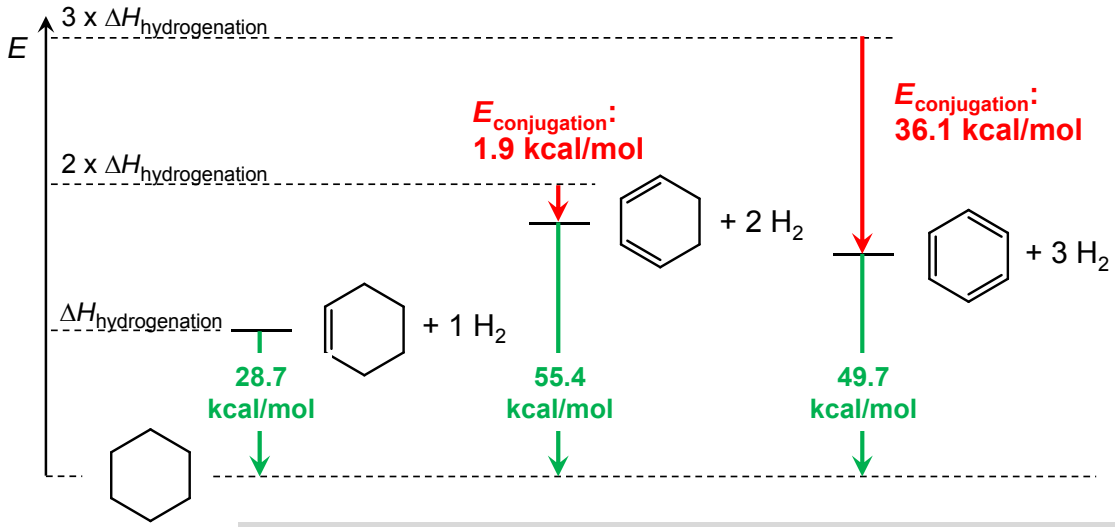
Benzene: An Unusually Stable Molecule

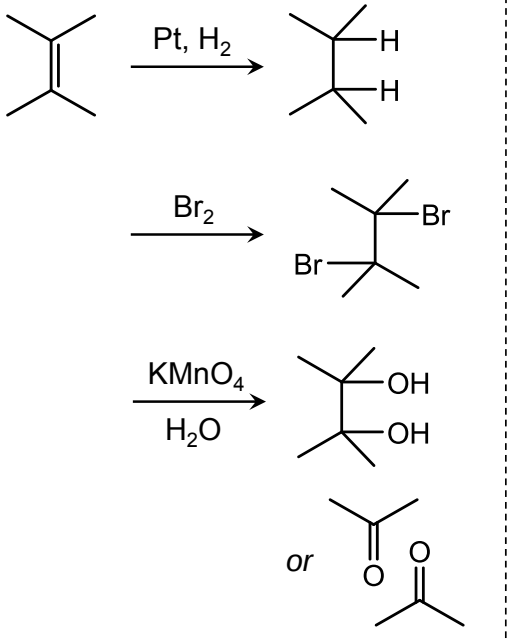
Not just an ordinary triene.

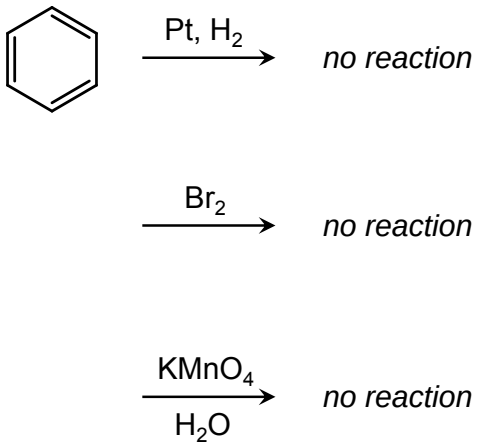
Comparing energies of hydrogenation,



So, benzene is stabilized by 36.1 kcal/mol relative to a typical triene.

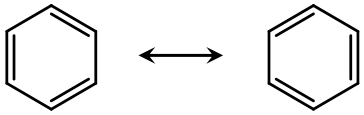
Benzene Does Not React Like a Typical Alkene





Benzene Stability Is Not Due To Cyclic Resonance Alone

Original hypothesis was that resonance responsible for benzene stability.

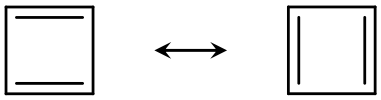


consensus structure

(all bonds equal length)

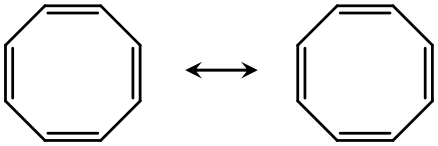
But…

cyclobutadiene



not stable.

cyclooctatetraene

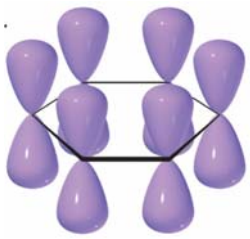


reacts like a typical alkene.

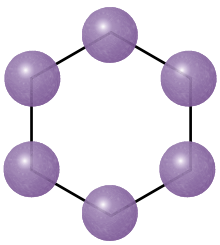
Molecular Orbital Diagrams of Cyclic π-Electron Systems

For continuous circle of *p* orbitals,

1. On an energy diagram, draw the ring of atoms as a polygon, point down.
2. Draw an energy level at each vertex of the polygon.
3. At the lowest level, draw an all-bonding molecular orbital.
4. At each energy level above previous one, draw orbital with one more node--evenly spaced, through the center.
5. Fill orbitals with electrons (keeping Hund's rule in mind).



viewed from the top:



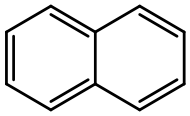
Hückel's Rule of Aromaticity

For a continuous, planar circle of *p* orbitals,

- Molecules with (4*n* + 2) electrons (where *n* is an integer) are stabilized, "aromatic".
- Molecules with (4*n*) electrons are destabilized, "anti-aromatic".

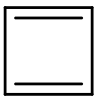
aromatic molecules

6 π electrons



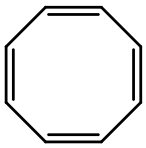
naphthalene
10 π electrons

anti-aromatic molecules



too reactive to isolate

4 π electrons

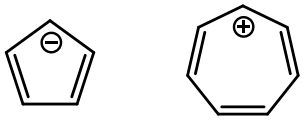


8 π electrons

puckers to avoid conjugation

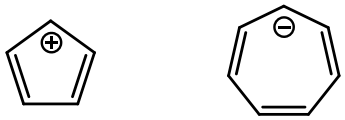
Aromatic and Anti-Aromatic Ions

aromatic (4n+2) ions

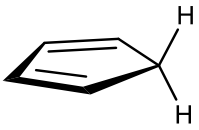


6 π electrons

anti-aromatic (4n) ions

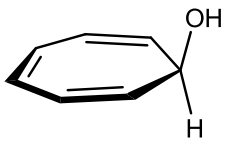


4 π electrons 8 π electrons



$pK_a \approx 16$

acidic for a hydrocarbon!



+ dilute HCl

unusually reactive for an alcohol!

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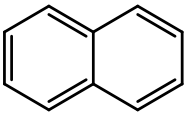
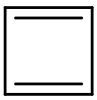
aromatic molecules

6 π electrons



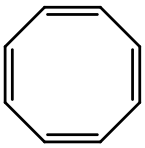
naphthalene
10 π electrons

anti-aromatic molecules



too reactive to isolate

4 π electrons



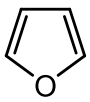
8 π electrons

puckers to avoid conjugation

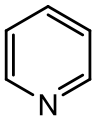
Aromatic Heterocycles

Heterocycle: A ring containing atoms other than carbon. ("Heteroatoms". Typically N, O, S, or P.)

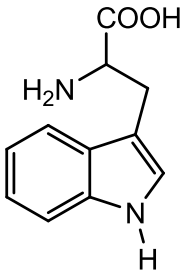
aromatic heterocycles



furan
6 π electrons



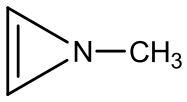
pyridine
6 π electrons



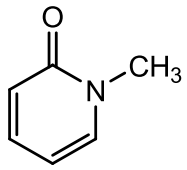
tryptophan
10 π electrons

Hybridization of heteroatoms is determined by aromaticity.

non-aromatic heterocycle



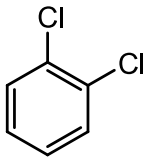
Aromaticity by Resonance



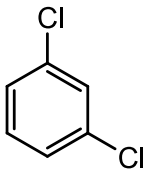
Is this molecule aromatic?

- Check to see if π orbital system is contiguous.
- Check resonance structures.
  If any of them have (4*n*+2) π electrons, the molecule is aromatic.

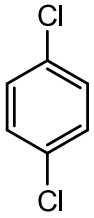
Naming Disubstituted Benzenes



1,2-dichlorobenzene
ortho-dichlorobenzene
o-dichlorobenzene



1,3-dichlorobenzene
meta-dichlorobenzene
m-dichlorobenzene



1,4-dichlorobenzene
para-dichlorobenzene
p-dichlorobenzene