

Aromaticity :

Aromaticity refers to the class of organic compounds based on the physiological property of odour. Many of these organic compounds resemble benzene in their chemical behaviour particularly in undergoing substitution reactions despite unsaturation in the molecule (and are said to exhibit aromatic character or aromaticity). It was also realised that the molecules of most of these organic compounds possess a benzene ring. Thus the term aromatic was synonymous to benzenoid. However, in recent years it has been pointed out that compounds other than benzene or its derivatives resemble them in chemical behaviour.

Ex: Azulenes, tropolones etc. are called non-benzenoid aromatics.

There are several theories proposed for explaining aromaticity. Some of these are aromatic sextet theory, Valence bond theory, Molecular Orbital Theory and Hückel theory.

Hückel theory:

(Hückel in 1937 carried out M.O calculation for monocyclic systems where each carbon atom contributed one πe^- and came to the conclusion)
It states
~ that stability and aromatic character is based on the presence of $(4n+2)\pi$ electrons in such systems, where 'n' is a positive integer.

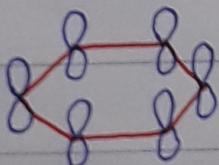
Requirements for Aromaticity:

Four structural criteria must be satisfied for a compound to be aromatic.

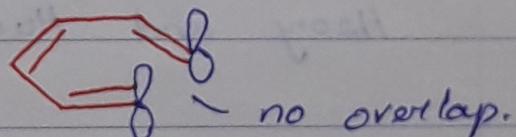
Rule 1 :

A molecule must be cyclic. To be aromatic, each p orbital must overlap with orbitals on two adjacent atoms.

Ex: The p orbitals on all six carbons of benzene continuously overlap, so benzene is aromatic. 1,3,5-hexatriene has six p orbitals, but the two on the terminal carbons can not overlap with each other, hence it is not aromatic.



Aromatic

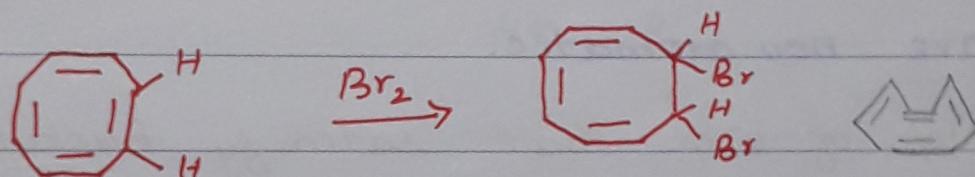


Not aromatic

Rule 2:

All the p orbitals must be aligned so that the πe^- density can be delocalised.

Ex: Cyclooctatetraene resembles benzene in that, it is a cyclic molecule with alternating single and double bonds. But it is tub shaped, however not planar, so overlap between adjacent π bonds is impossible. Hence, cyclooctatetraene is not aromatic, so it undergoes addition reactions like those of other alkenes.



Rule 3:

A molecule must be completely conjugated. Aromatic compounds must have a p orbital on every atom.

Not completely conjugated

A completely conjugated ring.



(a p orbital on every C)
Aromatic

no p orbitals

1,3 cyclohexadiene
Not aromatic



no p orbital.

1,3,5 cyclohepta triene.
Not aromatic.

Rule 4 :

A molecule must satisfy Hückel's rule, and contain a particular number of π electrons.

i.e 1) An aromatic compound must contain $4n+2 \pi$ e⁻s ($n = 0, 1, 2, 3, \dots$)

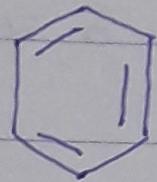
2) Cyclic, planar and completely conjugated compounds that contain $4n\pi$ e⁻s are especially unstable and are said to be antiaromatic.

3) A compound that lacks one or more of the four requirements to be aromatic or antiaromatic are non aromatic.

No. of e⁻s that satisfy Hückel's rule.

n	$4n+2$ AROMATIC	ANTI - AROMATIC	NON AROMATIC
0	2 cyclic	cyclic	Lacking in
1	6 Planar	Planar	1 (or)
2	10 Conjugated	Conjugated	more require
3	14 ($4n+2$) π e ⁻ s	$4n$ e ⁻ s	ments.
4 etc.	18		

Examples for Aromatic / Anti-aromatic / Non-aromatic.



Aromatic

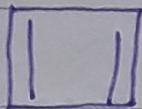
$$3 \times 2 = 6 \text{ e}^- \text{s.}$$

$$4n + 2 = 6$$

$$4n = 6 - 2 = 4$$

$$n = \frac{4}{4} = 1. \text{ - Integer.}$$

Planar, cyclic & conjugated.



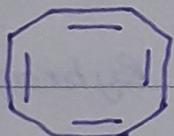
Anti aromatic.

$$2 \times 2 = 4 \text{ e}^- \text{s.}$$

$$4n = 4$$

$$\therefore n = \frac{4}{4} = 1 \text{ integer.}$$

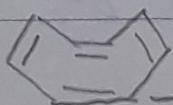
But does not follow $4n + 2$ rule. Hence, it is anti-aromatic.



~~Non~~ aromatic

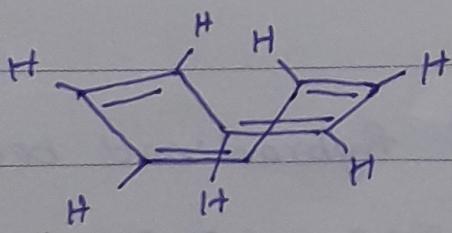
$$4 \times 2 = 8 \text{ e}^- \text{s.}$$

$$4n = 8$$

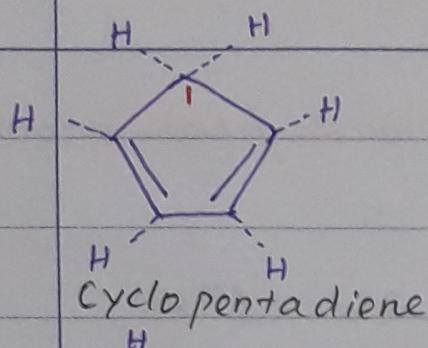


Not
planar.

Non-aromatic



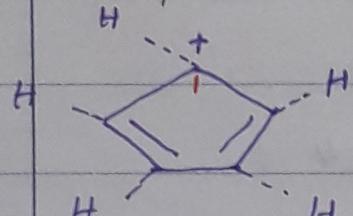
Not planar.



Non-aromatic

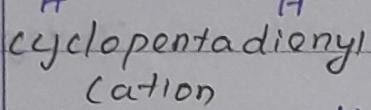
C_1 is not sp^2 hybridised.

π does not have a $\pi^- e^-$.



Anti-aromatic

$2 \times 2 = 4 \pi^- e^-$ s.

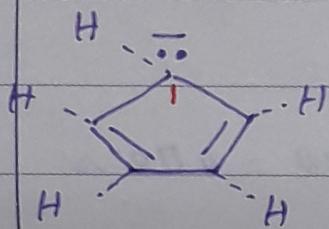


C_1 does not have a $\pi^- e^-$.

$$\text{Hence, } 4n = 4$$

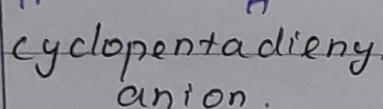
p orbital is vacant

$$n = \frac{4}{4} = 1.$$



Aromatic

C_1 has 1 $\pi^- e^-$.

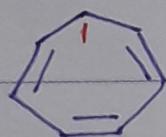


$$\text{Hence } 3 \times 2 = 6 \pi^- e^-$$
s.

$$4n + 2 = 6$$

$$4n = 6 - 2$$

$$n = \frac{4}{4} = 1.$$

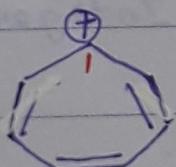


Non-aromatic

C_1 is not sp^2 hybridised and

cycloheptatriene

does not have a $\pi^- e^-$.



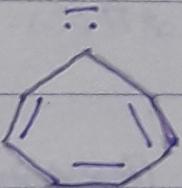
C_1 is not sp^3 hybridised because,

it has lost 2 e^- s. $\therefore 3 \times 2 = 6 \pi^- e^-$ s.
empty p orbital. Conjugation is possible.

$$4n+2 = 6$$

$$4n = 6-2$$

$$n = \frac{4}{4} = 1$$



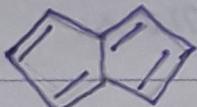
Anti-aromatic

$$4 \times 2 = 8 e^-s$$

cycloheptatrienyl : $4n = 8$

anion.

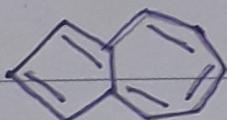
$$n = \frac{8}{4} = 2$$



Anti-aromatic. $4 \times 2 = 8 e^-s$

Pentalene

$$4n = 8 \quad \therefore n = \frac{8}{4} = 2.$$



Aromatic

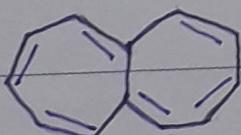
$$5 \times 2 = 10 e^-s.$$

Azulene

All c atoms are conjugated.

$$4n+2 = 10$$

$$n = \frac{10-2}{4} = 2.$$



Anti-aromatic

$$6 \times 2 = 12 e^-s.$$

All c atoms are conjugated.

$$4n = 12$$

$$n = \frac{12}{4} = 3.$$



Cyclopropene

Non-aromatic.

$C_1 - sp^3$ hybridised. Delocalisation

is not possible. Only $1 \times 2 = 2\pi e^-s$.



Cyclopropenyl
cation.

Aromatic. $1 \times 2 = 2\pi e^-s$.

$$4n+2 = 2$$

$$n = 0. \quad (4 \times 0 + 2 = 2)$$

Delocalisation of πe^-s possible, through empty P orbital of C.



Anti-aromatic. $2 \times 2 = 4\pi e^-s$.

$$4n = 4$$

$$n = \frac{4}{4} = 1. \quad (\underline{\text{even no.}} \text{ of } \underline{\text{pairs}})$$

Ex.

cyclic compds. like Furan
— O has 2 lone pairs — i.e.
—

→ 2nd v

Hence furan has 3 e⁻ pairs for

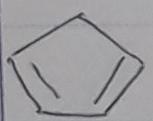
$$4n+2 = 6$$

$$4n = 6-2 = 4$$

$$n = 4/4 - 1 \text{ arc}$$



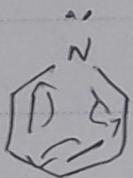
- Thiophene - Aromatic.



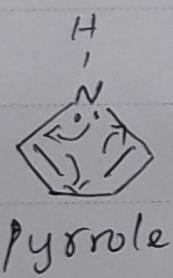
- Not fully conjugated, top C is sp^3 hybridized
- Non-aromatic.



- Anti aromatic, top C is not sp^2 hybridised
contains lone pair. Hence delocalization is
possible. $4n = 4 e^-$
 $n = 4/4 = 1$



6 e^- s Aromatic.. Pyridine does not use lone pair.



~~lone pair~~ uses its lone pair for resonance.

How to find out, the atom participating in
resonance?

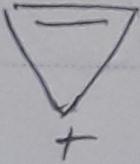
If an atom has a π bond, it means it is
participated in resonance. So, no need to count lone pair.

If the atom is not able to participate unless it
supplies its own e^- , it must provide its own
 e^- s to participate in resonance.



- Thiophene.

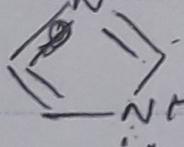
For resonance it has to use one lone pair
Other pair will be left out free
Aromatic $6 \pi e^-$ s.



$$4n+2 = 2 \quad \text{Aromatic.}$$

$n=0.$

... not participating - lone pair.

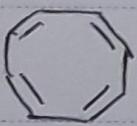


participating. $6\pi e^-s$ Aromatic.
Imidazole.



$10\pi e^-s$

Aro



$8\pi e^-s$

Anti



$6\pi e^-s$

Aro