Huckel Rule and Aromaticity

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Learning Outcomes

- After studying this lecture, you shall be able to:
- Explain Huckel rule
- Learn about the aromaticity of the organic compounds
- Understand the difference between aromatic, non-aromatic and anti-aromatic compounds
- Understand aromaticity in the benzenoid and non-benzenoid ring systems
- Learn about some other special cases

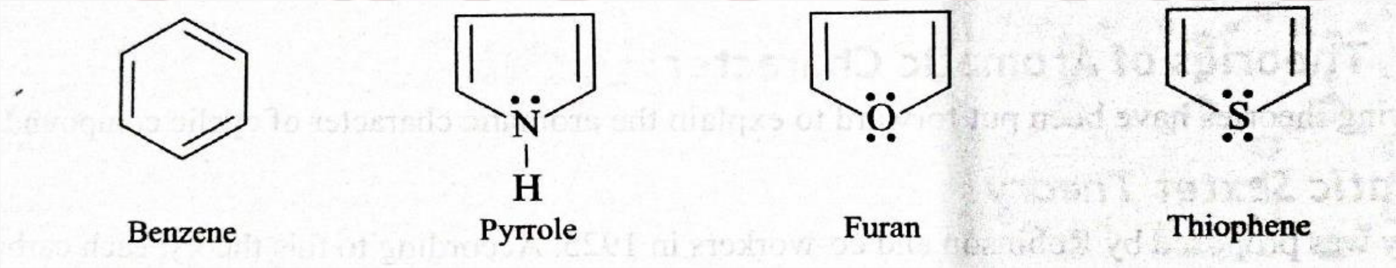
Aromaticity

- The name ‘aromatic’ was originated from the characteristic odor or ‘aroma’ of benzene-like compounds, chemists now have a completely different method of deciding whether a compound is aromatic or not.
- The aromatic compounds apparently contain alternate double and single bonds in cyclic structure and resemble benzene in chemical behaviour.
- They undergo substitution rather than addition reactions.
- The property of exhibiting aromatic character is called ‘**aromaticity’**.
- Aromaticty is, in fact, a property of sp^2 hybridized planner rings in which the p orbitlals (one on each atom) allow cyclic delocalization of π electrons.

Criteria for Aromaticity

In order that a compound may be aromatic in nature it must fulfill the following characteristics-

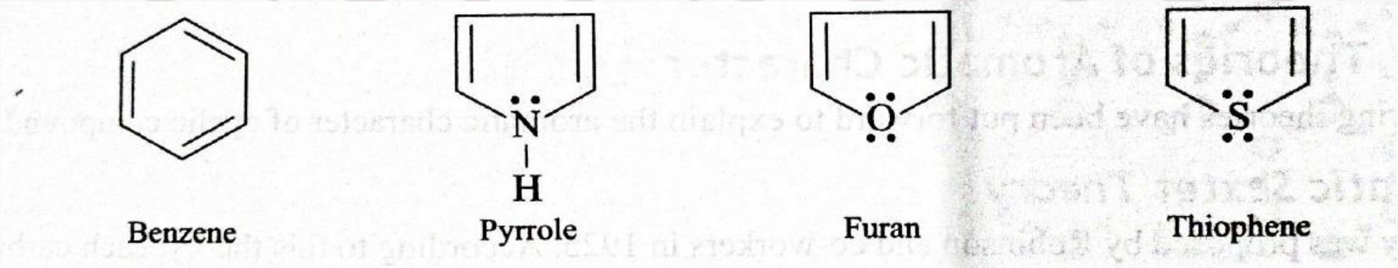
- The compound must be cyclic in nature.
- Planar with uninterrupted cloud of π electrons above and below the plane of the ring.
- It should have 4n+2 π electrons.
- Aromatic character is not confined merely to benzene and the compounds containing one or more benzene rings. There are many examples in which rings do not have six carbon atoms, it could be heterocyclic in nature.



Huckel's Rule

The aromatic character of cyclic compounds can be explained in terms of Huckel's rule. According to this rule

- The cyclic π molecular orbital (electron cloud) formed by overlap of p orbitals must contain 4n+2 π electrons, where n = integer 0,1,2,3 etc. This is known as Huckel's rule.
- Cyclic compounds having 2, 6, 10, 14 , 18, 22 π electrons are expected to show aromatic character.



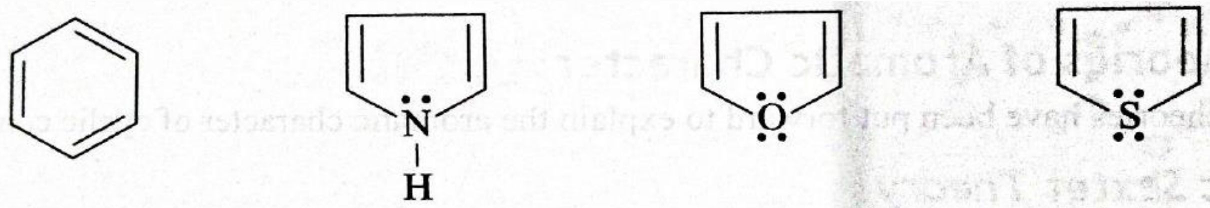
Terms of Aromaticity

Aromatic	Anti-Aromatic	Non-Aromatic
Cyclic	Cyclic	Non-cyclic
All sp^2 hybridized atoms	All sp^2 hybridized atoms	has sp^3 hybridized atoms
Planar	Planar	Non-planar
having 2, 6, 10, 14 , 18, 22 π electrons	having 4, 8. 12, 16, 20 π electrons	

Aromatic character of some cyclic compounds

Monocyclic systems

- All the monocyclic system shown here have a number of π electrons according to Huckel's rule i.e. 6 π electrons in the ring. They are, therefore aromatic in nature.
- In heterocyclic rings 4 π electrons are contributed by 2 double bonds in the ring while 2 electrons are contributed by the hetero atom.

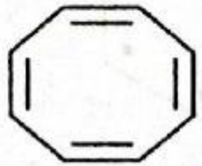


Benzene Pyrrole Furan Thiophene

$4n+2=6$ or $4n=6-2$

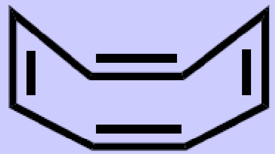
$\therefore 4n=4$ and $n=1$

It may be noted that cyclooctatetraene does not show any aromatic character although the ring has four double bonds in alternate positions. This is because it does not follow Huckel's rule.



The number of π-electrons (8) is not according to Huckel's rule.

$4n + 2 = 8$ equals $4n = 6$ $\therefore n = 1.5$

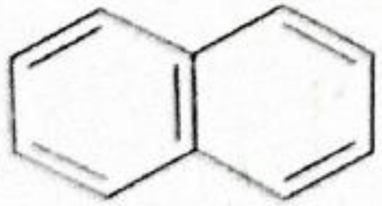


Cyclooctatetraene

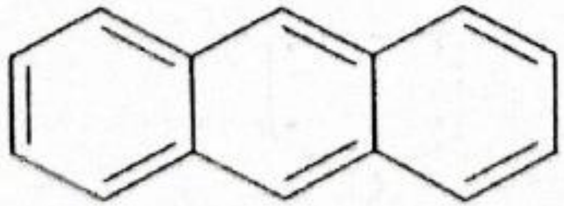
Tub shaped and non planner

Fused ring systems

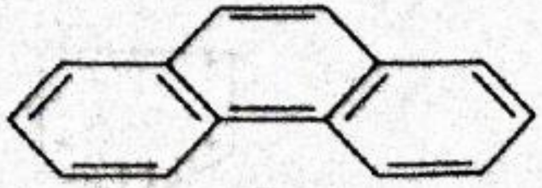
The polar nuclear hydrocarbons such as naphthalene, anthrocene and phenanthrene are aromatic in nature according to Huckel's rule (6 and 14 π electrons).



Naphthalene
(10 π-Electrons)



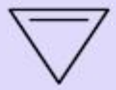
Anthracene
(14 π-Electrons)



Phenanthrene

Aromatic/Antiaromatic/Non-aromatic compounds

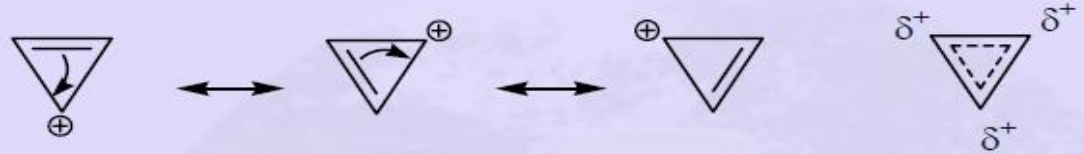
Cyclopropene

1) 

Cyclopropene
2 electrons (n = 0); the delocalization is inturrupted due to sp3 methylene;
Nonaromatic

2) 

Cyclopropenyl cation
2 electrons (4n+2; n = 0); the delocalization of 2 electrons is possible through the empty p orbital;
Aromatic



Resonance contributors in cyclopropenyl cation

Resonance Hybrid

3) 

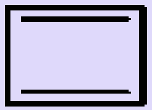
Cyclopropenyl anion
4 electron (even number of pairs; 4n, n = 1);
Theoretically antiaromatic; not stable

Aromatic/Antiaromatic/Non-aromatic compounds

Cyclobutadiene or [4]-annulene*

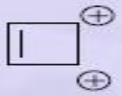
(* Monocyclic hydrocarbons with alternating single and double bonds are called annulenes. A prefix in brackets denotes the number of carbons in the ring)

1)



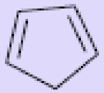
4 electrons (even number of pairs; 4n, n = 1)
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation)
Antiaromatic

2) Cyclobutadienyl dication



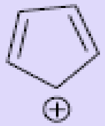
2 electrons (4n+2; n = 0); the delocalization of 2 electrons is possible through the empty p orbitals
Aromatic

Aromatic/Antiaromatic/Non-aromatic compounds

1) 

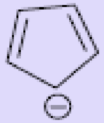
Cyclopentadiene

4 electron system(even number of pairs);
Does not have an uninterrupted ring of p orbital bearing atoms (conjugation);
Nonaromatic.

2) 

Cyclopentadienyl cation

4 electron (even number of pairs; 4n, n = 1;
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation);
antiaromatic

3) 

Cyclopentadienyl anion

6 electron system (4n+2, n = 1), cyclic, planar with conjugation;
Aromatic

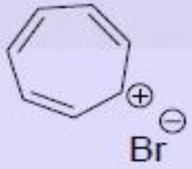
Aromatic/Antiaromatic/Non-aromatic compounds

Benzene [6]-Annulene.

A perfect example of cyclic planar molecule with uninterrupted ring of p orbital bearing atoms; 6 electron system (4n+2, n = 1)
Aromatic

7-membered rings- Cycloheptatriene

Although a 6π electrom system, one of the atoms in the cyclic structure can not contribute a p orbital for conjugation.
Nonaromatic



6π electron system, Cyclic, conjugated, planar with 4n+2 p electrons
Aromatic

References

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Thank You