(24) **Today**

Chap 15.2 – 15.6: Aromaticity

Next Class (25)

Chap 15.2 – 15.6: Aromaticity

(26) **Second Class from Today**

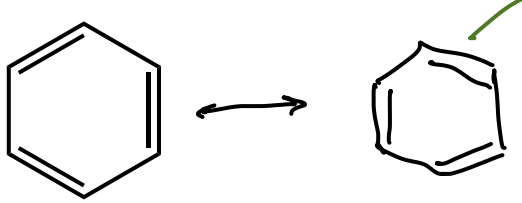
Chap 16.1 - 16.5: Electrophilic Aromatic Substitution

Third Class from Today (27)

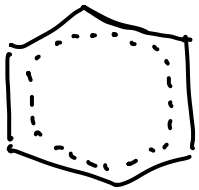
Chap 16.1 - 16.5: Electrophilic Aromatic Substitution

Reworked test 2 due Friday, April 11.

Benzene and resonance

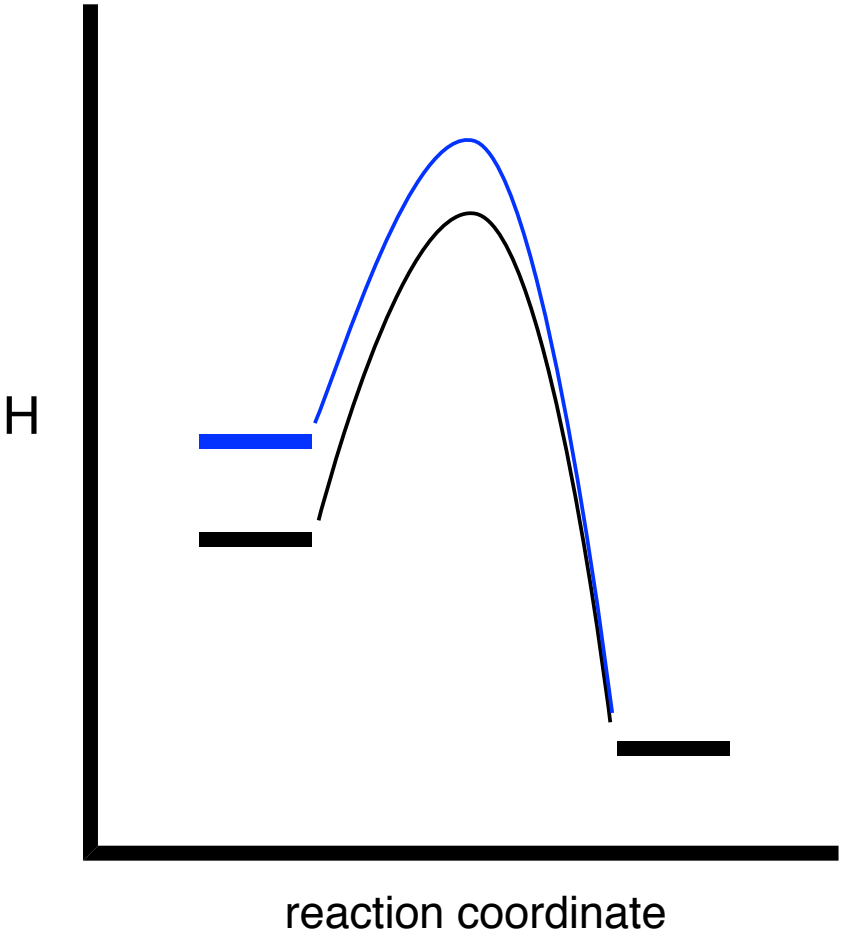


do not react like other C to C π bonds



delocalized e⁻'s into an extended π system

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



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

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

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

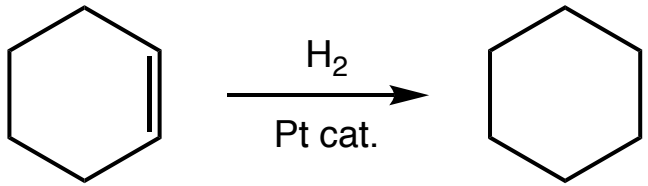
$\Delta H_{rxn} + H_{reactant} = H_{product}$

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

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

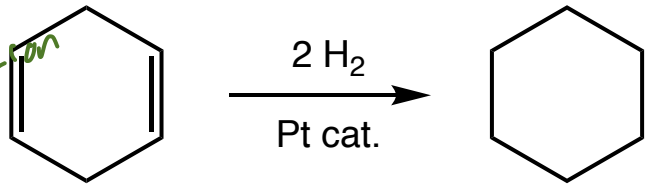
In other words, when two reactions end in the same place, the energy released or absorbed during the reaction can be used to compare the energies of the reactants.

Aromaticity: a special kind of resonance/electron delocalization



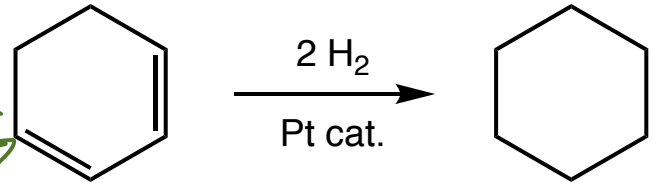
	$\Delta H_{reaction}$ (kcal/mol)	per bond (kcal/mol)
cyclohexene	–28.6	–28.6

no e⁻ delocalization

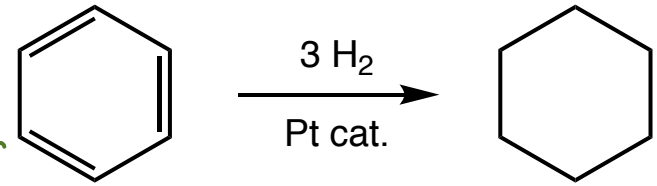


1,4 cyclohexadiene	–57.4	–28.7

e⁻ delocalized → resonance stabilized



1,3-cyclohexadiene	–55.4	–27.7

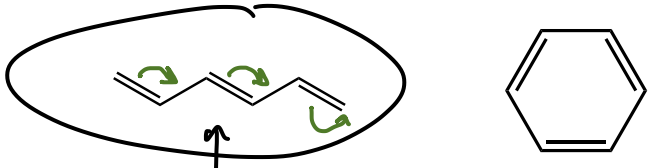


benzene	–79.8	-26.6

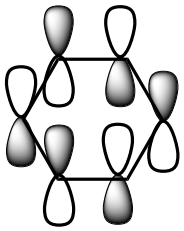
extra stabilization ... less E released per π bond as compared to "regular" resonance stabilization

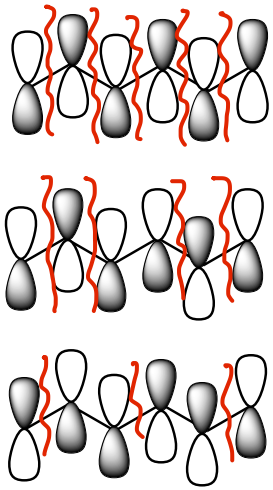
This extra stabilization is due to aromaticity

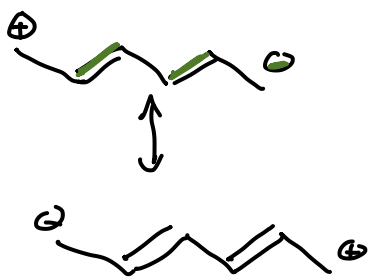
MO Basis for Aromaticity

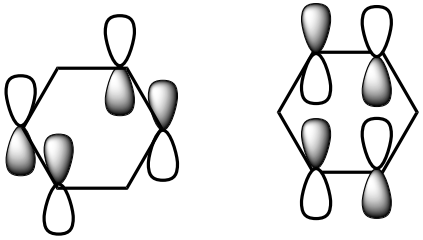


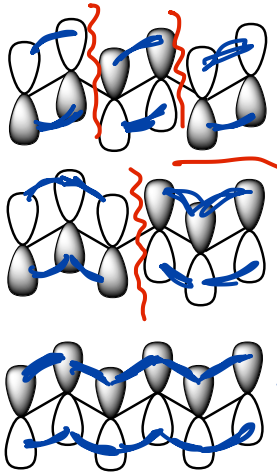
just looking at π bonds









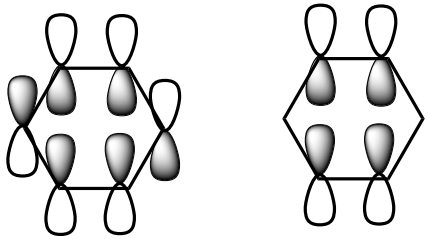


2 e⁻

node

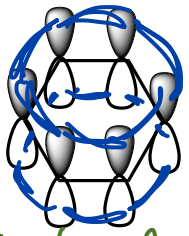
2 e⁻

2 e⁻



way out here e⁻'s only attracted to 1 nucleus but that never happens over here

every where in the orbital

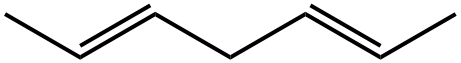


for 2e⁻ can experience attraction to 2 C nuclei

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

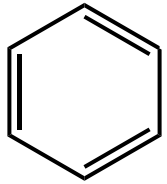
unconjugated π bonds

no resonance stabilization



No electron delocalization

conjugated aromatic π bonds



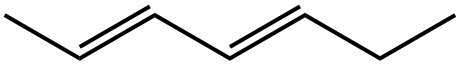
e⁻ delocalized

resonance contributors

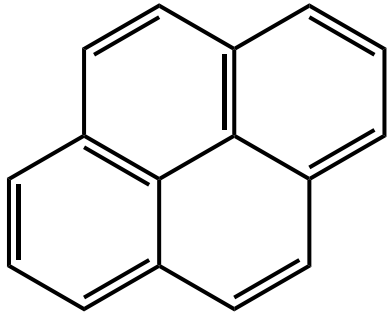
e⁻ delocalization

resonance stabilization

conjugated π bonds



conjugated antiaromatic π bonds



less stable than unconjugated π bonds

Rules for Aromaticity and Antiaromaticity

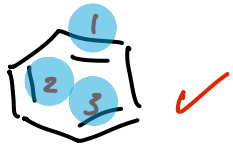
$4 \cdot 0 + 2 = 2e^-$

$4 \cdot 1 + 2 = 6e^-$

$4 \cdot 2 + 2 = 10e^-$

$4 \cdot 3 + 2 = 14e^-$

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

Criteria for Antiaromaticity

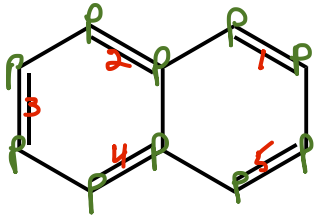
1. Uninterrupted π cloud

- cyclic
- p orbital on every atom
- planar

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

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

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



cyclic ✓

planar ✓

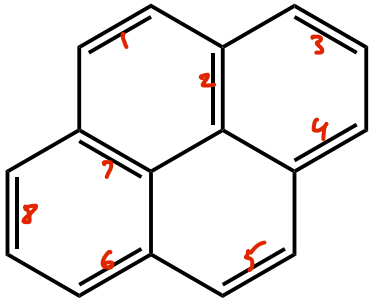
p orbitals everywhere ✓

5 pairs ✓

aromatic

do something different

electrophilic aromatic substitution



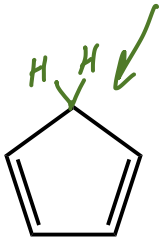
cyclic ✓

planar ✓

p orbitals everywhere ✓

8 pairs ∴

antiaromatic



cyclic ✓

planar ✓

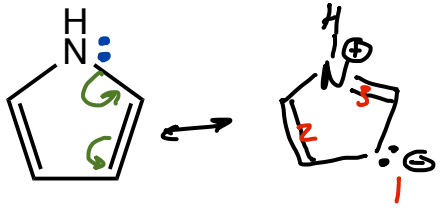
p orbs ✗

nope

regular resonance stabilization of π bonds

reacts like other C to C π bonds

electrophilic addition



✓

✓

✓

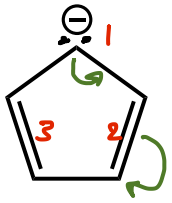
3 pairs

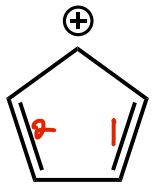
aromatic

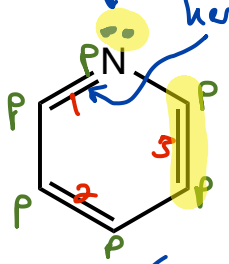
do something different

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

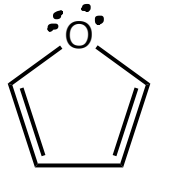
$FC_c = 4 - 5 = -1$







cannot enter π system 'cuz p orbital that we would need is already being used here



cyclic ✓ ✓ ✓ ✓

p orbs ✓ ✓ ✓ ✓

planar ✓ ✓ ✓ ✓

- sp^2 hybridized N
- p orbital used to form π bond
- lp e⁻'s in sp^2 hybrid that is ⊥ to π bond

3 pairs

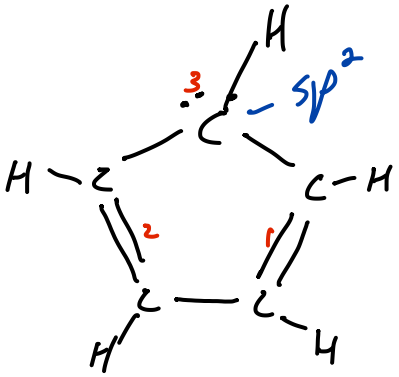
aromatic

2 pairs

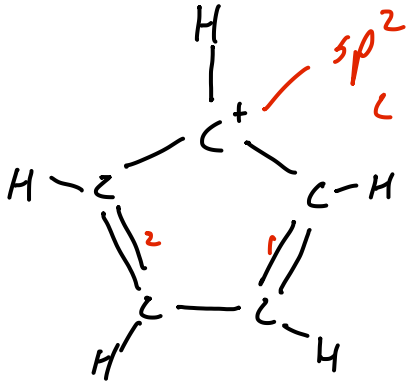
anti aromatic

aromatic ✓

aromatic



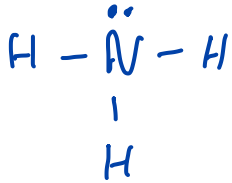
easier to make



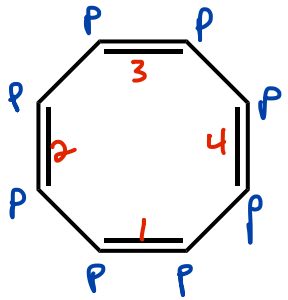
harder to make

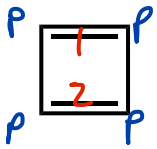
sp^2 hybridized C atom

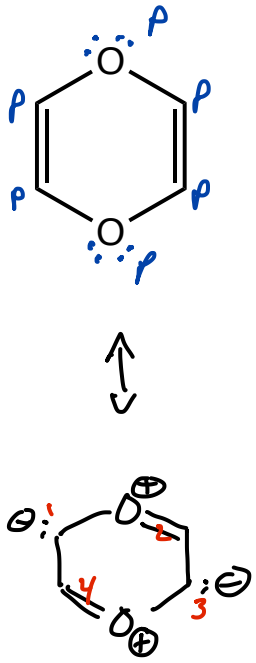
empty p orbital



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







if planar

even

antiaromatic

even

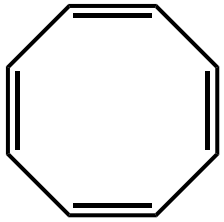
antiaromatic

even

antiaromatic

being antiaromatic is a thing to be avoided

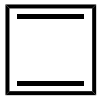
More on Antiaromaticity

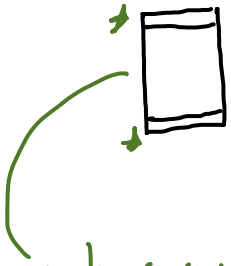


not planar

no electron delocalization

avoids being antiaromatic

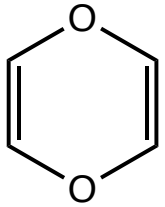


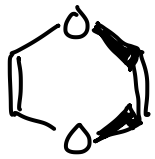


not square

sp orbitals don't overlap

thus not antiaromatic





not planar

no electron delocalization

avoids being antiaromatic