AROMATICITY.

Although the name 'aromatic' was originated from the characteristic odour or 'aroma' of benzene like compounds, chemists now have a completely different method of deciding whether a compound is aromatic or not. Based on the analysis of a number of compounds with unusual resonance stabilization energies, the following characteristics have been accepted as criteria for aromaticity.

- It must be cyclic,
- Every atom in the ring must be conjugated. Each atom in the ring must be sp^2 hybridised.
- The molecule must be flat. (planar).
- The molecule must have $[4n+2]\ \pi$-es. (Huckel's rule)

  where, $n = 0, 1, 2, 3 \ldots$

Condition 1: The molecule must be cyclic.

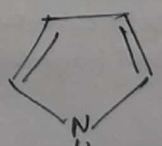
Determine if a molecule is cyclic. If yes move to 2nd condition. If there's no ring, it's not cyclic. (ie) to be aromatic each p-orbital must overlap with orbitals on two adjacent atoms.

Eg: (Z)-1,3,5-hexatriene has the same no of π-bonds (ie) π-es as benzene, but isn't aromatic.

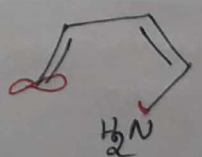
As it has no ring - no aromaticity.

Cyclic
Benzene
Aromatic

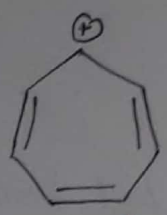
acyclic
(Z)-1,3,5-hexatriene
Not aromatic



cyclic
Pyrolle.
Aromatic



acyclic.
Not aromatic.



cyclic
Tropyllium ion
Aromatic

acyclic
Not-aromatic.

cyclohexene

tetrahydrofuran.

not aromatic

2) Every atom in the ring must be conjugated.

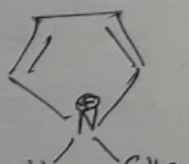
- Every atom in the ring must have an available p orbital
- Every atom in the ring must be able to participate in resonance.
- p-Orbital may be a part of a π-bond, also can bear a lone pair of e⁻s, a radical (or) may be an empty orbital.

i.e., Every atom around the ring must be capable of conjugation with each other.

- Each atom in the ring must be sp^2 hybridised

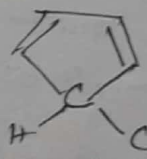
Eg:

Aromatic
(conjugation)

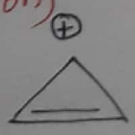


Not aromatic
(Nitrogen is not conjugated)
sp3

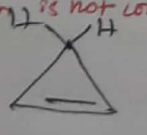
Aromatic
[all atoms are in conjugation



Not aromatic
[C - sp3 hybridised)
No conjugation



Aromatic
(conjugation)



Not aromatic
(sp3 hybridised, no conjugation)

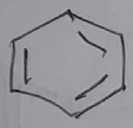
3) The Molecule Must have $[4n+2]$ π-e⁻s (Hückel's Rule)

$4n+2$ is a formula that you apply to see if your molecule is aromatic.

The condition that aromatic molecules must have $[4n+2]$ π-e⁻s is called as Hückel's rule. ($n=0,1,2,3$ ...)
[It should have 2, 6, 10, 14, 18, 22... π-e⁻s]

Hence the molecule which are cyclic, conjugated must have correct no of π-e⁻s.

Eg: Benzene



- cyclic
- conjugated
- Has 6 π-e⁻s.
- $n = 1$, $4n+2 = 6$ π-e⁻s.
  $4(1)+2 = 6$ π-e⁻s.

Aromatic

Cyclooctatetraene.

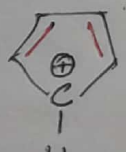
- cyclic
- conjugated.
- Has 8 π-e⁻s.
- $4n+2 \neq 8$ π e⁻s.

But it doesn't not satisfy.

Not aromatic.

6 π-e⁻s

Aromatic (cyclopentenyl anion)

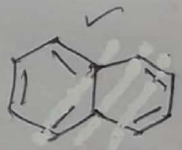


4 π e⁻s

non Aromatic (Cyclopentenyl cation)

4 π-e⁻s

Non-aromatic (cyclopropenyl cation)



10 π-e⁻s

Aromatic (Annulene)

4 π-e⁻s.

Non-aromatic cyclobutadiene

4 π e⁻s

Non-aromatic cyclopropenyl anion.

According to Hückel's rule a close system with π-e⁻s not in accordance with $(4n+2)$ π should be anti-aromatic. [Even though they are cyclic, have conjugation i.e) have resonance, they do not satisfy $(4n+2)$ π-e⁻ rule].

Generally System containing $4n$ π-e⁻s are ~~non-aromatic~~ & anti-aromatic

4). The Molecule must be Flat (planar)

Aromaticity is such a stabilizing property (~ 20-36 kcal/mol) that generally a molecule should be

- cyclic
- conjugated
- has [4n+2] pi electrons.

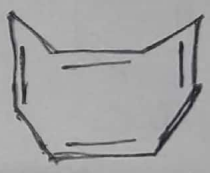
will also be flat (planar).

Eg: Benzene.

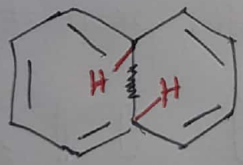
- cyclic
- conjugated
- 6 π-es.
- planar.

Aromatic.

Cyclooctatetraene.



- cyclic
- conjugated
- 8 π es (4n π es - anti-aromatic)
- Non-planar (tub-shaped) (non-aromatic)



[10] Annulene.

- cyclic
- conjugated
- 10 π-es. [4n+2] π-es satisfies.
- Non-planar.

Still Non-aromatic. (as it is non-planar due to two trans double bonds does not have a planar conformation, due to interaction between two H-atoms.

Hence compounds which are cyclic, conjugated, satisfies (4n+2) π-es rule, but are not planar — Non aromatic.

Summary:

For a compound to be

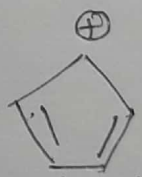
- Aromatic → cyclic, conjugated, satisfies $(4n+2)\pi$ e⁻s and planar.
- Anti aromatic → cyclic, conjugated, does not satisfy Huckel's rule ie) $(4n+2)\pi$ e⁻s and has $4n\pi$ e⁻s.
- Non aromatic → Cyclic, conjugated, satisfies $(4n+2)\pi$-e⁻s but are not planar (or) A compound that lacks one (or) more of above four requirements to be aromatic (or) antiaromatic are non-aromatic.

Cyclopropene (Non-aromatic) (No-conjugation)

Cyclopropene Cation (aromatic) (2π-e⁻s)

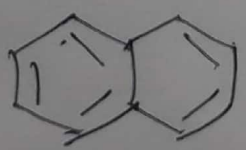
Cyclopropene anion. (Anti-aromatic). (4π e⁻s) [do not obey Huckel's rule]

Cyclopentadiene (Non-aromatic) (4π e⁻s) (no-conjugation)

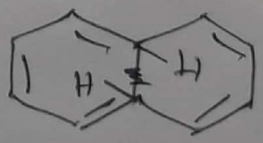


Cyclopentadienyl Cation. (Anti-aromatic) 4π e⁻s, has conjugation. ↓ donot obey Huckel's rule.

Cyclopentadienyl anion. 6π e⁻s. (aromatic)



Annulene. (Aromatic)



[10] Annulene. (Non-aromatic).
- Non planar.