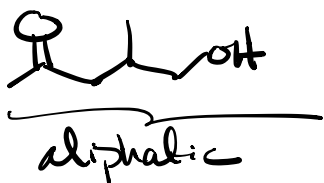# Aromaticity

Aliphatic

Something that is
not aromatic
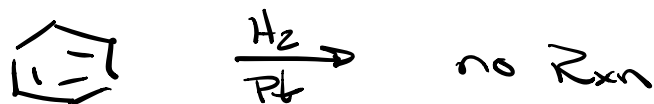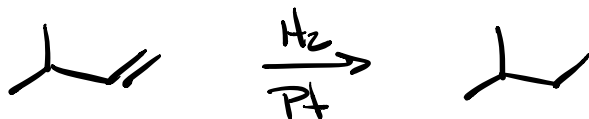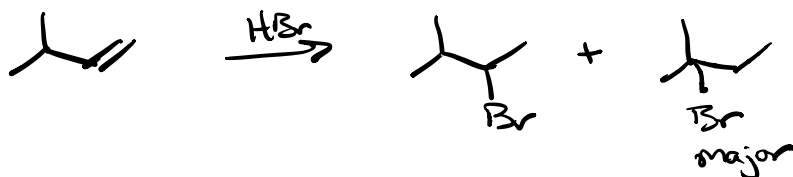
[structure drawing] OH

aliphatic

Aromatic

Not Simple

sp^2 ⟹ [benzene ring] Benzene

Vary Stable
does not do $SN^1 SN^2 E, E^2$

⟹ Electrophilic Substitution & Addition

[alkene structure] $\xrightarrow{HBr}$ [structure] Br + [structure] Br
major

[benzene ring] $\xrightarrow{HBr}$ no Rxn

[alkene structure] $\xrightarrow[Pt]{H_2}$ [structure]

[benzene ring] $\xrightarrow[Pb]{H_2}$ no Rxn

Stability

less stable

ΔE

$\begin{array}{c} H_2 \\ Pt \end{array}$

$\begin{array}{c} H_2 \\ Pt \end{array}$

ΔE

Isolated System

Conjugated

$\leftarrow$ Sp^3

More
Stable
Energy gained by Conjugation

2x

2eg H$_2$
Pt

Less than
2x

2eg H$_2$
Pt

ΔE
$= x$

H$_2$
Pt

3x

Conjugated

Not Simple Resonance
or Conjugation

Aromatic

3eg H$_2$
Pt

3eg H$_2$
Pt

much
more
Stable

3eg H$_2$
Pt

Molecules & Ions that demonstrate Aromaticity
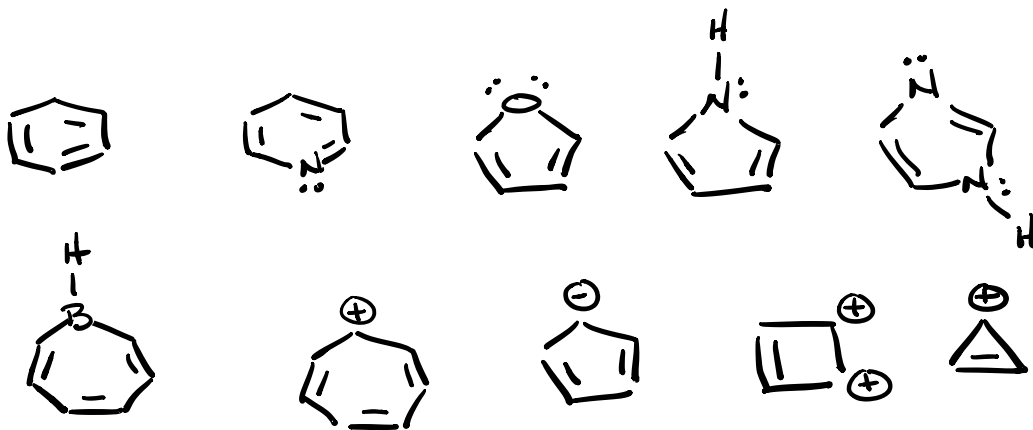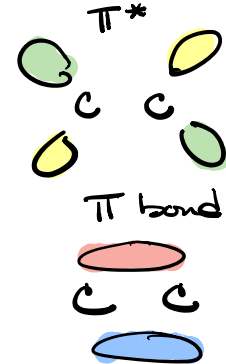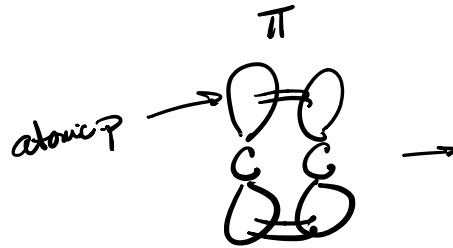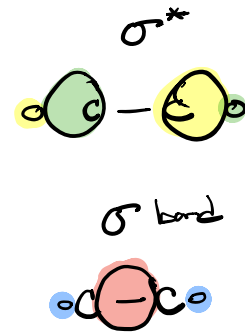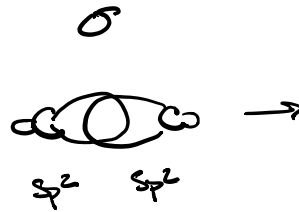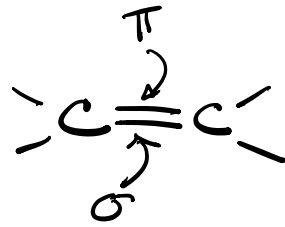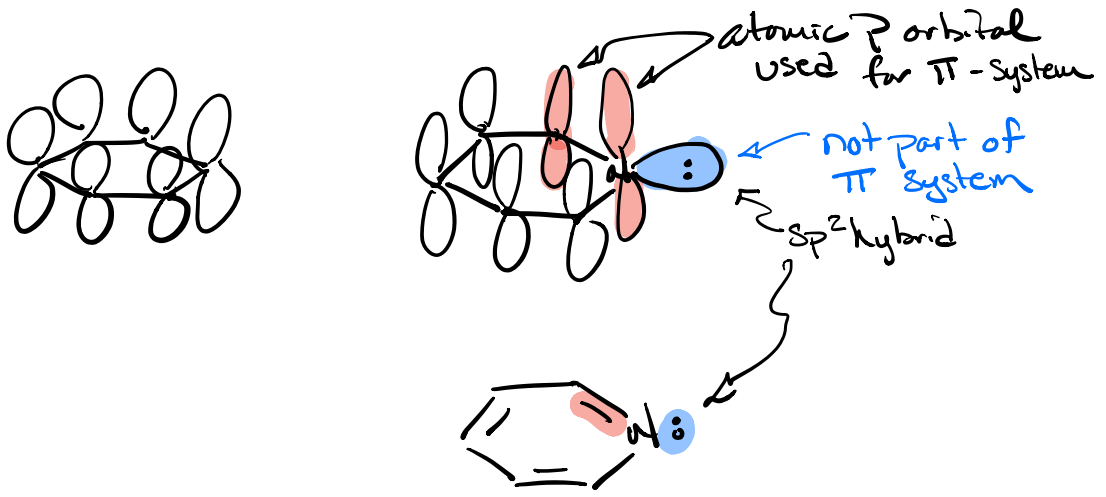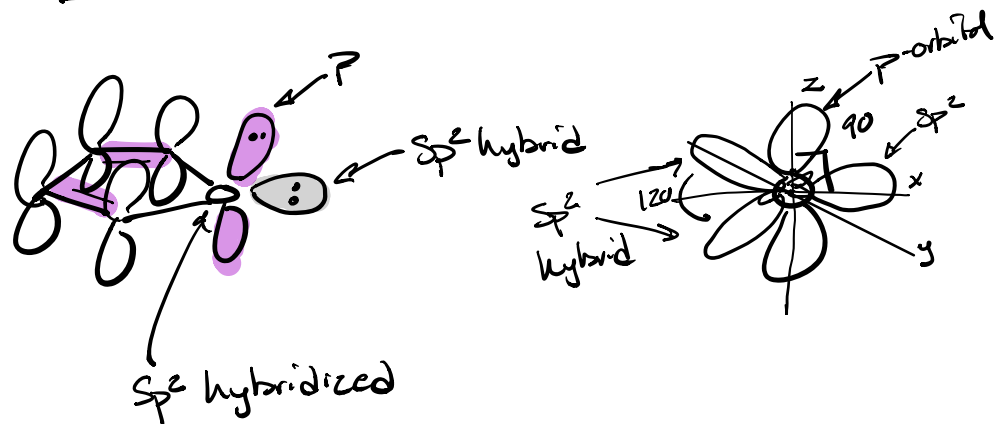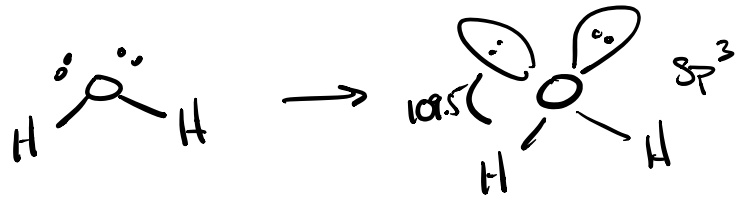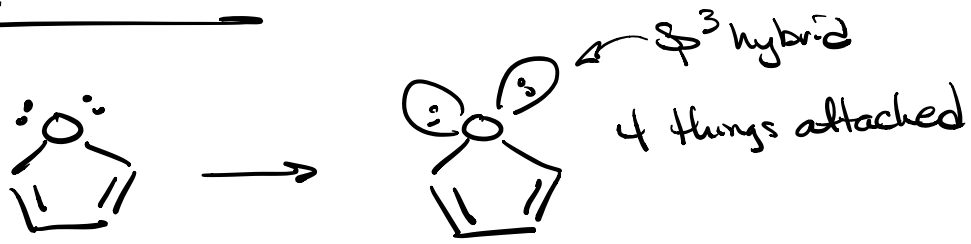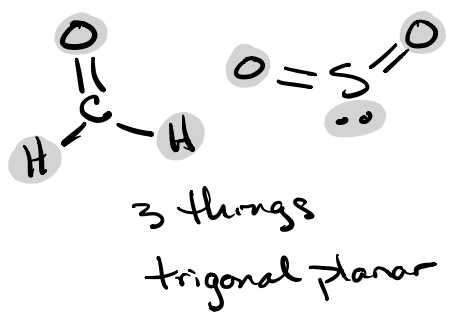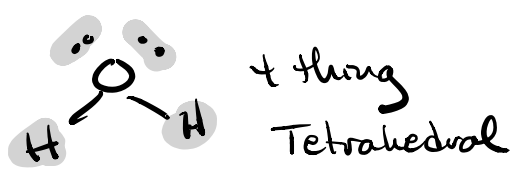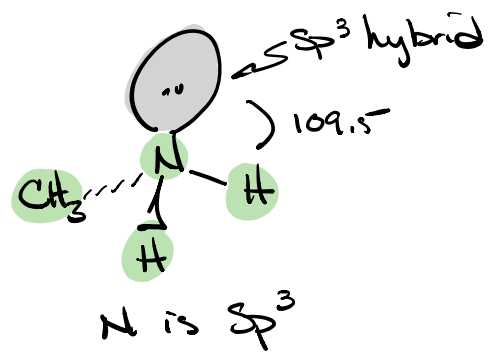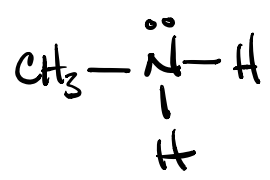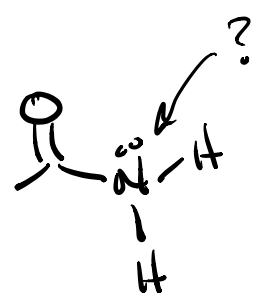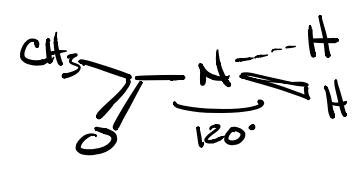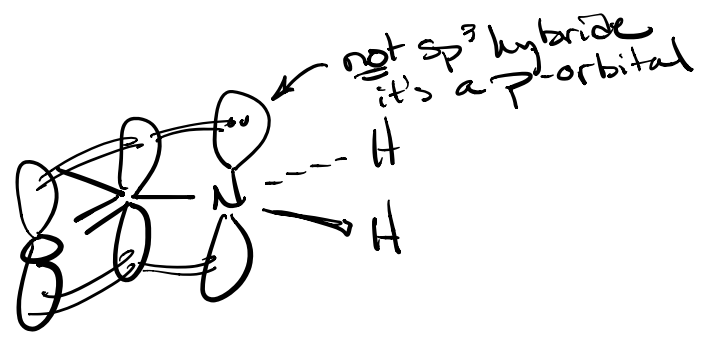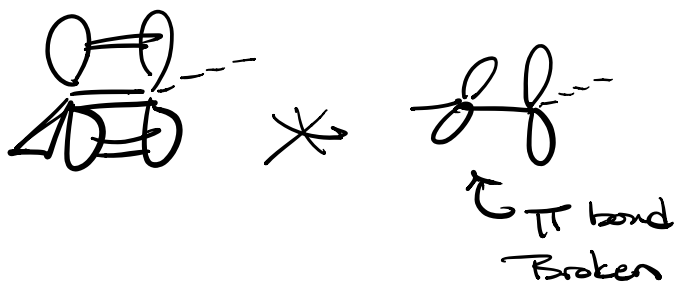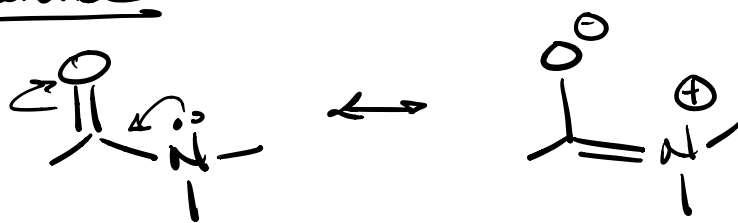
~~~~~~

Not Aromatic

Aromatic

- Flat
- All sp^2 hybridized atoms for ring (conjugated)
- Have a number of π electrons that fit the formula $4n + 2$ } n = integer value

n	# of π e$^-$ allowed for aromatic $4n+2$
0	$4(0) + 2 = 2e^-$
1	$6e^-$
2	$10e^-$
3	$14e^-$
⋮	

Benzene	Pyridine	Thiophene	Pyrrole

#πe$^-$ in System 6π 6π 6π 6π

Counting of e$^-$ is about MO theory & which e$^-$ are in the π system

Molecular Orbitals
of π-System

ψ_6 ——

ψ_5 ——   anti bonding

ψ_4 ——   π*

$\overline{\psi_3}$ ⥮   π

ψ_2 ⥮   Bonding
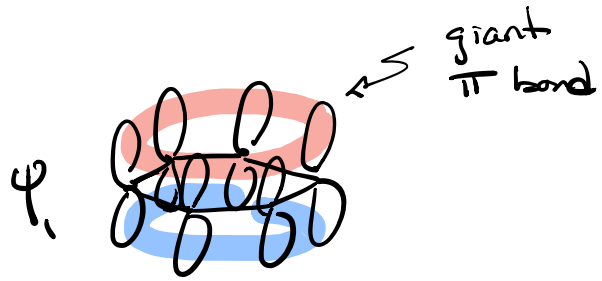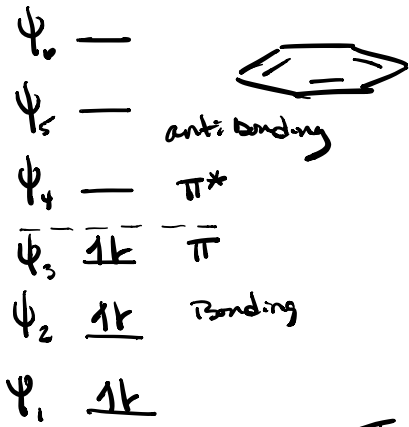
ψ_1 ⥮

giant
π bond

ψ_1

π
$>C=C<$
σ

σ

sp²   sp²

σ*

σ bond

π

atomic P

π*

C C

C C

π bond

C C

atomic p orbital
used for π-system

not part of
π system

sp² hybrid

Furan

p

sp² hybrid

sp² hybridized

sp² hybrid

p-orbital

sp²

120

Expectation

sp^3 hybrid

4 things attached

sp^3

105

Chem 3
Chem 1A
Chem 1B
} VSEPR

Count atoms & lone pairs
attached to an atom

4 thing
Tetrahedral

3 things
trigonal planar

Chem 12A   Natural Bonding theory   Localized bonds
            ↳ Hybridization
            sp^3, sp^2, sp
            Molecular Orbital Theory   Delocalized

VSEPR

$CH_3 - \overset{..}{\underset{|}{N}} - H$
$\qquad\;\; H$

Sp³ hybrid

} 109.5

$CH_3 \cdots \overset{}{N} \;\; H$
$\qquad\quad | \\ \qquad\quad H$

N is Sp³

Molecular Geometry — trigonal pyramidal

Electronic Geometry — tetrahedral

?

$\overset{O}{\underset{|}{||}} \; \overset{..}{N} - H \\ \qquad\quad | \\ \qquad\quad H$

VSEPR ⟹ Sp³

Observation

$CH_3 - \overset{}{\underset{||}{C}} - N \overset{---H}{\underset{\underset{120°}{\smile}}{\diagdown H}}$
$\qquad\qquad O$

Reality = Sp²

why

not Sp³ hybride
it's a P-orbital

$\overset{}{N} \cdots H \\ \qquad \searrow H$

More stable through
Conjugation

Resonance

$$\text{structures shown}$$

π bond
Broken

Molecular Orbital Theory

Focus just on π System

# of atomic P orbitals in = # of MO out

π-System

Antibonding

Bonding

⟵ valence e^-

Mass Spec

$\xrightarrow{-e^-}$

Valence e^-

Frost's Circle ⟹ A model that predicts the relative energies of the π System in an aromatic molecule.

point down

Antibonding
Empty

Antibonding

$\overline{\Psi_6}$

$\overline{\Psi_4}$ --- --- --- $\overline{\Psi_5}$

$\underline{\uparrow\downarrow}$ $\quad$ $\underline{\uparrow\downarrow}$
Ψ_2 $\qquad$ Ψ_3
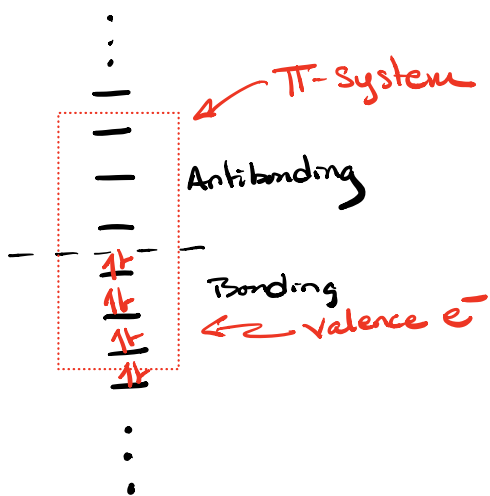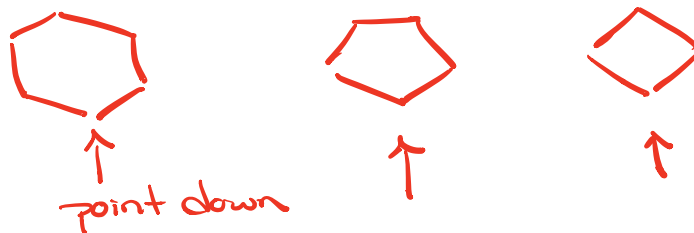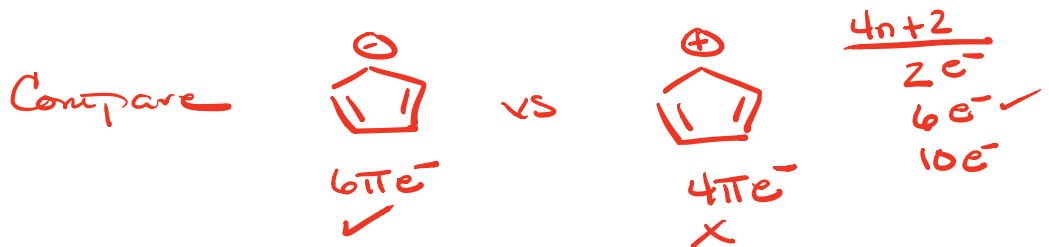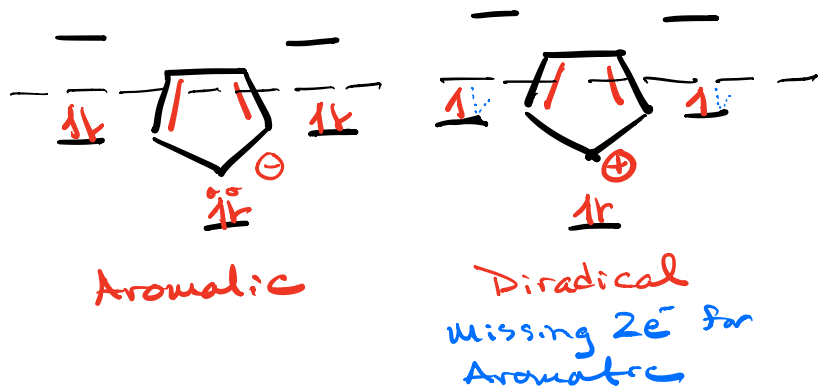
$\underline{\uparrow\downarrow}$
Ψ_1

Bonding
full

Bonding

Relative energies
of aromatic π system

$6 \pi e^-$

---

antibonding
Empty

$\overline{\Psi_4}$ $\qquad\qquad$ $\overline{\Psi_5}$

$\underline{\uparrow\downarrow}$ --- --- --- $\underline{\uparrow\downarrow}$ $\quad$ Bonding
Ψ_2 $\qquad\qquad$ Ψ_3 $\qquad$ full

$\underline{\uparrow\downarrow}$
Ψ_1

Compare $\qquad$ vs $\qquad$ $\dfrac{4n+2}{2e^-}$
$\qquad\qquad\qquad\qquad\qquad$ $6e^- \checkmark$
$\qquad\qquad\qquad\qquad\qquad$ $10e^-$

$6\pi e^-$ $\qquad\qquad$ $4\pi e^-$
$\checkmark$ $\qquad\qquad\qquad$ X

Frost's Circle analysis

$\underline{\uparrow\downarrow}$ $\qquad$ $\underline{\uparrow\downarrow}$ $\qquad\qquad$ $\underline{\uparrow}$ $\qquad$ $\underline{\uparrow}$

$\underline{\uparrow\downarrow}$ $\qquad\qquad\qquad\qquad$ $\underline{\uparrow\downarrow}$

Aromatic $\qquad\qquad$ Diradical
$\qquad\qquad\qquad\qquad$ Missing $2e^-$ for
$\qquad\qquad\qquad\qquad$ Aromatic

Anti Aromatic

Short

Long

Same length

empty p-orbitals

Aromatic

$4\pi e^-$

1 1 ← anti bonding orbitals

$1\uparrow\downarrow$ ← Bonding

$2\pi e^-$

anti bonding empty

$1\uparrow\downarrow$ ← bonding