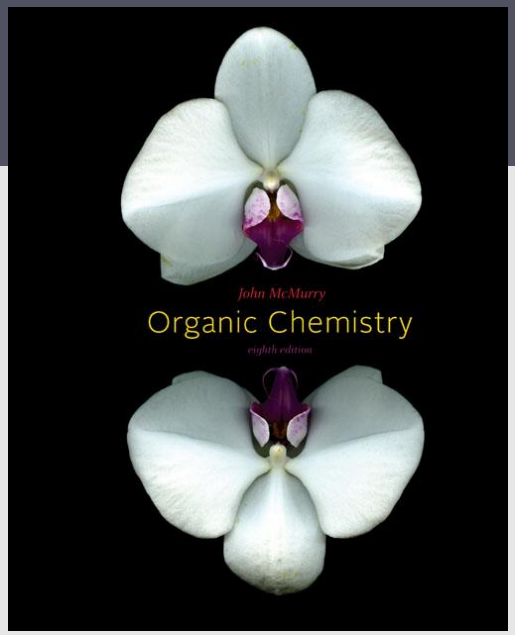


John E. McMurry

www.cengage.com/chemistry/mcmurry

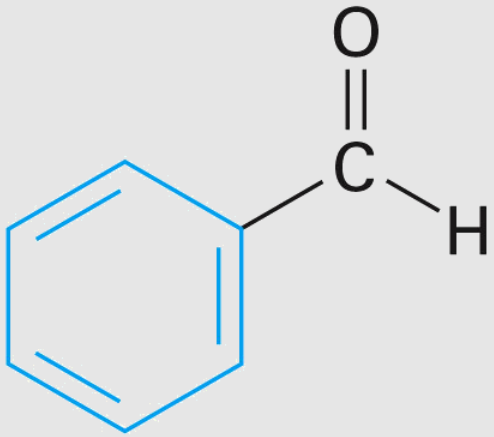
Chapter 15
Benzene and Aromaticity

Paul D. Adams • University of Arkansas

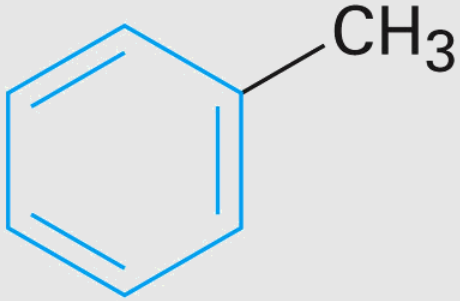
Aromatic Compounds

- *Aromatic* was used to described some fragrant compounds in early 19th century
  - Not correct: later they are grouped by chemical behavior (unsaturated compounds that undergo substitution rather than addition)
- Current: distinguished from *aliphatic* compounds by electronic configuration

Benzene



Benzaldehyde



Toluene

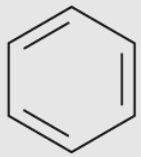
Why this Chapter?

- Reactivity of substituted aromatic compounds is tied to their structure

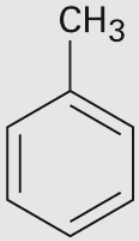
- Aromatic compounds provide a sensitive probe for studying relationship between structure and reactivity

15.1 Sources and Names of Aromatic Hydrocarbons

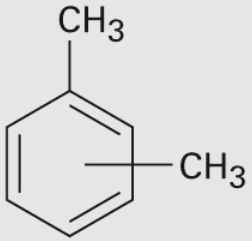
- From high temperature distillation of coal tar
- Heating petroleum at high temperature and pressure over a catalyst



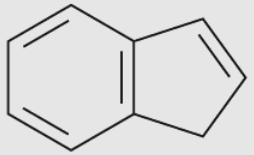
Benzene
(bp 80 °C)



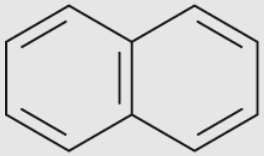
Toluene
(bp 111 °C)



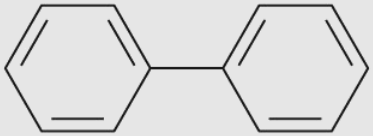
Xylene
(bp: ortho, 144 °C;
meta, 139 °C; para, 138 °C)



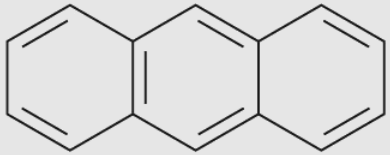
Indene
(bp 182 °C)



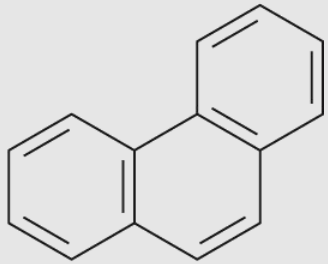
Naphthalene
(mp 80 °C)



Biphenyl
(mp 71 °C)



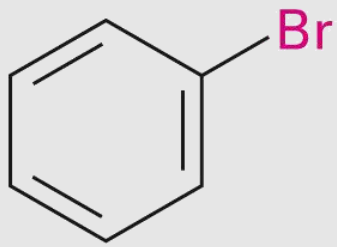
Anthracene
(mp 216 °C)



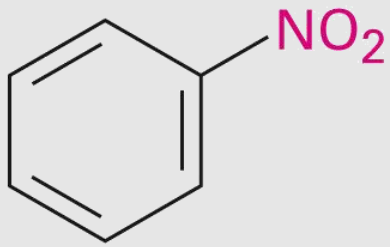
Phenanthrene
(mp 101 °C)

Naming Aromatic Compounds

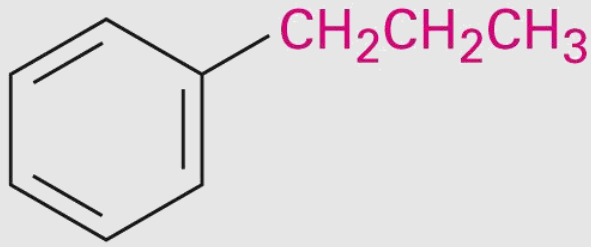
- Many common names (toluene = methylbenzene; aniline = aminobenzene)
- Monosubstituted benzenes systematic names as hydrocarbons with *–benzene*
  - C_6H_5Br = bromobenzene
  - $C_6H_5NO_2$ = nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ is propylbenzene



Bromobenzene



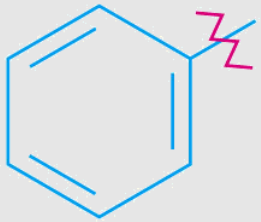
Nitrobenzene



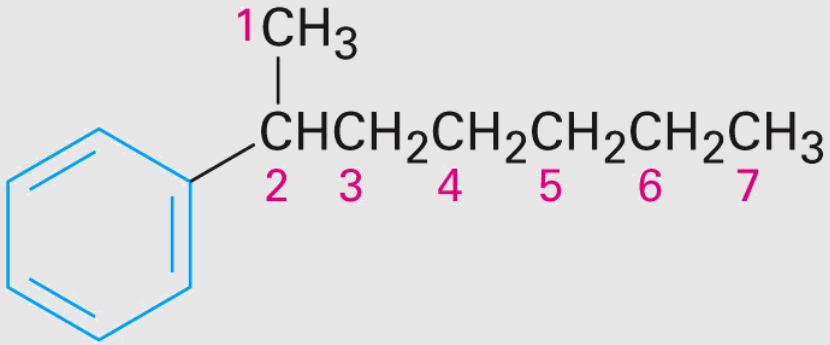
Propylbenzene

The Phenyl Group

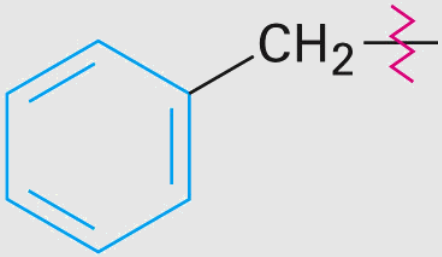
- When a benzene ring is a substituent, the term **phenyl** is used (for C_6H_5 羊?)
  - You may also see "Ph" or "ϕ" in place of "C_6H_5"
- "**Benzyl**" refers to "$C_6H_5CH_2$ 羊?"



A phenyl group



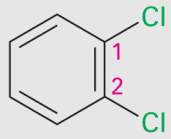
2-Phenylheptane



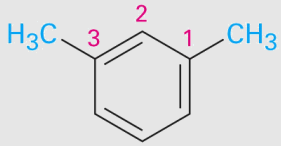
A benzyl group

Disubstituted Benzenes

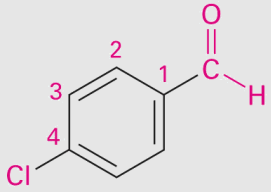
- Relative positions on a benzene ring
  - ***ortho- (o)*** on adjacent carbons (1,2)
  - ***meta- (m)*** separated by one carbon (1,3)
  - ***para- (p)*** separated by two carbons (1,4)
- Describes reaction patterns ("occurs at the *para* position")



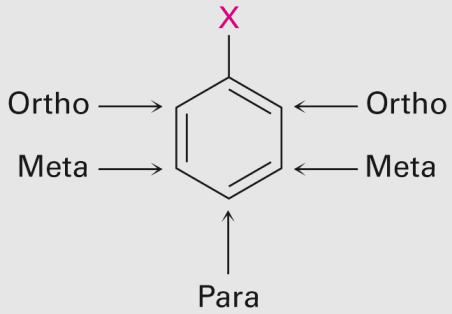
***ortho*-Dichlorobenzene**
1,2 disubstituted

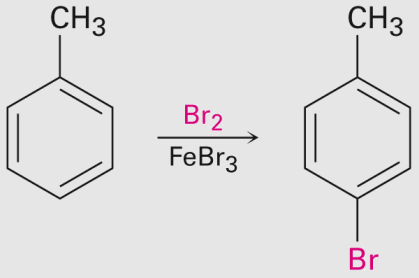


***meta*-Dimethylbenzene**
(*meta*-xylene)
1,3 disubstituted



***para*-Chlorobenzaldehyde**
1,4 disubstituted

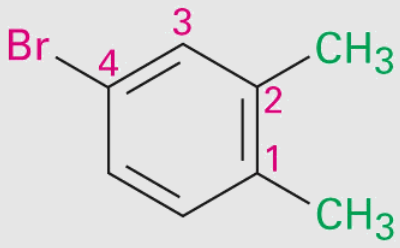




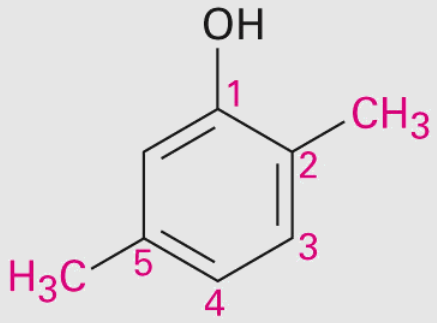
Toluene **p-Bromotoluene**

Naming Benzenes with More Than Two Substituents

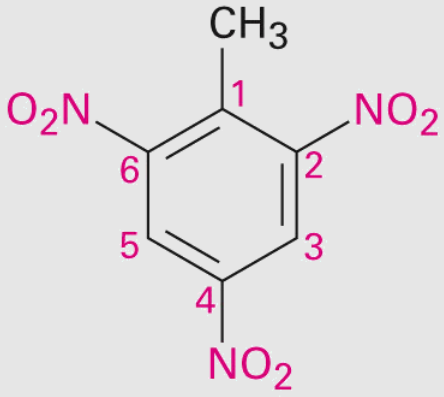
- Choose numbers to get lowest possible values
- List substituents alphabetically with hyphenated numbers
- Common names, such as “toluene” can serve as root name (as in TNT)



4-Bromo-1,2-dimethylbenzene



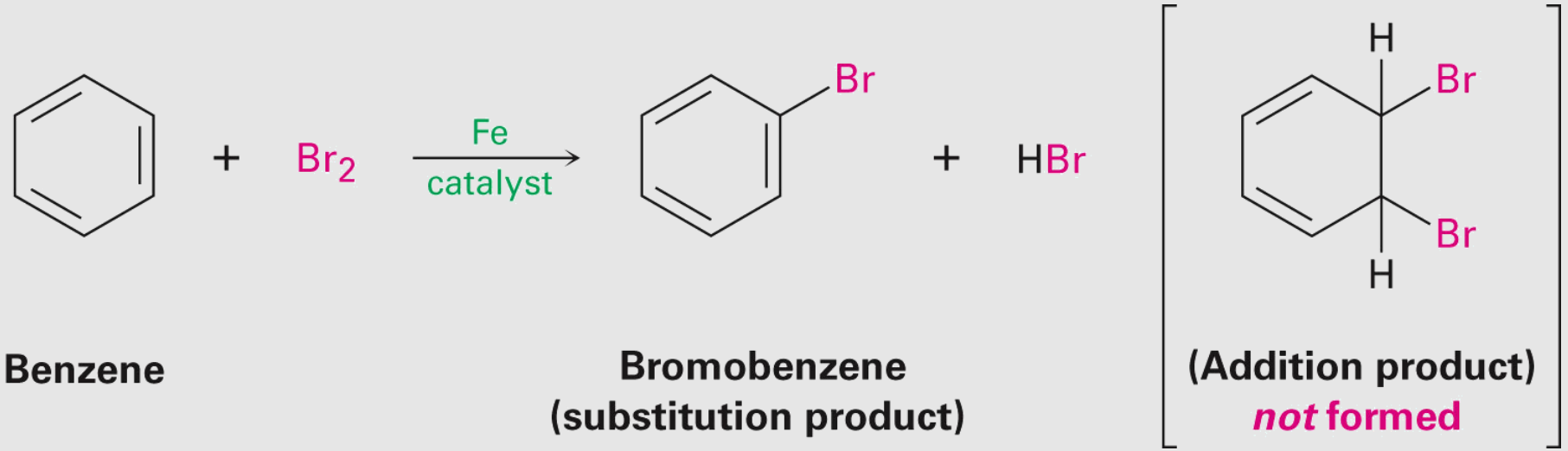
2,5-Dimethylphenol



2,4,6-Trinitrotoluene (TNT)

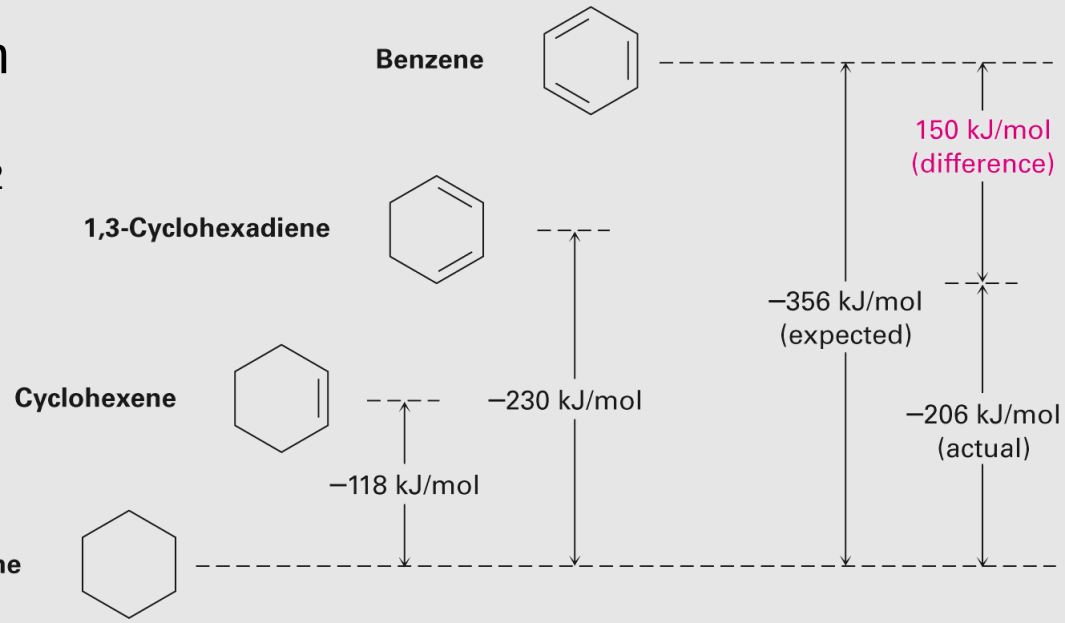
15.2 Structure and Stability of Benzene

- Benzene reacts slowly with Br_2 to give bromobenzene (where Br replaces H)
- This is substitution rather than the rapid addition reaction common to compounds with C=C, suggesting that, in benzene, there is a higher barrier



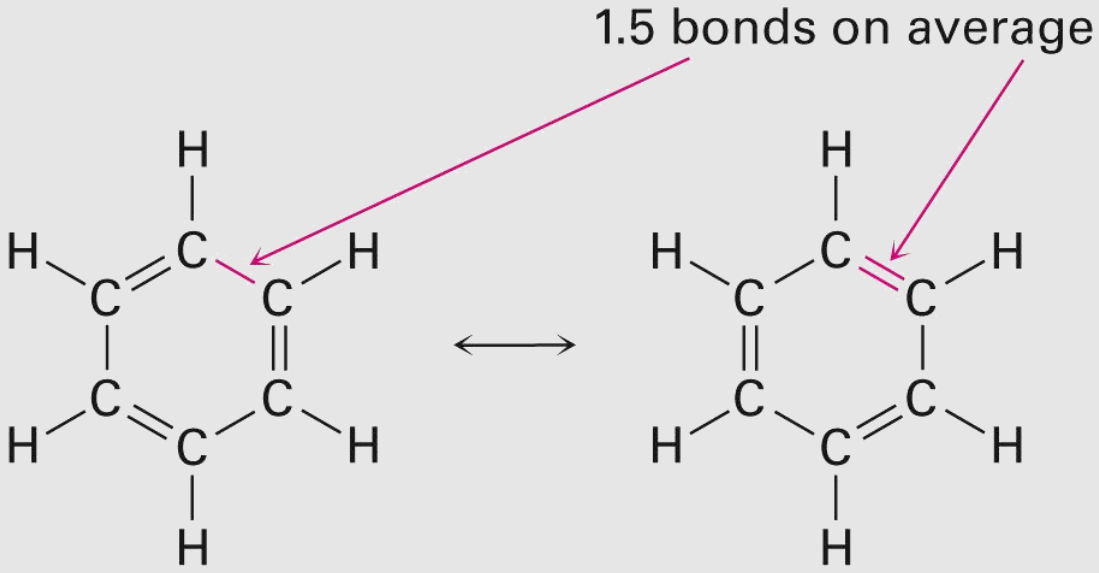
Heats of Hydrogenation as Indicators of Stability

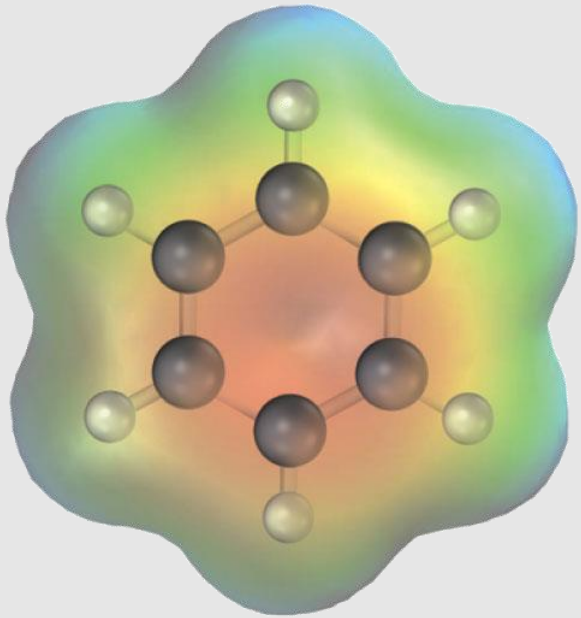
- The addition of H_2 to C=C normally gives off about 118 kJ/mol – 3 double bonds would give off 354kJ/mol
  - Two conjugated double bonds in cyclohexadiene add 2 H_2 to give off 230 kJ/mol
- Benzene has 3 unsaturation sites but gives off only 206 kJ/mol on reacting with 3 H_2 molecules
- Therefore it has about 150 kJ more “stability” than an isolated set of three double bonds



Benzene's Unusual Structure

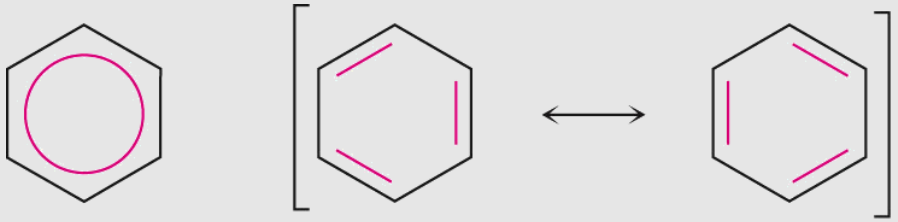
- All its C-C bonds are the same length: 139 pm — between single (154 pm) and double (134 pm) bonds
- Electron density in all six C-C bonds is identical
- Structure is planar, hexagonal
- C–C–C bond angles 120°
- Each C is sp^2 and has a *p* orbital perpendicular to the plane of the six-membered ring





Drawing Benzene and Its Derivatives

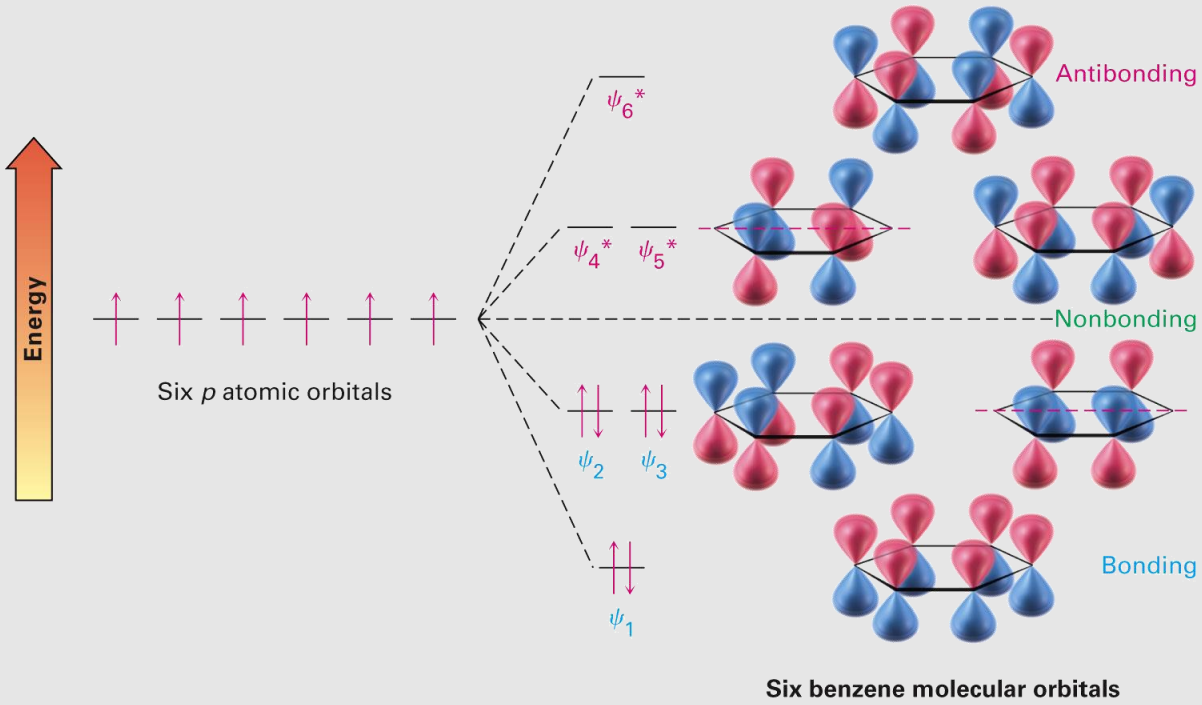
- The two benzene resonance forms can be represented by a single structure with a circle in the center to indicate the equivalence of the carbon–carbon bonds
- This does not indicate the number of π electrons in the ring but reminds us of the delocalized structure
- We shall use one of the resonance structures to represent benzene for ease in keeping track of bonding changes in reactions



Alternative representations of benzene. The "circle" representation must be used carefully since it doesn't indicate the number of π electrons in the ring.

Molecular Orbital Description of Benzene

- The 6 *p*-orbitals combine to give
  - Three bonding orbitals with 6 π electrons,
  - Three antibonding with no electrons
- Orbitals with the same energy are degenerate

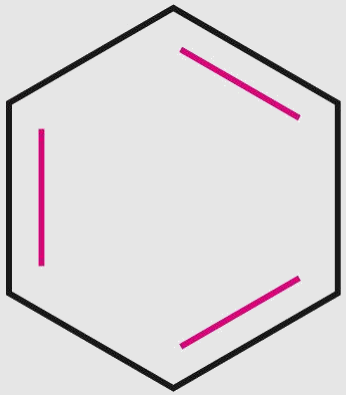


15.3 Aromaticity and the Hückel $4n+2$ Rule

- Unusually stable - heat of hydrogenation 150 kJ/mol less negative than a hypothetical cyclic triene
- Planar hexagon: bond angles are 120°, carbon–carbon bond lengths 139 pm
- Undergoes substitution rather than electrophilic addition
- Resonance hybrid with structure between two line-bond structures

Aromaticity and the $4n + 2$ Rule

- Hückel's rule, based on calculations – a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has ***4n+ 2*** π *electrons (n is 0,1,2,3,4*)
- For n=1: $4n$+2 = 6; **benzene** is stable and the electrons are delocalized



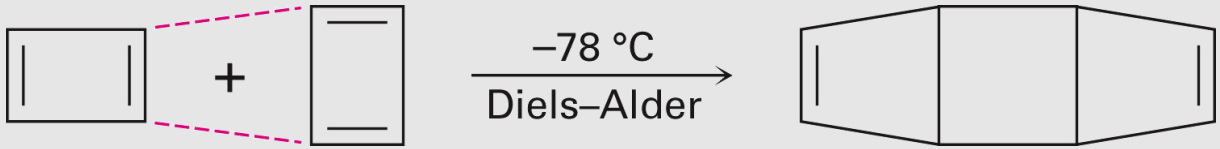
Benzene

Three double bonds;

six π electrons

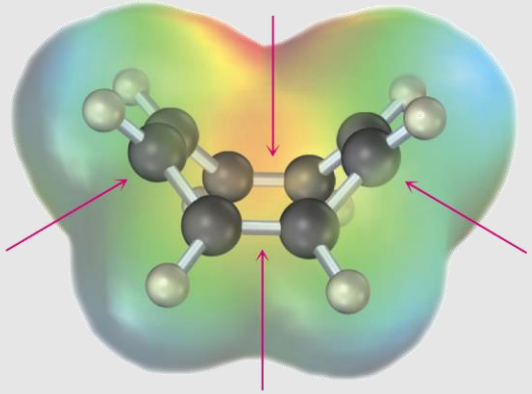
Compounds with 4n π Electrons Are Not Aromatic (May be Antiaromatic)

- Planar, cyclic molecules with ***4 n*** π electrons are much *less* stable than expected (antiaromatic)
- They will distort out of plane and behave like ordinary alkenes
- 4- and 8-electron compounds are not delocalized (single and double bonds)
- Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low temperature
- Cyclooctatetraene has four double bonds, reacting with Br_2, $KMnO_4$, and HCl as if it were four alkenes



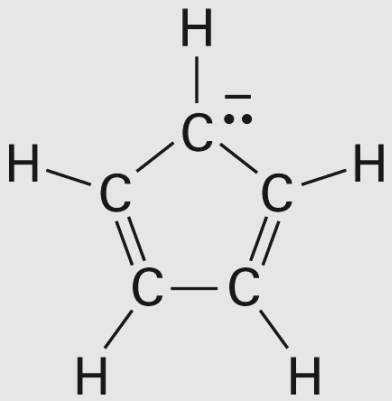
Cyclooctatetraene

Four double bonds;
eight π electrons

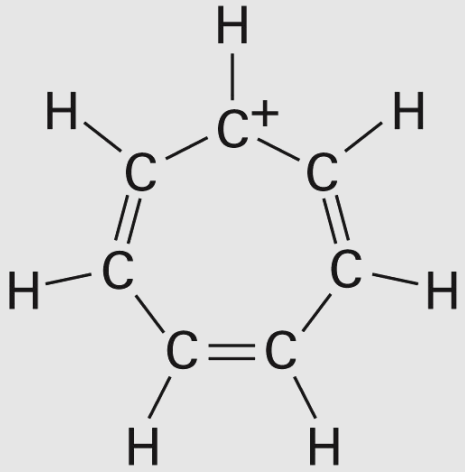


15.4 Aromatic Ions

- The $4n + 2$ rule applies to ions as well as neutral species
- Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic
- The key feature of both is that they contain 6 π electrons in a ring of continuous p orbitals



Cyclopentadienyl anion

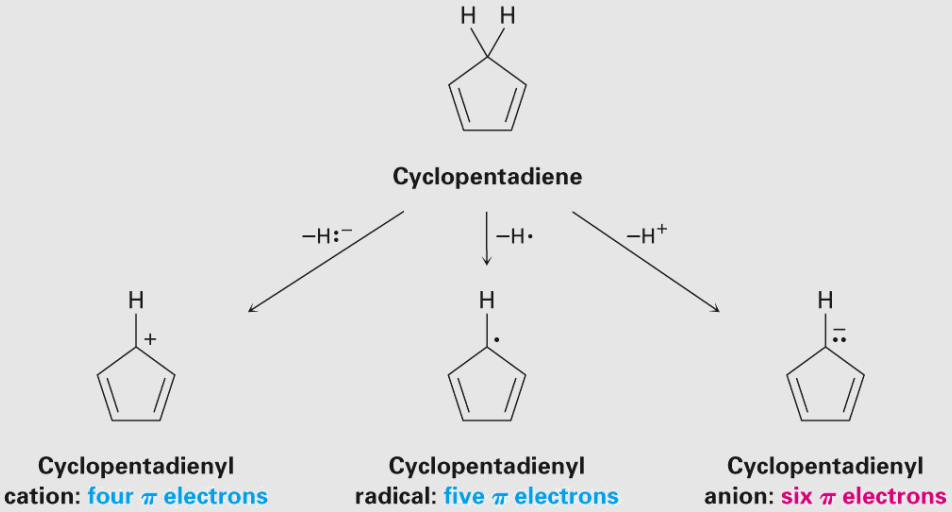


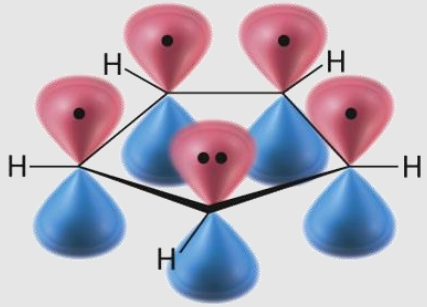
Cycloheptatrienyl cation

Six π electrons; aromatic ions

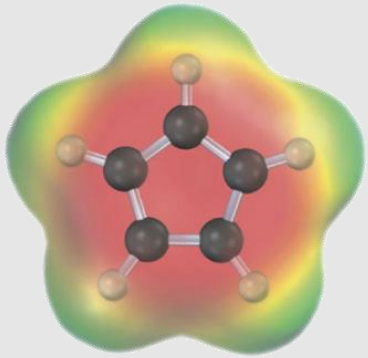
Aromaticity of the Cyclopentadienyl Anion

- 1,3-Cyclopentadiene contains conjugated double bonds joined by a CH_2 that blocks delocalization
- Removal of H^+ at the CH_2 produces a cyclic 6 π-electron system, which is stable
- Removal of H^- or H• generate nonaromatic 4 and 5 electron systems
- Relatively acidic (pK_a = 16) because the anion is stable



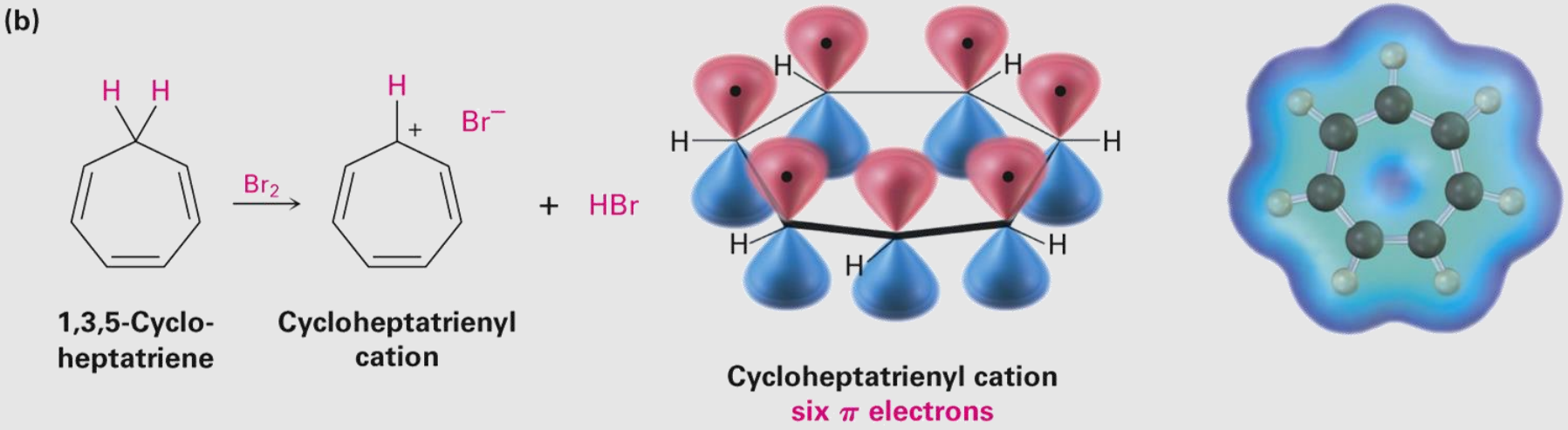


Aromatic cyclopentadienyl anion with six π electrons



Cycloheptatriene

- Cycloheptatriene has 3 conjugated double bonds joined by a CH_2
- Removal of "H^-" leaves the cation
- The cation has 6 π–electrons and is aromatic

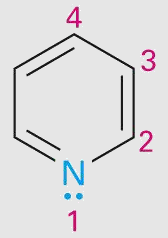


15.5 Aromatic Heterocycles: Pyridine and Pyrrole

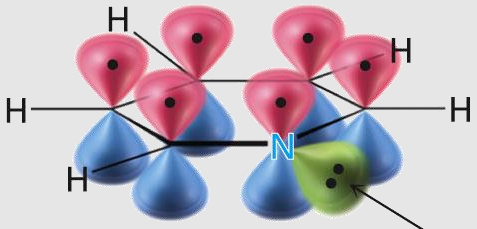
- Heterocyclic compounds contain elements other than carbon in a ring, such as N,S,O,P
- Aromatic compounds can have elements other than carbon in the ring
- There are many heterocyclic aromatic compounds and many are very common
- Cyclic compounds that contain only carbon are called carbocycles (not homocycles)
- Nomenclature is specialized

Pyridine

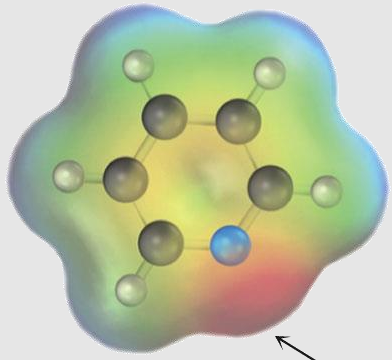
- A six-membered heterocycle with a nitrogen atom in its ring
- π electron structure resembles benzene (6 electrons)
- The nitrogen lone pair electrons are not part of the aromatic system (perpendicular orbital)
- Pyridine is a relatively weak base compared to normal amines but protonation does not affect aromaticity



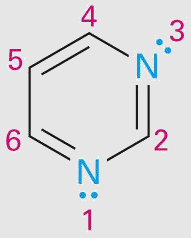
Pyridine



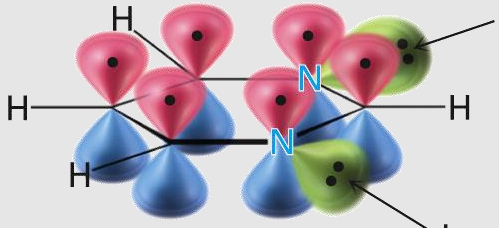
(Six π electrons)



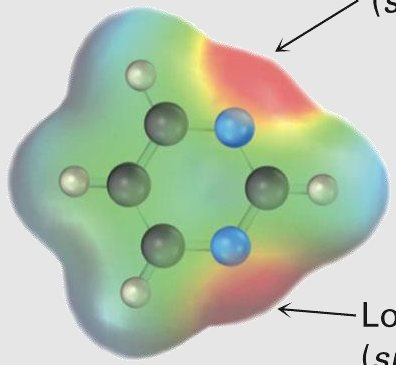
Lone pair
(sp^2)



Pyrimidine



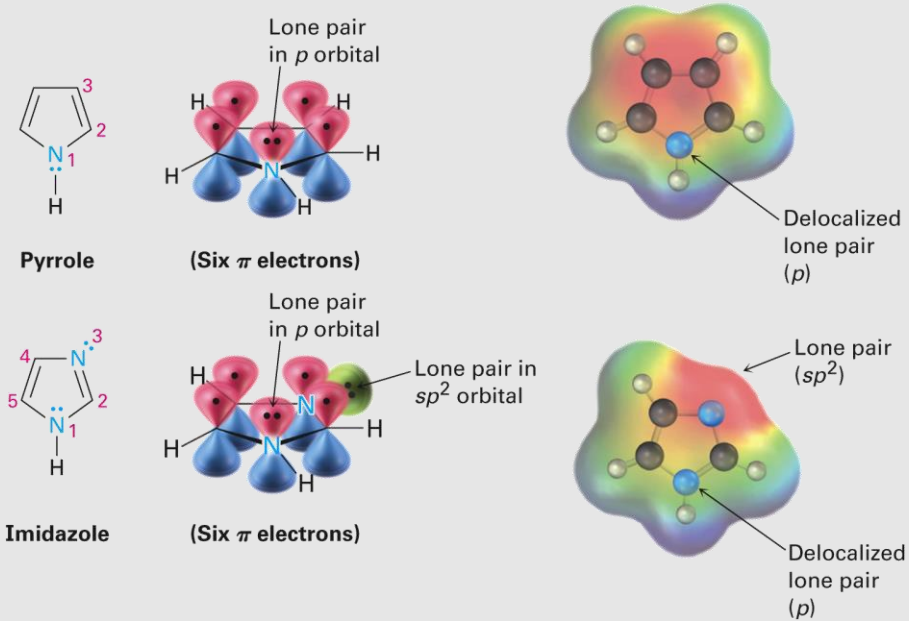
(Six π electrons)



Lone pair
(sp^2)

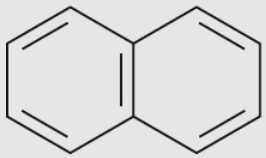
Pyrrole

- A five-membered heterocycle with one nitrogen
- 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
- Nitrogen atom is sp^2-hybridized, and lone pair of electrons occupies a p orbital (6 π electrons)
- Since lone pair electrons are in the aromatic ring, protonation destroys aromaticity, making pyrrole a very weak base

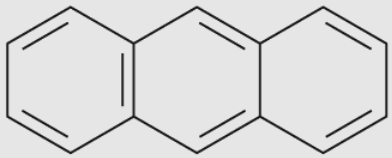


15.6 Polycyclic Aromatic Compounds

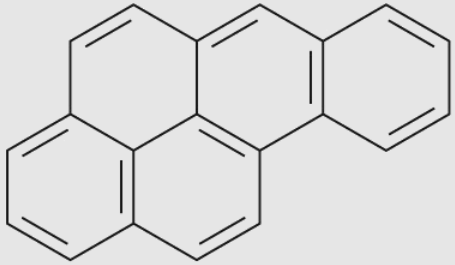
- Aromatic compounds can have rings that share a set of carbon atoms (fused rings)
- Compounds from fused benzene or aromatic heterocycle rings are themselves aromatic



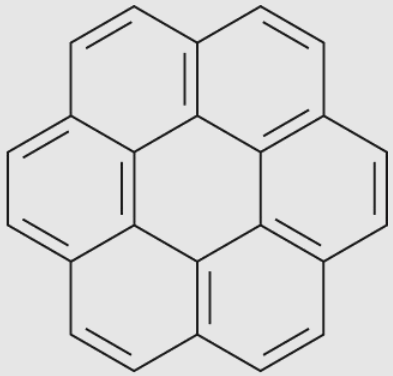
Naphthalene



Anthracene



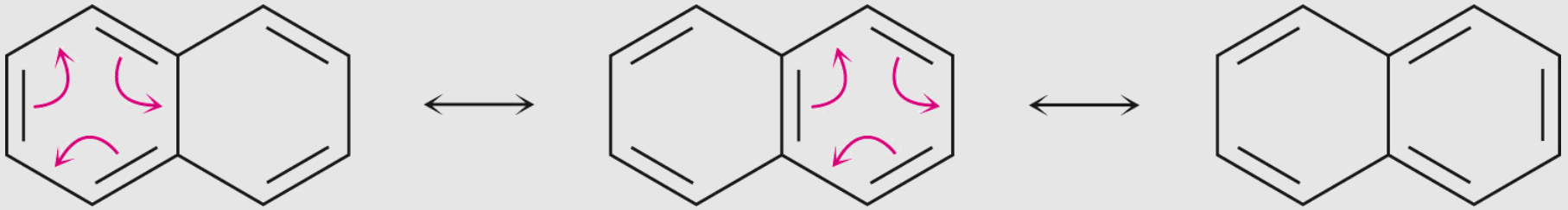
Benzo[a]pyrene



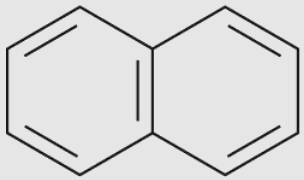
Coronene

Naphthalene Orbitals

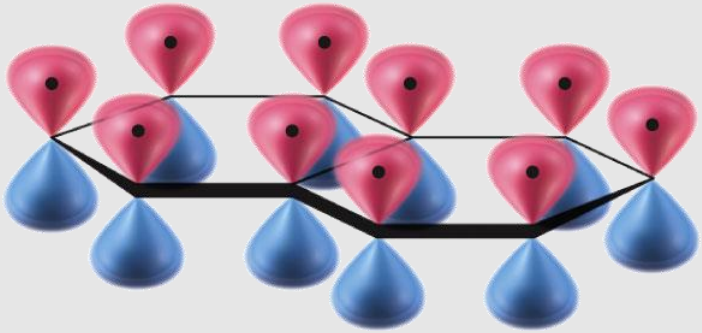
- Three resonance forms and delocalized electrons

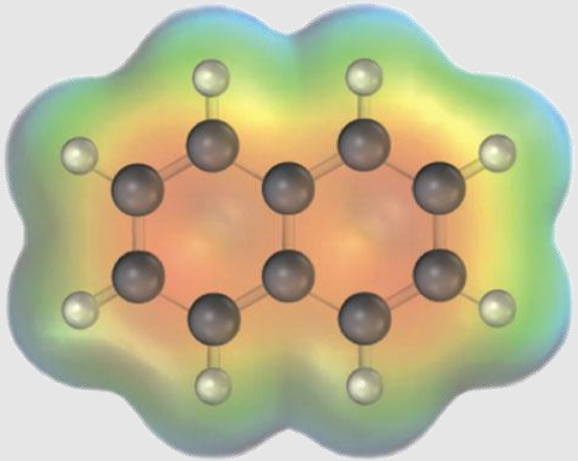


Naphthalene



Naphthalene



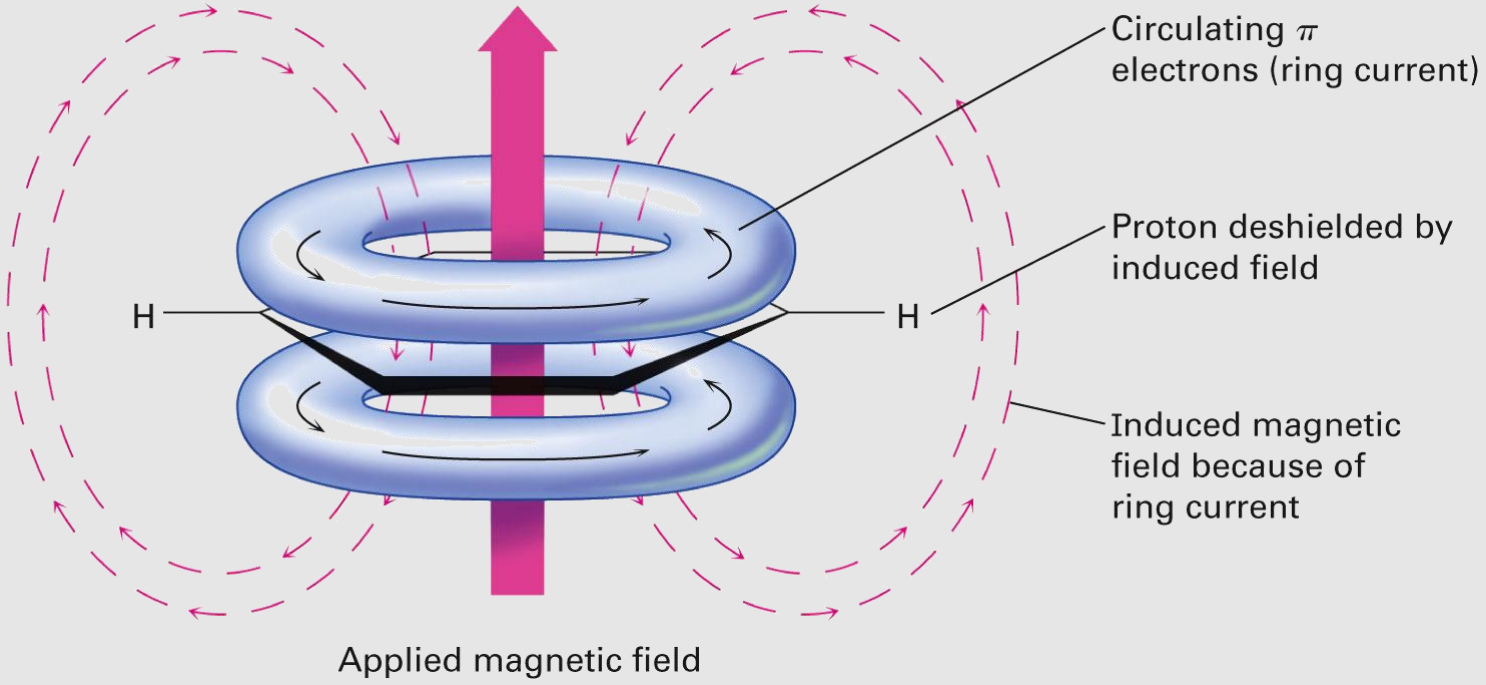


15.7 Spectroscopy of Aromatic Compounds

- IR: Aromatic ring C–H stretching at 3030 cm^{-1} and peaks 1450 to 1600 cm^{-1} (See Figure 15-13)
- UV: Peak near 205 nm and a less intense peak in 255-275 nm range
- ^1H NMR: Aromatic H's strongly deshielded by ring and absorb between δ 6.5 and δ 8.0
  - Peak pattern is characteristic of positions of substituents

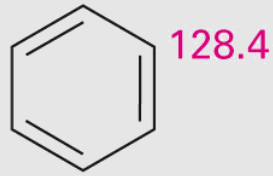
Ring Currents

- 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

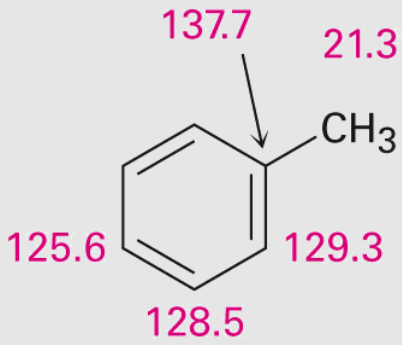


^{13}C NMR of Aromatic Compounds

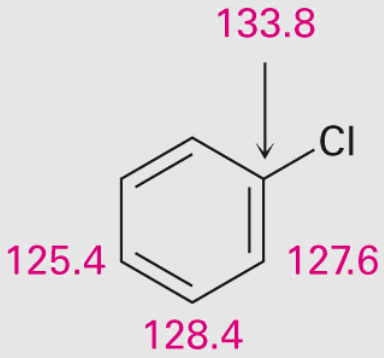
- Carbons in aromatic ring absorb at δ 110 to 140
- Shift is distinct from alkane carbons but in same range as alkene carbons



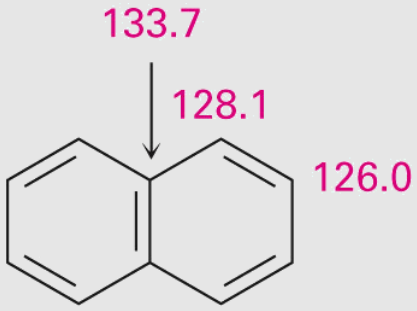
Benzene



Toluene



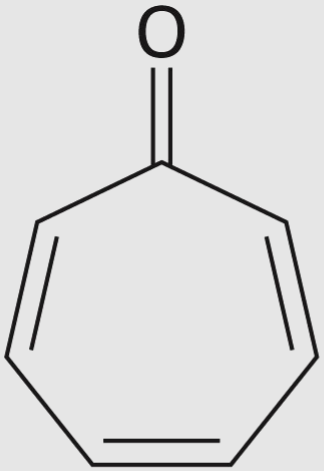
Chlorobenzene



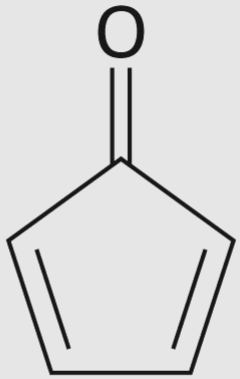
Naphthalene

Let's Work a Problem

Cycloheptatrienone is stable, but cyclopentadienone is so reactive that it can't be isolated. Explain, taking the polarity of the carbonyl group into account?



Cycloheptatrienone



Cyclopentadienone

Answer

Draw the resonance forms of the molecules in which both carbonyl π electrons are on the oxygen. The cycloheptatrienone ring possesses 6 π electrons and is aromatic according to Hückel's rule. When we do this with the cyclopentadienone ring, we see that it contains 4 π electrons and thus is antiaromatic and does not obey Hückel's rule, resulting in its extreme reactivity.