.

Aromaticity and Aromatic Compounds

Dr. Ahmed A. Ahmed

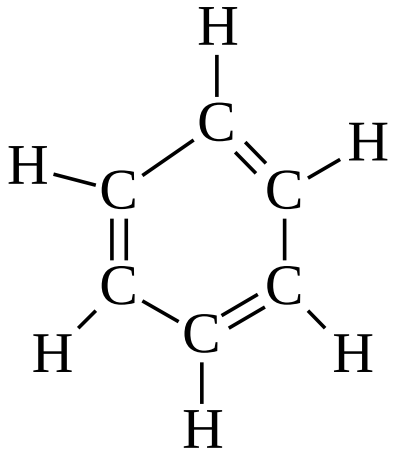
Lect. 14

Discovery of Benzene

- Isolated in 1825 by Michael Faraday who determined C:H ratio to be 1:1.
- Synthesized in 1834 by Eilhard Mitscherlich who determined molecular formula to be C_6H_6.
- Other related compounds with low C:H ratios had a pleasant smell, so they were classified as aromatic.

Kekulé Structure

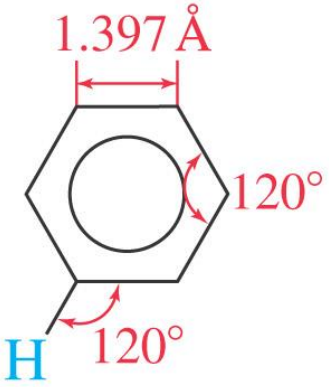
- Proposed in 1866 by Friedrich Kekulé, shortly after multiple bonds were suggested.
- Failed to explain existence of only one isomer of 1,2-dichlorobenzene.

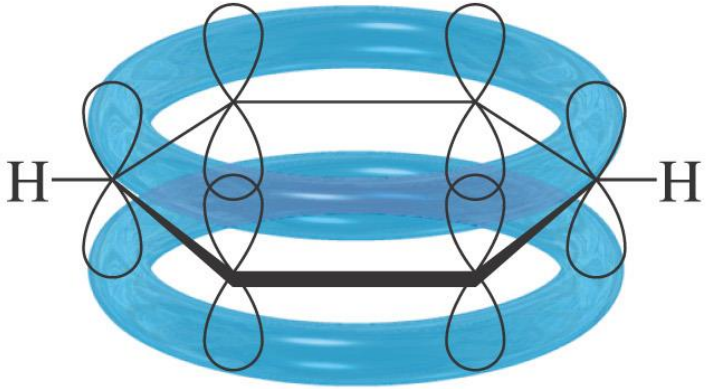


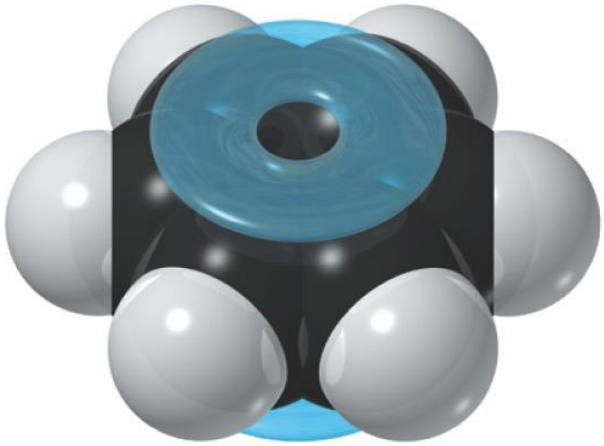
=>

Resonance Structure

Each sp^2 hybridized C in the ring has an unhybridized *p* orbital perpendicular to the ring which overlaps around the ring.







=>

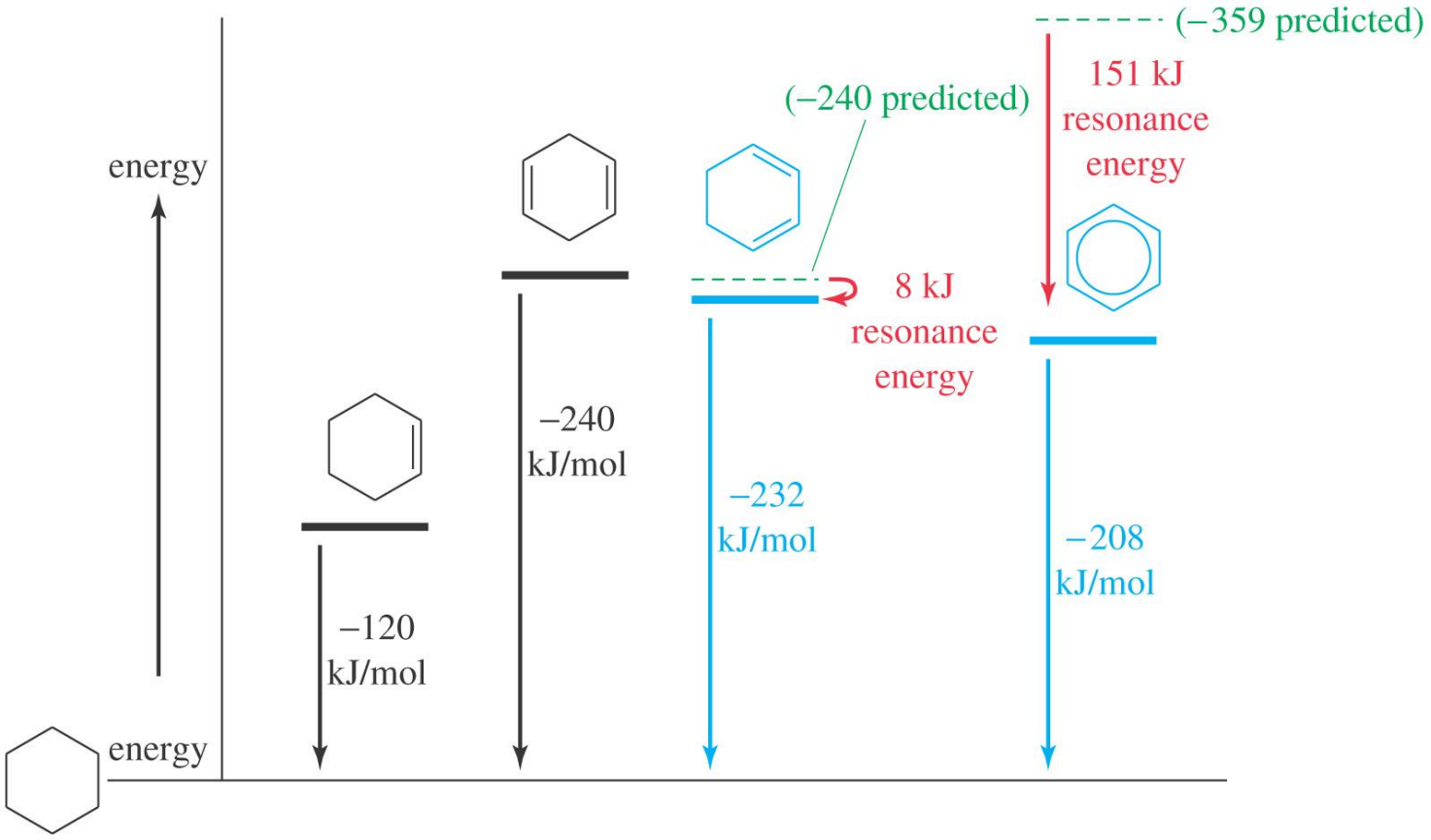
Unusual Reactions

- Alkene + $KMnO_4 \rightarrow$ diol (addition)
  Benzene + $KMnO_4 \rightarrow$ no reaction.
- Alkene + $Br_2/CCl_4 \rightarrow$ dibromide (addition)
  Benzene + $Br_2/CCl_4 \rightarrow$ no reaction.
- With $FeCl_3$ catalyst, Br_2 reacts with benzene to form bromobenzene + HBr (substitution!). Double bonds remain.

=>

Unusual Stability

Hydrogenation of just one double bond in benzene is endothermic!



=>

Aromatic Requirements

- Structure must be cyclic with conjugated pi bonds.
- Each atom in the ring must have an unhybridized *p* orbital.
- The *p* orbitals must overlap continuously around the ring. (Usually planar structure.)
- Compound is <u>more</u> stable than its open-chain counterpart. =>

Anti- and Nonaromatic

- Antiaromatic compounds are cyclic, conjugated, with overlapping *p* orbitals around the ring, but the energy of the compound is <u>greater</u> than its open-chain counterpart.
- Nonaromatic compounds do not have a continuous ring of overlapping *p* orbitals and may be nonplanar. =>

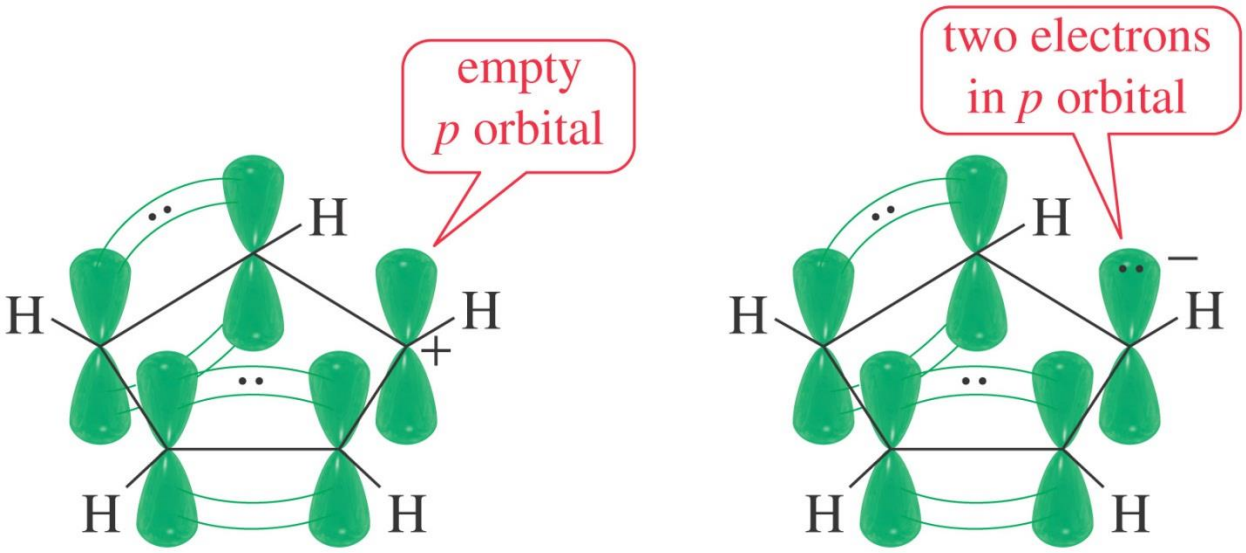
Hückel's Rule

- If the compound has a continuous ring of overlapping *p* orbitals and has $4N + 2$ electrons, it is aromatic.
- If the compound has a continuous ring of overlapping *p* orbitals and has $4N$ electrons, it is antiaromatic.

=>

Cyclopentadienyl Ions

- The cation has an empty *p* orbital, 4 electrons, so antiaromatic.
- The anion has a nonbonding pair of electrons in a *p* orbital, 6 e^-'s, aromatic.



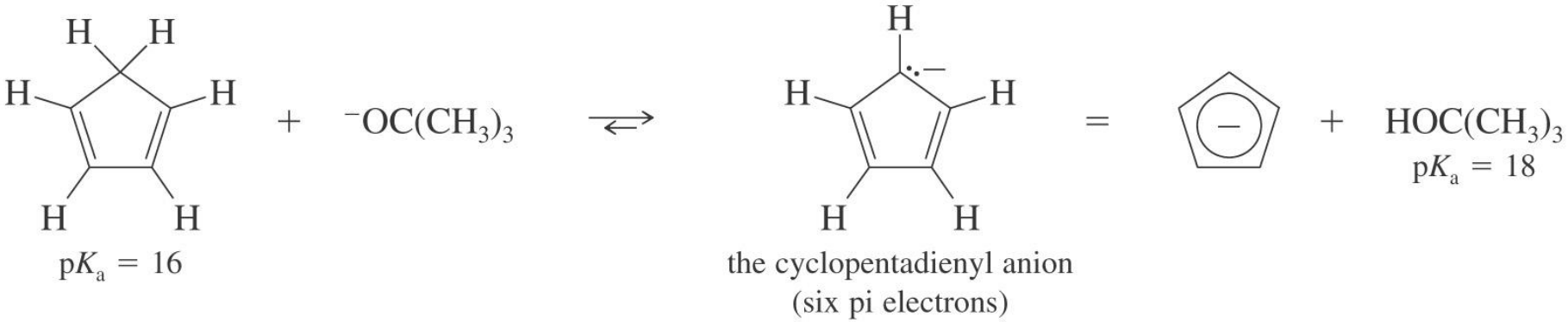
four electrons
cyclopentadienyl cation

six electrons
cyclopentadienyl anion

=>

Acidity of Cyclopentadiene

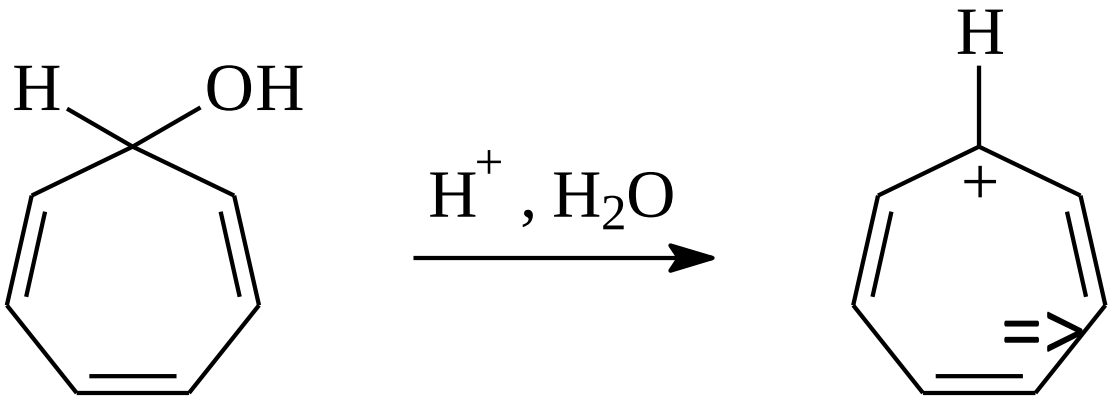
pK_a of cyclopentadiene is 16, much more acidic than other hydrocarbons.



=>

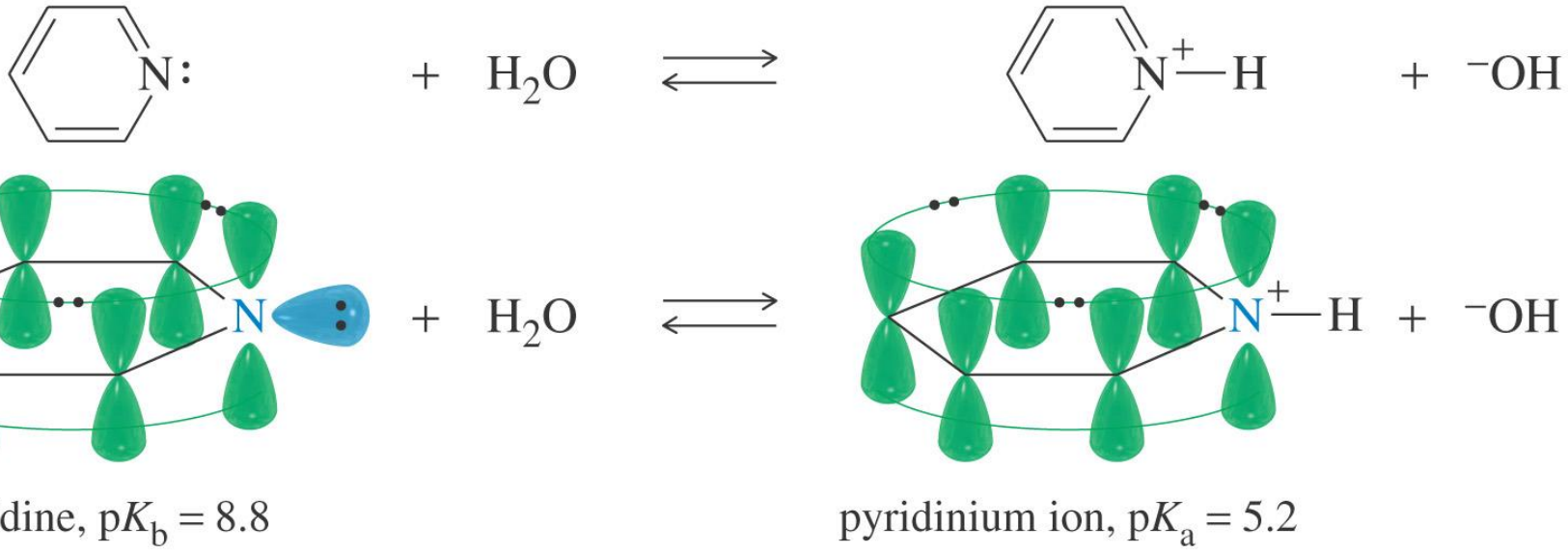
Tropylium Ion

- The cycloheptatrienyl cation has 6 *p* electrons and an empty *p* orbital.
- Aromatic: more stable than open chain ion.



Pyridine

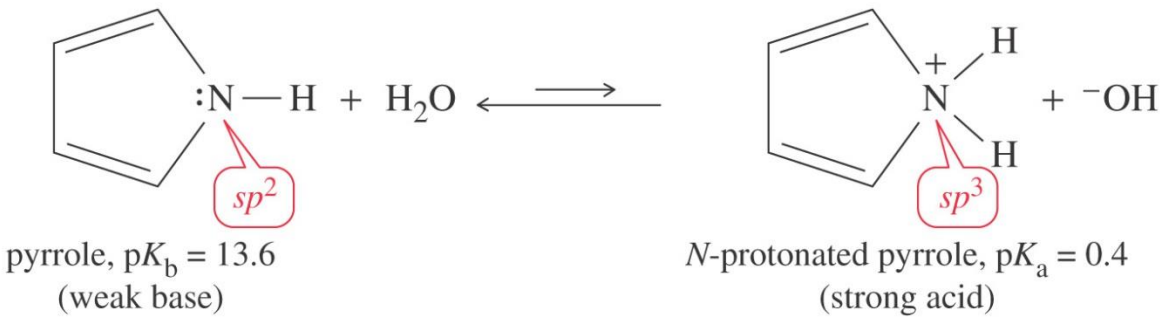
- Heterocyclic aromatic compound.
- Nonbonding pair of electrons in sp^2 orbital, so weak base, pK_b = 8.8.

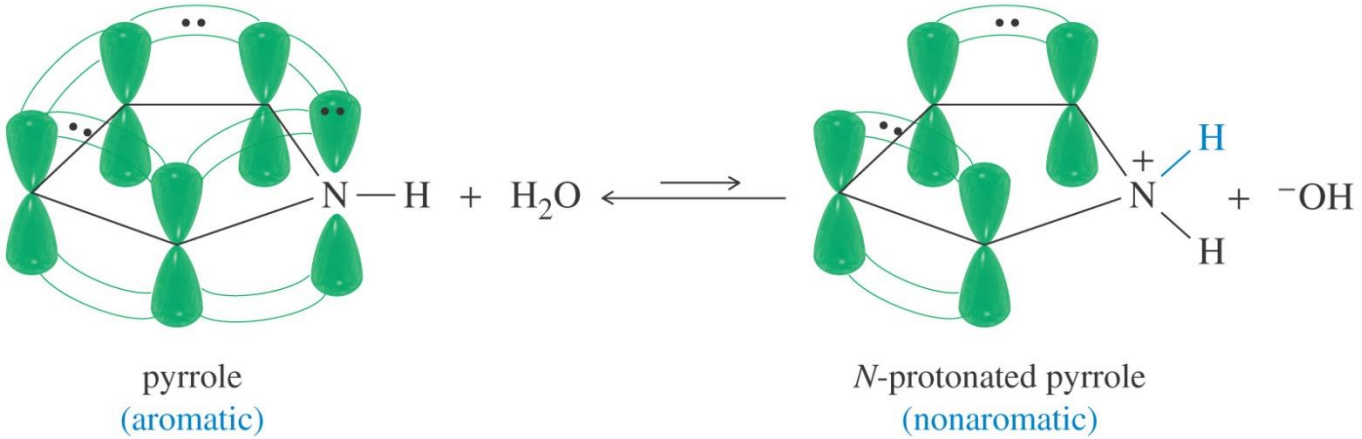


=>

Pyrrole

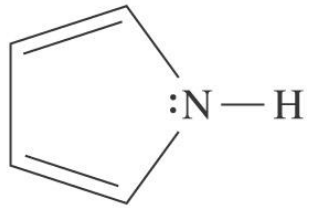
Also aromatic, but lone pair of electrons is delocalized, so much weaker base.



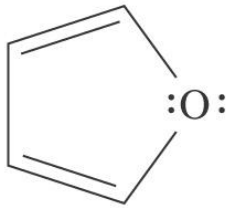


=>

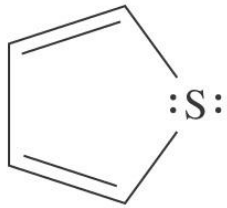
Other Heterocyclics



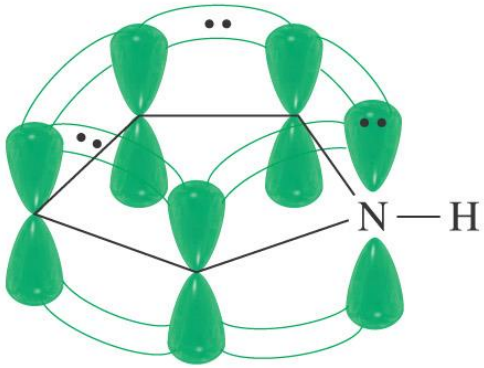
pyrrole



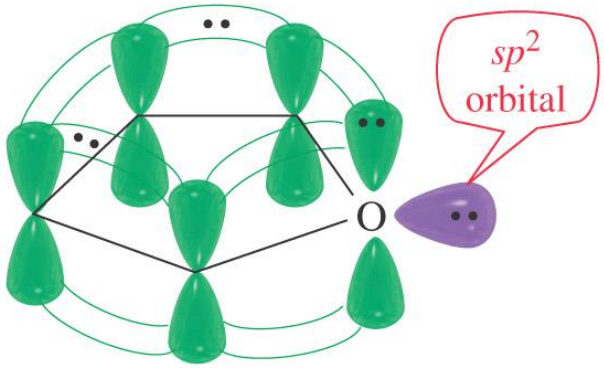
furan



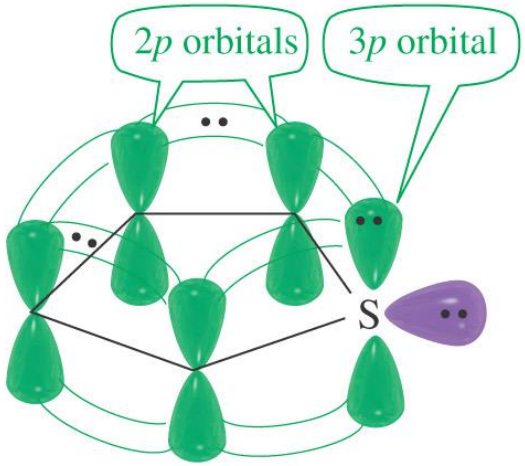
thiophene



six pi electrons



six pi electrons

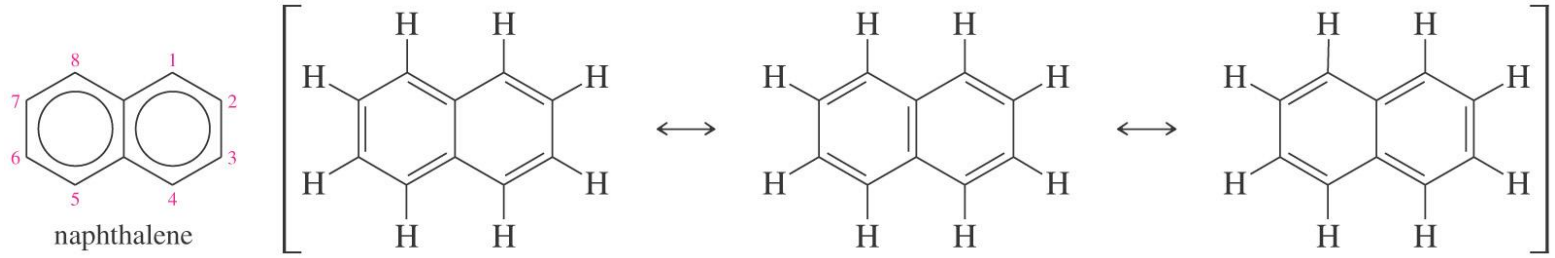


six pi electrons

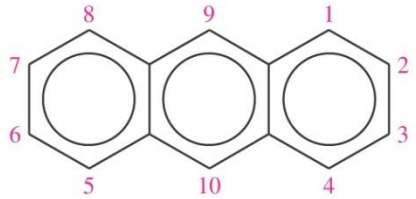
=>

Fused Ring Hydrocarbons

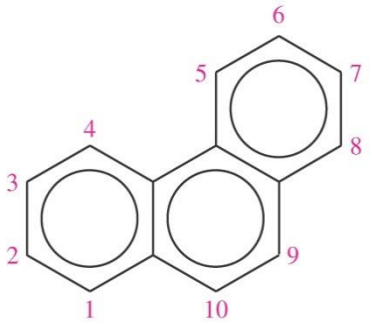
- Naphthalene



- Anthracene



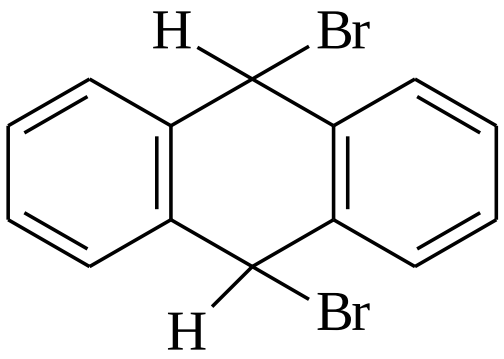
- Phenanthrene

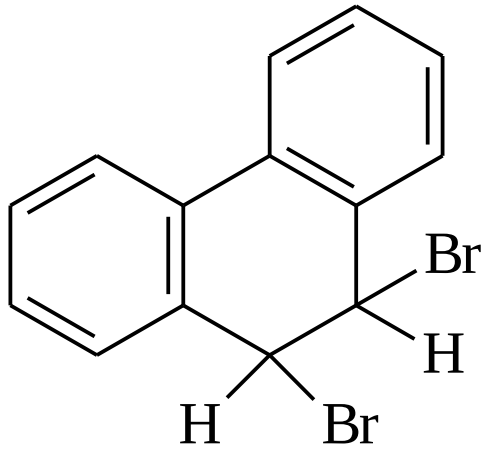


=>

Reactivity of Polynuclear Hydrocarbons

As the number of aromatic rings increases, the resonance energy per ring decreases, so larger PAH's will add Br_2.

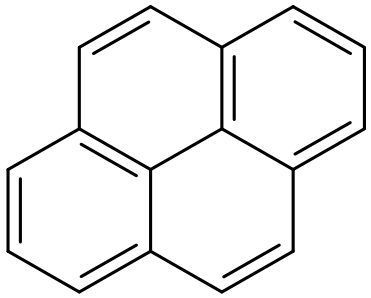




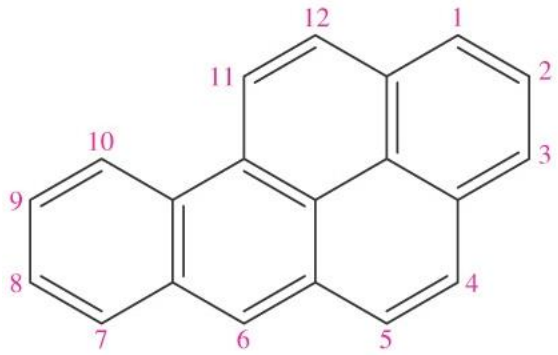
(mixture of cis and trans isomers) =>

Larger Polynuclear Aromatic Hydrocarbons

- Formed in combustion (tobacco smoke).
- Many are carcinogenic.
- Epoxides form, combine with DNA base.



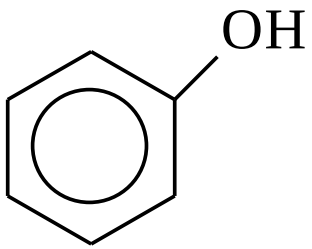
pyrene



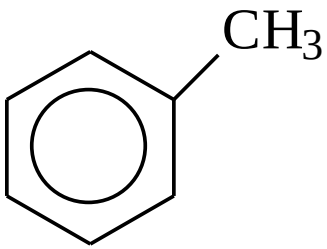
benzo[*a*]pyrene

=>

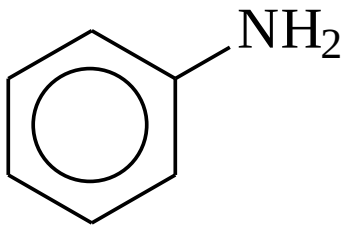
Common Names of Benzene Derivatives



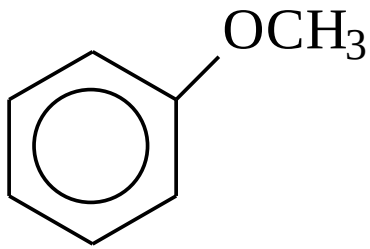
phenol



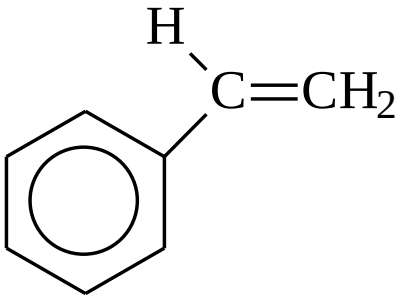
toluene



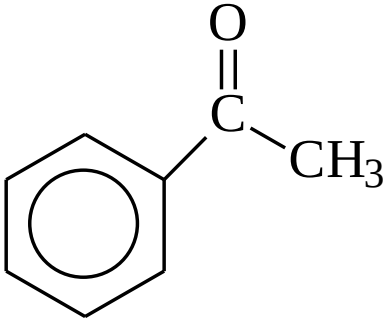
aniline



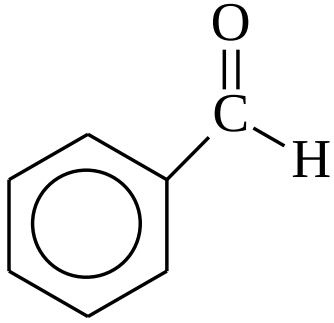
anisole



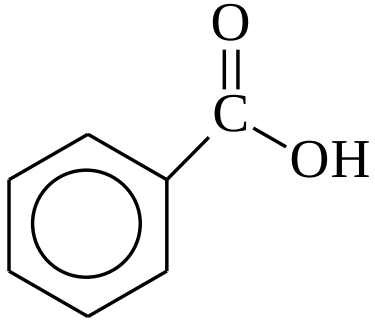
styrene



acetophenone



benzaldehyde

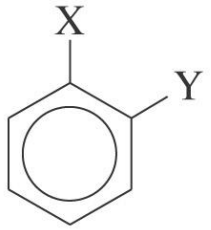


benzoic acid

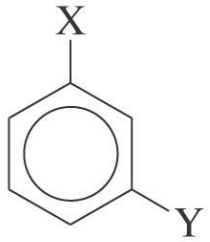
=>

Disubstituted Benzenes

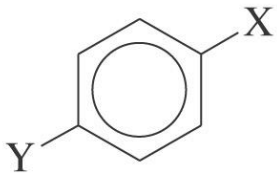
The prefixes *ortho*-, *meta*-, and *para*- are commonly used for the 1,2-, 1,3-, and 1,4-positions, respectively.



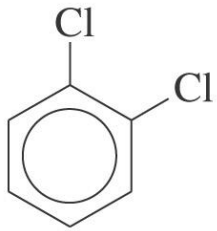
1,2 or ortho

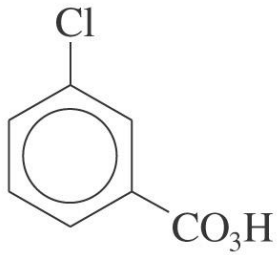


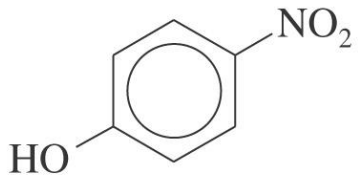
1,3 or meta



1,4 or para





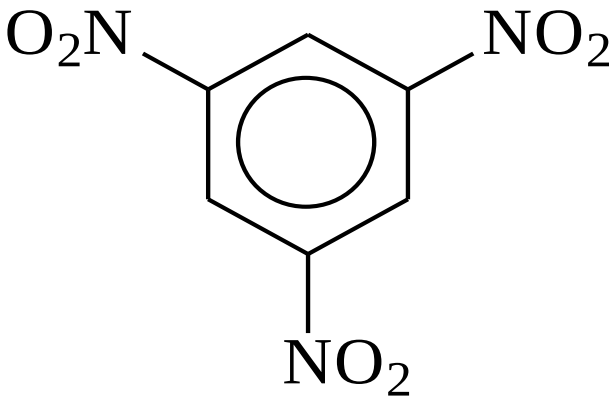


common name:	*o*-dichlorobenzene	*m*-chloroperoxybenzoic acid	*p*-nitrophenol
IUPAC name:	1,2-dichlorobenzene	3-chloroperoxybenzoic acid	4-nitrophenol

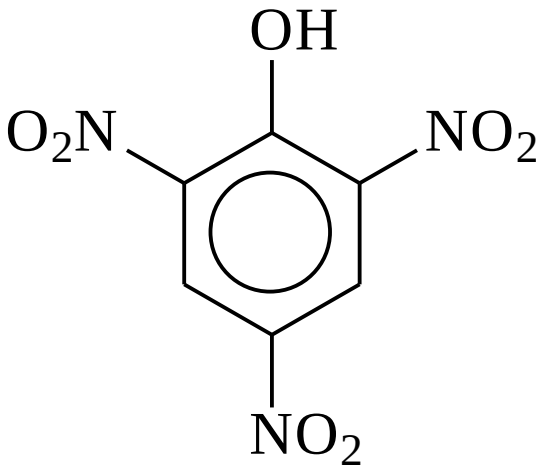
=>

3 or More Substituents

Use the smallest possible numbers, but the carbon with a functional group is #1.



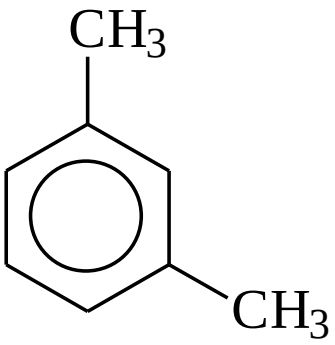
1,3,5-trinitrobenzen



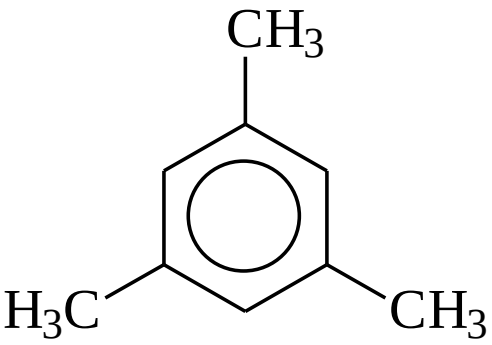
2,4,6-trinitrophenol

=>

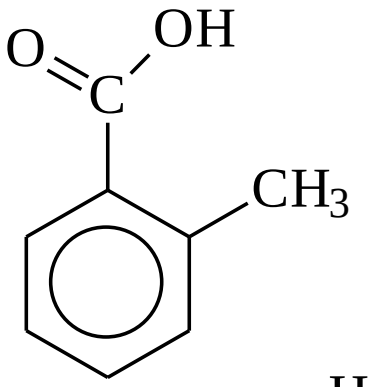
Common Names for Disubstituted Benzenes



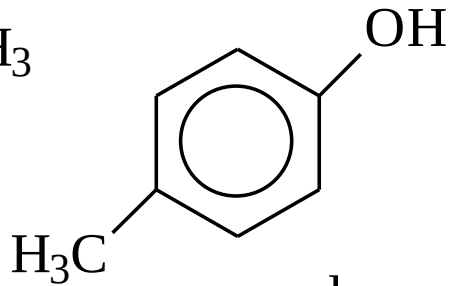
m-xylene



mesitylene



o-toluic acid

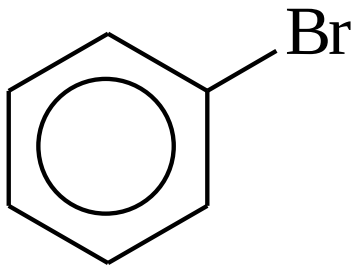


p-cresol

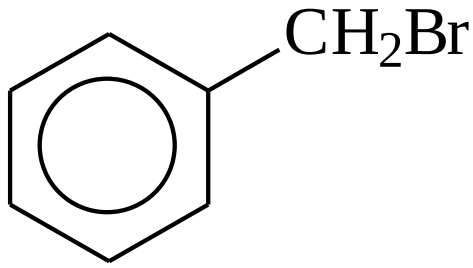
=>

Phenyl and Benzyl

Phenyl indicates the benzene ring attachment. The benzyl group has an additional carbon.



phenyl bromide



benzyl bromide

=>

Physical Properties

- Melting points: More symmetrical than corresponding alkane, pack better into crystals, so higher melting points.
- Boiling points: Dependent on dipole moment, so *ortho* > *meta* > *para*, for disubstituted benzenes.
- Density: More dense than nonaromatics, less dense than water.
- Solubility: Generally insoluble in water. =>