(27) **Today**

**Chap 15.2 – 15.6: Aromaticity**

**Next Class** (28)

**Chap 15.2 – 15.6**: Aromaticity

(29) **Second Class from Today**

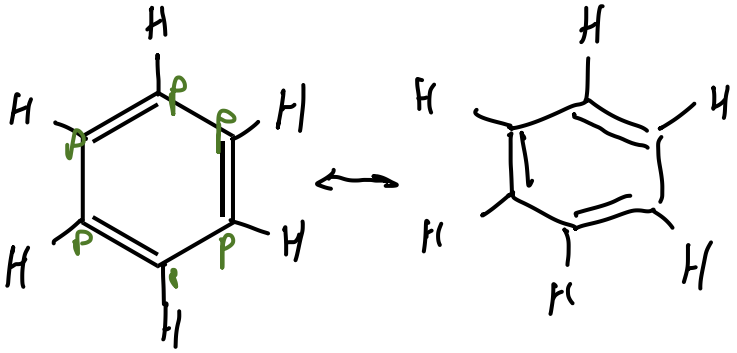
**Chap 16.1 - 16.5**: Electrophilic Aromatic Substitution

**Third Class from Today** (30)

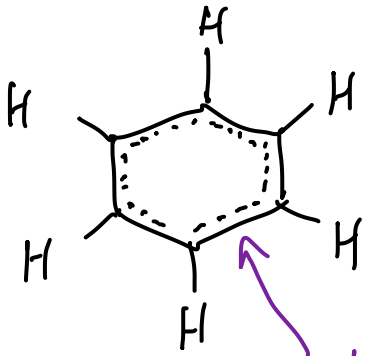
Test 3
**Chap 21**: 21.3, 21.4, 21.6. 21.7
**Chap 10**: 10.6
**Chap 19**: 19.4, 19.7, 19.5, 19.10, 19.8, 19.11

Withdrawal Deadline is Tuesday, April 14 at 4:30 pm

Benzene and resonance



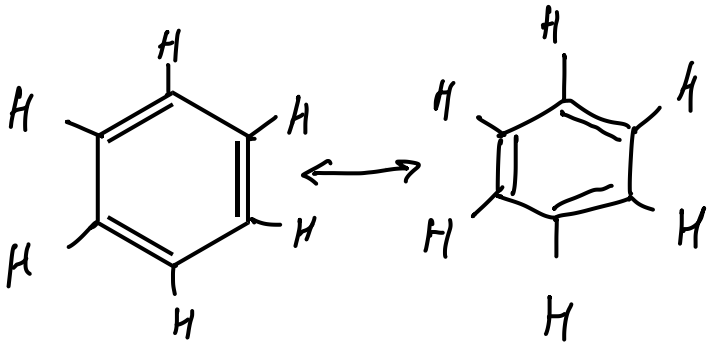
resonance contributors



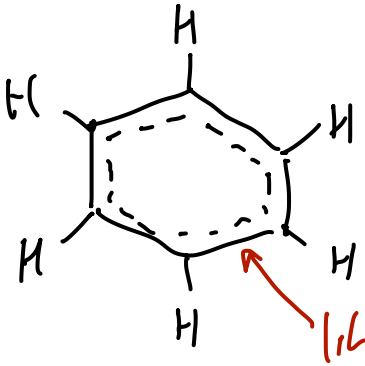
resonance hybrid

1 σ bond and "½" a π bond

# Benzene and resonance



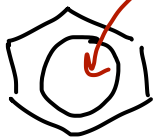
resonance contributors



like a

Hand and a half

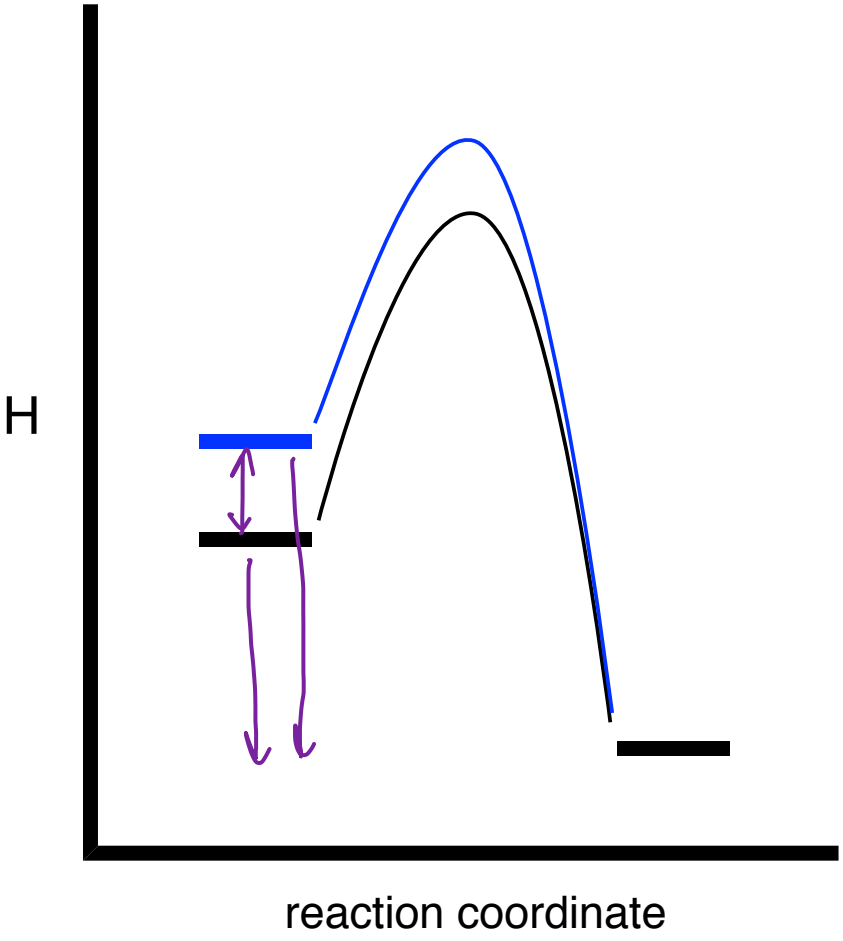
resonance hybrid (the actual molecule)



circle indicates a special kind of resonance...

aromaticity

Reactions that produce the same products can be used to compare the stabilities of the reactants




$\Delta H_{rxn} = H_{product} - H_{reactant}$

$\Delta H_{rxn} + H_{reactant} = H_{product}$

$\Delta H_{rxn} = H_{product} - H_{reactant}$

$\Delta H_{rxn} + H_{reactant} = H_{product}$

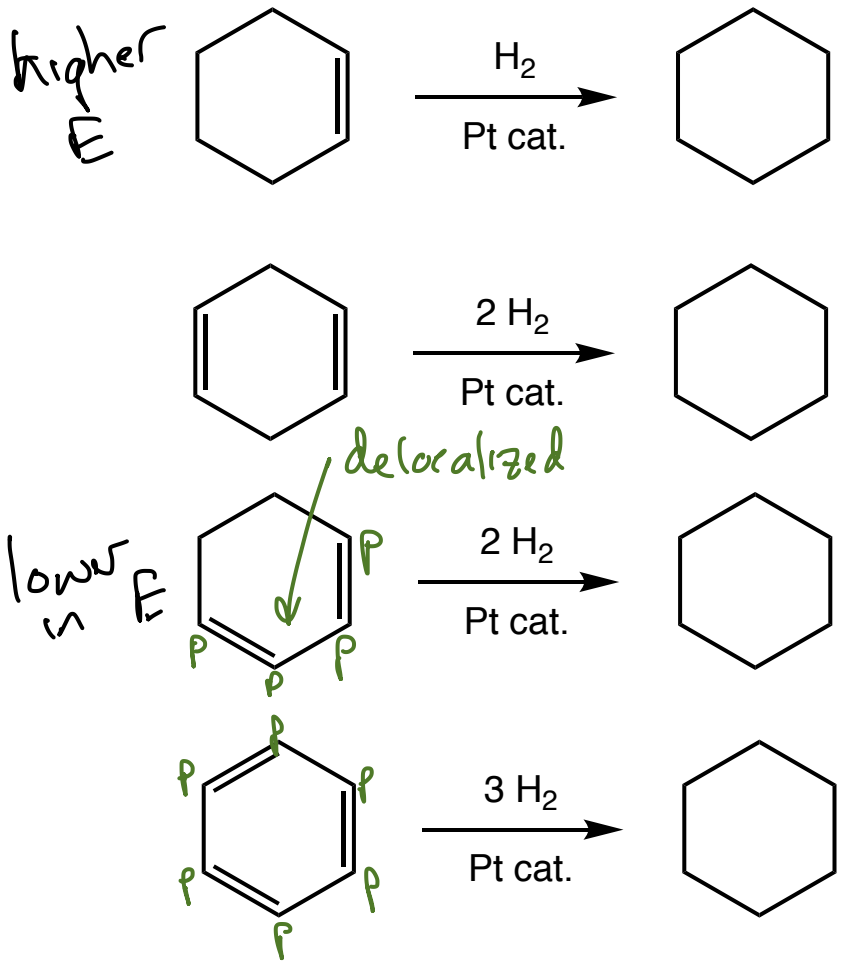
$\Delta H_{rxn} + H_{reactant} = \Delta H_{rxn} + H_{reactant}$

$\Delta H_{rxn} - \Delta H_{rxn} = H_{reactant} - H_{reactant}$

compare energy of reactants by comparing energy of the rxn

In other words, when two reactions end in the same place, the energy released or absorbed during the reaction can be used to compare the energies of the reactants.

# Aromaticity: a special kind of resonance/electron delocalization




| | $\Delta H_{reaction}$ (kcal/mol) | per bond (kcal/mol) |
|---|---|---|
| cyclohexene | –28.6 | –28.6 |
| 1,4 cyclohexadiene | –57.4 | –28.7 |
| 1,3-cyclohexadiene | –55.4 | –27.7 |
| benzene | –79.8 | 26.6 |

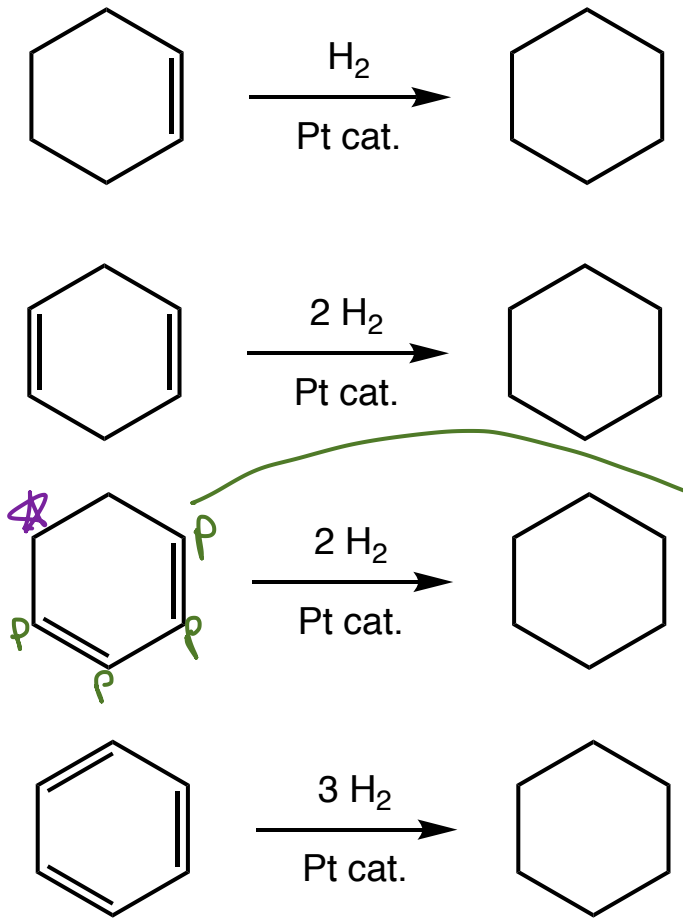
ΔH per π bond

less due to resonance

less energy released per bond hydrogen

even less due to aromaticity

# Aromaticity: a special kind of resonance/electron delocalization

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| benzene | –79.8 | 26.6 |

same

4 p orbtals in a row, e⁻ will be delocalized

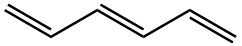
resonance

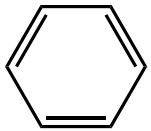
less energy was released when we hydrogenated these π bonds

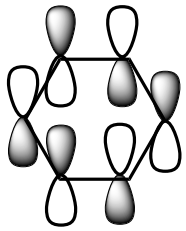
this extrastabilized by aromaticity

these π bonds are lower in E than the resonance stabilized π bonds in 1,3-cyclohexdiene*

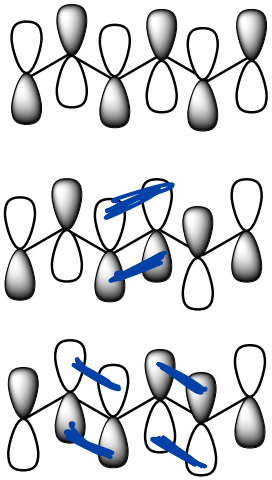
# MO Basis for Aromaticity

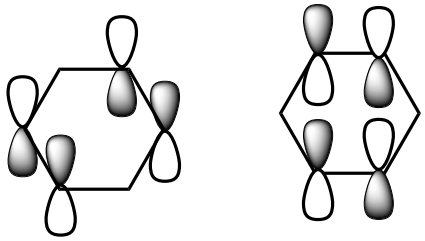


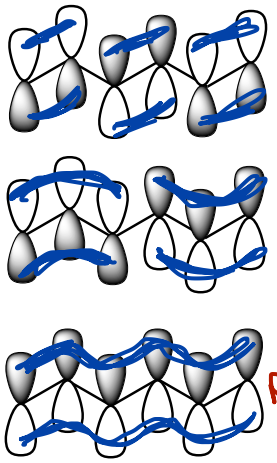




higher







π

π

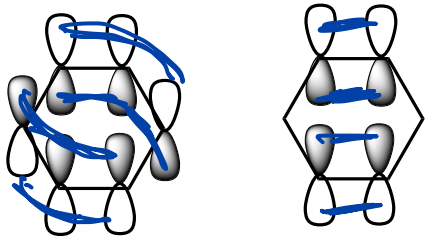
π

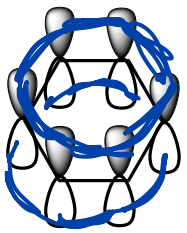
lower

e⁻ out here not between 2 nuclei

e⁻ always get to be between 2 nuclei

lowered





orbital is in E

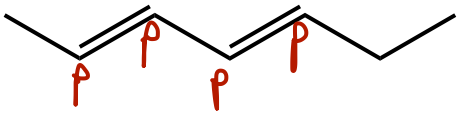
# Aromatic, Antiaromatic, Resonance Stabilized, and None of the Above

Nothing special happening here

unconjugated π bonds

$CH_2$ interrupts the string of p orbitals ... no e⁻ delocalization

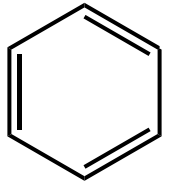
conjugated π bonds




3 or more p orbs in a row ... e⁻ delocalization

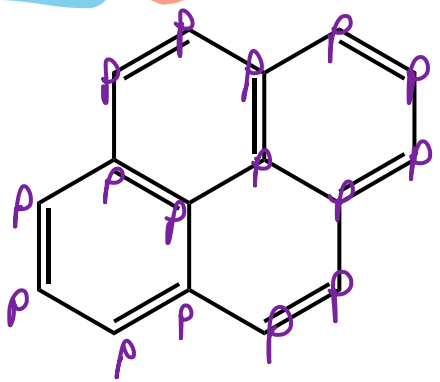
resonance is stabilizing the π bonds

conjugated aromatic π bonds



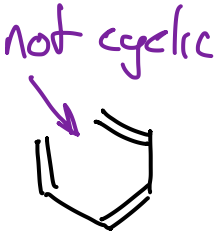
something extra special here more stable than just resonance stabilized

conjugated antiaromatic π bonds




something extra special (in a bad way) here ... less stable than just resonance stabilized

Rules for Aromaticity and Antiaromaticity


## Criteria for Aromaticity

1. Uninterrupted π cloud
   - •cyclic ✓
   - •p orbital on every atom ✓
   - •planar ✓

2. odd number of pairs of electrons or 4n+2 e⁻'s

3 pairs of e⁻'s in the π system

$4(1)+2 = 6\ e^-$'s

$4(2)+2 = 10\ e^-$'s

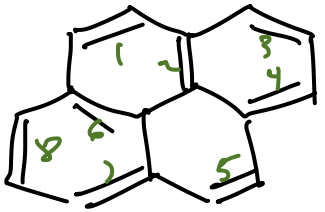
$4(3)+3 = 14\ e^-$'s

## Criteria for Antiaromaticity

1. Uninterrupted π cloud
   - •cyclic
   - •p orbital on every atom
   - •planar

2. even number of pairs of electrons or 4n e⁻'s in the π system

8 pairs of e⁻'s in π system



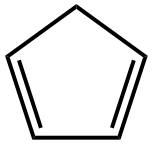

n is just a number not the number of C, H's or anything else

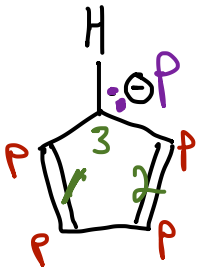
Aromatic, Antiaromatic, Resonance Stabilized, or None of the Above

$FC = 4 - (ab)$

$-1 = 4 - (ab)$

$5 = ab$





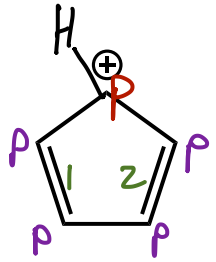
e⁻'s are delocalized so C⊖ is $sp^2$ so there is a p orbital for the lp e⁻'s to delocalize

planar

p orbs all the way around

3 is odd

aromatic



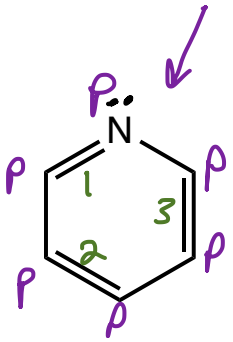
$sp^2$ hybridized C⊕

there is an unhybridized empty p orbital on the C⊕

planar ✓

uninterupted ring of p orbitals ✓

2 pairs even so antiaromatic

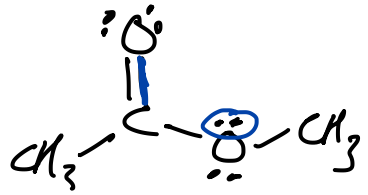


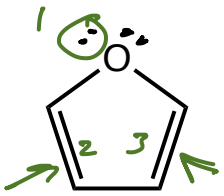
planar

p orbs all the way around

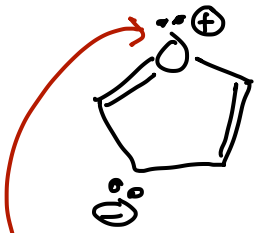
3 is odd

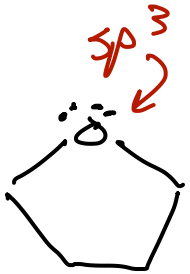
aromatic





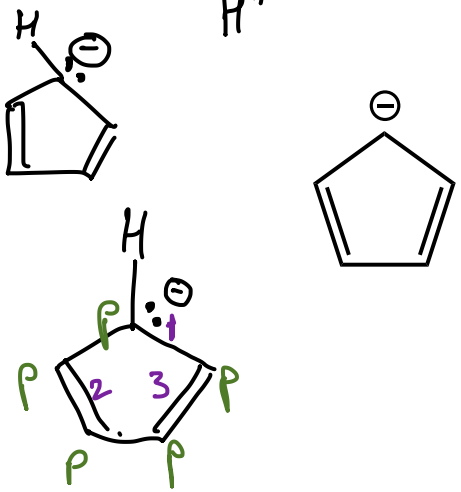
aromatic





$sp^2$ due to the e⁻ delocalization

Aromatic, Antiaromatic, Resonance Stabilized, or None of the Above



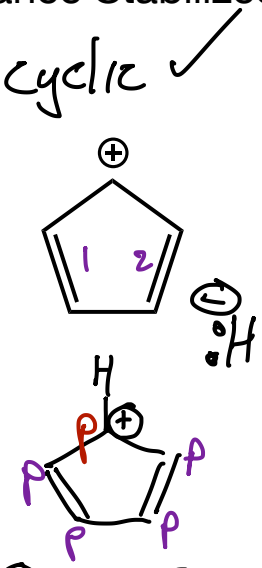
$C^{\ominus}$ is $sp^2$ because lp $e^-$'s on $C^{\ominus}$ are delocalized into π bond

- $sp^2$ C's all the way around

planar ✓

uninterrupted ring of p orbitals ✓

aromatic



cyclic ✓

$C^{\oplus}$ is $sp^2$ hybridized

planar ✓

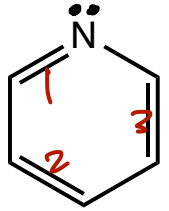
$sp^2$ all the way around

there is an empty p orbital on the $C^{\oplus}$

p orbs everywhere ✓

2 is even

antiaromatic



cyclic ✓

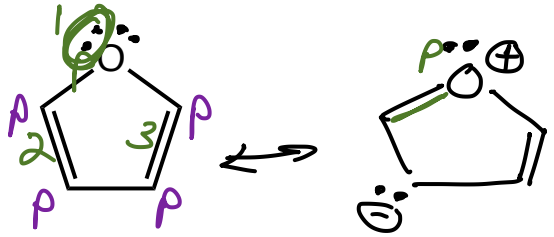
all $sp^2$ atoms

planar ✓

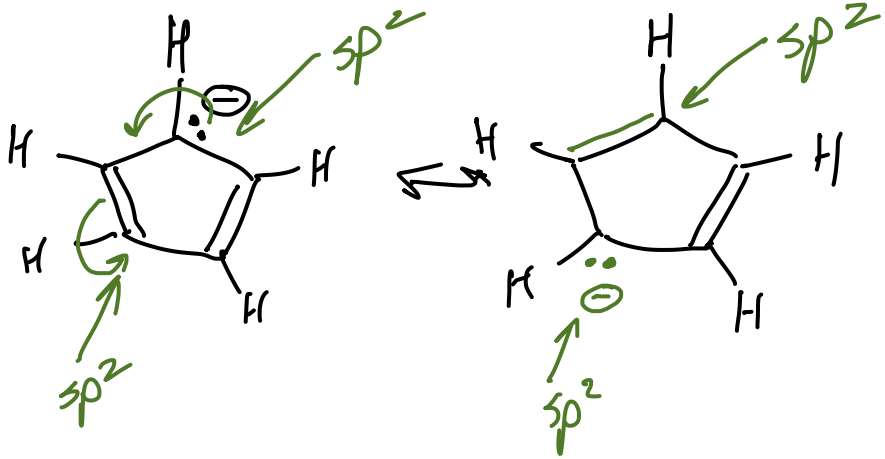
# pairs of $e^-$'s in π system?

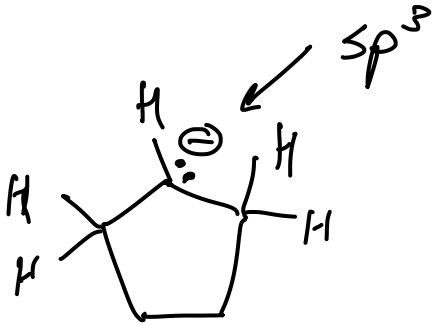
3 odd

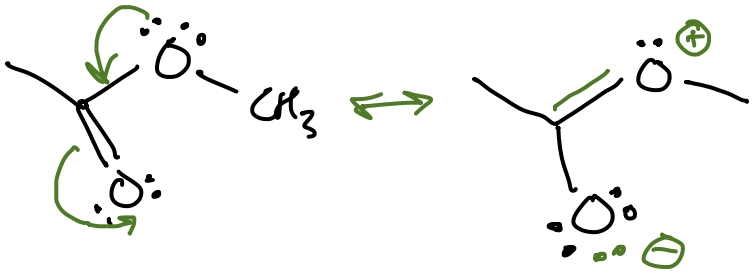
aromatic



aromatic


H
sp²
H
H
H
H
sp²
H
sp²
H
H
H
H
sp²


sp³
H
H
H
H


O
CH₃
O
O
O