

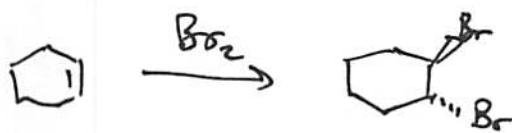
Aromaticity.

The case of Benzene.

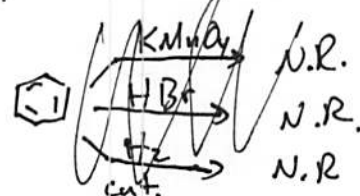


- Resonance.
- Highly delocalized π electrons
- Very stable
- Does not undergo traditional electrophilic addition.

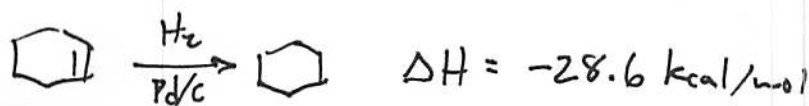
compare:



but

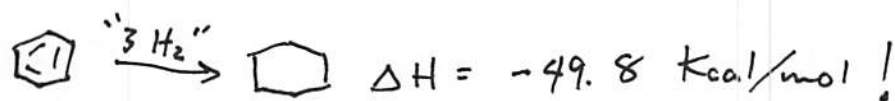


To understand stability, study heat of hydrogenation.



if "cyclohexatriene" $\xrightarrow{3 \text{ H}_2}$ Cyclohexane $\Delta H = -85.8 \text{ kcal/mol}$ Expected.

However.
Real value



The difference in expected heat of hydrogenation and the observed " " " is 36 kcal/mol

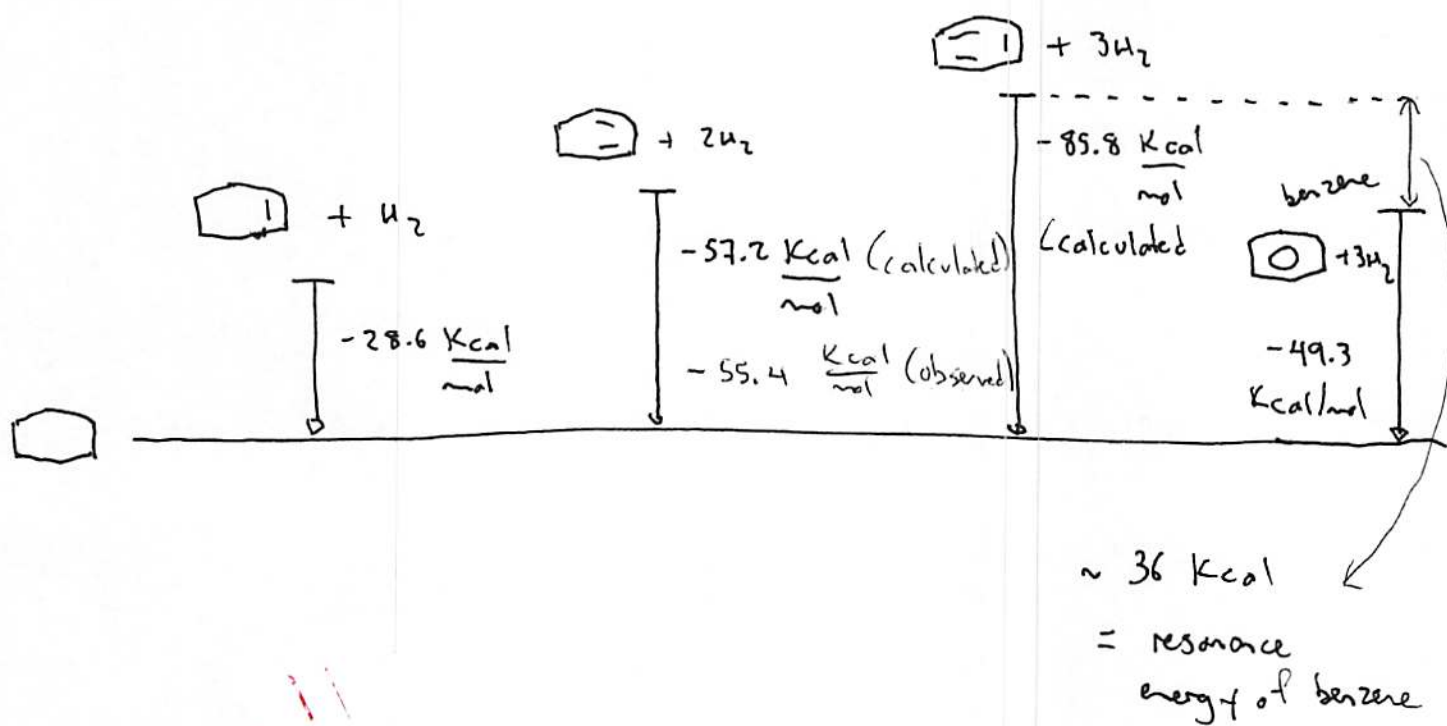
That is the Energy Stabilization, due to electron delocalization.

Compounds like benzene are considered as a class of Aromatic Compounds.

How to classify Aromatic compounds? - Wow 1
2

• Heat of hydrogenation

1,3,5-cyclohexatriene




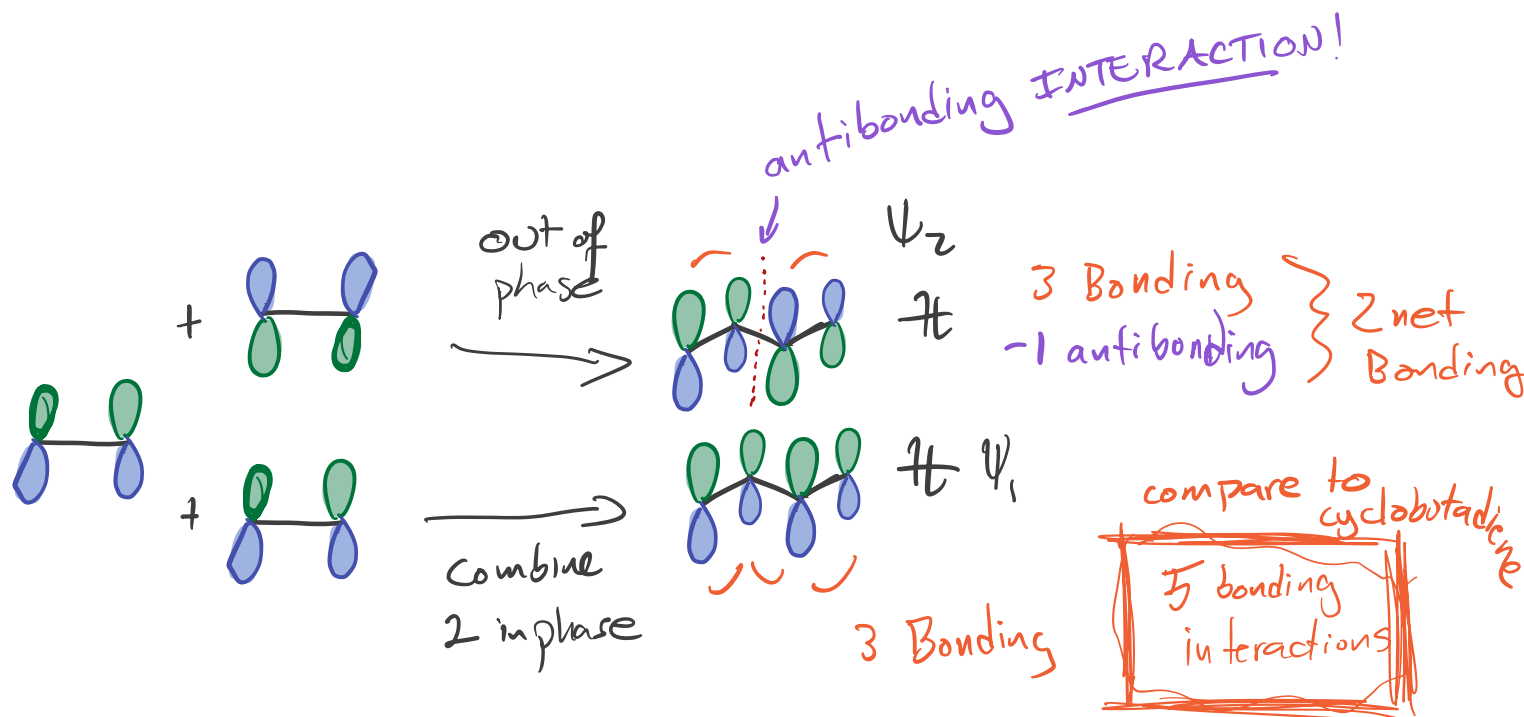
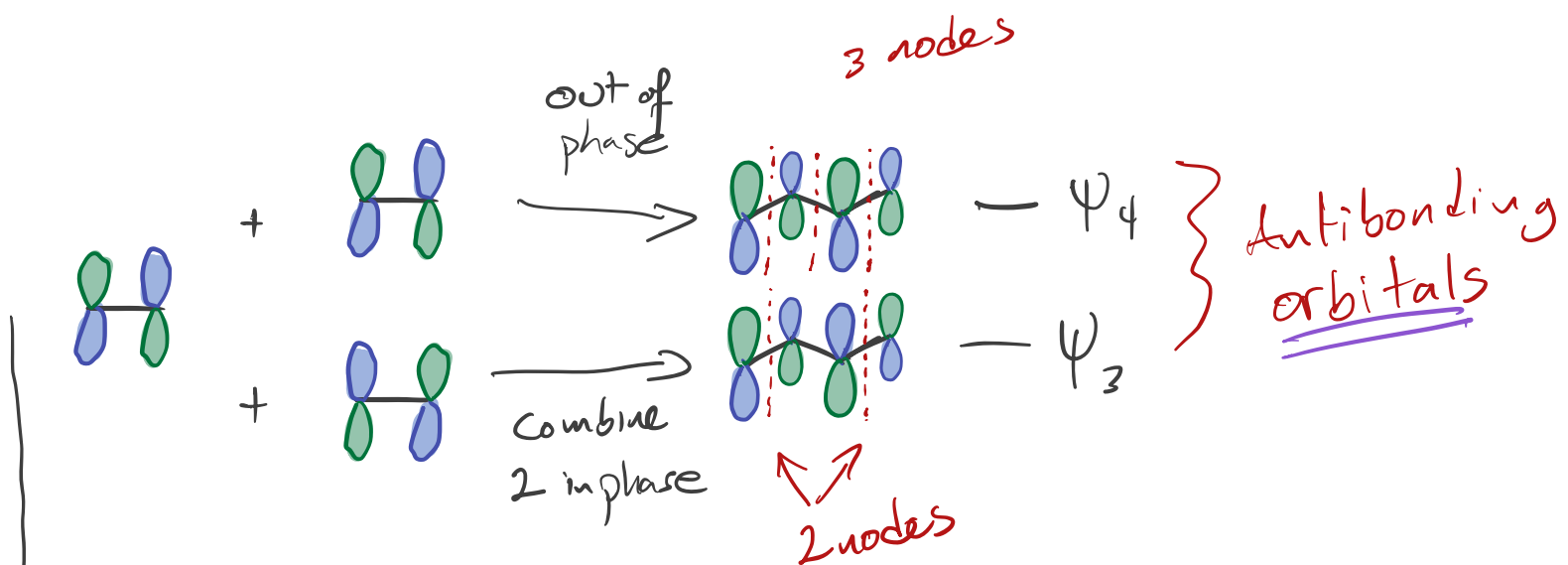
Lets consider Conjugation: Hexatriene vs. Benzene

conjugation: the sequential arrangement of double bonds in an alternating fashion, separated by a single bond.



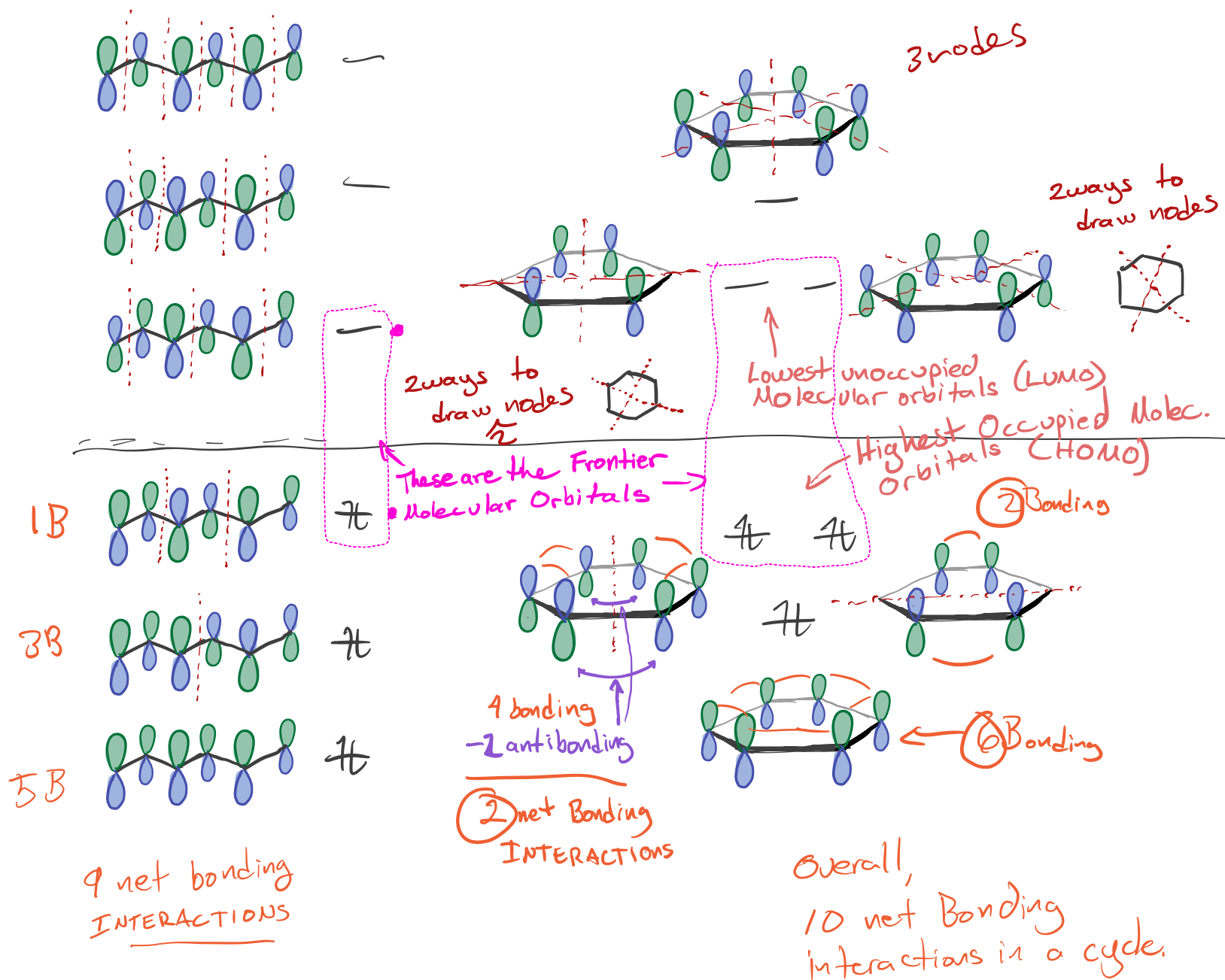
MO Diagram

 \Rightarrow 2 π bonding orbitals,
2 π^* antibonding
4 p atomic orbitals connect 2



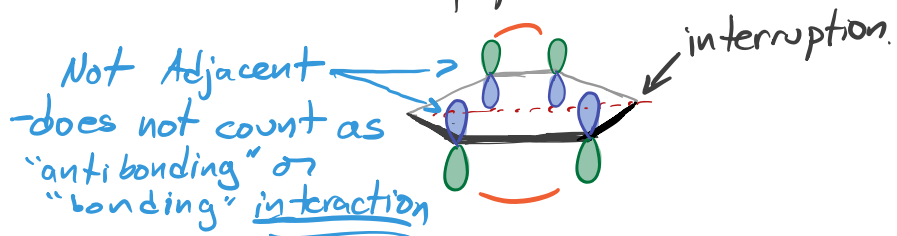
Hexatriene

Benzene



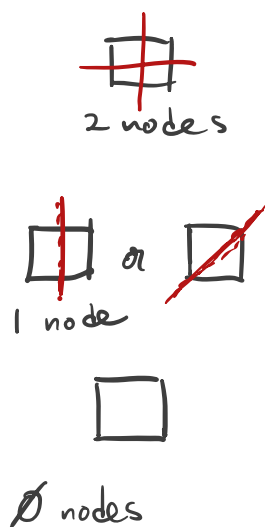
The "Bonding interactions" are between adjacent p-orbitals that are in-phase.

Anti bonding interactions are between adjacent p-orbitals that are out of phase.

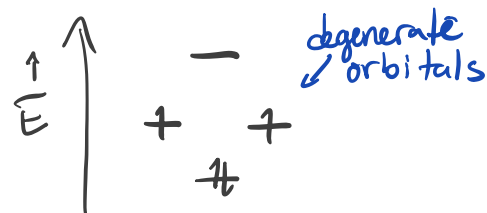


What about cyclobutadiene? As you will see, \square has less bonding interactions than \approx

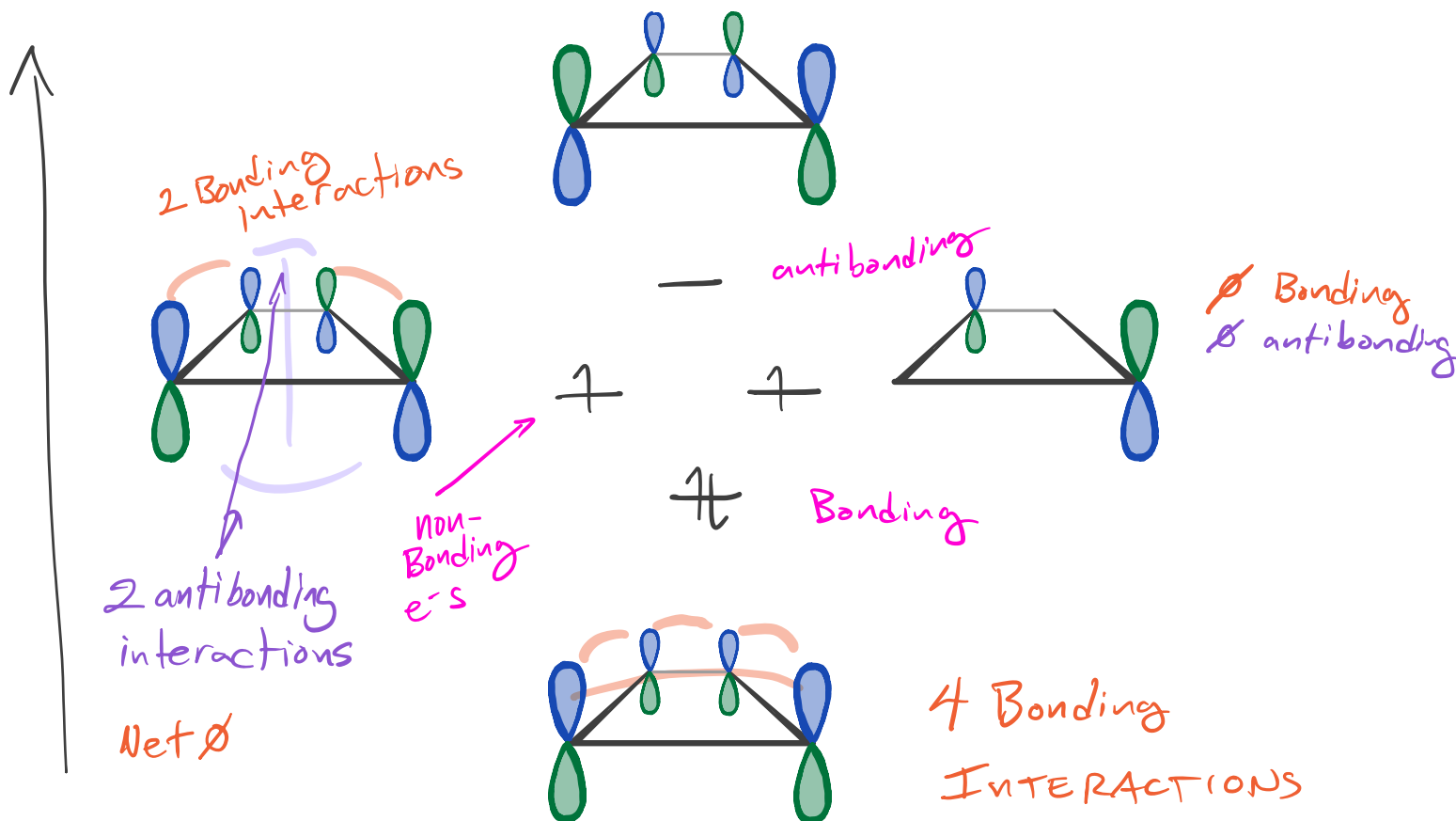
\square 4 π e⁻s, 4 p orbitals



Therefore:



"diradical" character
 $\frac{1}{2}$ unstable.
 e⁻s in non-bonding orbitals



Only 4 Bonding interactions
 in cyclobutadiene

compare to \approx , which has
5 bonding interactions

Handout

Classification of Aromatic Compounds

(2)

1) Compound must be cyclic and have an ~~un~~interrupted cloud of π -e's (a π -cloud), above and below the plane of the molecule.

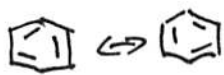
Need:

- cyclic molec, planar
- every atom has p-orbital
- each p-orbital must overlap w/ neighbor

2) The π cloud must have an ~~odd~~^{even} # of pairs of e's.
- Hückel's rule $\Rightarrow 4n + 2$, where n = whole number.

That is, if planar, cyclic molecule w/ p-orbitals contains 2, 6, 10, 14, 18, etc. π -electrons, molec. is aromatic.

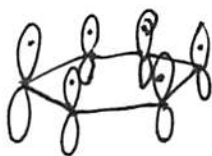
ex. Benzene



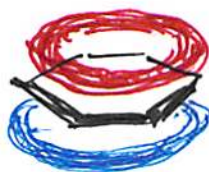
3 pairs of π e's
= 6 e's

Falls under the
 $4n + 2$ category
when $n=1$

p-orbitals



π -cloud

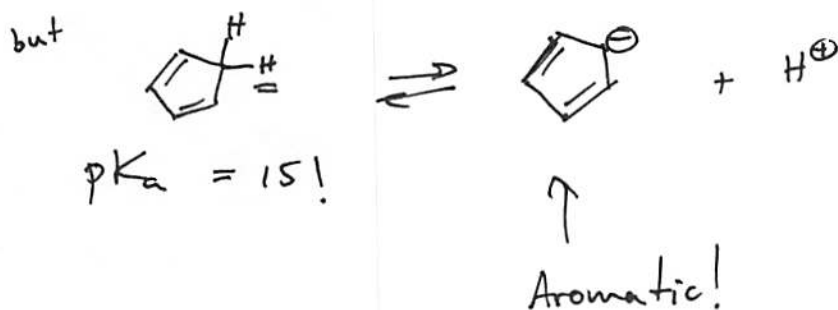


\therefore Aromatic!

Note: if the molecule fulfills item (1) but not (2), the compound is considered **Antiaromatic**

That is, the number of π e's falls within a value of $4n$; ex \Rightarrow 4, 8, 12, etc.

Now consider Acidity & Basicity



Another class:

Aromatic Heterocyclic Compounds.

→ one or more atoms in the ring is other than carbon.
ex. N, S, O

~~OK. 20~~

Classification of Aromatic Compounds

Hückel's rule is a qualitative classification of aromatic compounds.

Part 1. An aromatic compound must be cyclic and have an uninterrupted cloud of π -electrons (a π -cloud). Interruptions can arise from sp^3 atoms in the cycle or p -orbitals engaged in bonding outside of the ring (ex. exocyclic double bonds).

In other words:

- the molecule must be cyclic and planar.
- every atom in the cycle has a p -orbital.
- each p -orbital must overlap with both neighboring atoms in the cycle.

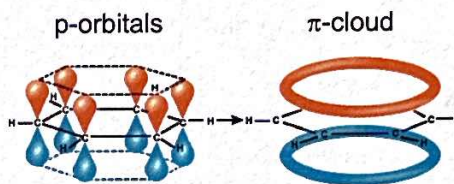
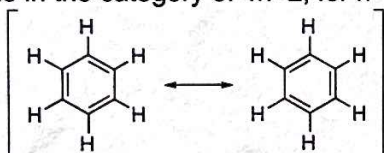
Part 2. Hückel rule is satisfied for aromaticity if the π -cloud has an odd number of pairs of electrons.

- i.e., the molecule contains $4n + 2$ number of electrons, where $n = \text{an integer}$ (0, 1, 2, etc).
- from above, the molecule should contain 2, 6, 10, 14, etc. number of π -electrons.

Note: If the molecule fulfills **Part 1**, but **not Part 2**, then the molecule is considered **Antiaromatic** (when the number of π -electrons falls within the value of $4n$, where $n = \text{an integer}$ (1, 2, 3, etc)). If the molecule does not fulfill both parts, then the molecule is **non-aromatic**.

Example: **Benzene** is aromatic.

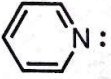

3 pairs of π -electrons = 6 electrons
(falls in the category of $4n+2$, for $n=1$)



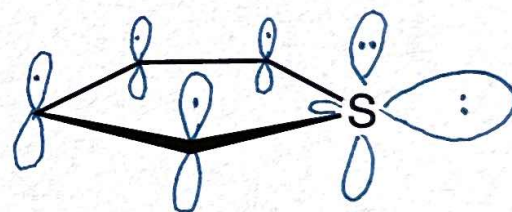
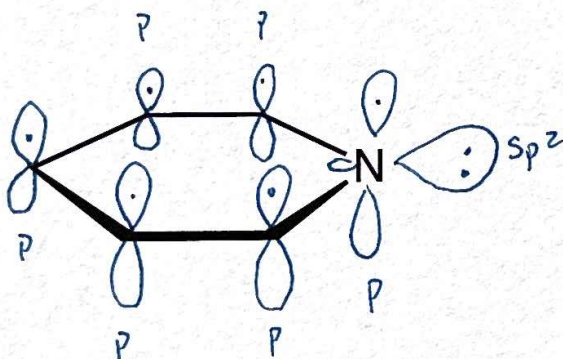
Your task: For the compounds below, fill in the appropriate boxes, answering the questions on the left.

# of electrons in p-orbitals?	2	4	6	6	10	10	8	8
# of electrons in an uninterrupted cycle?	2	4	N/A	N/A	5	10	8	N/A
aromatic? (yes / no)	Y	N	N	N	Y	Y	N	N
antiaromatic? (yes / no)	N	Y	N	N	N	N	Y	No

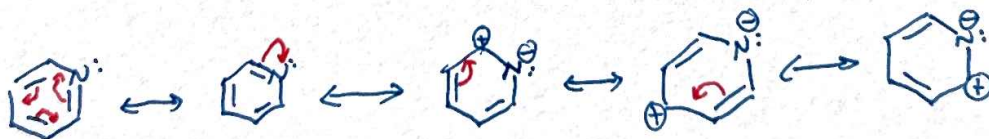
Consider the heterocycles below:

		what is the hybridization of:	# of electrons in p-orbitals?	# of electrons in an uninterrupted cycle?	aromatic? (yes / no)
pyridine		<div> sp^2 Nitrogen </div>	<div>6</div>	<div>6</div>	<div>Y</div>
thiophene		<div> sp^2 Sulfur </div>	<div>6</div>	<div>6</div>	<div>Y</div>

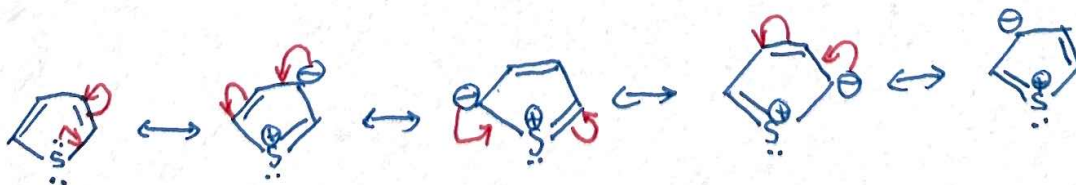
Draw the orbitals for all non-bonding electrons, i.e. the single and lone pair electrons found in p-orbitals and other hybrid orbitals. Note that the planar structures are drawn sideways.



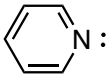
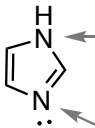
Draw the resonance structures of **pyridine**.



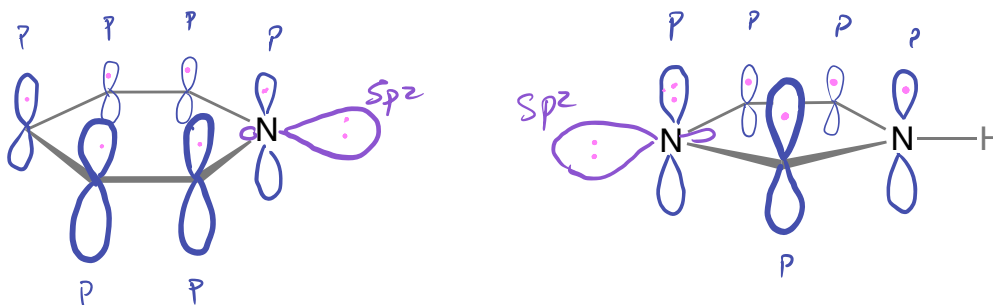
Draw the resonance structures of **thiophene**.



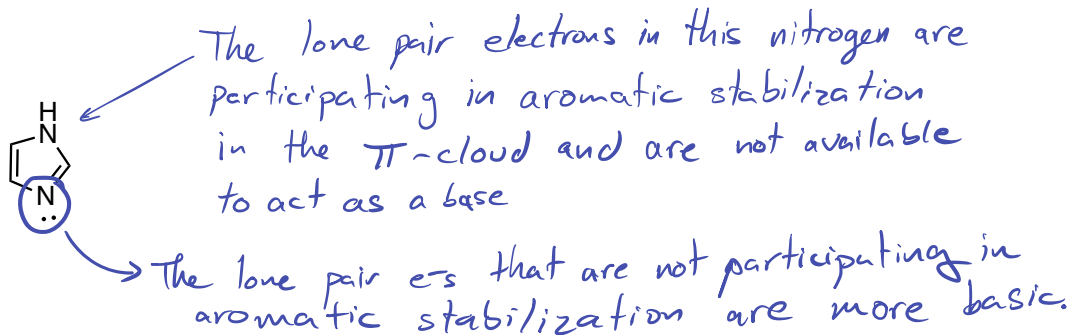
Consider the heterocycles below:

		what is the hybridization of nitrogen:	# of electrons in p-orbitals?	# of electrons in an uninterrupted cycle?	aromatic? (yes / no)
Pyridine		sp^2	6	6	yes
Imidazole		sp^2	6	6	yes
		sp^2			

Draw the orbitals for all electrons that are not participating in σ -bonds. Note that the planar structures are drawn sideways.



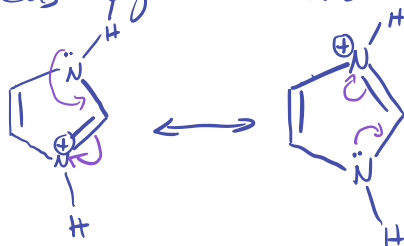
In **imidazole**, which nitrogen is more basic and why (circle it in the structure below)?



Which compound do you expect to be more basic, **pyridine**, or **imidazole**, and why?

Imidazole is more basic.

When imidazole is protonated, there are two resonance contributors bearing the charge on nitrogen, whereas pyridine has only one.



Nitrogen stabilizes \oplus better than Nitrogen

