Benzene and Aromaticity 8.1, 8.2, 8.16 - 8.18

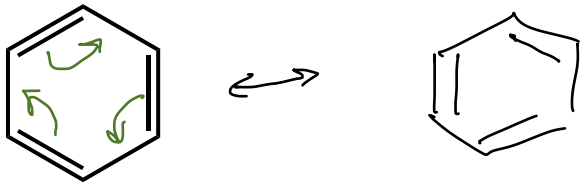
Reactions of Benzenes
Chap 18

Rework Test 3 by Monday May 2

all bonds in benzene are the same length

more 2p orbitals in a row or

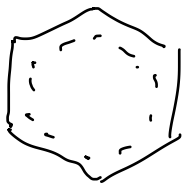
2p orbitals + lp e⁻



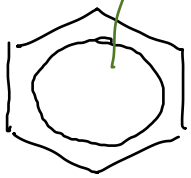
there are resonance contributors

electron delocalization occurs and we represent that e⁻ delocalization by drawing resonance contributors moving only π e⁻ + lp e⁻'s

The average of the resonance contributors is called the resonance hybrid



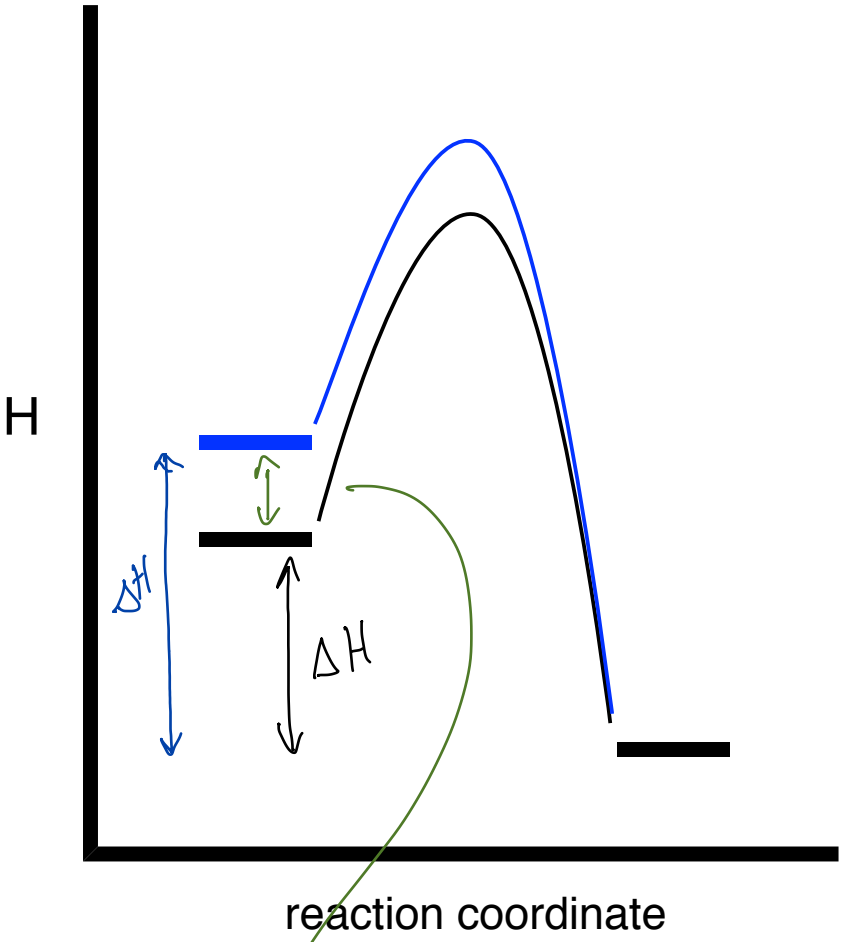
like a bond + a half



the circle is used to emphasize the aromaticity

not alternating single + double bonds

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



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

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

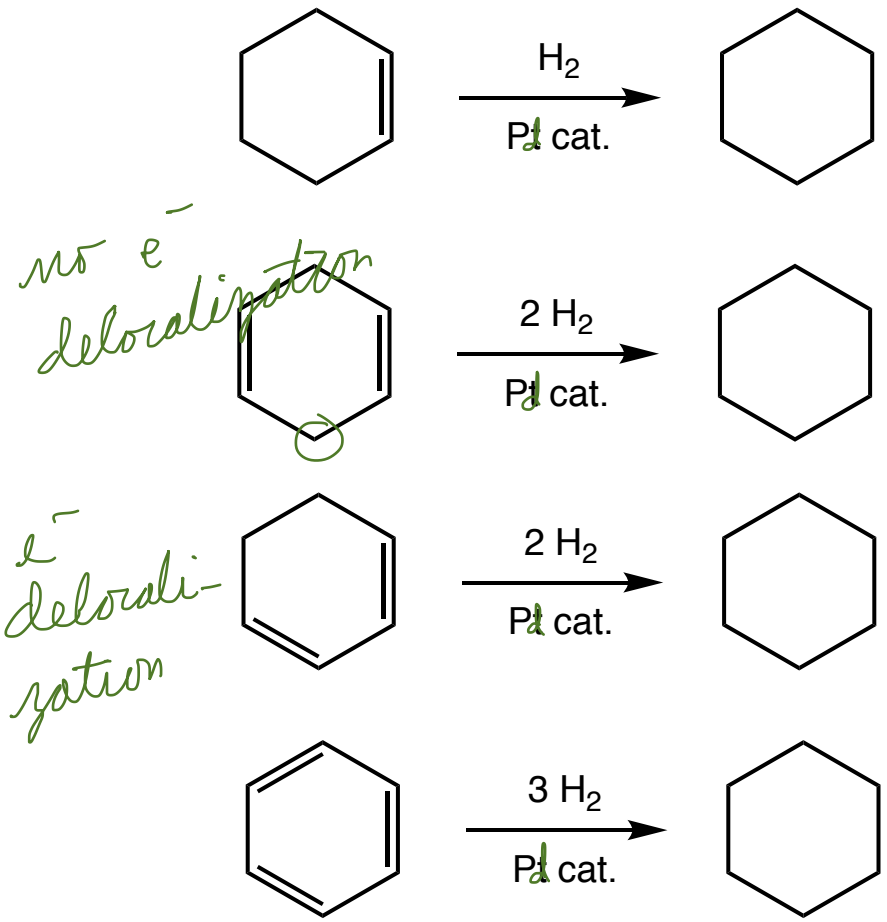
$\Delta H_{rxn} = H_{product} - H_{reactant}$

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

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

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

comparing reactions that give the same products is a convenient way to compare the stabilities of the reactants



no e⁻ delocalization

e⁻ 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

no resonance same stabilities

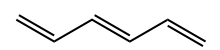
resonance has stabilized the π bond

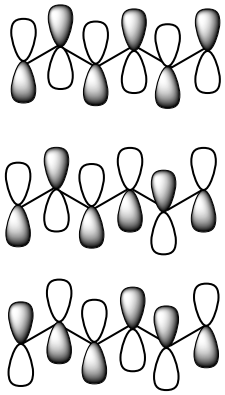
the π bond in

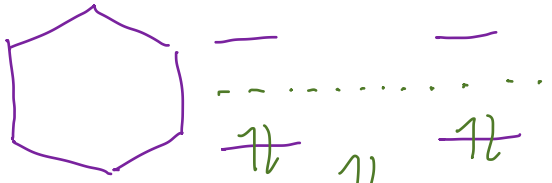
The "extra" stability (26.6 vs 27.7) is what we refer to as aromaticity

benzene are more stable than resonance would predict

6 p orbitals in a row

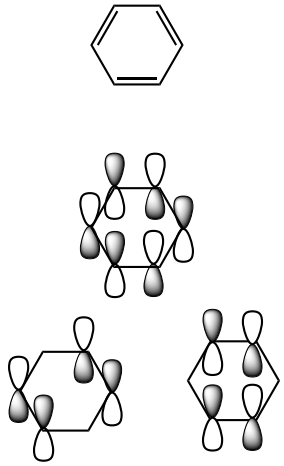


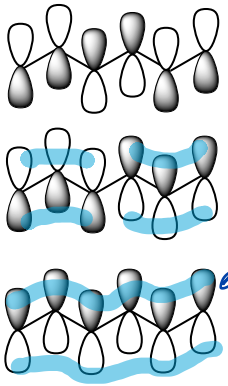




antibonding

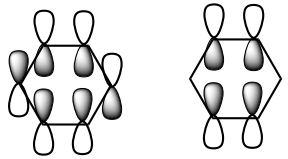
bonding

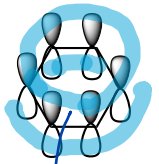




e⁻ over here can only be attracted to 1 nucleus

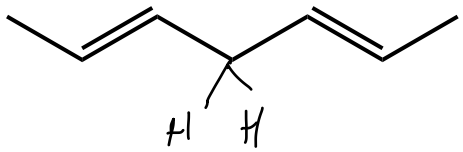
the e⁻'s always being between the two nuclei stabilizes the molecule





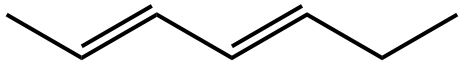
the e⁻ in this orbital can always be between 2 C nuclei

unconjugated π bonds



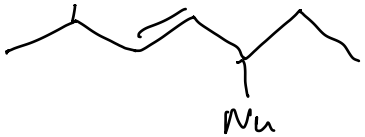
NO electron delocalization because CH_2 is between π bonds. Behave like all other unconjugated π bonds

conjugated π bonds

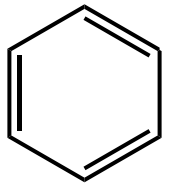


e⁻'s are delocalized

e⁻'s are lower in E as compared to above. Have additional reactivity like unconjugated π bonds plus "long range" reactions



conjugated aromatic π bonds



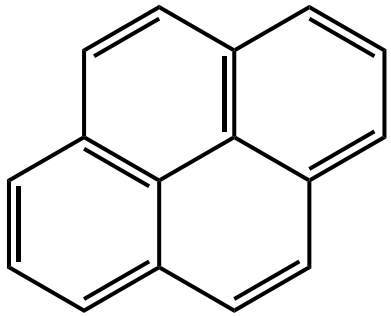
totally different chem

e⁻ delocalization

e⁻ more stable

do not react like alkenes

conjugated antiaromatic π bonds



e⁻ delocalization, but it DESTABILIZES the π e⁻'s

Criteria for Aromaticity

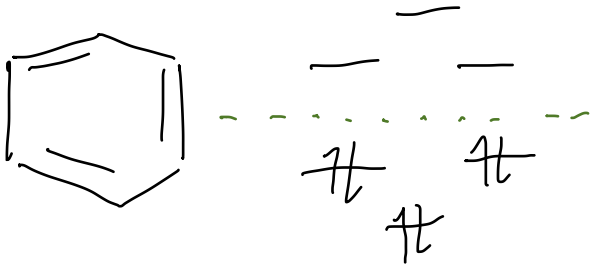
1.Uninterupted π cloud
- cyclic
- p orbital on every atom
- planar

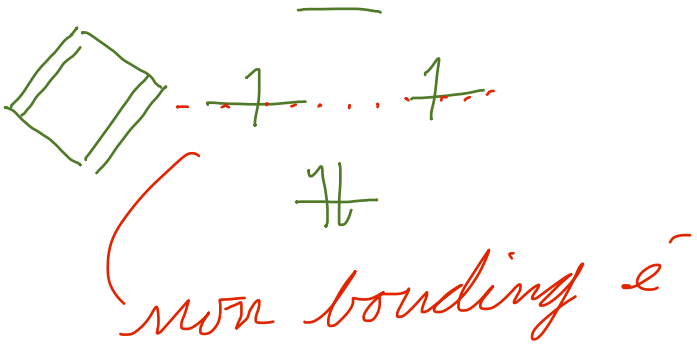
2. odd number of pairs of electrons or 4n+2 e⁻'s

Criteria for Antiaromaticity

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

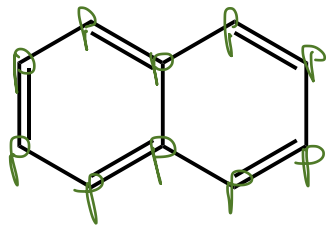
2. even number of pairs of electrons or 4n e⁻'s in the π system





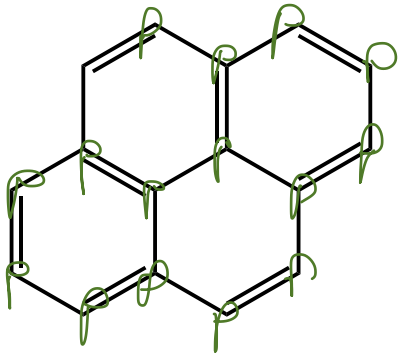
n is just a number not the number of C, H's or anything else

aromatic

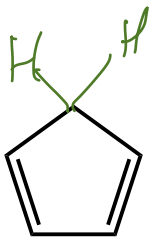


ring of p orbitals planar odd # of pairs of e⁻

antiaromatic

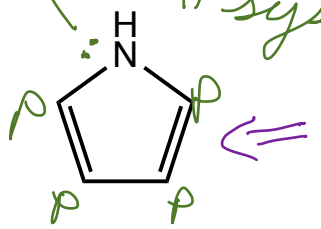


even # of pair of e⁻'s



NotA

part of π system



aromatic

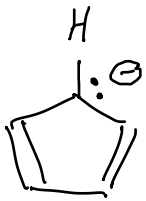
lp e⁻'s or N participate in π system

3 pairs e⁻'s

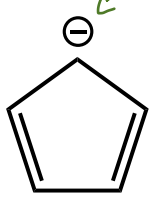
sp²

ring of p orbitals

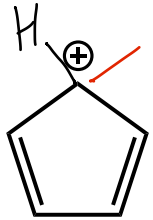
aromatic



2 π bonds + lp e⁻'s makes ring of p orbitals



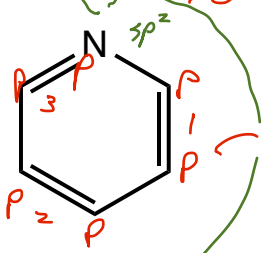
aromatic 3 pairs of e⁻



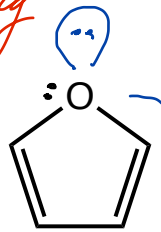
empty p orbital

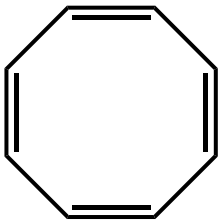
antiaromatic

in the plane of the ring

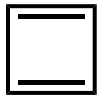


aromatic 3 pairs these e⁻'s are in an sp² hybrid and ⊥ to π system



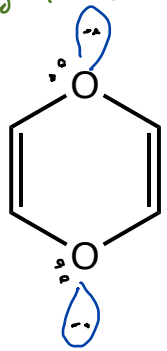


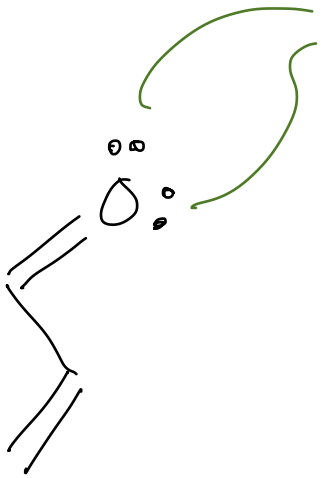
combine 3 AO's = 3 HO's =>



sp² sp² sp²

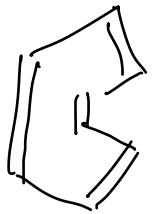
s p_x p_y p_z

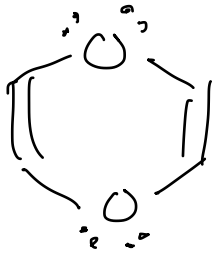


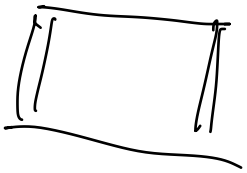


cannot participate in e^- delocalization because the already present π bond locks the lp e^- out

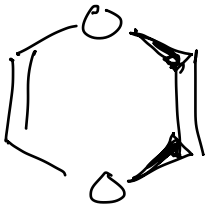
one set of lp e^-'s can participate







becomes a boat shape to avoid being antiaromatic



puckers at the C atoms to avoid becoming antiaromatic