

CYI101

Common CHEMISTRY(Organic)

Stereochemistry: Aromaticity

Aromaticity-2

Summary: Anti-Aromaticity

Aromatic

*unusually
stable*

- Cyclic
- Conjugated
- $(4n+2)$ Pi electrons
- Flat

e.g.



benzene

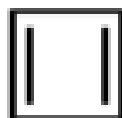
(resonance
energy of 36 kcal/mol)

Anti-Aromatic

*unusually
unstable*

- Cyclic
- Conjugated
- $(4n)$ Pi electrons
- Flat

e.g.



cyclobutadiene

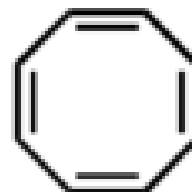
(only stable below
 $-100\text{ }^{\circ}\text{C}$)

Non-Aromatic

everything else

*Fails any one
of the 4 criteria
on the left*

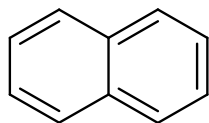
e.g.



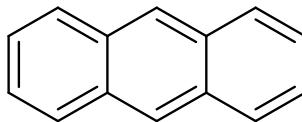
cyclooctatetraene

(adopts a tub-like
shape to "escape"
anti-aromaticity)

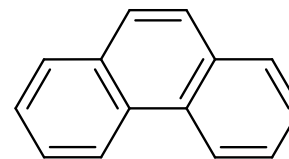
Aromatic/Heteroaromatic



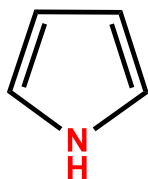
naphthalene



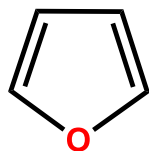
anthracene



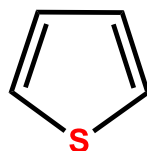
phenanthrene



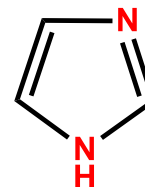
Pyrrole



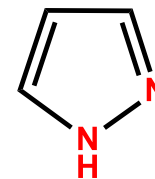
Furan



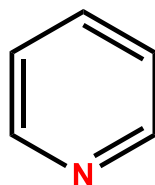
Thiophene



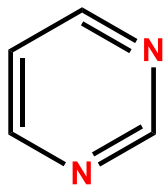
Imidazole



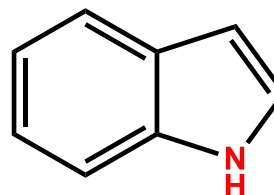
Pyrazole



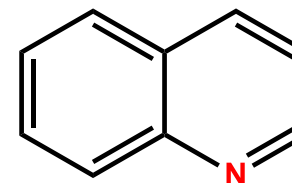
Pyridine



Pyrimidine



Indole



Quinoline

Aromaticity

- The molecule must be Cyclic
- Every atom in the ring must be conjugated
- The molecule must be Flat
- The molecule must contain $4n+2$ π electron

Hückel's Rule

Among planar, cyclic, completely conjugated polyenes, only those with $4n + 2$ π electrons possess special stability are aromatic

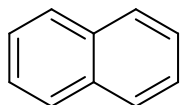
So for $n = 0$, we have $[4 (0) + 2] = 2$

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

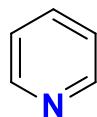
for $n = 2$, we have $[4 (2) + 2] = 10$

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

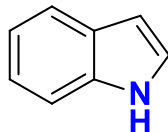
for $n=4$, we have $[4 (4) +2] = 18$



Napthalene



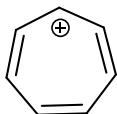
Pyridine



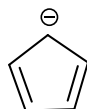
Indole



Furan



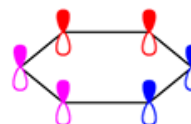
Tropylium ion



Cyclopenta
dienyl anion

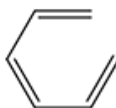


benzene

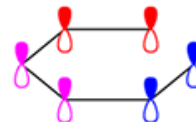


1. Cyclic
2. p -orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. $4n+2$ π -bond electron count.

Aromatic



hexatriene

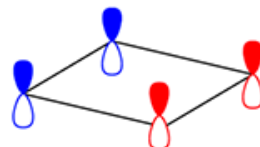


1. NOT Cyclic
2. p -orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. $4n+2$ π -bond electron count.

Non-Aromatic



cyclobutadiene

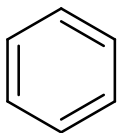


1. Cyclic
2. p -orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. Closed $4n$ π -bond electron count.

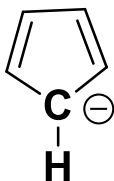
Anti-Aromatic

Aromaticity

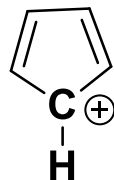
- Where $[4n + 2]$ is a formula describing the number series: **2, 6, 10, 14, 18, 22, 26....**
- These are “**magic numbers**” for **aromaticity**; the number of pi electrons in the molecule in order for the molecule to be aromatic
(We often call number **must be in this series** in this series, “**Huckel numbers**”)



6 π electrons



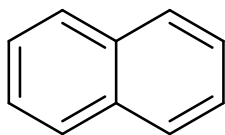
6 π electrons



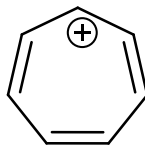
4 π electrons



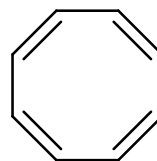
2 π electrons



10 π electrons



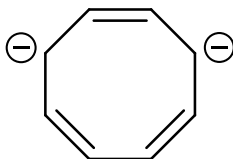
6 π electrons



8 π electrons



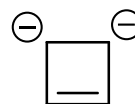
4 π electrons



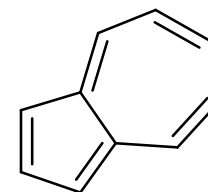
10 π electrons



4 π electrons



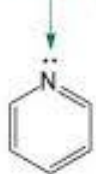
6 π electrons



10 π electrons

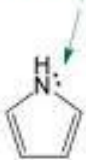
Heterocyclic

This lone pair is *not* part of the π system.



Pyridine

This lone pair is part of the π system.

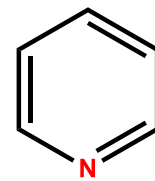


Pyrrole

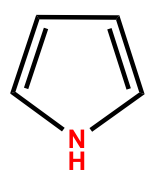
One of these lone pairs is part of the π system.



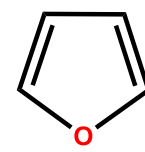
Furan



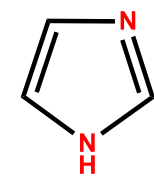
Pyridine



Pyrrole

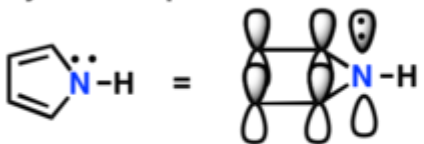


Furan



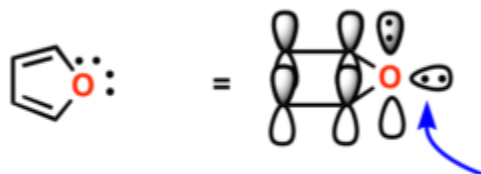
Imidazole

Pyrrole : 6 pi electrons



- Similar to cyclopentadiene anion.
- 2 electrons from lone pair contribute to pi system
- When added to 4 pi electrons from the 2 pi bonds, we get 6 pi electrons total (a "Huckel number")

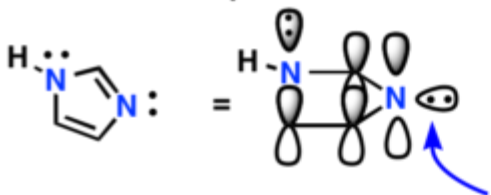
Furan : 6 pi electrons



- Here the oxygen has 2 lone pairs, but only **one** can be part of the pi system
- When added to 4 pi electrons from the 2 pi bonds, we get 6 pi electrons total (a "Huckel number")

Lone pair at 90 degrees to pi system (don't count as "pi electrons")

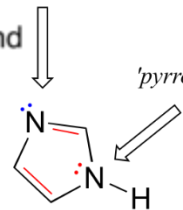
Imidazole : 6 pi electrons



- Only the nitrogen which is not part of a pi bond can donate a lone pair

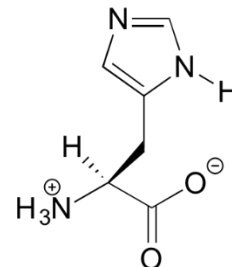
Lone pair at 90 degrees to pi system (don't count as "pi electrons")

'pyridine-like' nitrogen



imidazole

'pyrrole-like' nitrogen



histidine

Four Rules For Aromaticity

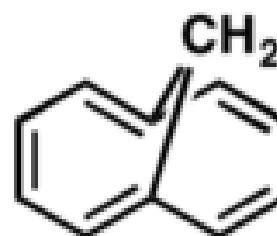
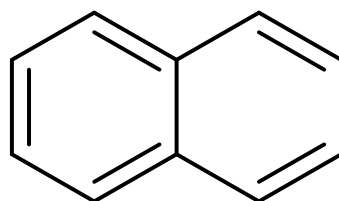
Condition #4: The molecule must be flat

Generally, if the first three conditions are met then it's usually safe to assume that the molecule is flat. .

A prominent exception is the isomer of [10]-annulene below left.



not aromatic



aromatic !

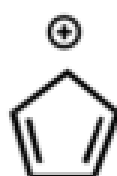
Although it is cyclic, conjugated, and has 10 pi electrons, it is not flat due to repulsions between hydrogens that arise when it is in the flat conformation.

Since it is not flat, it is not aromatic.

However, replacing the hydrogens with bonds to a bridging carbon allows all C-C pi bonds to be in the same plane - aromatic!

Anti-Aromaticity

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



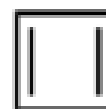
4



4



4



4



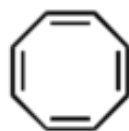
8

Pi-electrons

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

WAIT! Isn't cyclooctatetraene anti-aromatic?

Only if it's flat!
(and it's not)



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

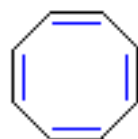
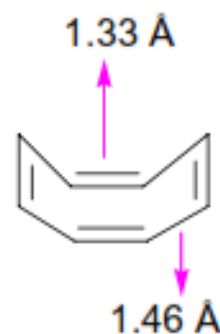
(18 kcal/mol more stable than the
flat, anti-aromatic form)

8 π electron system;

If completely planar, this molecule will become antiaromatic
(bond angle for planar structure = 135° which can give considerable
angle strain in a cyclic structure involving sp^2 carbon atoms);

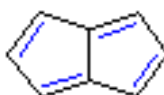
The molecule is actually boat shaped and *nonaromatic*.

(Nonaromatic form is more stable than an antiaromatic form)

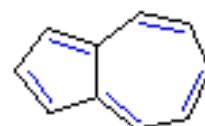


tub conformer
(non-planar)

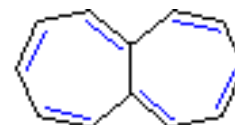
cyclooctatetraene **stable** b.p. 142°C
gives alkene-like reactions
8 π -electrons



pentalene (planar)
very unstable
8 π -electrons

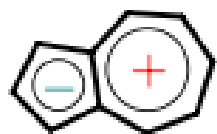


azulene (planar)
aromatic stability
10 π -electrons



heptalene (planar)
very unstable
12 π -electrons

Azulene

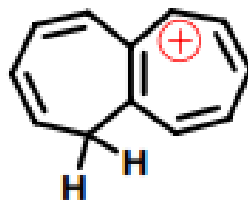


Pentalene

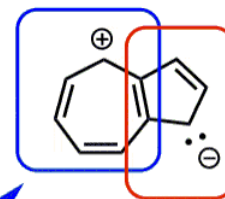


unstable,
readily
dimerises

Heptalene



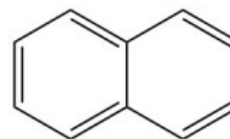
Important resonance form of azulene



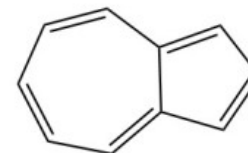
Cyclopentadiene anion
(aromatic)

Cycloheptatriene
cation
(aromatic)

Isomers



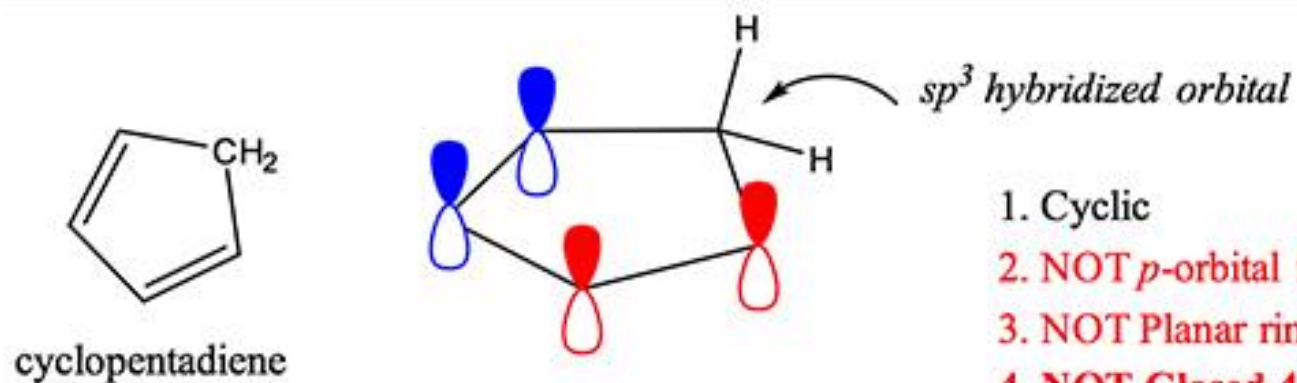
Naphthalene
(White)



Azulene
(Blue)

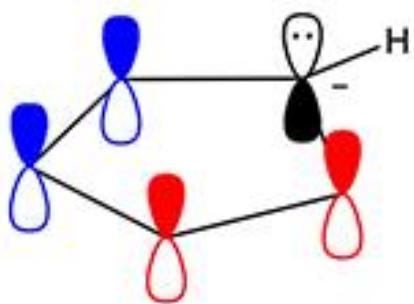
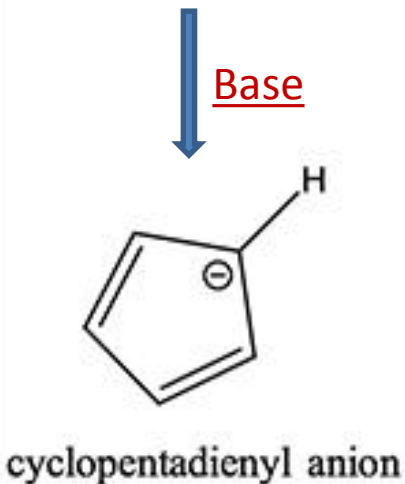


Cyclopentadiene Vs Cyclopentadienyl anion



- 1. Cyclic
- 2. NOT *p*-orbital for each member of the ring
- 3. NOT Planar ring (sp^2 hybridized)
- 4. NOT Closed $4n+2$ π -bond ring.

Not Aromatic



- 1. Cyclic
- 2. *p*-orbital for each member of the ring
- 3. Planar ring (sp^2 hybridized)
- 4. Closed $4n+2$ π -bond ring.

Aromatic

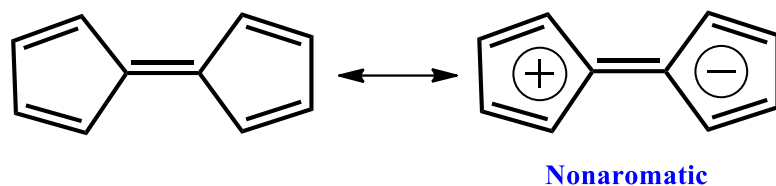
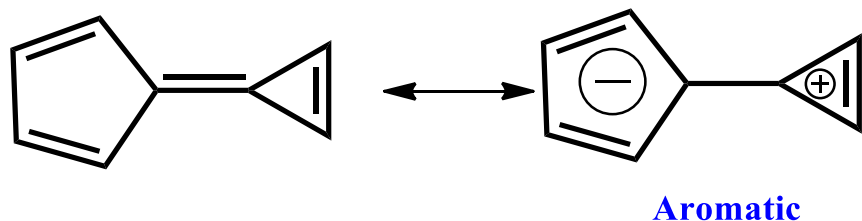
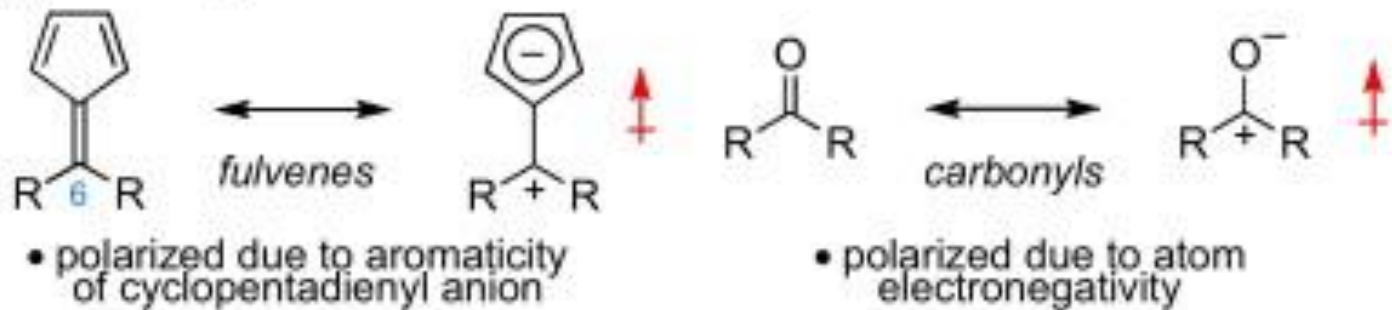
Exocyclic Double bond (Fulvenes)

(a) fulvenes



- First prepared by Thiele in 1900
- 6 electron cross conjugated π -system
- polarized due to aromaticity
- useful for cycloadditions, organometallic ligands, complex molecule synthesis, etc.

(b) fulvene polarization



M.O- Explanation

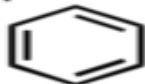
Summary: Anti-Aromaticity

Aromatic

*unusually
stable*

- Cyclic
- Conjugated
- $(4n+2)$ Pi electrons
- Flat

e.g.



benzene

(resonance energy of 36 kcal/mol)

Anti-Aromatic

*unusually
unstable*

- Cyclic
- Conjugated
- $(4n)$ Pi electrons
- Flat

e.g.



cyclobutadiene

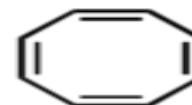
(only stable below $-100\text{ }^{\circ}\text{C}$)

Non-Aromatic

everything else

*Fails any one
of the 4 criteria
on the left*

e.g.



cyclooctatetraene

(adopts a tub-like shape to "escape" anti-aromaticity)

In Terms of M.O Theory:

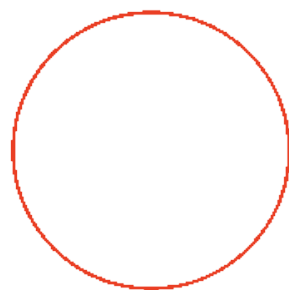
All the bonding MO's are **Filled** (Contain Paired e's)

All the bonding/non-bonding/anti-bonding MO's are **Partially Filled** (Contain unpaired e's)

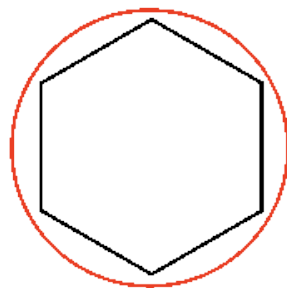
All the bonding/non-bonding/anti-bonding MO's are **Partially Filled** (Contain unpaired e's)

Huckel Aromaticity and Frost Circles

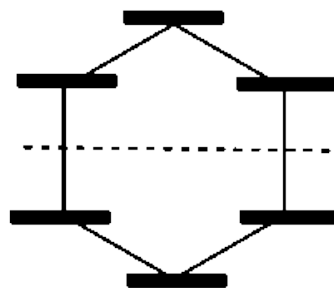
- The molecule must be Cyclic
- Every atom in the ring must be conjugated
- The molecule must be Flat
- The molecule must contain $4n+2$ p electron



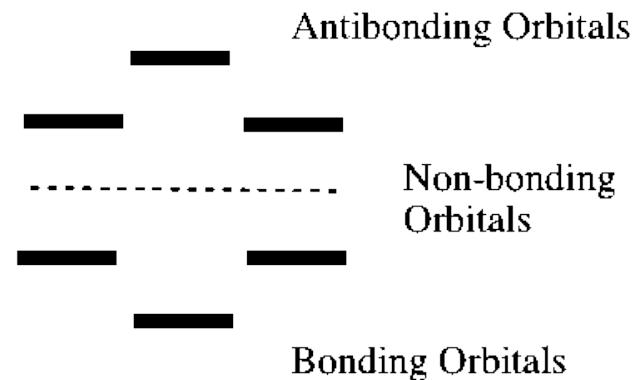
Step 1



Step 2



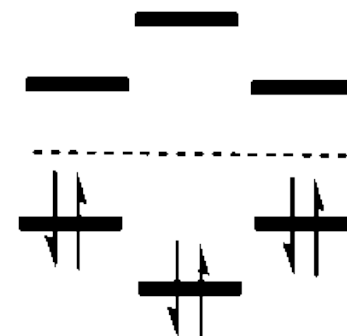
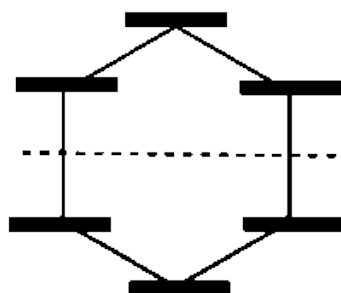
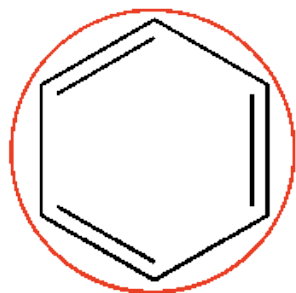
Step 3



Step 4

1. Draw a circle
2. Connect the carbon atoms to the circle such that **one is always pointed at the bottom**
3. Draw a **horizontal line at each carbon** – this represents the pi bond molecular orbitals
4. Draw a dotted line through the middle of the circle – this is the boundary between bonding and antibonding orbitals.
 1. Anything pi electrons occupying an orbital below the line are in a bonding orbital and are **STABLE**
 2. Any pi electrons on the line or above the line are in non-bonding & anti-bonding orbital and are **UNSTABLE**.

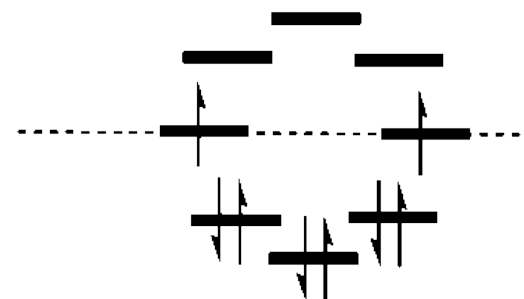
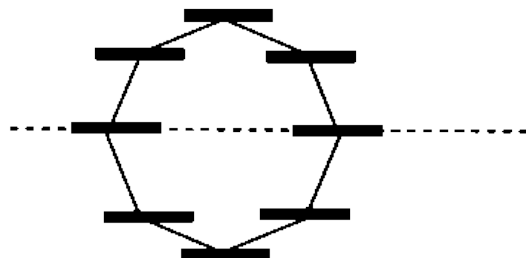
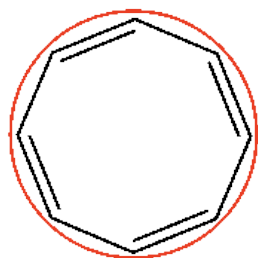
Benzene



Three double bonds = 6 pi electrons. Paired together, all of the pi electrons are in bonding orbitals so benzene is in fact aromatic.

Benzene
6 pi electrons
STABLE

Cyclooctatetraene



Four double bonds = 8 pi electrons, Pairing the first 6 electrons in the bonding orbitals, we place last 2 electrons in each of the non-bonding orbitals. Because of these two electrons, this molecule is anti-aromatic!

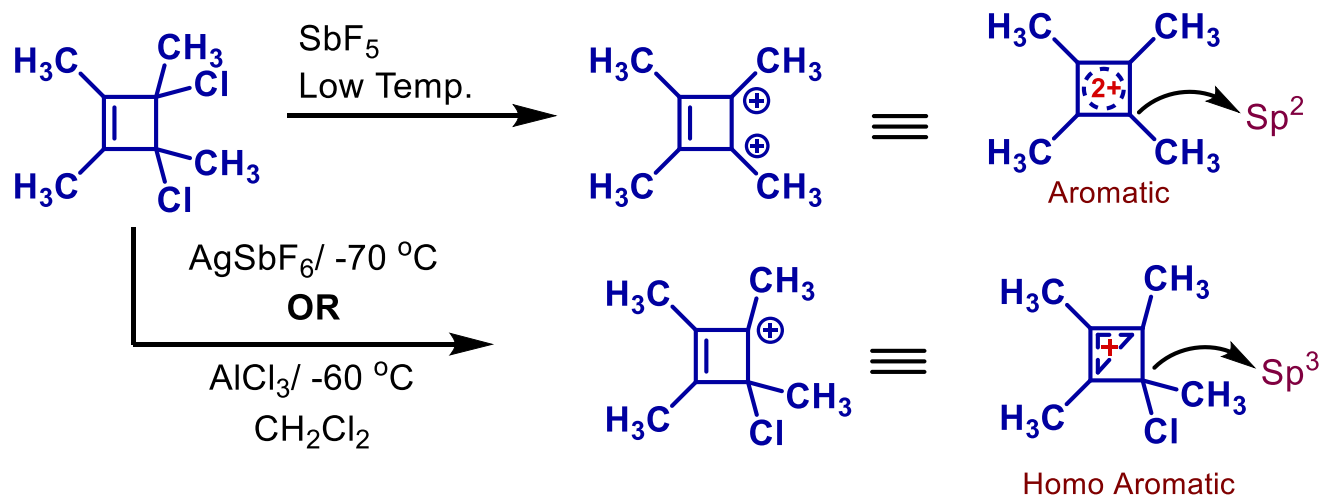
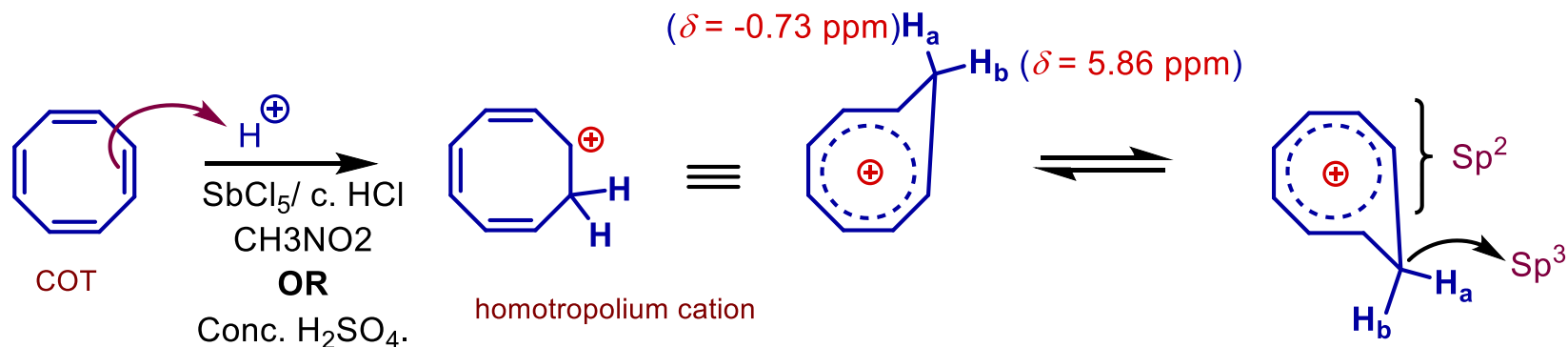
Cyclooctatetraene
8 pi electrons
UNSTABLE

Frost diagrams - Illustrative examples

		<div>Antibonding</div> <div>Nonbonding</div> <div>Bonding</div>	Antiaromatic
		<div>Antibonding</div> <div>Bonding</div>	Aromatic
		<div>Antibonding</div> <div>Bonding</div>	Aromatic
		<div>Antibonding</div> <div>Bonding</div>	Aromatic
		<div>Antibonding</div> <div>Nonbonding</div> <div>Bonding</div>	Antiaromatic (chooses to be nonaromatic by adopting tub-shaped conformation)

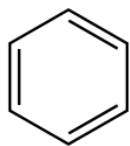
Homoaromatic

A **homoaromatic** compound is defined as a compound that contains one or more **sp³ hybridised carbon atom** in a conjugated cycle. In order for the **pi orbitals** to overlap more effectively so as to close a loop the **sp³ atoms** are forced to lie almost vertically above the plane of the aromatic system

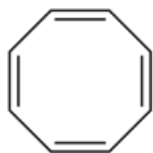


Annulenes:

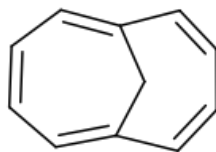
Completely conjugated monocyclic hydrocarbons are called annulenes.



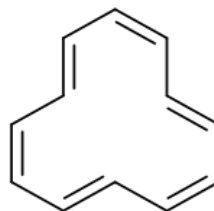
Benzene
[6]annulene
(Aromatic)



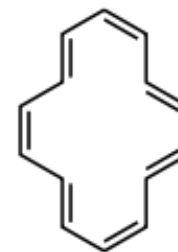
Cyclooctatetraene
[8]annulene
(Not Aromatic)



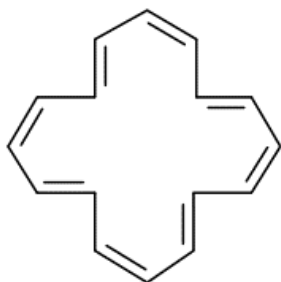
(Aromatic)



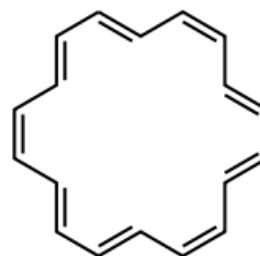
Cyclododecahexaene
[12]annulene
(Not aromatic)



Cyclotetradecaheptaene
([14]annulene) (Aromatic)



([16]annulene)
(Not Aromatic)



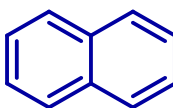
Cyclooctadecanonaene
[18]annulene (Aromatic)

Annellation Effect:

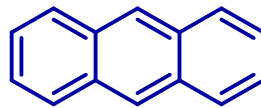
The phenomenon, whereby some rings in fused systems give up part of their aromaticity to adjacent rings is called Annellation.



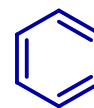
Resonance
Energy Kcal/mol: 36



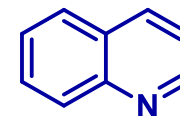
61



84

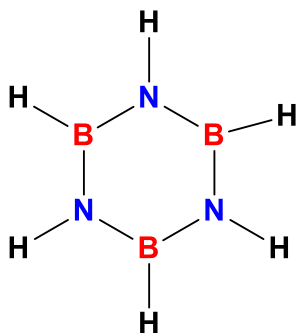


21



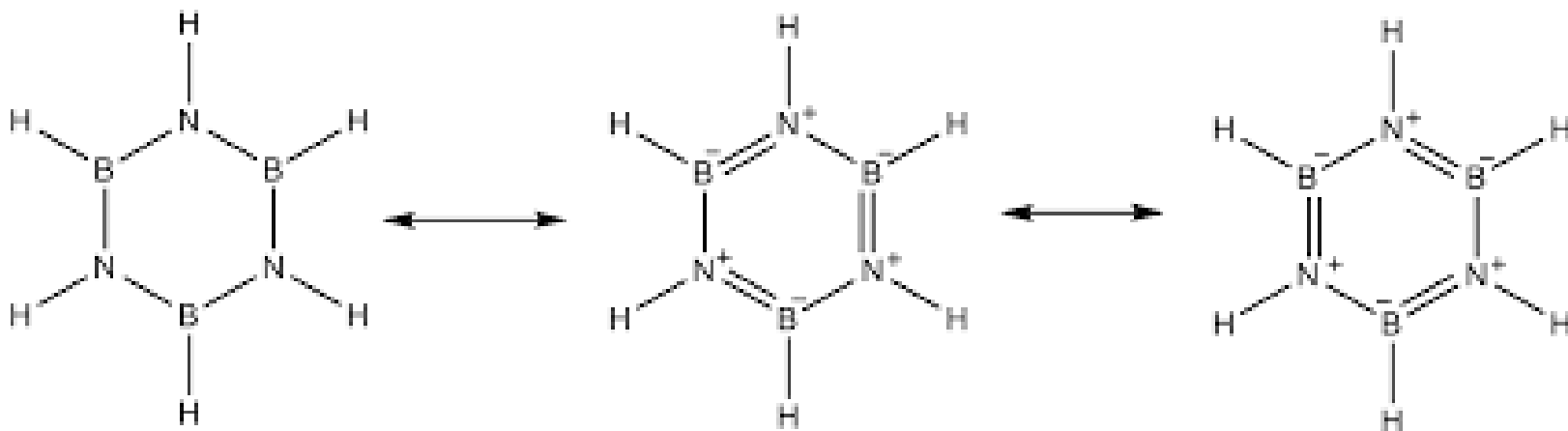
47.3

Borazine



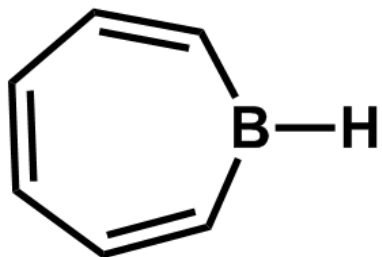
Borazine is **aromatic** as there are 3 nitrogen atoms in the structure of **borazine** that donate two electrons each. Boron doesn't donate any, but it has an empty p-orbital available through which the electrons can delocalize. Hence, in total it has 6 π -electrons

"inorganic benzene"

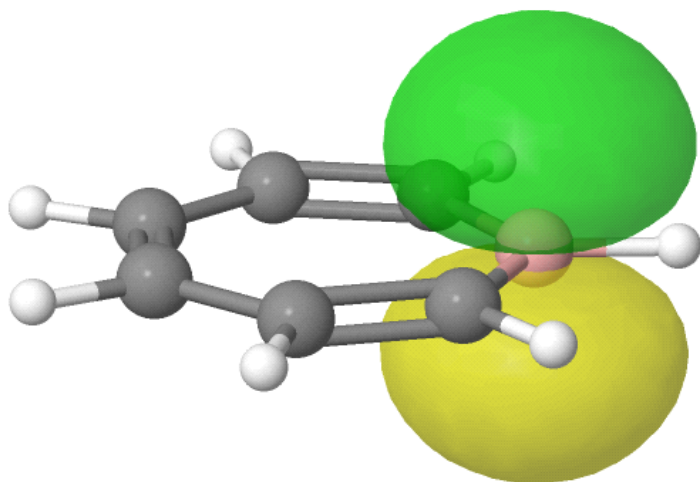


The **electronegativity of boron** (2.04 on the Pauling scale) compared to that of nitrogen (3.04) and also the electron deficiency on the boron atom and the lone pair on nitrogen favor alternative mesomer structures for borazine

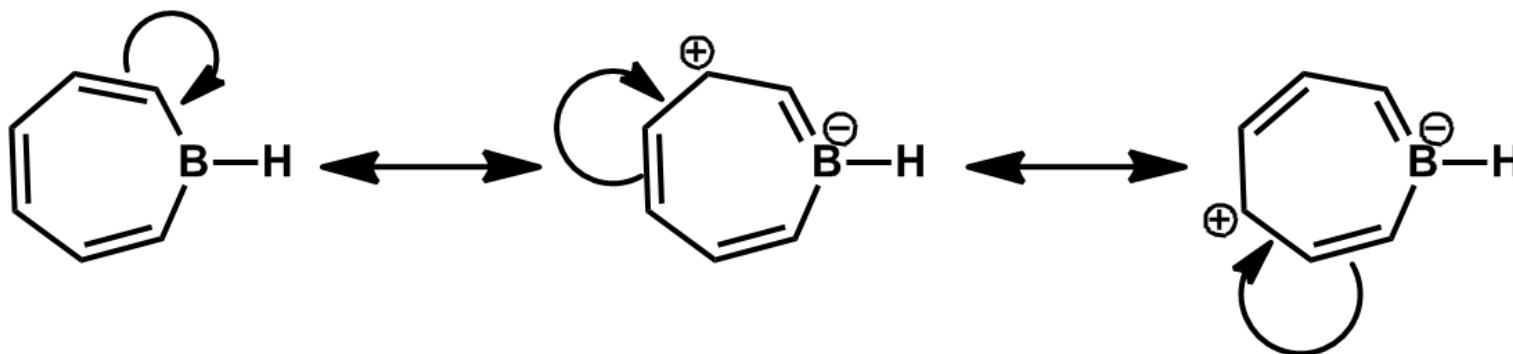
Borepin



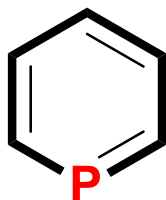
Borepin is planar and has three double-bonds, bringing the total π -electron count to six, satisfying Hückel's Rule. However, for a ring to be aromatic there needs to be conjugation around the entire ring



For **Borepin**, there is full conjugation across the ring. The boron atom has an **empty** p-orbital that allows for full conjugation with the adjacent double bonds. As it is an empty orbital, there are no electrons to add to the π -system, so the count stays at six and the molecule is **aromatic**.

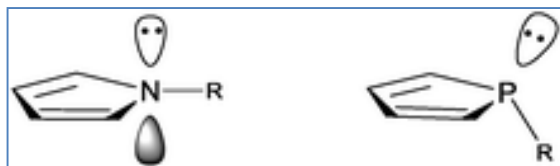
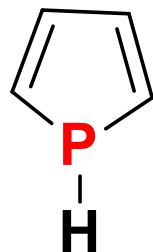


OrganoPhosphorus: Phosphinine



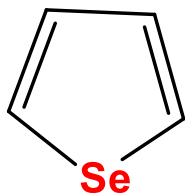
Just like pyridine, phosphinine, having 6 π -electrons in a molecule, is an **aromatic compound**. Depending on the aromaticity index applied it can be shown that the aromaticity of the phosphabenzene is 88–97% of that of benzene.

Phospholes



Unlike the related 5-membered heterocycles **pyrrole, thiophene, and furan**, the aromaticity of **phospholes** is diminished, reflecting the reluctance of phosphorus to delocalize its lone pair.

Selenophene



It is a heterocycle with reduced aromatic character compared to thiophene