}$  ions sandwiched between two cyclopentadienyl anions on the opposite sides and held to each other by  $\pi$  complexation.



There are no C-Fe bonds as the two rings are free to rotate. The x-ray crystallographic studies point towards the staggered conformation of the two rings as the most stable one, in the condensed phase due to crystal packing while the gas phase electron diffraction studies point towards the stable conformation to be eclipsed in the gas phase.

Ferrocene consists of the ion center in the +2 oxidation state (full valence shell of  $18e^-$ , six of its own, present in its five 3d AO'S) and six from each cyclopentadienyl anion (Each cyclopentadienyl ring is then allocated a negative charge bringing the number of  $\pi e^-$  each ring to be six and hence making it aromatic) These twelve electrons (six from each ring) are shared covalently with the metal ion having six d electrons on  $\text{Fe}^{2+}$  with complex attaining stability and aromaticity with 18 electron configuration.

## 6. Summary

- A fused aromatic ring is one which shares one side of the ring. These are monocyclic rings that shares their connecting bond.
- Fused ring systems are classified into two categories depending on the number of atoms and bonds shared by the rings.

**Ortho-fused rings** – If the two rings of the fused system that have only two atoms and one bond is common between the rings.

**Ortho and peri fused rings** – If three atoms are common between the first ring and the other two rings then it is said to be *Ortho and peri fused rings*.

- The criteria for the aromaticity in the fused rings also follows the same rule as applied to the monocyclic systems

1. It is *cyclic, planar* and has *continuous delocalization* of  $\pi$  electrons (electrons in p orbitals) with or without the participation of lone pair(s)/- charge/ + charge (*i.e.*, having electrons or vacant p orbital).

2. The delocalized  $\pi$ -electron cloud must contain a total of  $(4n+2)\pi$  electrons, where n is a whole number (*i.e.*, n =0,1,2,3 and so on).

- Aromaticity of some benzenoid fused rings like naphthalene, anthracene and phenanthrene
- The resonance energy of fused system is generally less than of the number of benzene ring present in that system.
- Aromaticity of some non-benzenoid fused rings like azulene and oxazulones.
- Aromaticity of some special molecules like phenalene, ferrocene and benzo cyclobutadiene.