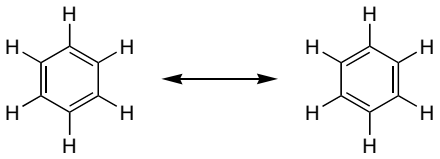
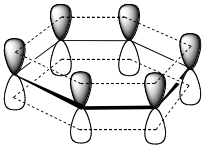
# Chapter 15: Benzene and Aromaticity

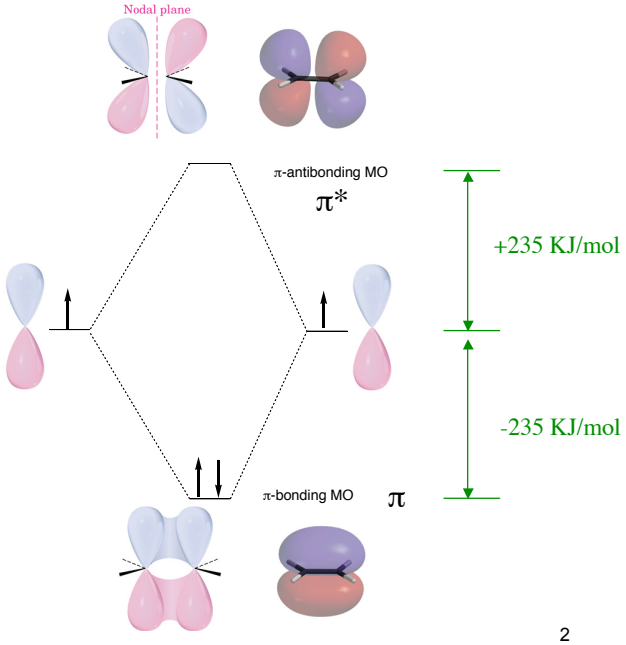


$C_6H_6$



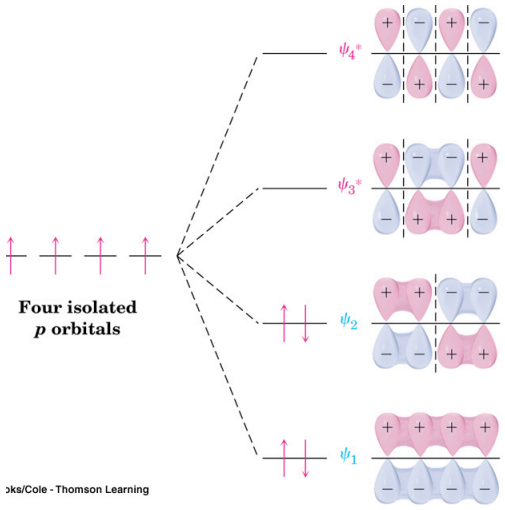


MO's of a
C=C π-bond




from Chapter 1

## π-molecular orbitals of butadiene




3 Nodes
0 bonding interactions
3 antibonding interactions
ANTIBONDING MO

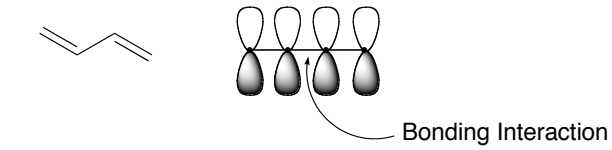
2 Nodes
1 bonding interactions
2 antibonding interactions
ANTIBONDING MO

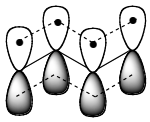
1 Nodes
2 bonding interactions
1 antibonding interactions
BONDING MO

0 Nodes
3 bonding interactions
0 antibonding interactions
BONDING MO

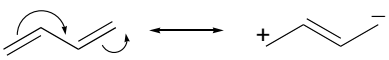
$\psi_2$ is the Highest Occupied Molecular Orbital (HOMO)
$\psi_3$ is the Lowest Unoccupied Molecular Orbital (LUMO) 3

## $\psi_1$ of Butadiene (no nodes, bonding MO)



The four π-electrons in $\psi_1$ are delocalized over the four p-orbitals



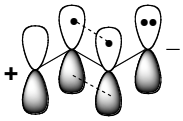


Table 14.2 (p. 528): Bond lengths in pm

| $H_3C—CH_3$ | $H_2C=CH_2$ | $H_2C=CH—CH_3$ | $H_2C=CH-CH=CH_2$ | $H_2C=CH-CH=CH_2$ |
|---|---|---|---|---|
| 154 | 133 | 149 | 148 | 134 |

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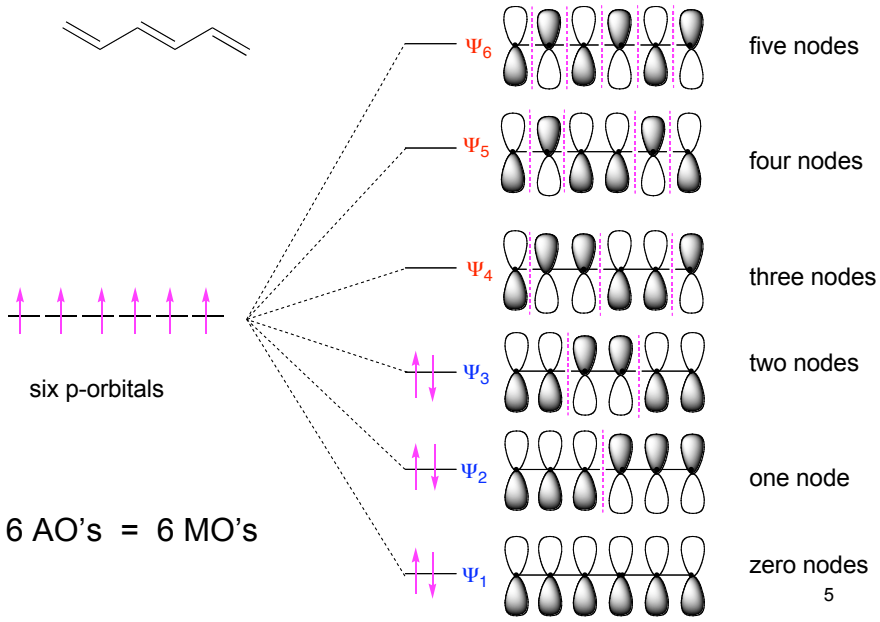
π-molecular orbitals of hexatriene




6 AO's = 6 MO's

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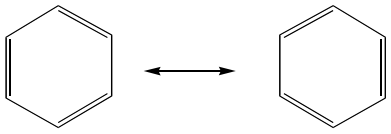
**Conjugation**: series of overlapping p-orbitals

**Aromaticity**: cyclic conjugated organic compounds such as benzene, that exhibit special stability due to resonance delocalization of π-electrons.



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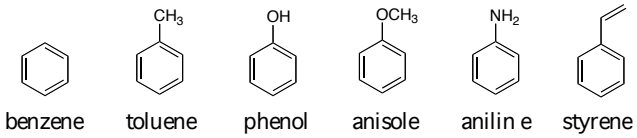
## 15.2: **Naming aromatic compounds:** (arenes)

large number on non-systematic names (Table 15.1)




benzene toluene phenol anisole anilin e styrene

Generally, mono-substituted benzenes are named in a similar manner as hydrocarbons with -benzene as the parent name


bromobenzene ethylbenzene (1-methylethyl)benzene (isopropylbenzene) nitrobenzene

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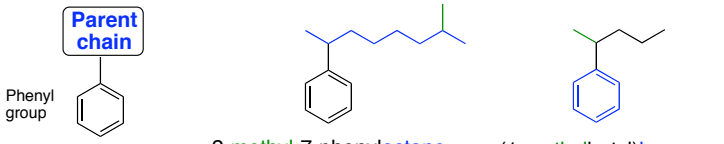
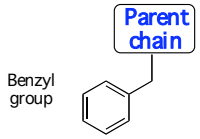
When the benzene ring is a substituent of a parent chain, referred to as a phenyl group. The benzene ring is is regarded as a substituent when the parent chain has greater than six carbons. The benzene ring is the parent when the longest alkyl chain substituent is six carbons or less




2-methyl-7-phenyloctane (1-methylbutyl)benzene

A phenyl substituent ($C_6H_5$-) is often abbreviates as Ph-

A $C_6H_5$-$CH_2$- susbtitutent is often referred to as a benzyl group (Bn-)

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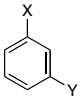
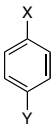
Disubstituted benzene: relative position of the substitutents


1,2-disubstituted: *ortho* (*o*-)



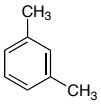

1,3-disubstituted: *meta* (*m*-)



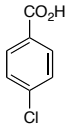

1,4-disubstituted: *para* (*p*-)

Note: ortho, meta, and para are not used in systematic nomenclaure


2-chlorotoluene
*ortho*-chlorotoluene
*o*-chlorotoluene




1,3-dimethylbenzene
*meta*-xylene
*m*-xylene




4-chlorobenzoic acid
*para*-chlorobenzoic acid
*p*-chlorobenzoic acid

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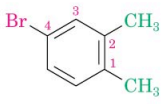
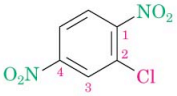
Benzenes with two or more substituents:

Choose numbers to get lowest possible values

List substituents alphabetically with hyphenated numbers




**4-Bromo-1,2-dimethylbenzene**

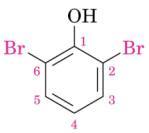



**2-Chloro-1,4-dinitrobenzene**


**2,4,6-Trinitrotoluene (TNT)**

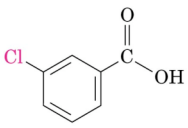


Common names, such as “toluene” can serve as root name (as in TNT)




***2,6-Dibromophenol***






***m*-Chlorobenzoic acid**

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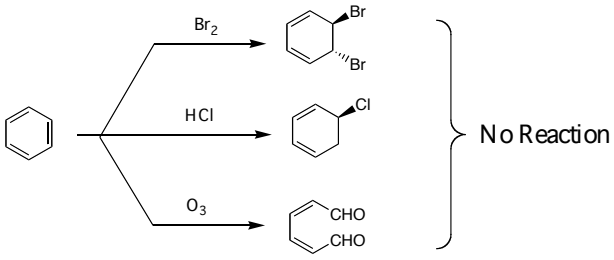
## 15.3: Structure and Stability of Benzene

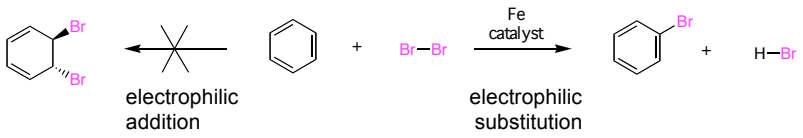
Formula: $C_6H_6$, four degrees of unsaturation (section 6.2)
three double bonds + one ring

The π-bonds of benzene are resistant to the normal reactions of alkenes and alkynes

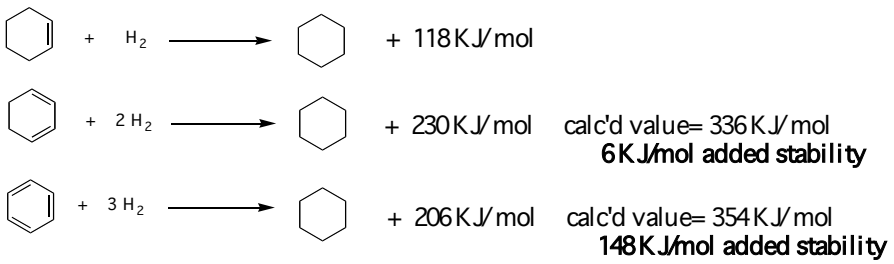



Benzene's cyclic conjugated structure gives it special stability

Benzene undergoes electrophilic substitution reactions (chapter 16) rather than electrophilic addition




Stability of Benzene: Heats of Hydrogenations

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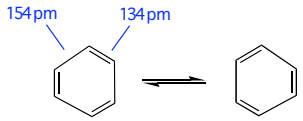
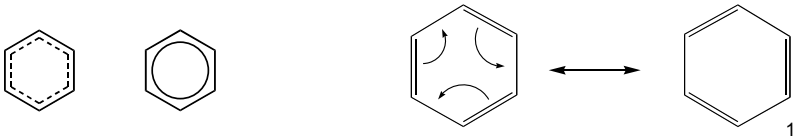
Structure of Benzene:

Kekule benzene: two forms are in rapid equilibrium




- All bonds are ~139 pm (intermediate between C-C and C=C)
- Electron density is distributed evenly between the six carbons
- Structure is planar, hexagonal
- C–C–C bond angles are 120°
- Each carbon is $sp^2$ and has a *p* orbital perpendicular to the plane of the six-membered ring



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Arrows in organic chemistry



Reaction arrow



Equilibrium arrow



Resonance arrow

Mechanism arrows

Double-headed arrow

Single-headed arrow

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## Drawing and Interpreting Resonance Forms
## (chapter 2.5 and 2.6)

1. No one resonance forms accurately depicts the structure of the molecule. The real structure is a composite or hybrid of all resonance forms
2. Resonance forms differ only by the placement of π- or non-bonding electrons. Neither the position or hybridization of the atoms changes.
3. Resonance forms are not necessarily equivalent. While all resonance forms contribute to the actual structure (resonance hybrid), some forms may contribute more.
4. All resonance forms must be proper Lewis structures.
5. The actual resonance hybrid is more stable than any single resonance form.
6. In general, the greater the number of resonance forms, the more stable the resonance hybrid.

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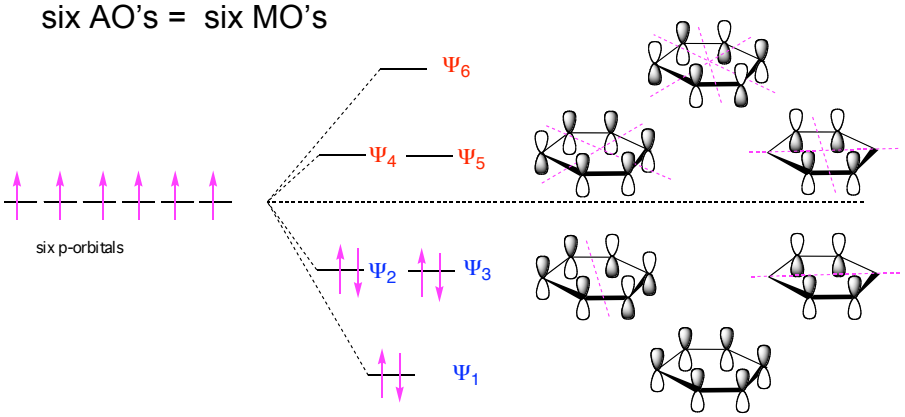
## 15.4: Molecular orbitals of benzenes: (figure 15.3)

six AO's = six MO's




Degenerate orbitals: orbitals that have the same energy

$\Psi_1$: zero nodes
$\Psi_2$ and $\Psi_3$: one node

Bonding

$\Psi_4$ and $\Psi_5$: two nodes
$\Psi_6$: three node

Anti-bonding

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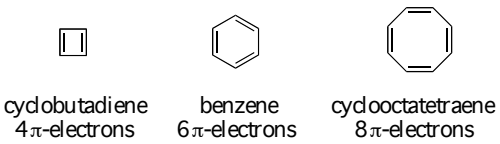
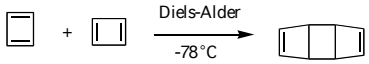
## 15.5 & 15.8: Aromaticity and the Hückel 4*n* + 2 Rule

Cyclic conjugated molecules: not all cyclic conjugated systems are aromatic (no special stability)



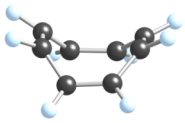
cyclobutadiene 4π-electrons | benzene 6π-electrons | cyclooctatetraene 8π-electrons

Cyclobutadiene: highly reactive
two different C-C bonds




Cyclooctatetraene: reactivity similar to normal C=C

Exists in a boat-like conformation:
little overlap between
double bonds



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Aromatic:

- Cyclic
- Conjugated: "alternating single and double bonds"
- Flat: maximum overlap between conjugated π-bonds
- Must contain 4*n*+2 π-electrons, where *n* is an integer
  - (**Hückel's rule**)

Anti-aromatic:

- cyclic, conjugated, flat molecules that contain 4*n* π-electrons (where *n* is an integer).
- Destabilized (highly reactive) relative to the corresponding open-chain conjugated system

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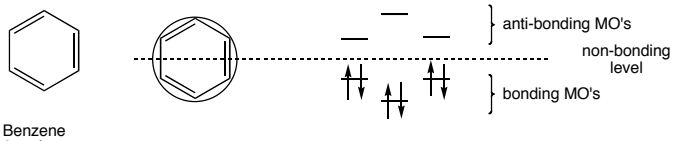
**Frost Circles**: relative energies of the molecular orbitals of cyclic, conjugated systems

Inscribe the cyclic, conjugated molecule into a circle so that a vertex is at the bottom. The relative energies of the MO's are where the ring atoms intersect the circle

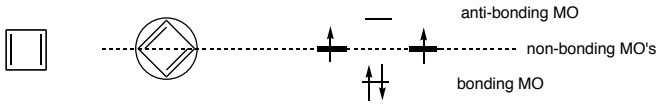
benzene:




Benzene
6 π-electrons

For aromatic compounds, such as benzene, the bonding MO's will be filled.

cyclobutadiene:




Cyclobutadiene
4 π-electrons

For anti- aromatic compounds, such as cyclobutadiene, there will be unpaired electrons in bonding, non-bonding or antibonding MO's.

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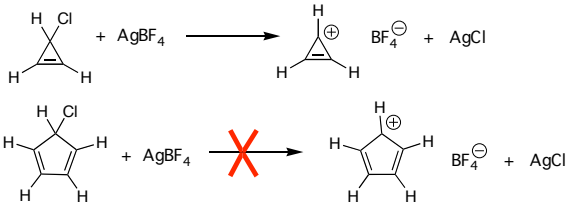
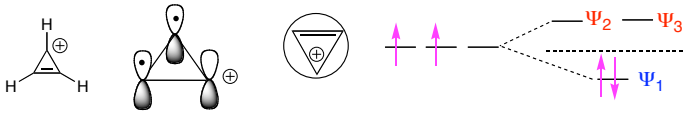
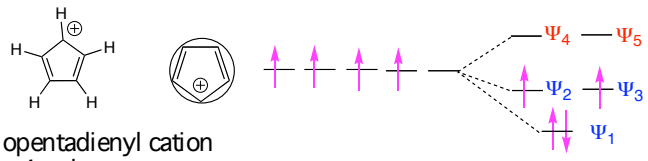
## 15.6: Aromatic ions




cyclopropenyl cation
2 π-electrons

4*n*+2=2
*n*=0
aromatic




cyclopentadienyl cation
4 π-electrons

4*n*=4
*n*=1
anti-aromatic

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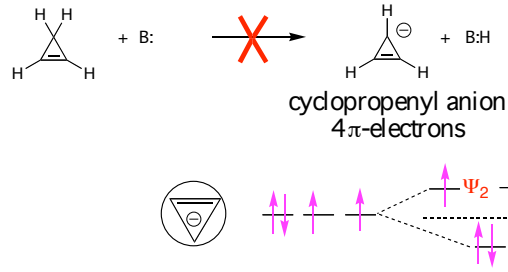
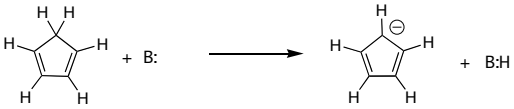



cyclopropenyl anion
4π-electrons

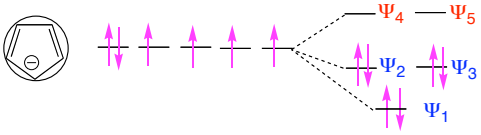



4*n*=4
*n*=1
anti-aromatic




$pK_a \sim 15$

cyclopentadienyl anion
6π-electrons




4*n*+2=6
*n*=1
aromatic

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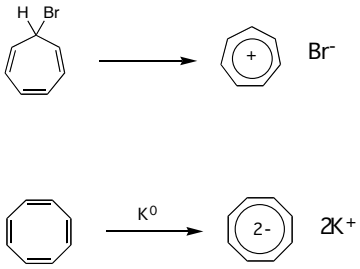


6 π-electron

10 π-electron

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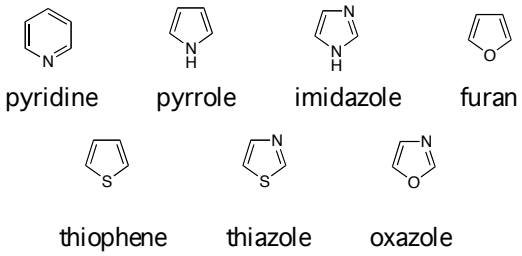
## 15.7: Aromatic Heterocycles

Heterocycle: any cyclic compound that contains ring atom(s) other than carbon (N, O, S, P)




Cyclic compounds that contain only carbon are called carbocycles

Heterocyclic aromatic compounds are numerous, common and a very important class of organic compounds

Nomenclature for heterocyclic compounds is specialized

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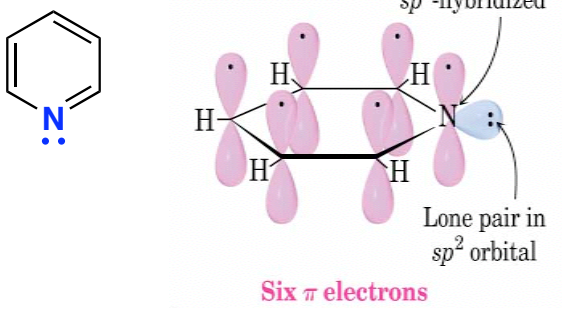
Pyridine

π-electron structure resembles benzene (6 π-electrons)

The nitrogen lone pair electrons are not part of the aromatic system (perpendicular orbital)

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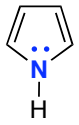
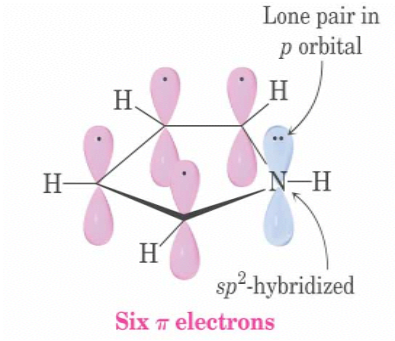
**Pyrrole:**

6 π-electron system similar to that of cyclopentadienyl anion

Four *sp*2-hybridized carbons with 4 *p* orbitals perpendicular to the ring and 4 p electrons

lone pair of electrons in an $sp^2$ orbital; part of the aromatic sextet




Pyrrole is much less basic than pyridine. Why?

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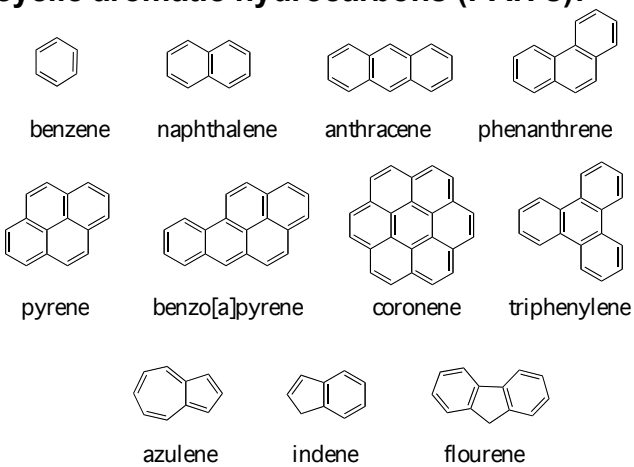
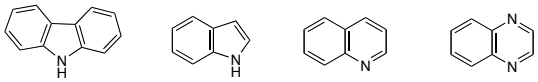
## 15.9: Polycyclic aromatic hydrocarbons (PAH's):




**Polycyclic heterocycles**

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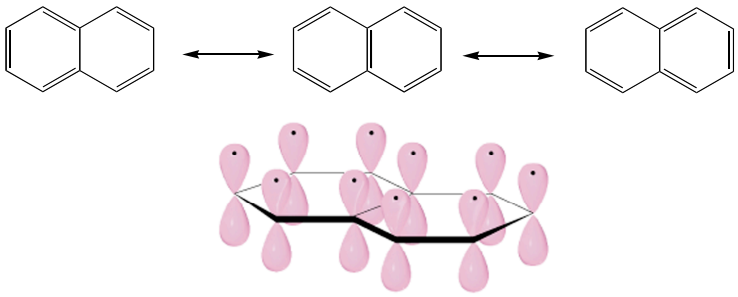
Polycyclic aromatic hydrocarbons

Aromatic compounds can have rings that share a set of carbon atoms (fused rings)

Compounds from fused benzene or aromatic heterocyclic rings are themselves aromatic

Naphthalene: $4n+2=10$, $n=2$ note: Hückels rule is strictly for monocyclic aromatic compound, its application to polycyclic aromatic compounds is tenuous.



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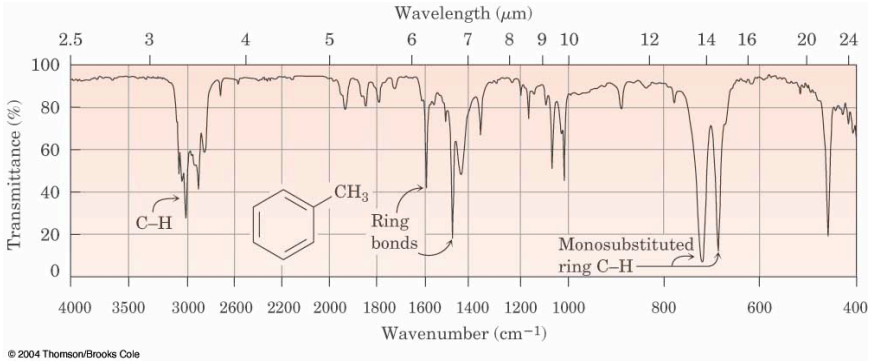
**15.10: Spectroscopy of Aromatic Compounds**

**IR:** Aromatic ring C–H stretching at 3030 $cm^{-1}$ and peaks from 1450 to 1600 $cm^{-1}$



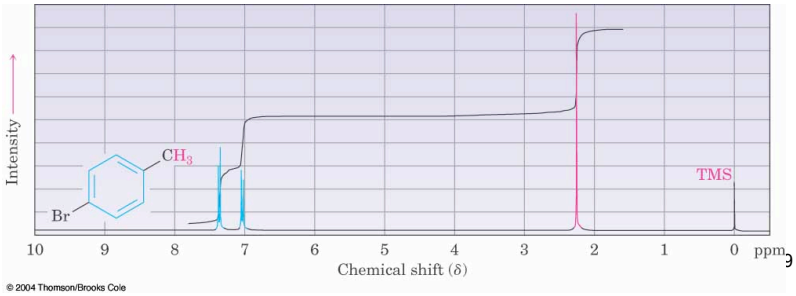

monosubstituted: 690-710 $cm^{-1}$ and 730-770 $cm^{-1}$
*o*-disubstituted: 735-770 $cm^{-1}$
*m*-disubstituted: 690-710 $cm^{-1}$ and 810-850 $cm^{-1}$
*p*-disubstituted: 810-840 $cm^{-1}$

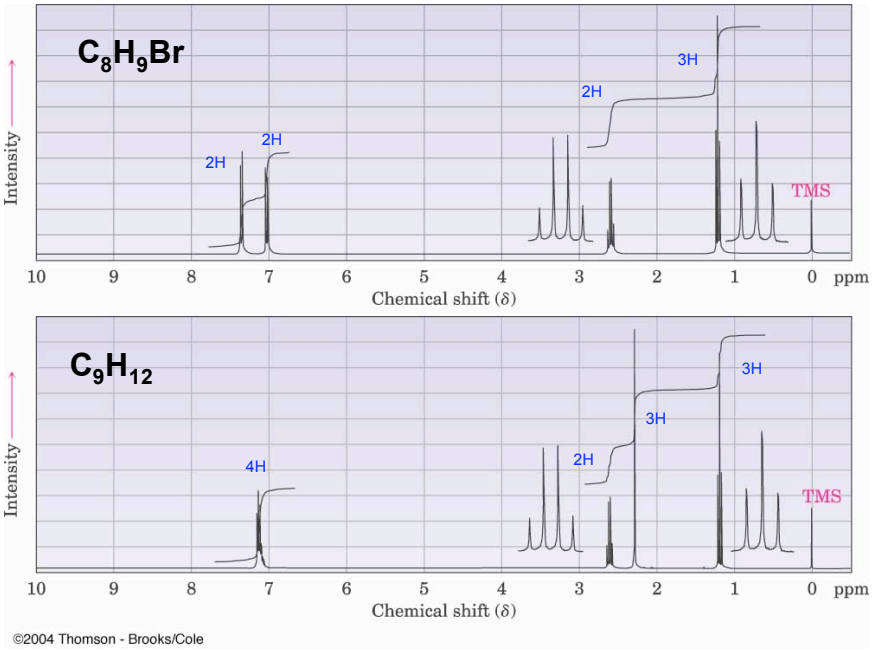
28

**UV:** Absorbance near 205 nm and a less intense peak in 255-275 nm range. Substitution and increased conjugation moves the absorbance to longer wavelengths

**$^1$H NMR:** Aromatic H's strongly deshielded by ring and absorb between δ 6.5 and δ 8.0

Peak pattern is characteristic positions of substituents



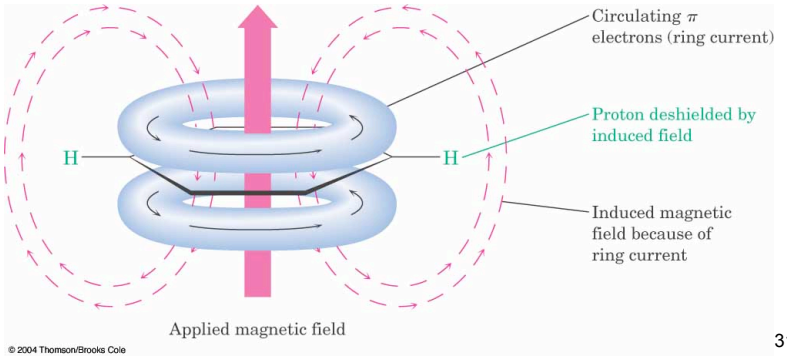



**Ring Current: (please read)**

Aromatic ring oriented perpendicular to a strong magnetic field, delocalized π electrons producing a small local magnetic field

*Opposes* applied field in middle of ring but *reinforces* applied field outside of ring

Results in outside H's resonance at lower field

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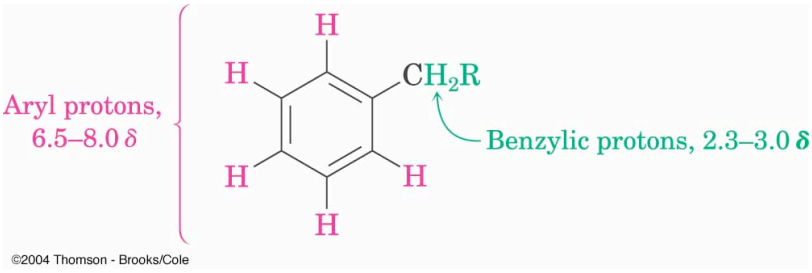
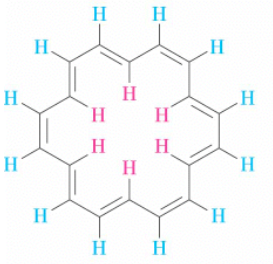
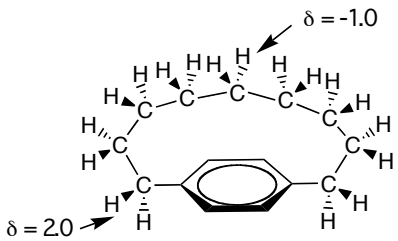


[18]Annulene

Inside H: −3.0 δ

Outside H: 9.3 δ

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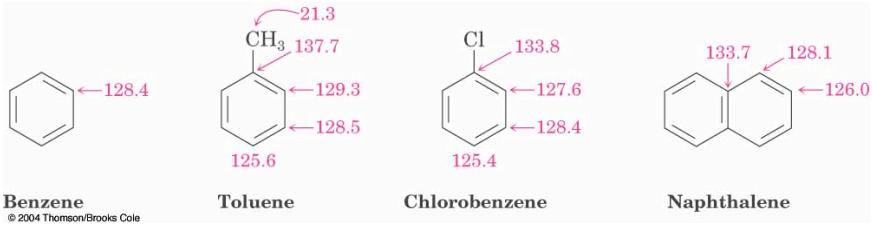
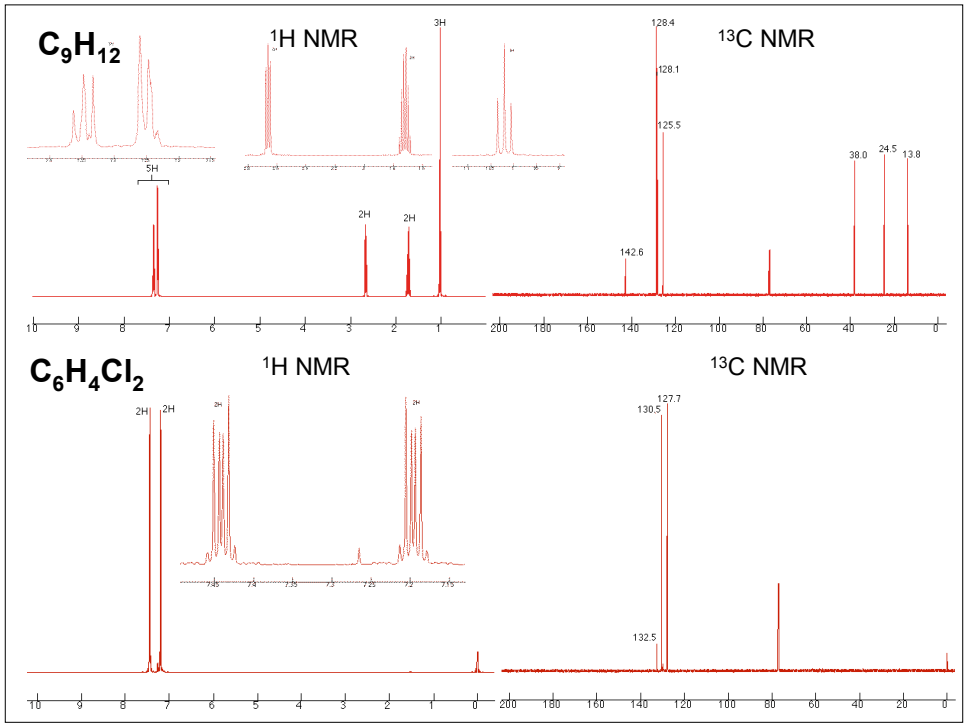
**$^{13}$C NMR:**

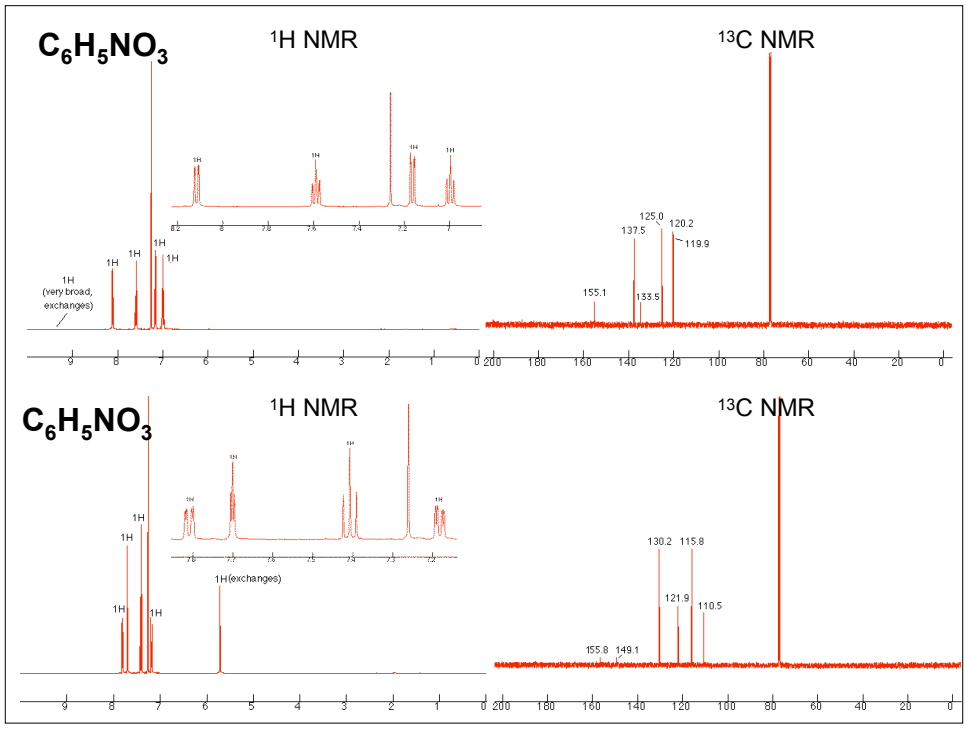
Carbons in aromatic ring absorb at δ 110 to 140

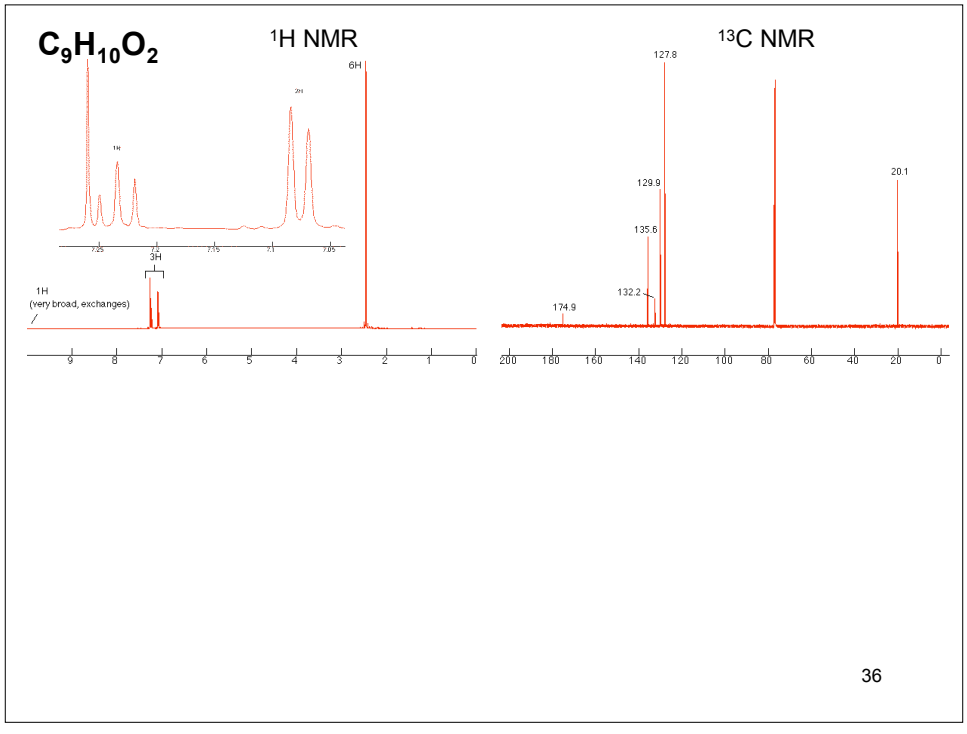
Shift is distinct from alkane carbons but in same range as alkene carbons




33




C6H5NO3
1H NMR
13C NMR
1H
(very broad, exchanges)
155.1
137.5
133.5
125.0
120.2
119.9
C6H5NO3
1H NMR
13C NMR
1H(exchanges)
155.8
149.1
130.2
115.8
121.9
110.5


C9H10O2
1H NMR
13C NMR
6H
3H
1H
(very broad, exchanges)
174.9
132.2
135.6
129.9
127.8
20.1

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