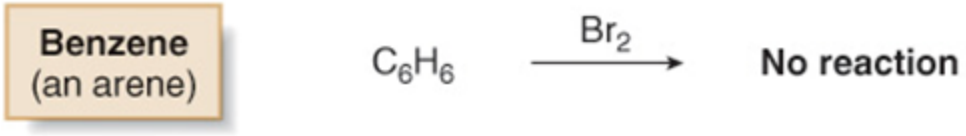
# Benzene and Aromatic Compounds

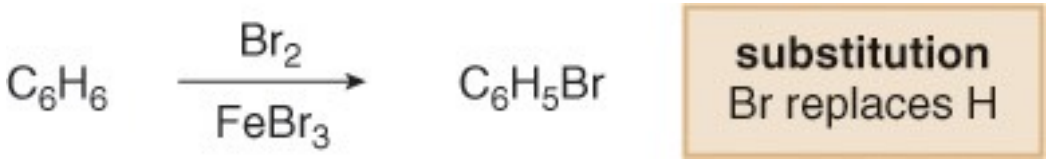
Chapter 15
Organic Chemistry, *8th Edition*
John McMurry

# Background

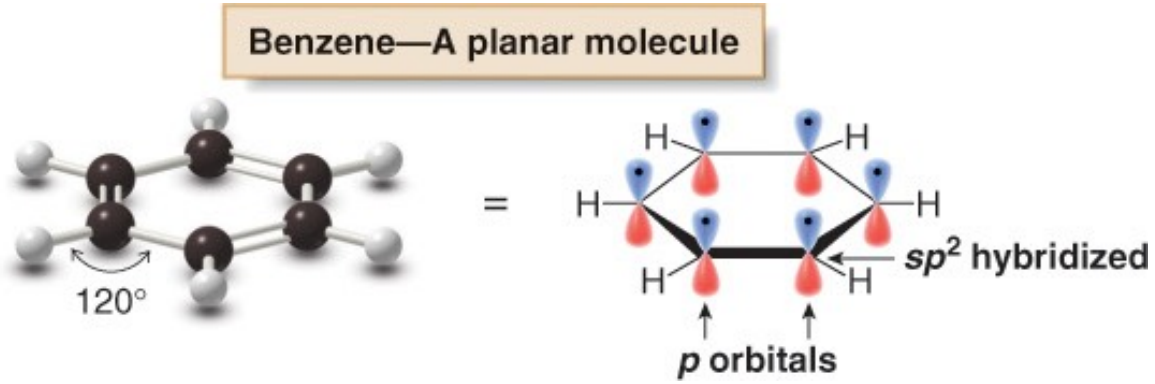
- Benzene ($C_6H_6$) is the simplest aromatic hydrocarbon (or arene).
- Four degrees of unsaturation.
- It is planar.
- All C—C bond lengths are equal.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not.

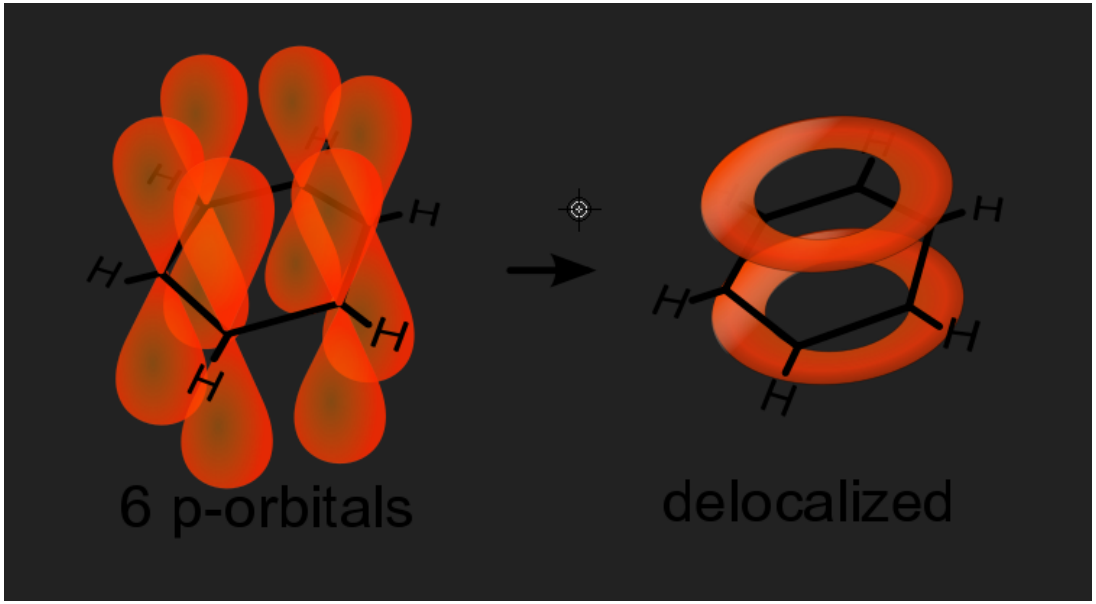



- Benzene reacts with bromine only in the presence of $FeBr_3$ (a Lewis acid), and the reaction is a substitution, not an addition.



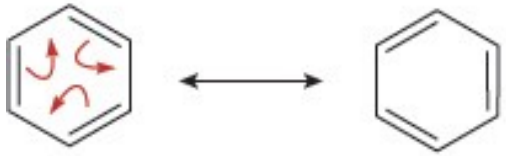
# The Structure of Benzene: MO



# The Structure of Benzene: Resonance

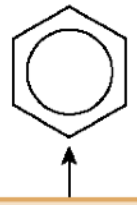
The true structure of benzene is a resonance hybrid of the two Lewis structures.



The hybrid

The electrons in the π bonds are **delocalized** around the ring.

Some texts draw benzene as a hexagon with an inner circle:



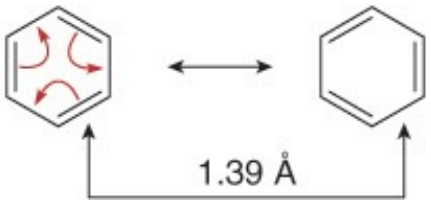
The circle represents the **six π electrons,** distributed over the six atoms of the ring.

$CH_3-CH_3$

1.53 Å

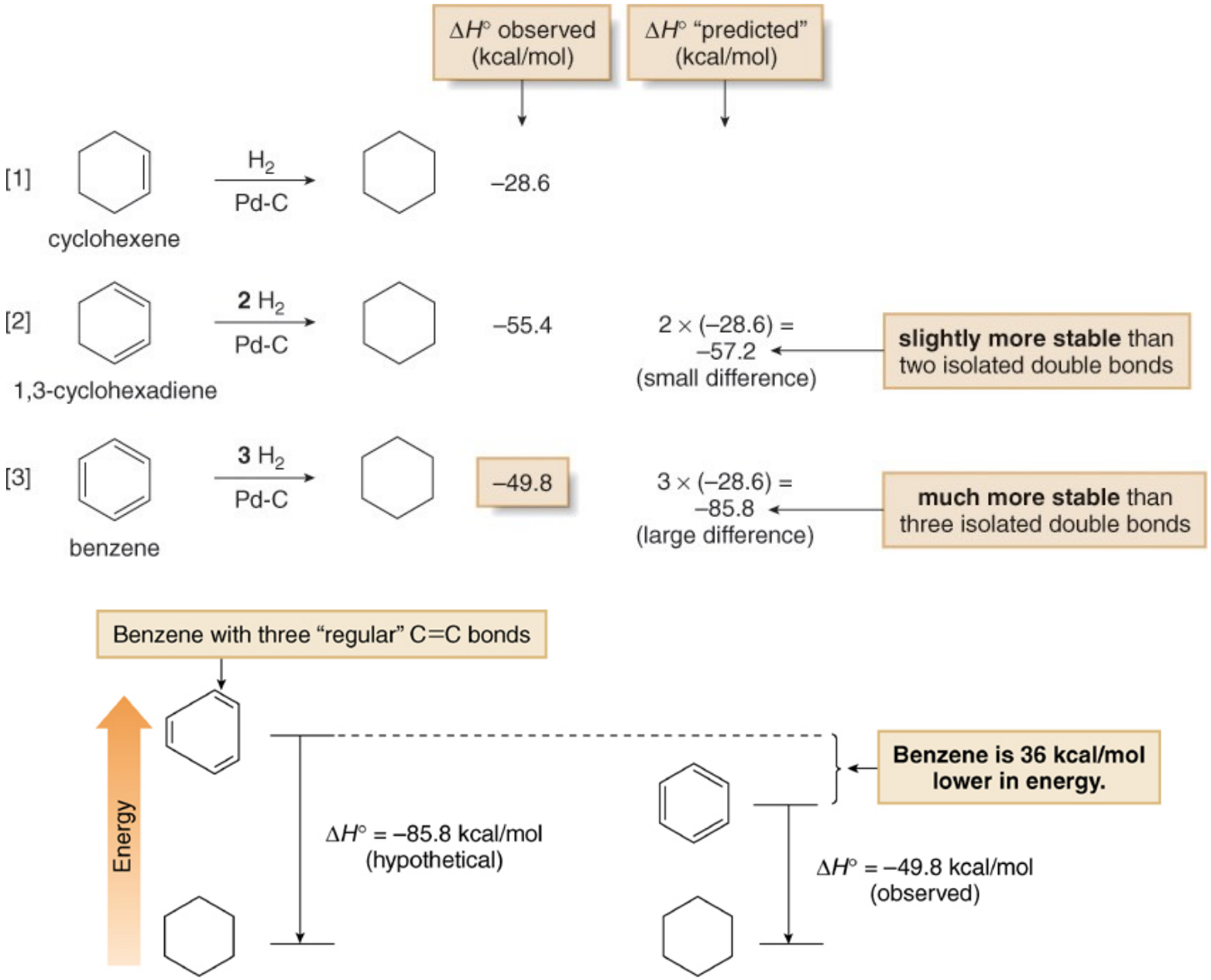
$CH_2=CH_2$

1.34 Å



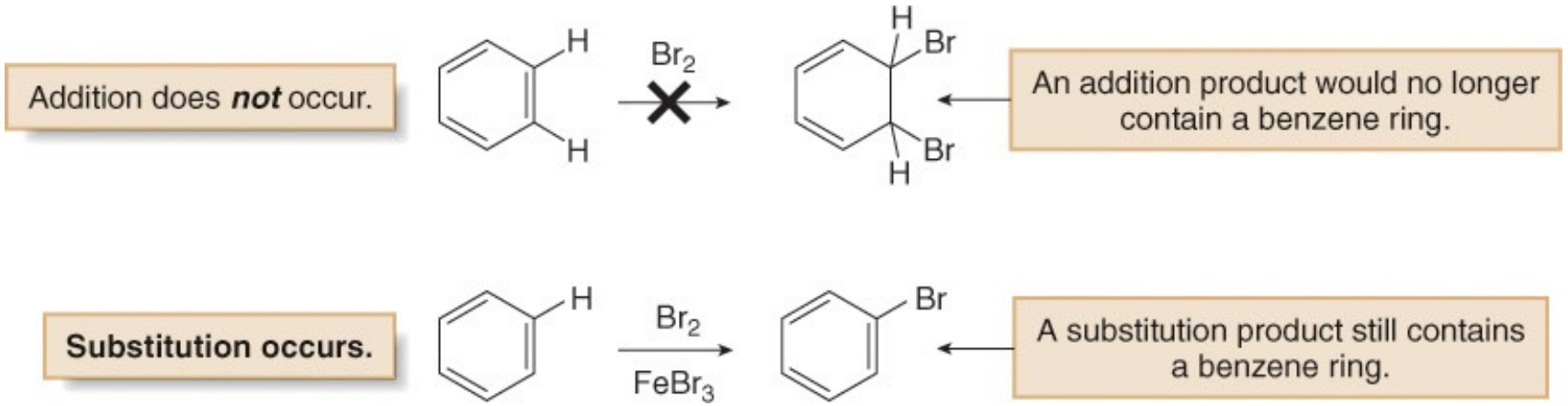

**The C–C bonds in benzene are equal and intermediate in length.**

# Aromaticity – Resonance Energy



# Stability of Benzene - Aromaticity

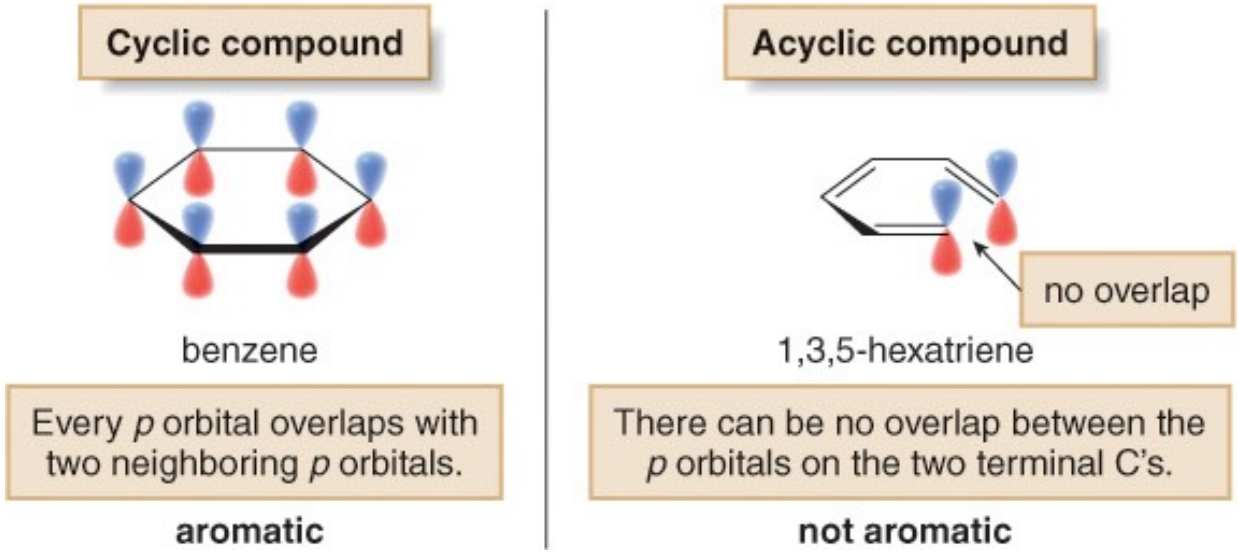
Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.



# The Criteria for Aromaticity

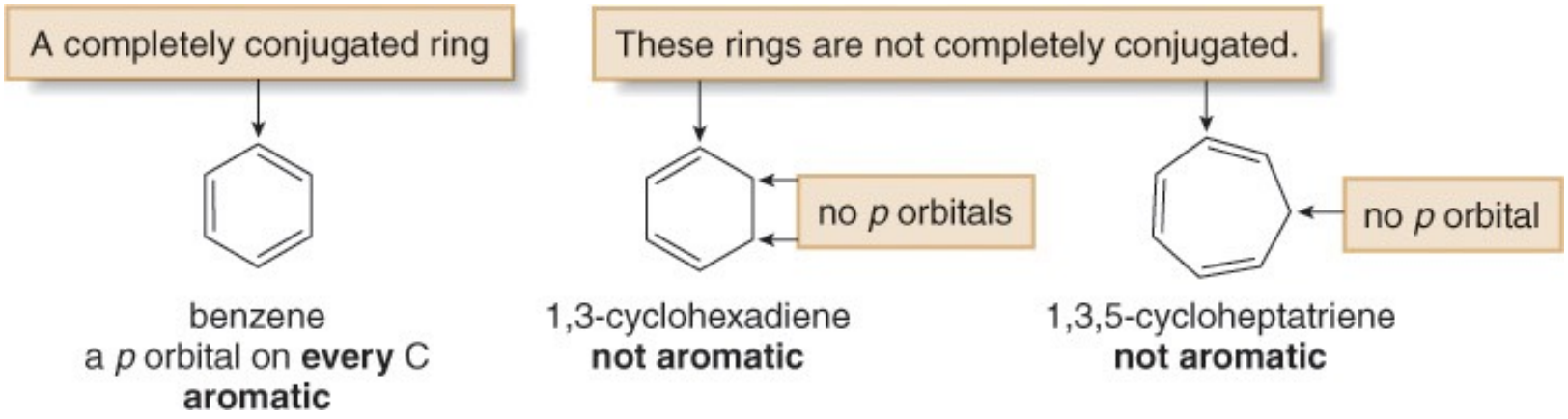
Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.



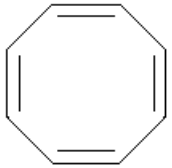
# The Criteria for Aromaticity

[2] A molecule must be completely conjugated (all atoms $sp^2$).

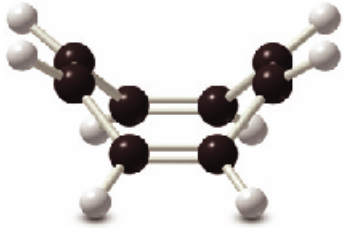


# The Criteria for Aromaticity

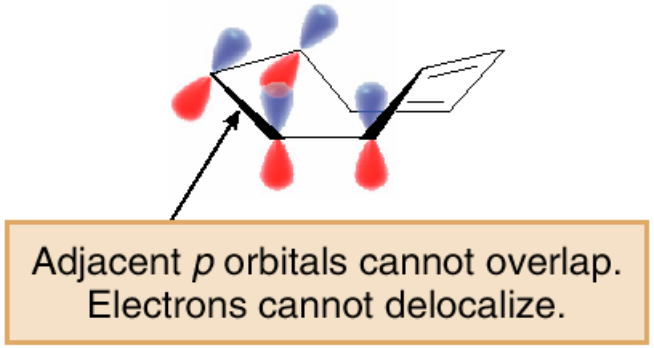
[3] A molecule must be planar.



cyclooctatetraene
**not aromatic**



a tub-shaped,
eight-membered ring



# The Criteria for Aromaticity—Hückel's Rule

[4] A molecule must satisfy Hückel's rule.

- An aromatic compound must contain $4n + 2$ π electrons ($n$ = 0, 1, 2, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic.*

**Benzene**
**An aromatic compound**

**$4n + 2 = 4(1) + 2 =$**
**6 π electrons**
**aromatic**

**Cyclobutadiene**
**An antiaromatic compound**

**$4n = 4(1) =$**
**4 π electrons**
**antiaromatic**



***Table 17.2*** **The Number of π Electrons That Satisfy Hückel's Rule**

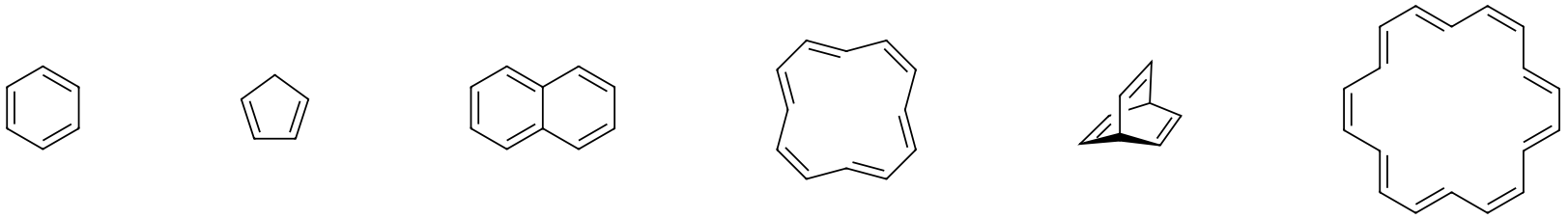
| $n$ | $4n + 2$ |
|---|---|
| 0 | 2 |
| 1 | 6 |
| 2 | 10 |
| 3 | 14 |
| 4, etc. | 18 |

# The Criteria for Aromaticity—Hückel's Rule

1. Aromatic—A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.

3. Antiaromatic—A cyclic, planar, completely conjugated compound with $4n$ π electrons.

5. Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.

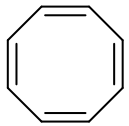


aromatic nonaromatic aromatic antiaromatic nonaromatic aromatic

modelli 3D

# Annulenes

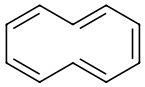
Cyclooctatetraene
**8** π electrons



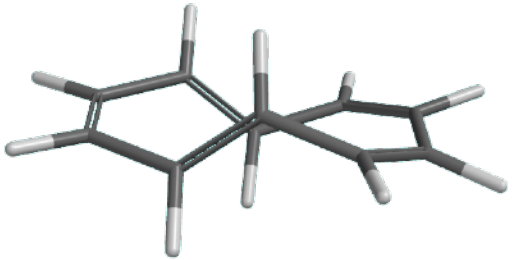
antiaromatic

nonaromatic

10-Annulene
**10** π electrons



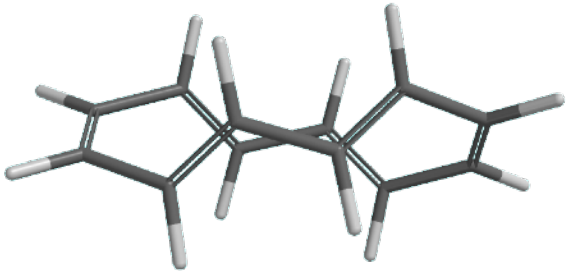
aromatic



nonaromatic

12-Annulene
**12** π electrons

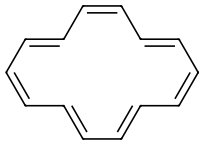
antiaromatic



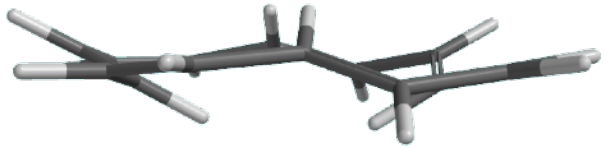
nonaromatic

# Annulenes

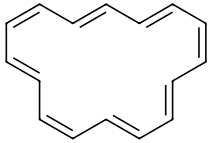
14-Annulene
**14** π electrons



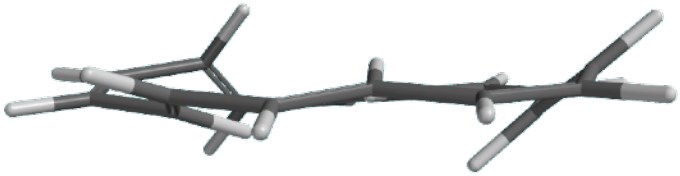
aromatic



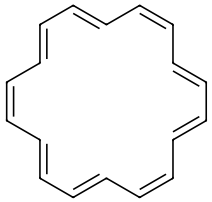
16-Annulene
**16** π electrons



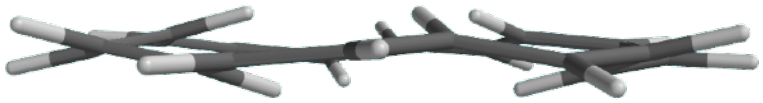
antiaromatic



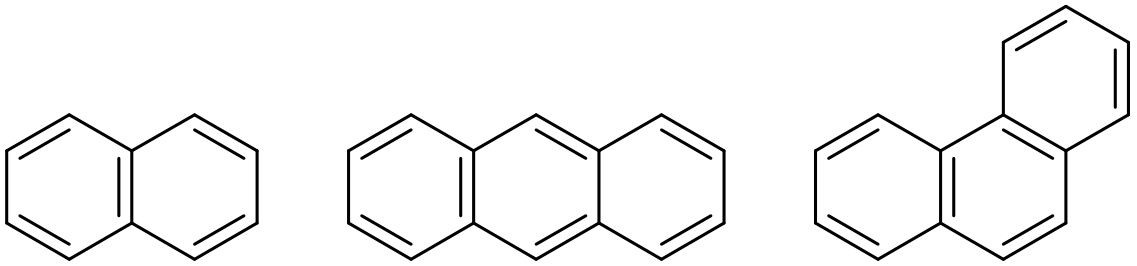
18-Annulene
**18** π electrons



aromatic



# Polycyclic Aromatic Hydrocarbons (PAH)

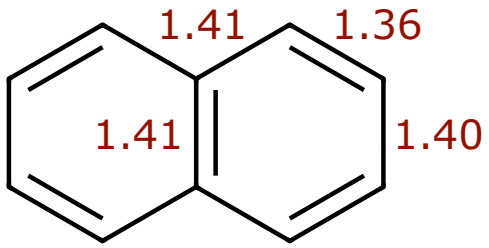


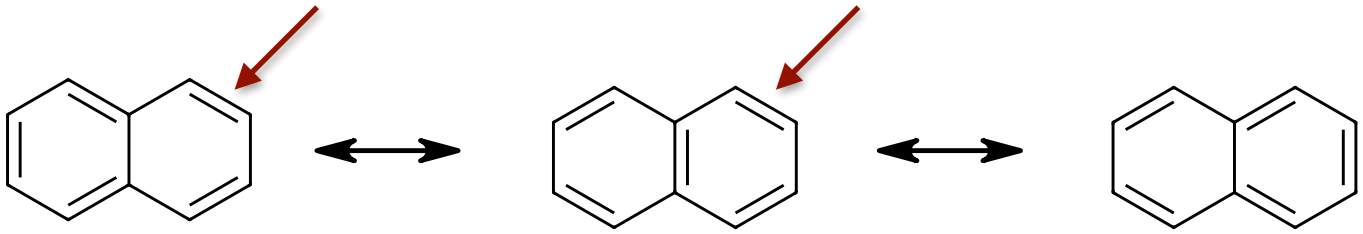
10 π 14 π

naphthalene anthracene phenanthrene

| | | | |
|---|---|---|---|
| resonance energy | 61 | 83 | 91 |
| per ring | 30.5 | 27.7 | 30.3 |

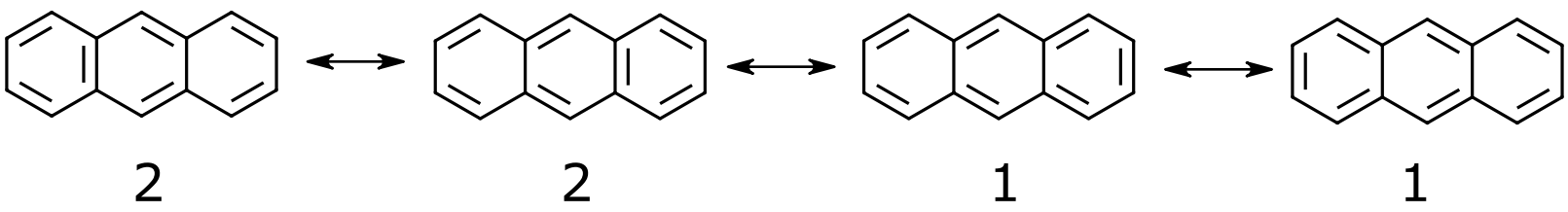
# Polycyclic Aromatic Hydrocarbons (PAH)

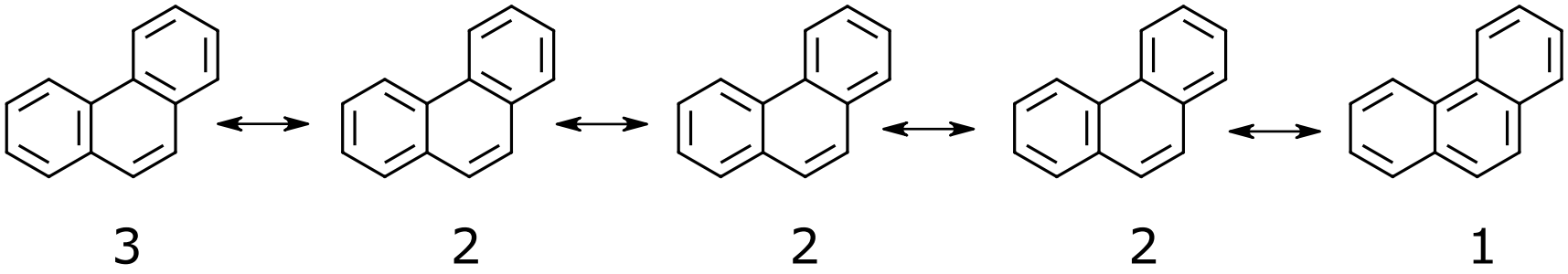


In 2 resonance structures there is a double bond between C1 and C2

# Polycyclic Aromatic Hydrocarbons (PAH)

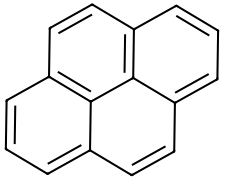


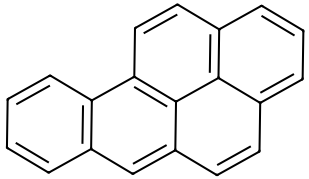

In phenanthrene there are more resonance structures containing 6-electron benzene rings

# Polycyclic Aromatic Hydrocarbons (PAH)

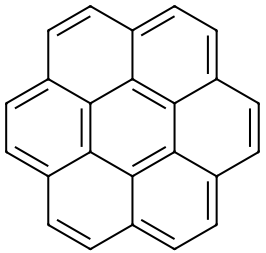
the Hückel rule does not apply to large fused systems: the following are all aromatic



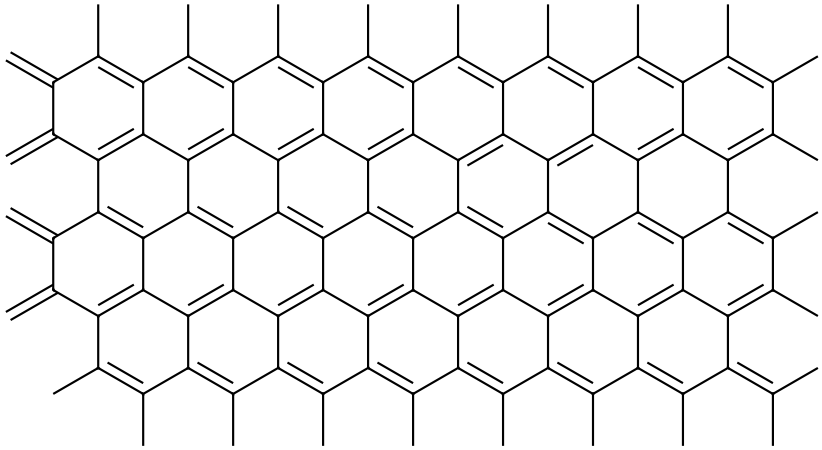
pyrene
16 π



benzopyrene
20 π

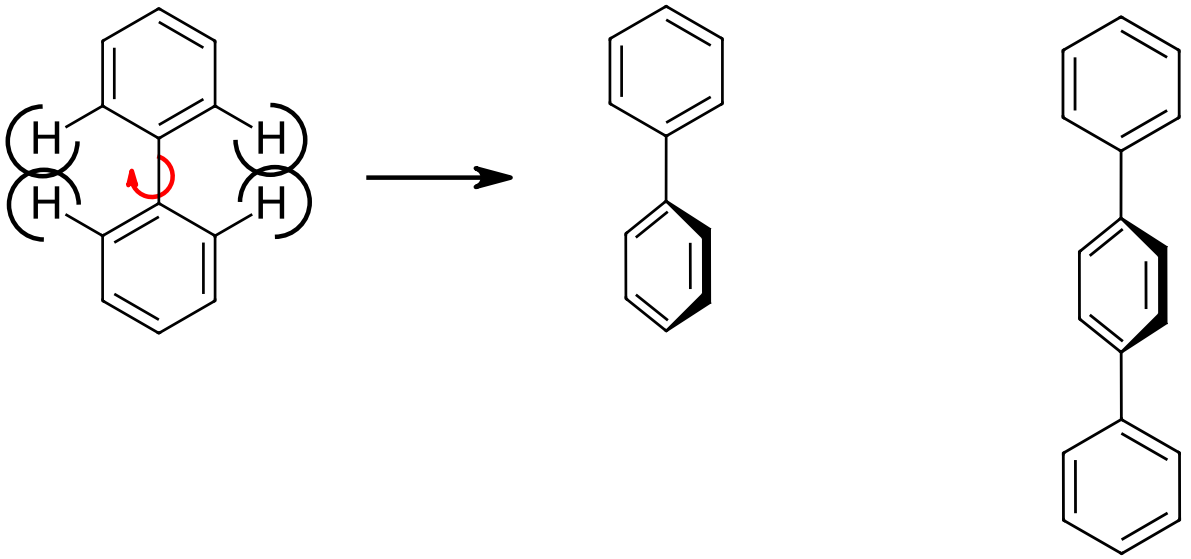


coronene
24 π



graphene

# Diphenyl and Terphenyl




- In diphenyl and terphenyl the rings are twisted around the central single bond to avoid torsional strain.

- The aromatic rings are independent.

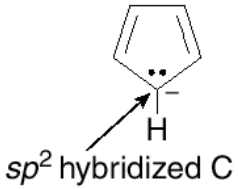
# Other Aromatic Compounds

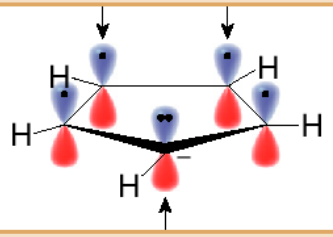

cyclopentadiene
**not aromatic**
$pK_a = 15$

cyclopentadienyl anion
**aromatic**
**a stabilized conjugate base**

**The cyclopentadienyl anion**

The ring is completely conjugated with **6 π electrons**.




The lone pair resides in a *p* orbital.

- **The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.**

# Other Aromatic Compounds

**cyclopentadienyl anion**
- **6** π electrons
- contains $4n + 2$ π electrons

**aromatic**

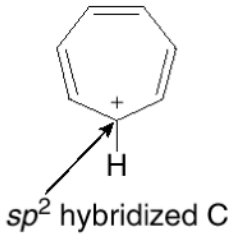
**cyclopentadienyl cation**
- **4** π electrons
- contains $4n$ π electrons

**antiaromatic**

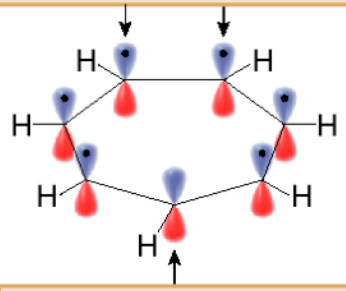
**cyclopentadienyl radical**
- **5** π electrons
- does not contain either $4n$ or $4n + 2$ π electrons

**nonaromatic**

**The tropylium cation**

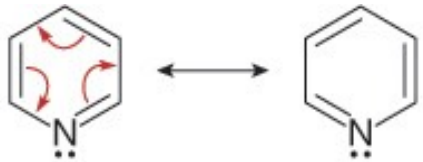



The ring is completely conjugated with **6 π electrons**.

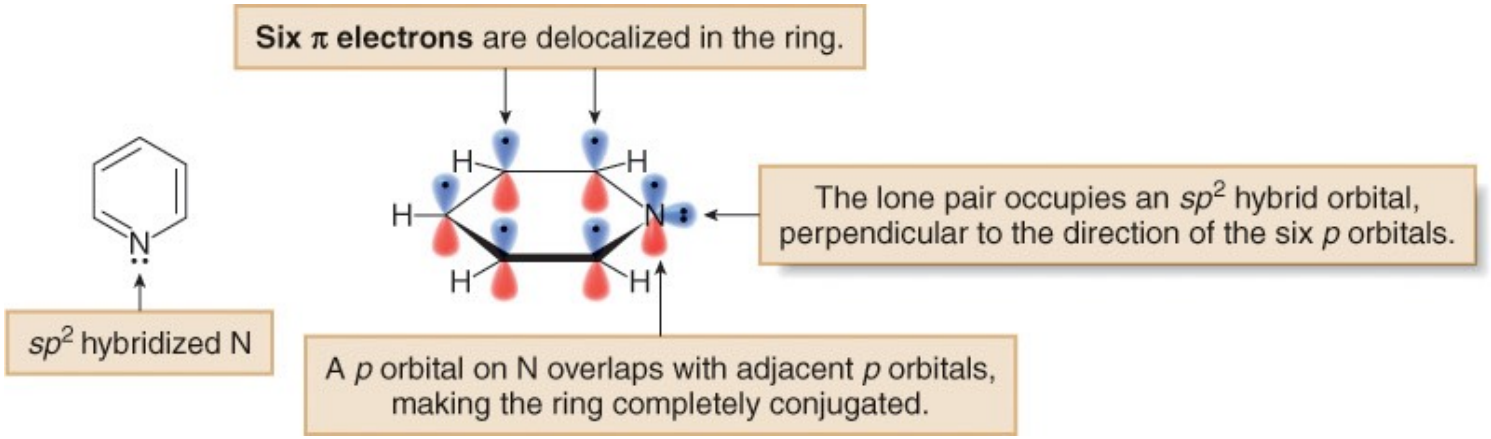



- The tropylium cation is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.

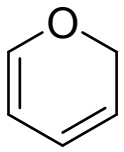
# Aromatic Heterocycles: Pyridine



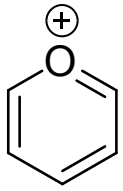
two resonance structures for pyridine
**6 π electrons**



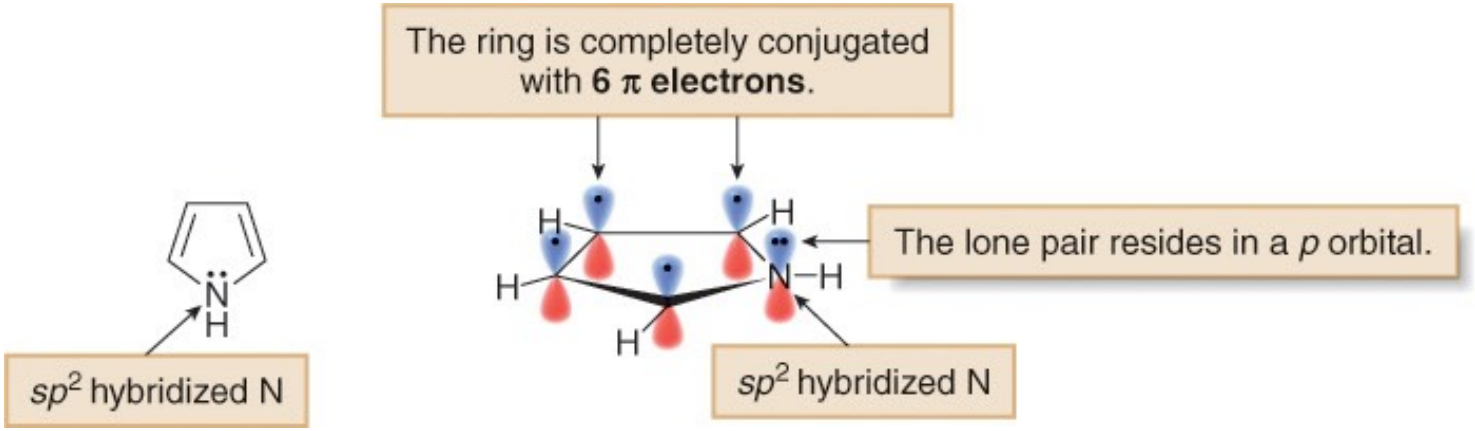

2H-pyran
4 π electrons
nonaromatic

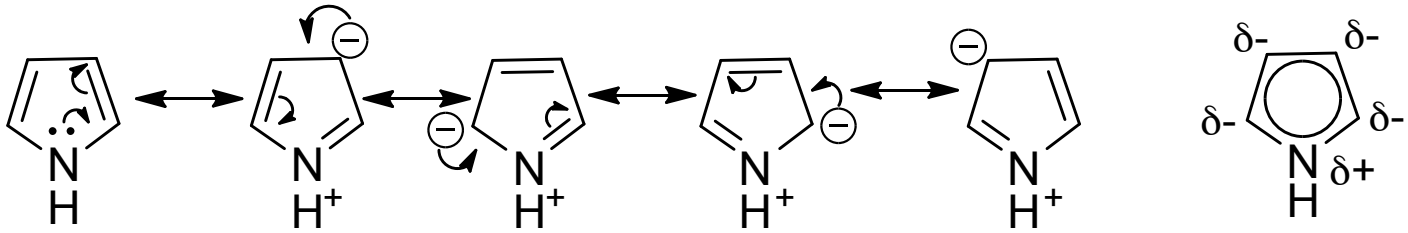


pyrilium ion
6 π electrons
aromatic

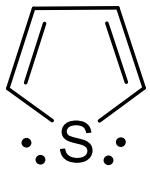


# Aromatic Heterocycles: Pyrrole

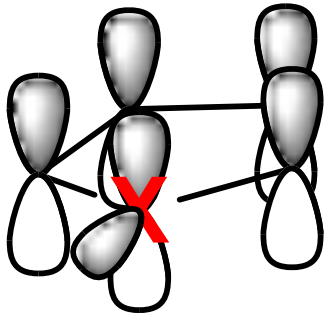


furan

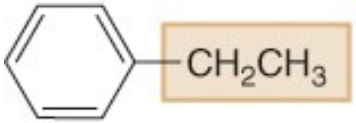


thiophen



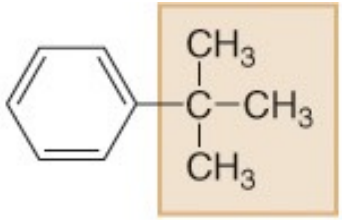
# Nomenclature: 1 Substituent

Systematic:



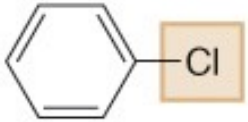

ethyl group

ethylbenzene




*tert*-butyl group

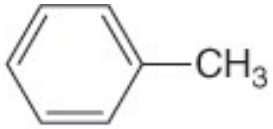
*tert*-butylbenzene



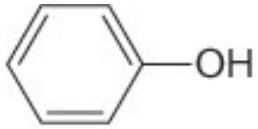

chloro group

chlorobenzene

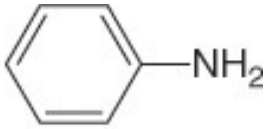
Common:




toluene
(methylbenzene)




phenol
(hydroxybenzene)

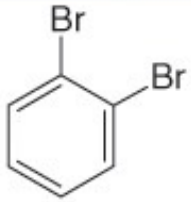



aniline
(aminobenzene)

# Nomenclature: 2 Substituents

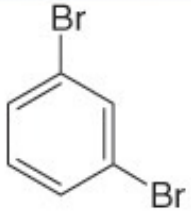
Identical:

**1,2**-disubstituted benzene
**ortho** isomer




1,2-dibromobenzene
*o*-dibromobenzene

**1,3**-disubstituted benzene
**meta** isomer



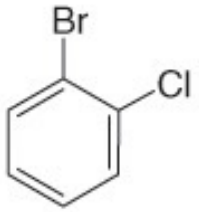

1,3-dibromobenzene
*m*-dibromobenzene

**1,4**-disubstituted benzene
**para** isomer

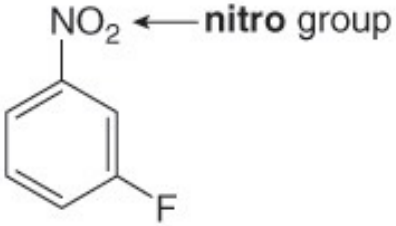

1,4-dibromobenzene
*p*-dibromobenzene

Different:

**Alphabetize two different substituent names:**

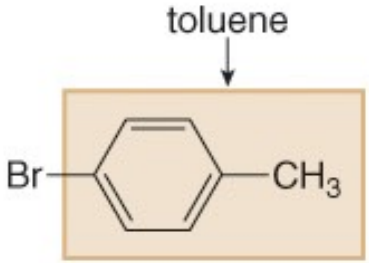



***o*-bromochloro-benzene**

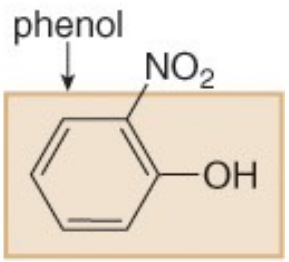



***m*-fluoronitro-benzene**

**Use a common root name:**




***p*-bromo**toluene

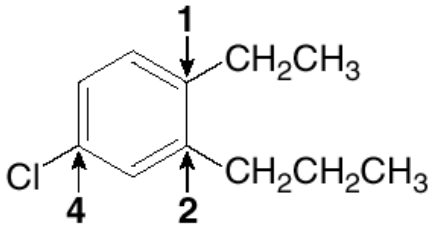



***o*-nitro**phenol

# Nomenclature: 3 or More Substituents

**Examples of naming polysubstituted benzenes**

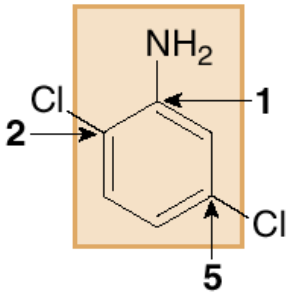
[1]




- Assign the lowest set of numbers.
- Alphabetize the names of all the substituents.

**4-chloro-1-ethyl-2-propylbenzene**

[2]

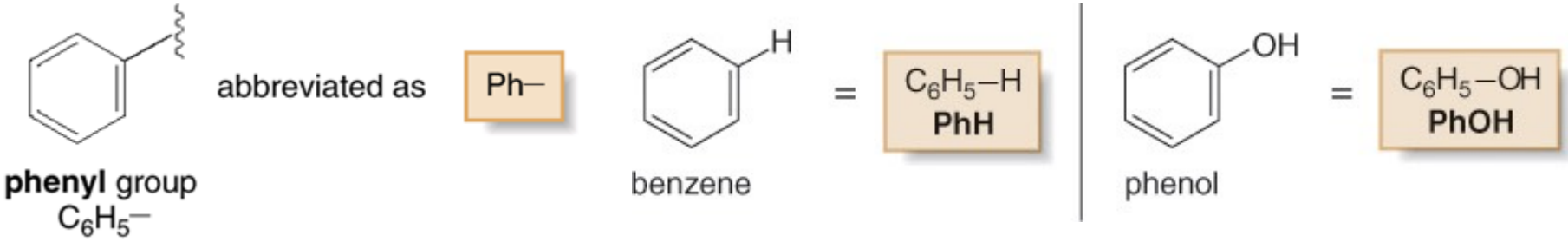



- Name the molecule as a derivative of the common root **aniline.**
- Designate the position of the $NH_2$ group as "1," and then assign the lowest possible set of numbers to the other substituents.

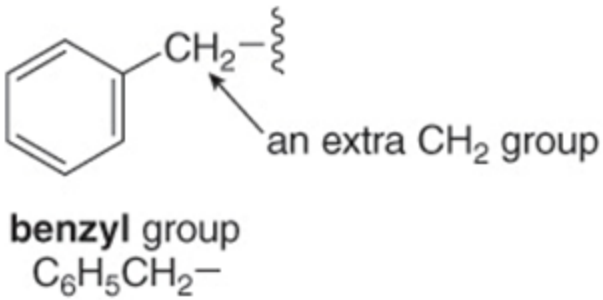
**2,5-dichloroaniline**

# Nomenclature

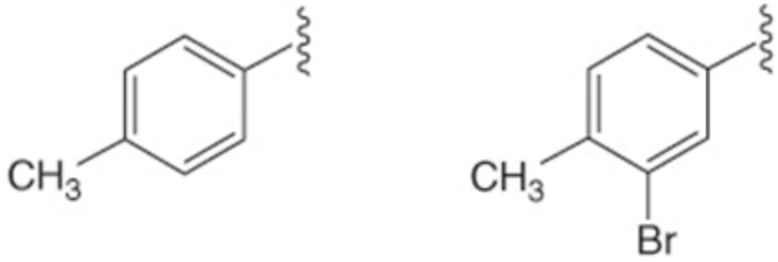
A benzene substituent is called a phenyl group, and it can be abbreviated in a structure as "Ph-".




## The benzyl group:




## Aryl groups:

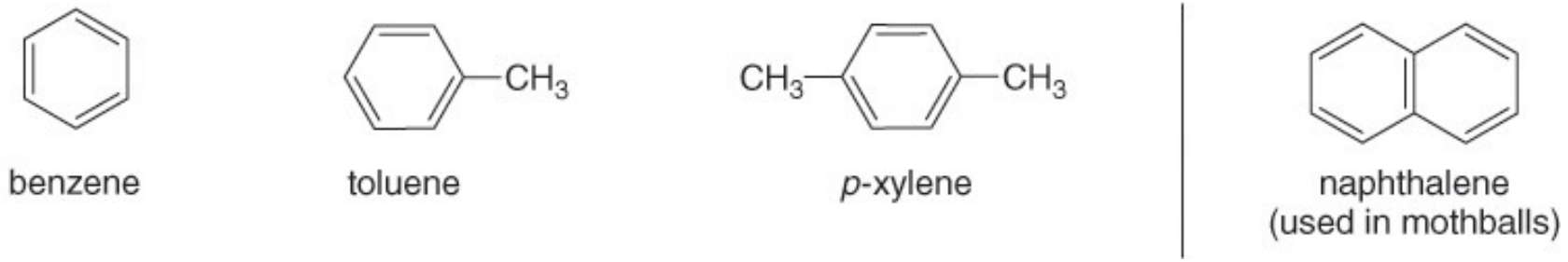


# Interesting Aromatic Compounds

- Benzene and toluene, are obtained from petroleum refining and are useful starting materials for synthetic polymers.

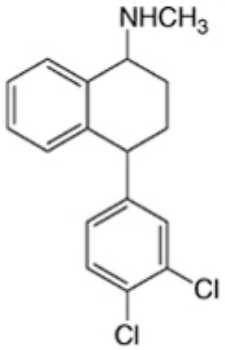
- Compounds containing two or more benzene rings that share carbon—carbon bonds are called polycyclic aromatic hydrocarbons (PAHs). Naphthalene, the simplest PAH, is the active ingredient in mothballs.

**The components of the gasoline additive BTX**

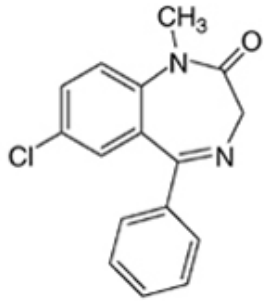



benzene | toluene | *p*-xylene | naphthalene (used in mothballs)

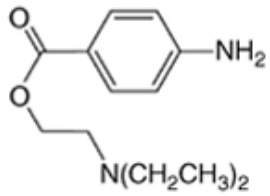
# Interesting Aromatic Compounds



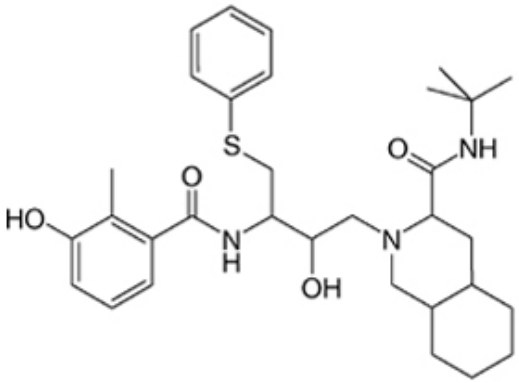

- Trade name: **Zoloft**
- Generic name: **sertraline**
- Use: a psychotherapeutic drug for depression and panic disorders



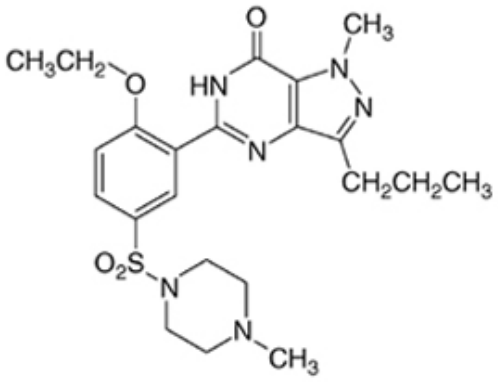

- Trade name: **Valium**
- Generic name: **diazepam**
- Use: a sedative



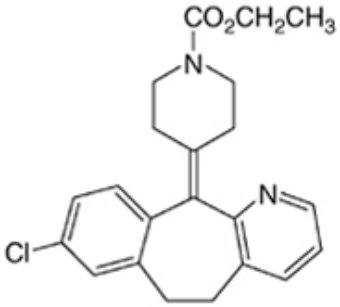

- Trade name: **Novocain**
- Generic name: **procaine**
- Use: a local anesthetic




- Trade name: **Viracept**
- Generic name: **nelfinavir**
- Use: an antiviral drug used to treat HIV



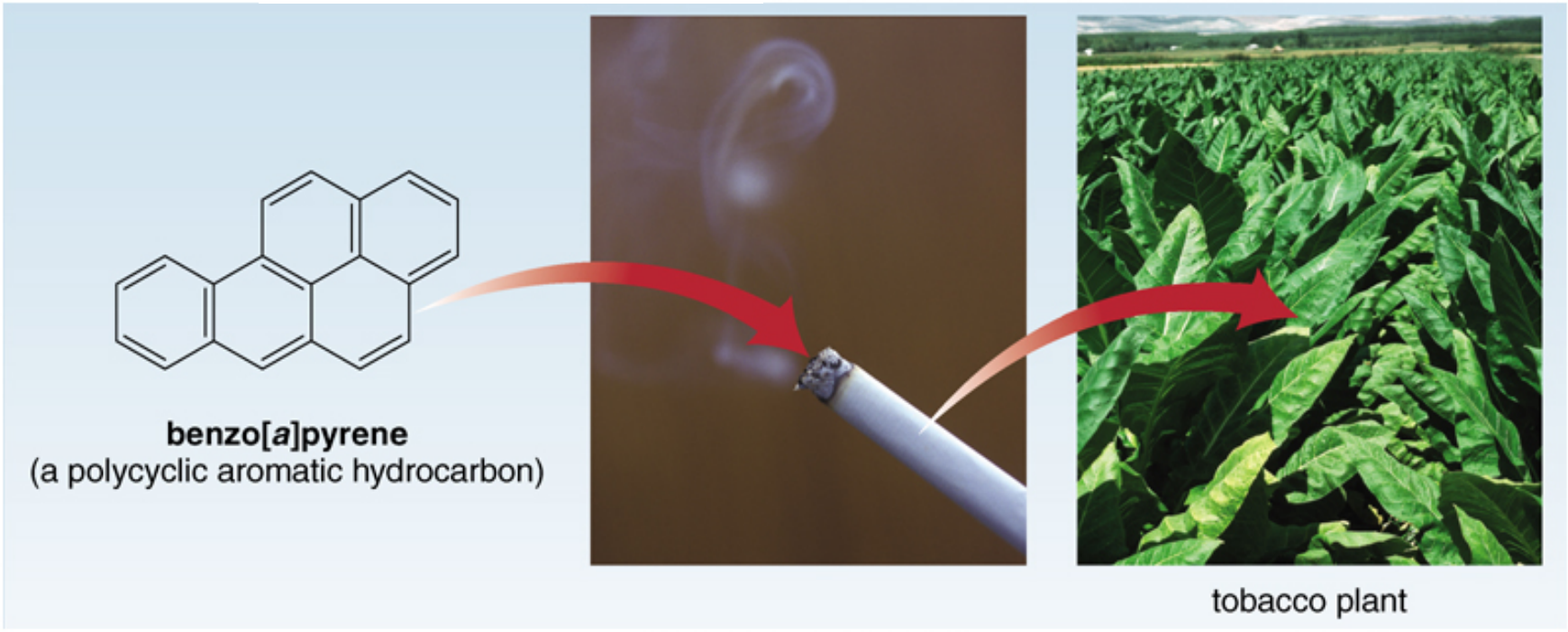

- Trade name: **Viagra**
- Generic name: **sildenafil**
- Use: a drug used to treat erectile dysfunction




- Trade name: **Claritin**
- Generic name: **loratadine**
- Use: an antihistamine for seasonal allergies

# Interesting Aromatic Compounds

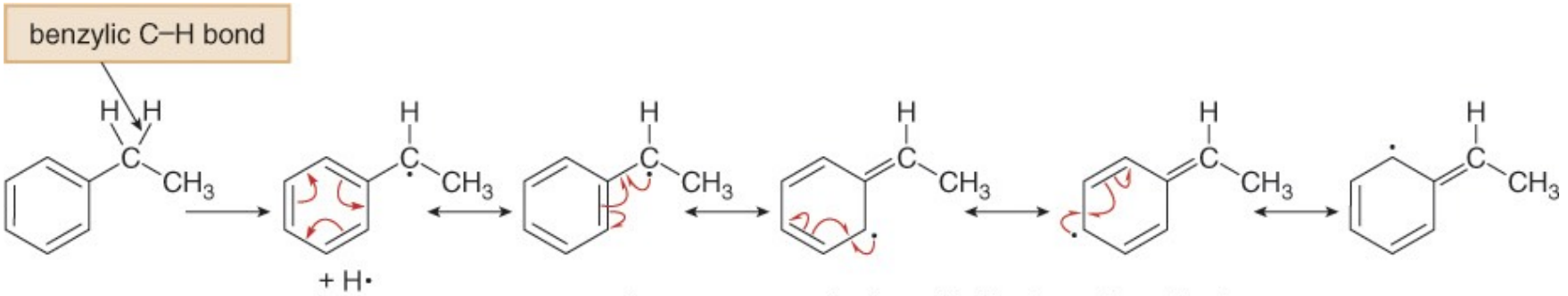
- Benzo[*a*]pyrene, produced by the incomplete oxidation of organic compounds in tobacco, is found in cigarette smoke.



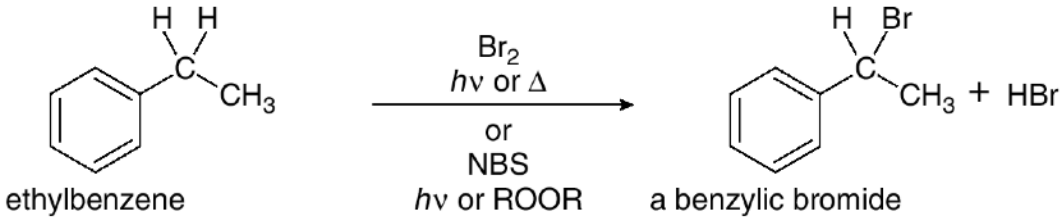

- When ingested or inhaled, benzo[a]pyrene and other similar PAHs are oxidized to carcinogenic products.

# Side Chain Reactivity: Radical Halogenation

Benzylic C—H bonds are weaker than most other $sp^3$ hybridized C—H bonds, because homolysis forms a resonance-stabilized benzylic radical.



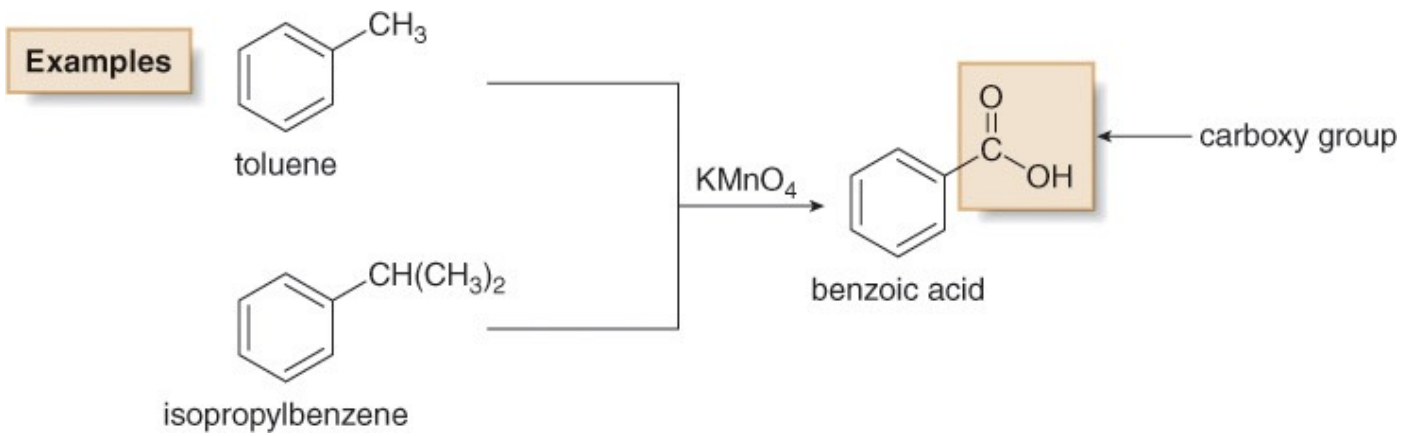

five resonance structures for the benzylic radical

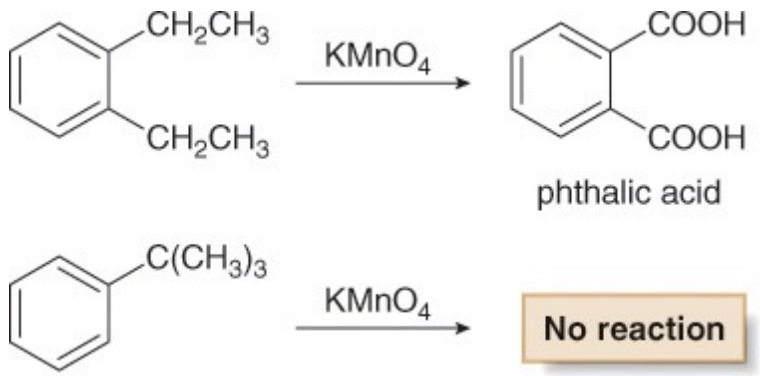



ethylbenzene — a benzylic bromide

**radical conditions**

# Side Chain Reactivity: Oxidation



# Side Chain Reactivity: Reduction