

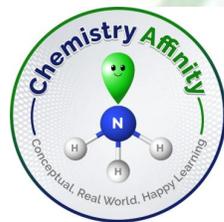
Fundamental Concept

  Organic Chemistry

Aromatic Non-aromatic Antiaromatic

Designed by Dr. Anuradha Mukherjee

Chemistry Affinity
Conceptual, Real world and Happy Learning

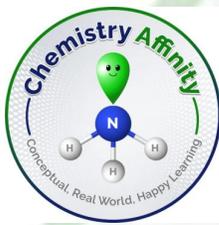


Characteristics of Aromatic Compound

Aromaticity is a property of some unusually stable organic molecules such as benzene

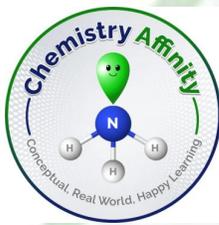
Aromatic molecules have

- (i) have an extremely high resonance energy (36 kcal/mol for benzene)**
- (ii) undergo substitution rather than addition reactions**
- (iii) have delocalized pi-electrons**



Rules of Aromaticity

- (i) it must be cyclic and planar**
- (ii) every atom in the ring must be conjugated**
- (iii) the molecule must have $[4n+2]$ pi electrons**



Rule 1: The Molecule Must be Cyclic

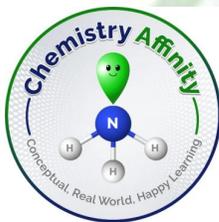
Determine if a molecule is cyclic

Is there a ring?

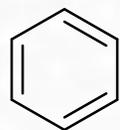
If yes, move to check second rule

If no

Ignore it



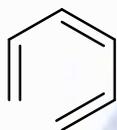
RULE 1: THE MOLECULE MUST BE CYCLIC



Benzene

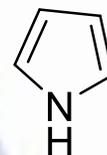
Cyclic

Aromatic



hexa-1,3,5-triene

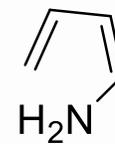
Acyclic



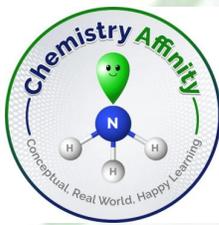
pyrrole

Cyclic

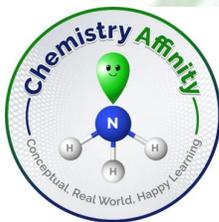
Aromatic



Acyclic

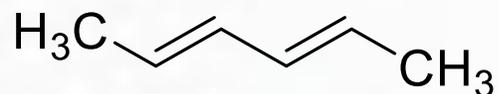


Rule 2: Every Atom in the Molecule Must Be Conjugated



What is conjugation?

The word "conjugation" is derived from a Latin word that means "to link together"



Conjugation



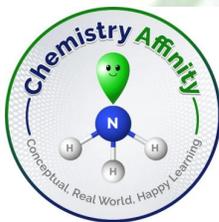
Conjugation



Non-Conjugation

[https://chem.ucalgary.ca/courses/351/Carey5th/Ch10/ch10-1-](https://chem.ucalgary.ca/courses/351/Carey5th/Ch10/ch10-1-1.html#:~:text=The%20word%20%22conjugation%22%20is%20derived,atoms%20(e.g.%20C%3DC)

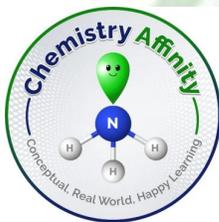
[1.html#:~:text=The%20word%20%22conjugation%22%20is%20derived,atoms%20\(e.g.%20C%3DC\)](https://chem.ucalgary.ca/courses/351/Carey5th/Ch10/ch10-1-1.html#:~:text=The%20word%20%22conjugation%22%20is%20derived,atoms%20(e.g.%20C%3DC)



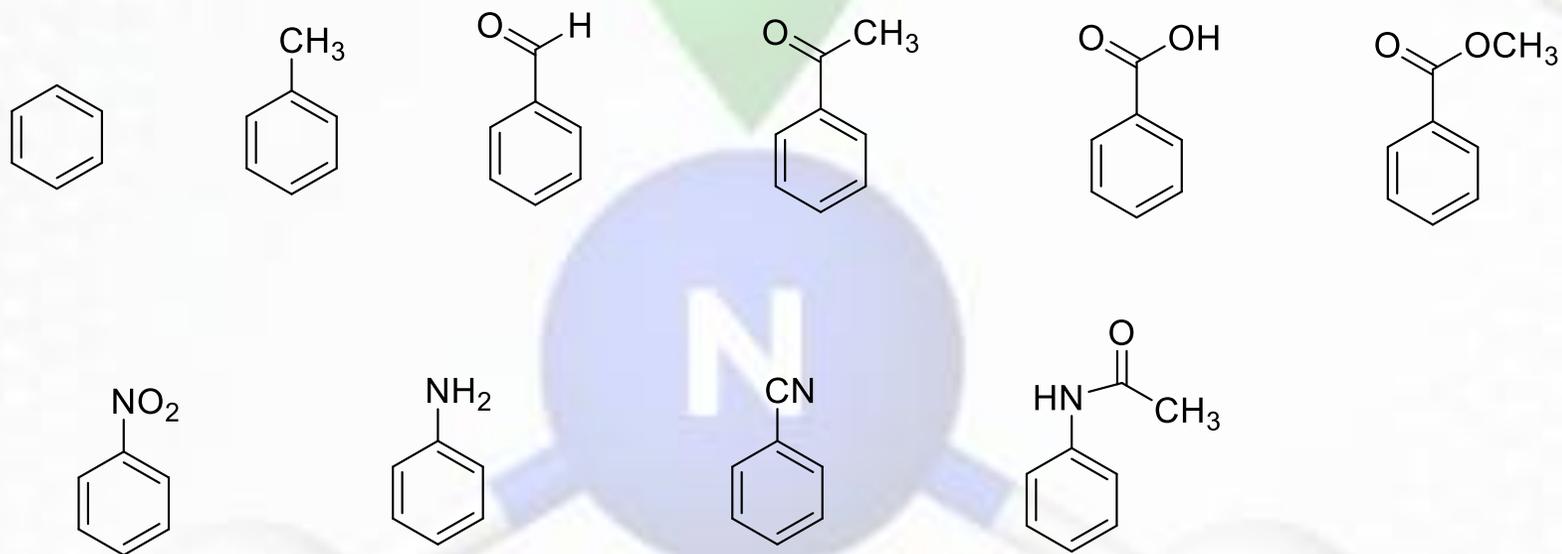
Rule 2: Every Atom in the Molecule Must Be Conjugated

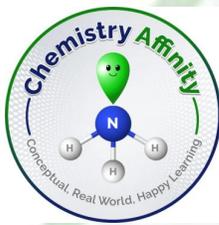
Being cyclic isn't a sufficient condition for aromaticity

In order for aromaticity to exist, there must be a continuous ring of p-orbitals inside the ring that build up cyclic “pi system” or “conjugated system”

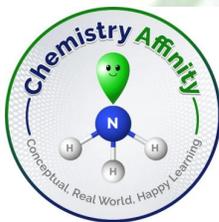


Aromatic compounds are conjugated





Rule 3: $[4n+2]\pi$ Electrons: Huckel's Rule

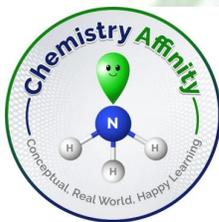


Huckel's Rule

$4n+2$ is a formula that tells the numbers in the magic series. The "magic series" is: 2, 6, 10, 14, 18, 22.....

("n" = 0, 1, 2, 3, 4...)

If the pi electron value matches any number in this series then the molecule is considered as aromatic.



[4n+2]π Electrons: Huckel's Rule

The “magic series” is: 2, 6, 10, 14, 18, 22.....

(“n” = 0, 1, 2, 3, 4...)

Those values of “n” have nothing to do with molecules.

We are just using them to generate the series

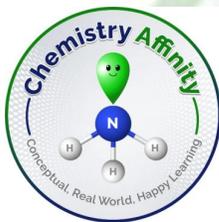
$$n = 0, 4n+2 = [4 (0) + 2] = 2$$

$$n = 1, 4n+2 = [4 (1) + 2] = 6$$

$$n = 2, 4n+2 = [4 (2) + 2] = 10$$

$$n = 3, 4n+2 = [4 (3) +2] = 14$$

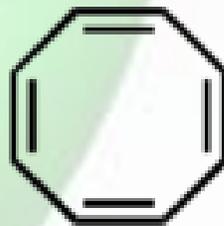
The numbers in this “magic series” are referred as “Hückel Numbers” after Erich Hückel, who proposed this rule in 1931



Benzene

- cyclic
- conjugated
- 6 π electrons

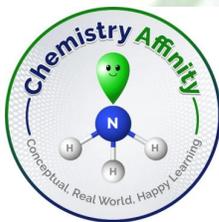
Aromatic



Cyclooctatetraene

- cyclic
- conjugated
- 8 π electrons

Not Aromatic



**Which lone pair of heteroatom
in heterocyclic compounds
take part in resonance or
conjugation?**

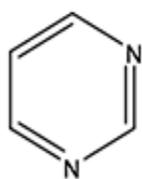


Heterocyclic Compounds

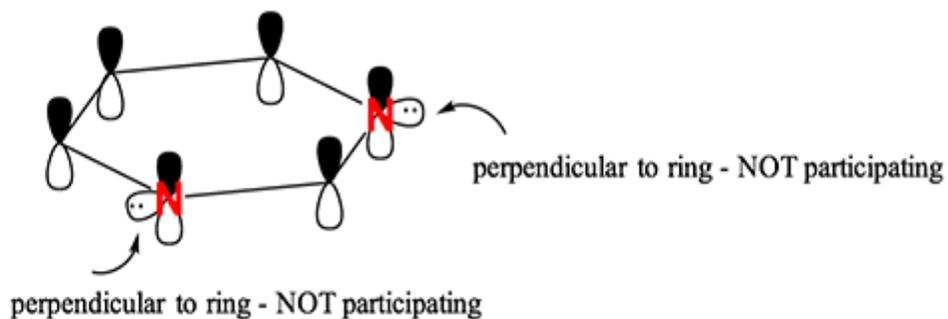
What about when atoms with lone pairs of electrons are involved in a cyclic structure?

If the hetero atom is already participating in the pi-bond forming in the ring, then the lone pair of electrons are perpendicular to the ring and therefore are NOT participating to aromaticity

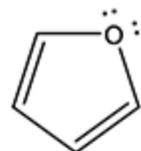
That means if the heteroatom has adjacent double bond, then the LP does not take part in resonance



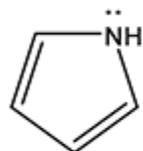
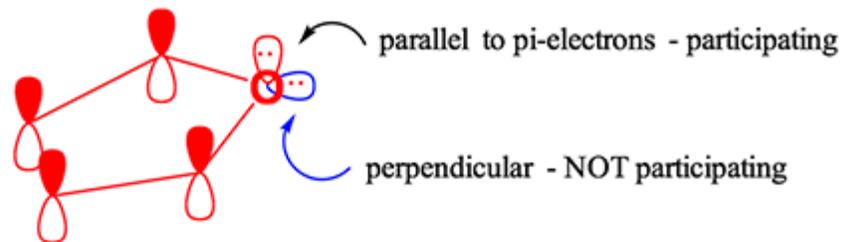
pyrimidine



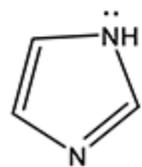
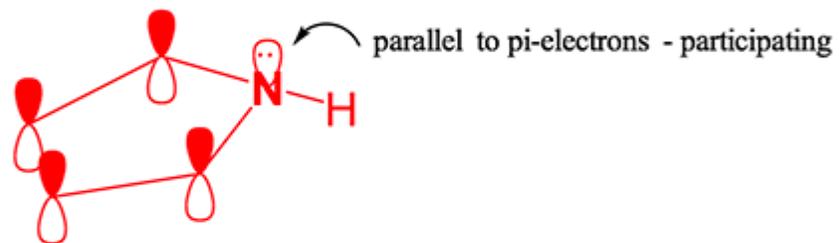
Example: pyrimidine: Both nitrogens are already contributing to the pi-bond ring and therefore, the lone pairs of electrons are not accessible for resonance



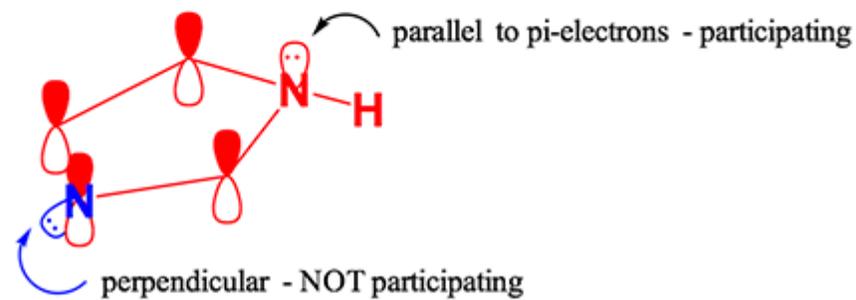
furan

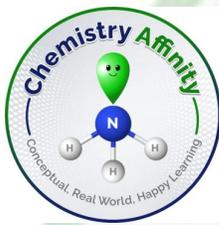


pyrrole



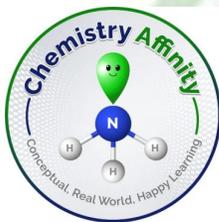
imidazole





Lone pair on heteroatom in heterocyclic compounds decides whether the heterocyclic compound behave as base or not

Let's Explain with examples



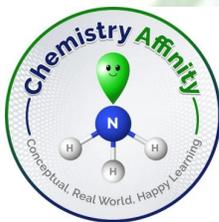
Which one is more basic pyridine or pyrrole?



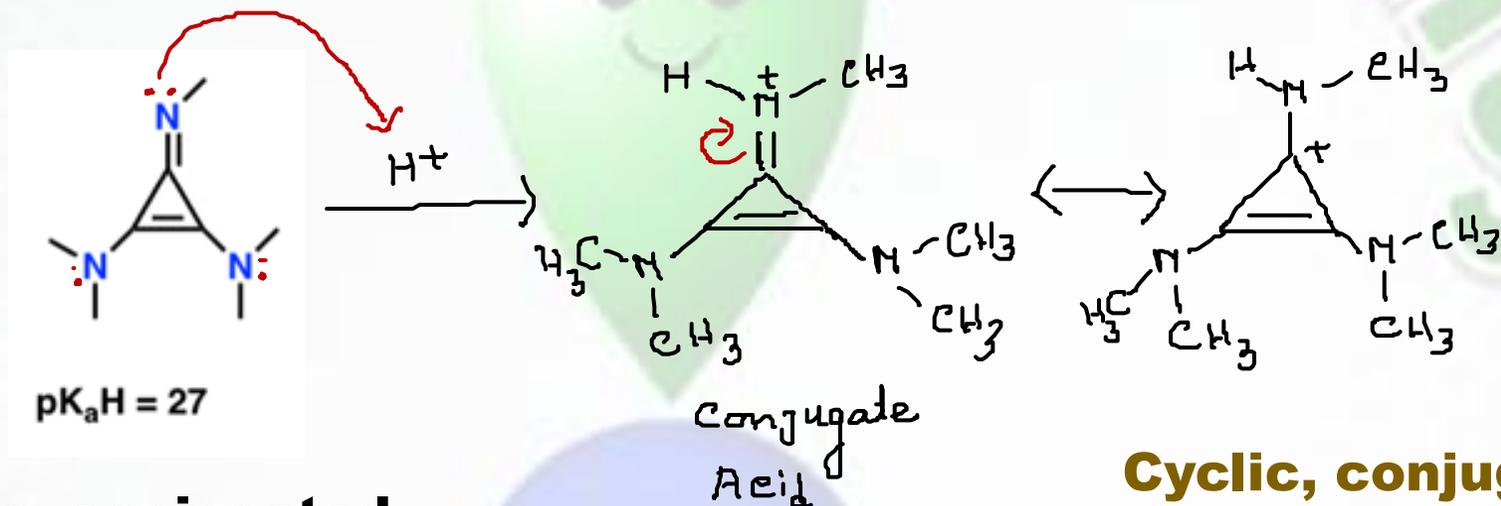
If pyrrole donates electron, it loses aromaticity, so it does not behave as base

Pyrrole nitrogen LP can take part in resonance but pyridine nitrogen LP does not

Therefore, pyridine nitrogen LP is available for donation and thus behaves as base



Why the following compound is basic?



**Cyclic, conjugated
and 4π electrons,
so antiaromatic**

**Cyclic, conjugated
and 2π electrons,
[($4n+2$) π] so aromatic**

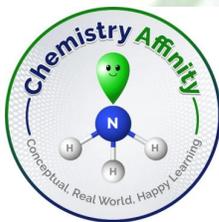
Due to protonation, it gets aromaticity, thus behaves as a stronger base

Aromatic

And

Antiaromatic



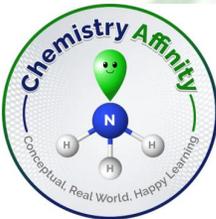


Key Factors: Antiaromaticity

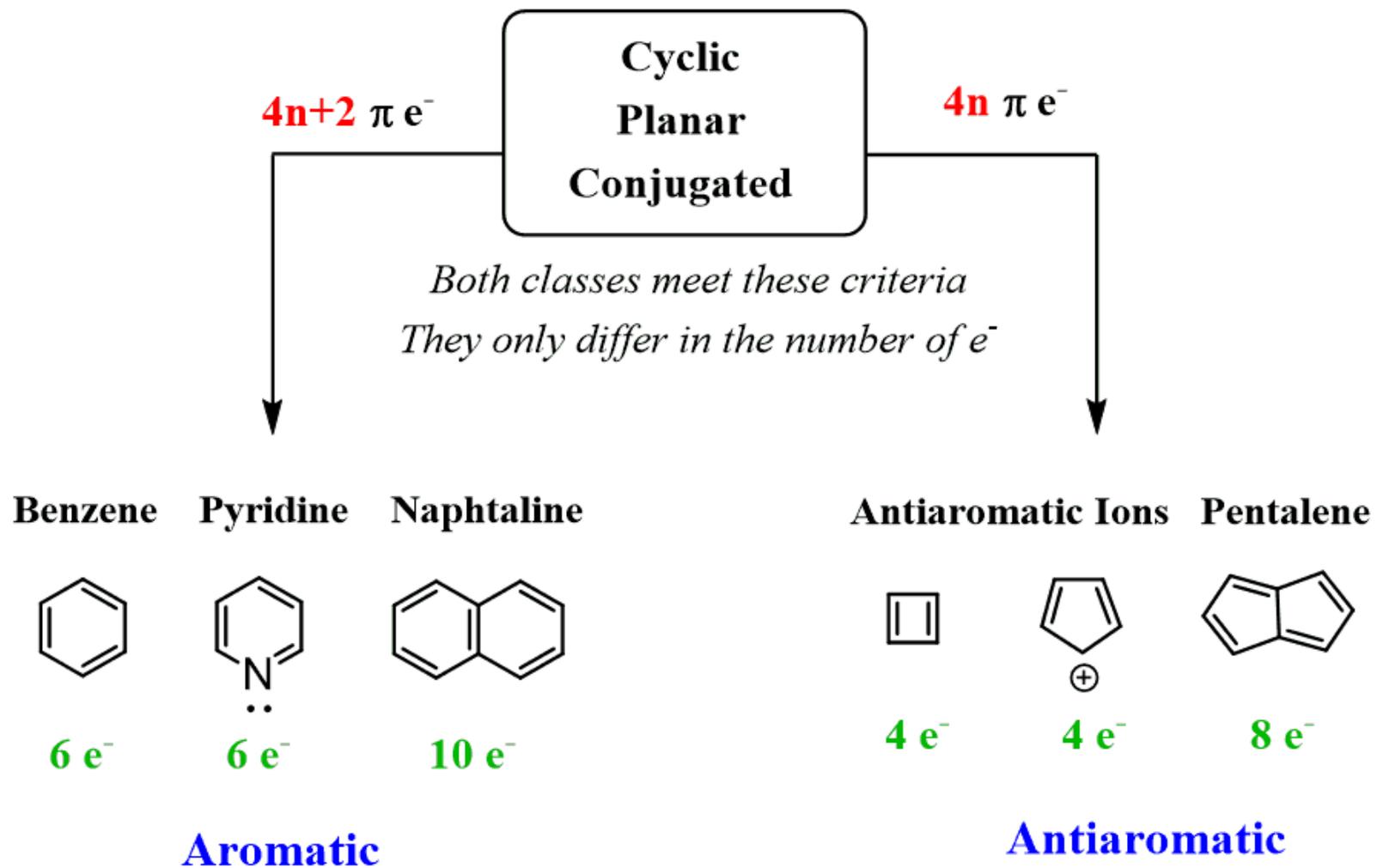
- 1. The molecule must be cyclic and planar**
- 2. The molecule must be conjugated**
- 3. The molecule must have $4n$ pi electrons
(4, 8, 12, 16...) pi electrons**

Contrast this with aromatic molecules, which must have $(4n+2)$ pi electrons (2, 6, 10, 14, 18...)

Antiaromatic compounds are *unusually* unstable



Classification of Aromatic and Antiaromatic Compounds

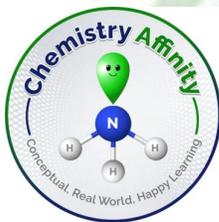


Key Difference: Aromatic Vs Antiaromatic

Antiaromatic is closed to the aromatic compounds as these also have cyclic, planar and conjugated structures

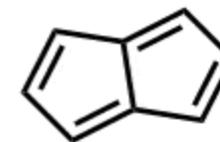
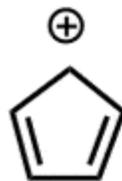
But these molecules have $4n$ pi electrons instead having $4n+2$ electrons

This makes antiaromatic compounds very rare and energetically unfavorable



Examples: Antiaromatic

- Each of these unusually unstable molecules is cyclic, conjugated, and flat.
- The number of Pi electrons is 4 or 8 ($= 4n$)



Pi-electrons

4

4

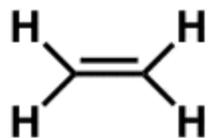
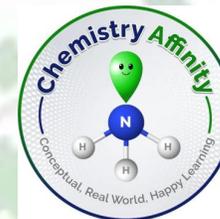
4

4

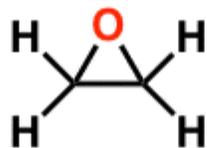
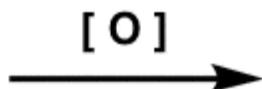
8

We call this unusual instability **anti-aromaticity**

<https://www.masterorganicchemistry.com/2017/03/27/antiaromaticity/>



Ethene

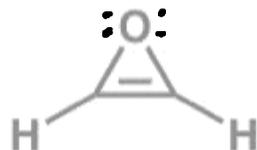


Ethylene oxide

annual production: 15 million tons



Acetylene



Antiaromatic: 4π electrons

Acetylene oxide
(Oxirene)

Has never been observed
(antiaromatic)

Some Elusive Three-Membered Rings



Oxirene

(never observed)



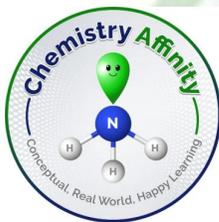
1H-Azirene

(never observed)



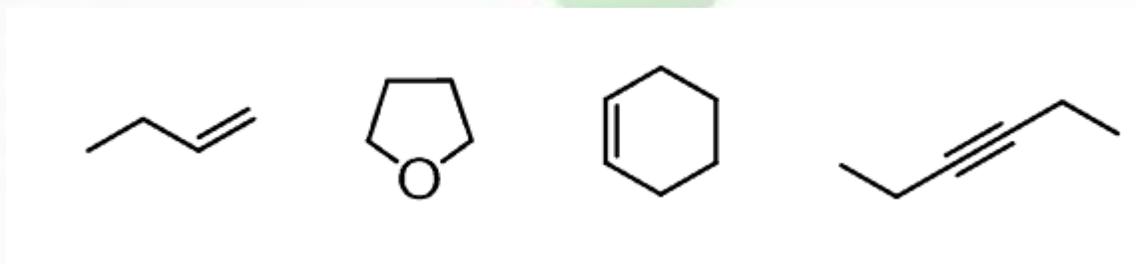
Thiirene

(never observed)



Non aromatic

There is another set of molecules which are called non aromatic

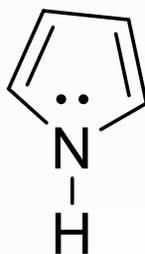


if any of these factors; cyclic, planar, fully conjugated does not match – the compound is said to be nonaromatic

<https://www.chemistrysteps.com/identify-aromatic-antiaromatic-or-nonaromatic-compounds/>



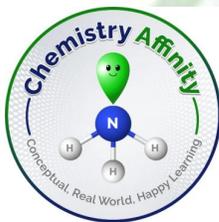
Is Pyrrole aromatic or non-aromatic or anti-aromatic?



1H-pyrrole

**Cyclic, planar,
Conjugated
and 6 π electrons
[(4n+2) π]**

Aromatic



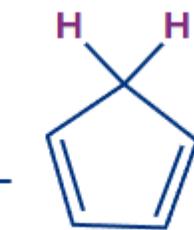
Predict Non-aromatic or Antiaromatic or Aromatic

Cyclic, conjugated and 4π electrons:

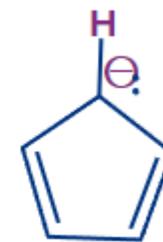
Cyclopentadienyl cation: **Antiaromatic**



Cyclopentadienyl cation



Cyclopentadiene



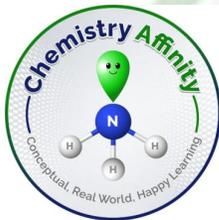
Cyclopentadienyl anion

Cyclic, conjugated and 6π electrons:

Cyclopentadienyl anion: **aromatic**

Cyclic, Non-conjugated and 4π electrons:

Cyclopentadiene: **Non-aromatic**



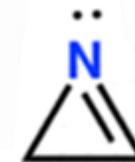
Predict Non-aromatic or Antiaromatic or Aromatic



[1H]-Azirine

**Cyclic,
Conjugated
and 4π electrons:**

Antiaromatic



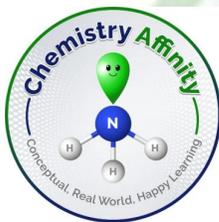
[2H]-Azirine

**Cyclic but non-conjugated
as the LP does not take
part in resonance**

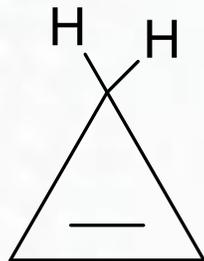
4π electrons:

Non-aromatic

Conclusion: [2H]-Azirine is found but [1H]-Azirine is not formed

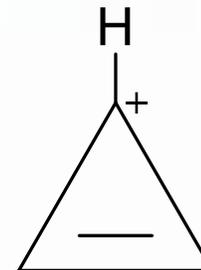


Predict Non-aromatic or Antiaromatic or Aromatic



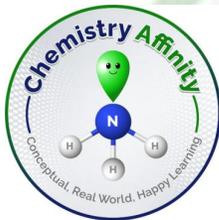
Cyclic, Non-Conjugated
and 2π electrons:

Non-aromatic

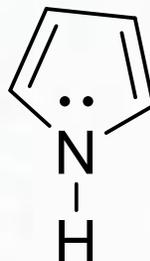


Cyclic, planar, Conjugated
and 2π electrons
[$(4n+2)\pi$]

Aromatic

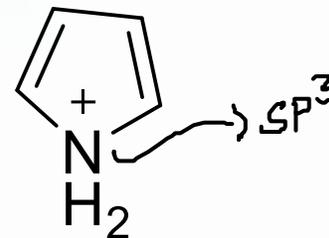


Predict Non-aromatic or Antiaromatic or Aromatic



**Cyclic, Conjugated
and 6π electrons
[($4n+2$) π]**

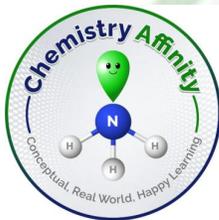
Aromatic



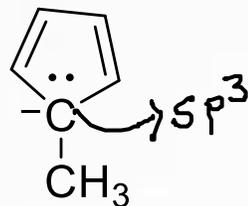
**Cyclic, Conjugated
and 4π electrons**

Antiaromatic

This compound shows aromaticity but nitrogen part of the ring is sp^3 hybridized. This type of aromatic compound is also known as **homoaromatic**



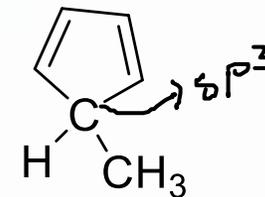
Predict Non-aromatic or Antiaromatic or Aromatic



**Cyclic, Conjugated
and 6π electrons
[($4n+2$) π]**

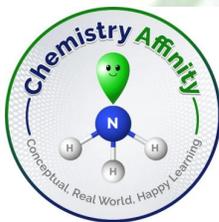
Aromatic

This compound shows aromaticity but one of the carbon which is a part of the ring is sp^3 hybridized. This type of aromatic compound is also known as **homoaromatic**

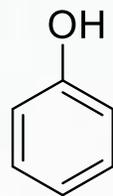


**Cyclic, Non-conjugated
and 4π electrons**

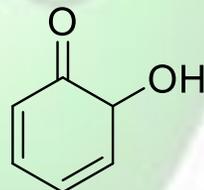
Non Aromatic



Why phenol does not undergo keto form?



Phenol

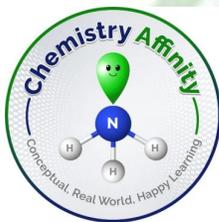


Keto-enol form of phenol

**Cyclic, planar
conjugated, 6π
electrons, so
aromatic**

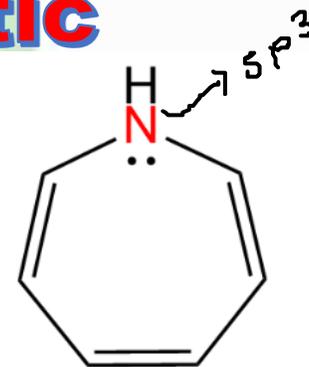
**Cyclic, non-
conjugated, 6π
electrons, so
non-aromatic**

Conclusion: Phenol cannot undergo keto enol tautomerism

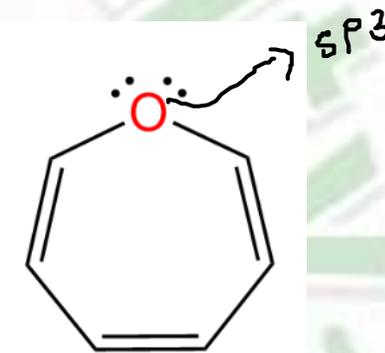


Predict Non-aromatic or Antiaromatic or Aromatic

Lone pairs of electrons present in sp^3 orbital which can take part in conjugation



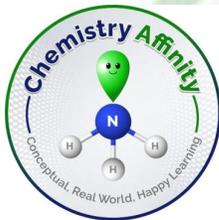
Azepine



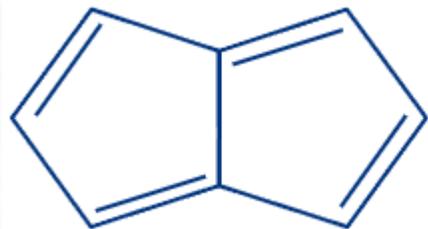
Oxepin

These molecules have 8 π electrons so we can be considered them as antiaromatic

These molecules are known as antiaromatic

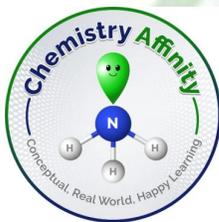


Predict Non-aromatic or Antiaromatic or Aromatic

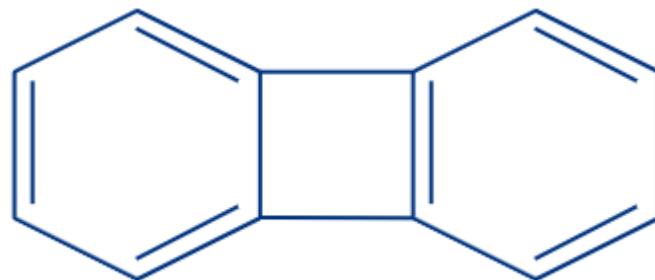


Two fused cyclopentadiene rings make up the polycyclic hydrocarbon known as pentalene.

**It contains $4n\pi$ electrons (8π electrons), where $n = 2$
It is antiaromatic compound**

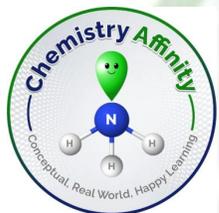


Predict Non-aromatic or Antiaromatic or Aromatic

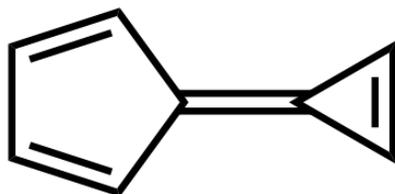


A polycyclic hydrocarbon called biphenylene which is made up of two benzene rings connected by two bridging bonds (instead of a typical ring fusion), resulting a 6-4-6 arene system

12 pi electrons ($4n$ pi electrons) : **Antiaromatic**

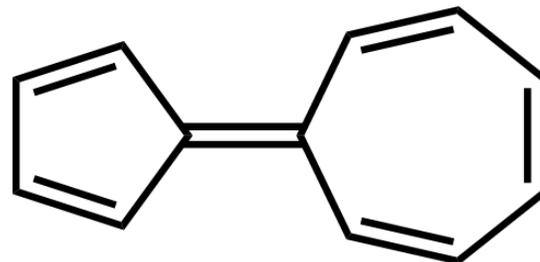


Would you classify the following two molecules as aromatic or not? Explain your answer.



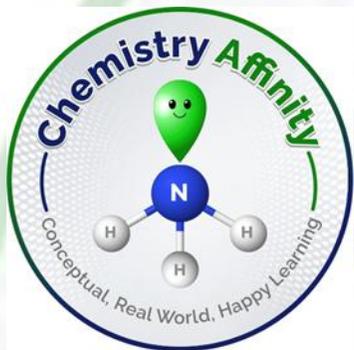
**Cyclic, Conjugated
and 8π electrons
[$4n\pi$]**

Anti aromatic

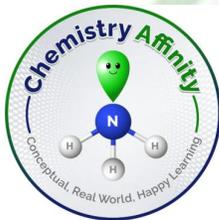


**Cyclic, Conjugated
and 12π electrons
($4n\pi$)**

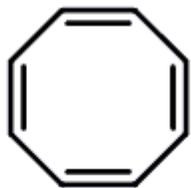
Anti aromatic



Interesting Molecules: Cyclooctatetraene And [10]Annulene



Cyclooctatetraene looks antiaromatic but avoids antiaromaticity. How??



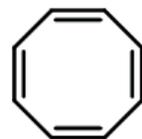
cyclooctatetraene

1. **cyclic and planar**
2. **conjugated**
3. **$4n\pi$ electrons: 8π**

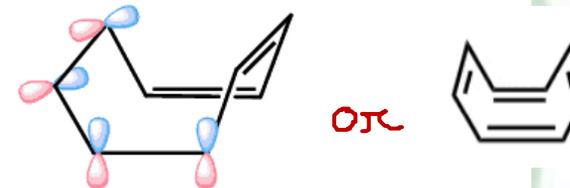
A perfect candidate to be named antiaromatic

It adopts a geometry that is not planar (flat):

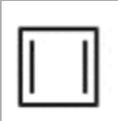
Cyclooctatetraene is not planar - Nonaromatic



Cyclooctatetraene
Nonaromatic

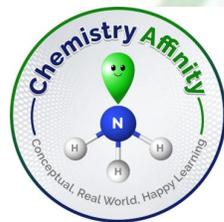


p orbitals of adjacent double bonds **cannot overlap.**

Aromatic	Antiaromatic	Non-aromatic
Cyclic and planar	Cyclic and planar	Falls any of the four criteria: flat/planar/conjugated
Conjugated	Conjugated	
		
Benzene: 6 pi electrons: (4n+2) Π electrons	Cyclobutadiene: 2 Π electrons	Cyclooctatetraene: 8Π electrons

Cyclooctatetraene "escapes" from anti-aromaticity by twisting into a "tub" shape

(18 kcal/mol more stable than the flat, anti-aromatic form)

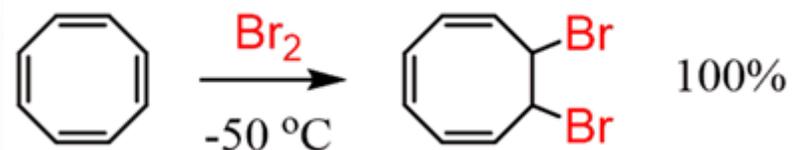


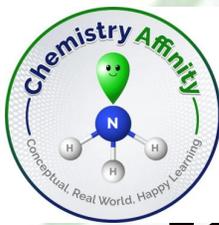
Due to this non-planar structure, double bonds in cyclooctatriene are not in resonance

Their p orbitals of adjacent double bonds cannot overlap

They are like separate alkenes and that is why cyclooctatetraene undergoes electrophilic addition reactions at very lower temperature (normal alkene cannot undergo electrophilic addition in such lower temperature)

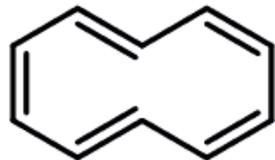
This electrophilic addition takes place in lower temperatures as the molecule wants to get rid of the double bond so that it can release some of the strain associated with this geometry



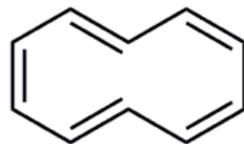


Annulene: Non aromatic

[10]-annulene has 10 π electrons which satisfies the Huckel's $(4n+2)\pi$ rule

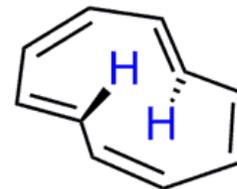


[10]-annulene



[10]-annulene

Nonaromatic

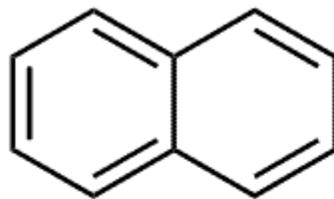
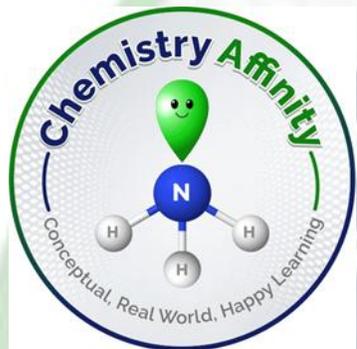


The molecule is
not planar

Still, it is nonaromatic

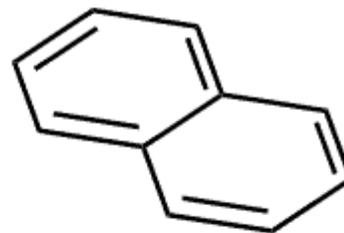
Reason:

[10]annulene cannot adopt a planar geometry due to the lack of space for the inner hydrogen. It lost its planarity thus behaves as nonaromatic



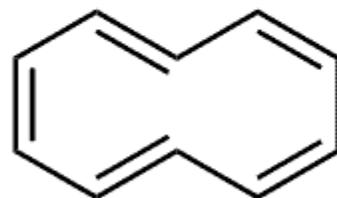
Naphthalene

Aromatic



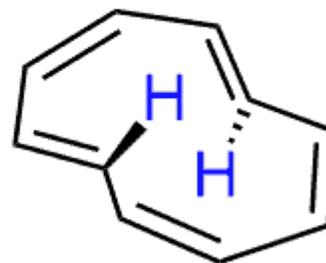
The molecule is

planar



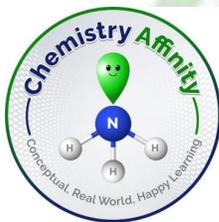
[10]-annulene

Nonaromatic



The molecule is

not planar



Annulenes: Aromatic, Nonaromatic and Antiaromatic



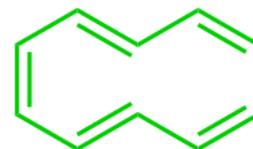
[2]Annulene
Antiaromatic



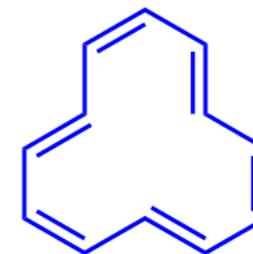
[6]Annulene
Aromatic



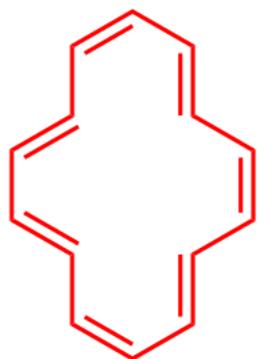
[8]Annulene
Nonaromatic



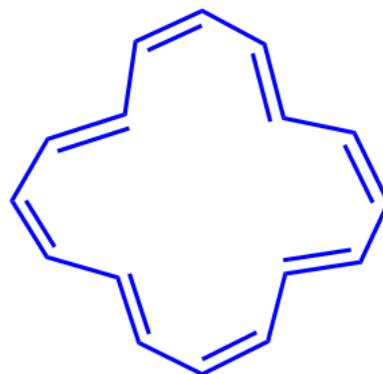
[10]Annulene
Nonaromatic



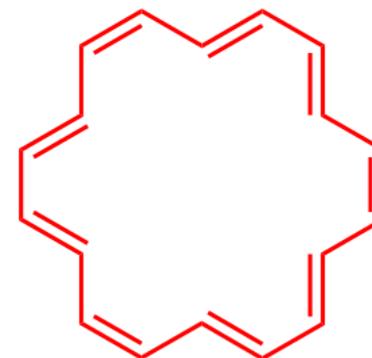
[12]Annulene
Antiaromatic



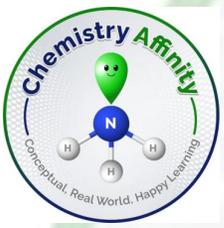
[14]Annulene
Aromatic



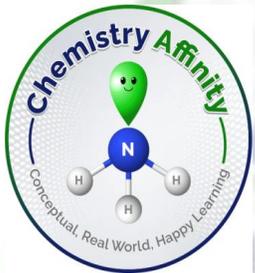
[16]Annulene
Antiaromatic



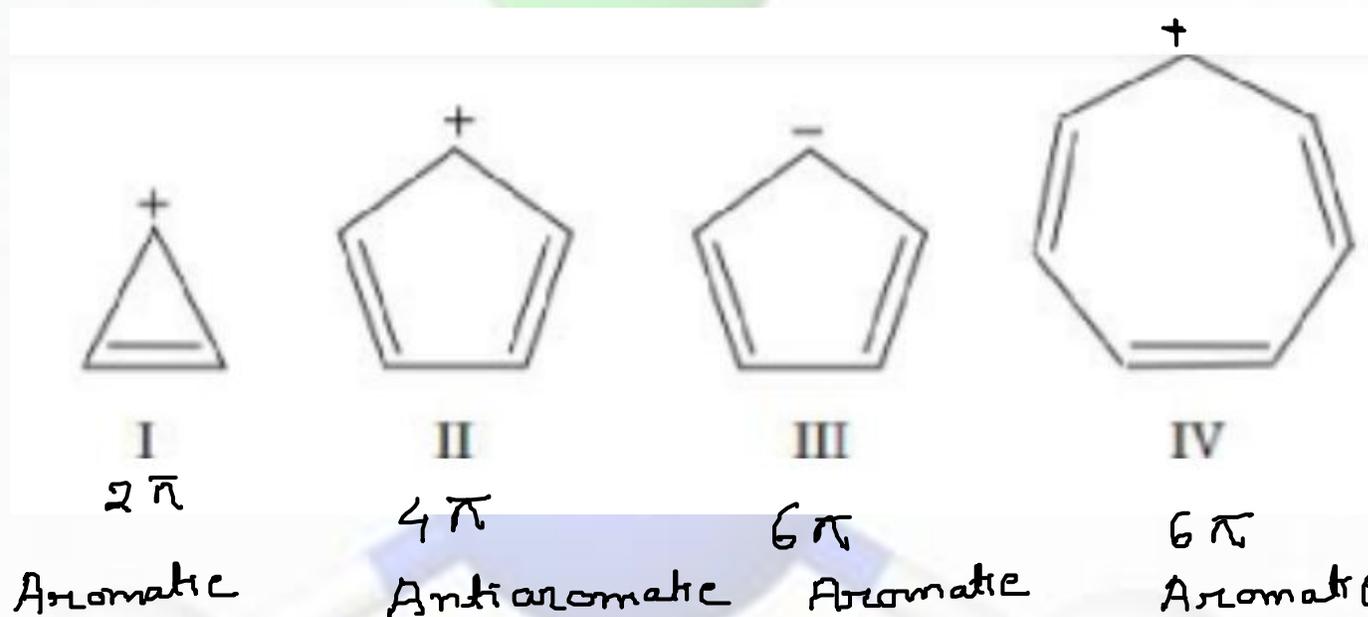
[18]Annulene
Aromatic

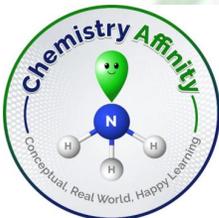


Check Your Learning

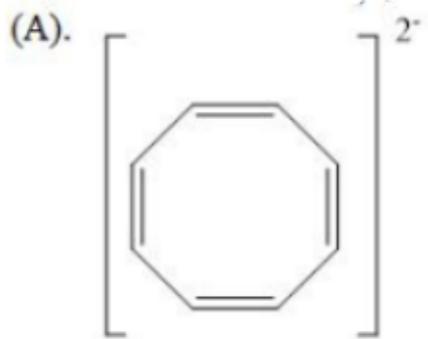


According to Huckel's rule which of the following is not aromatic?





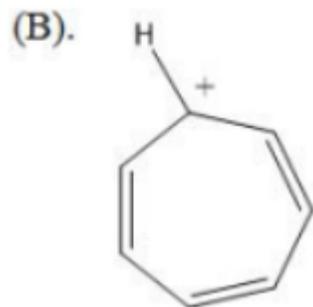
Which of the following is aromatic?



10π

$$(4n+2)\pi \quad [n=2]$$

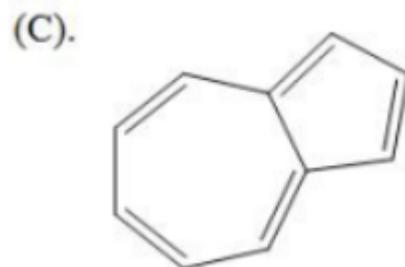
Aromatic



6π

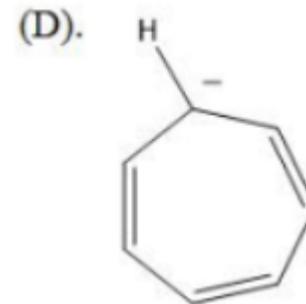
$$(4n+2)\pi \quad [n=1]$$

Aromatic



10π

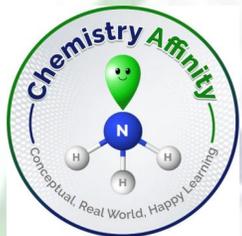
Aromatic



8π

$$4n\pi \quad [n=2]$$

Antiaromatic



Which one of the following compounds is non-aromatic?



**Cyclic, Conjugated
and 6π electrons :
Aromatic**



**Cyclic, Non-Conjugated:
Non- Aromatic**



**Cyclic, Conjugated, 2π
electrons : Aromatic**



**Cyclic, Conjugated, 14π
electrons : Aromatic**

Designed by Dr. Anuradha

Mukherjee



All the Best