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Organic Chemistry

Benzene and Aromatic compounds

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Expected Outcomes

In the completion of this chapter, student will have the ability to:

- Compare and identify aromatic, antiaromatic and nonaromatic compounds

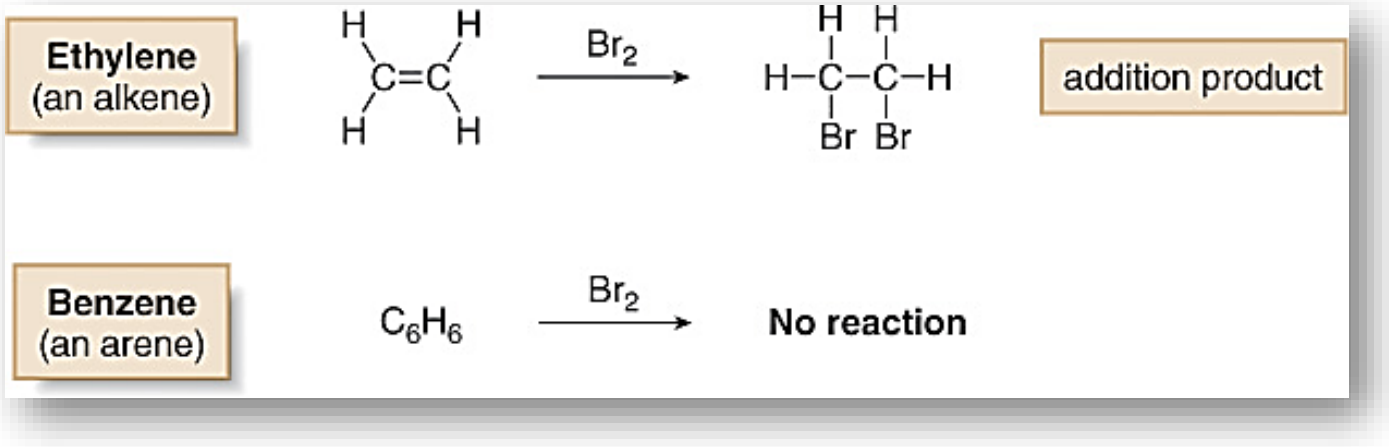
Contents

- Benzene structure
- Nomenclature
- Huckel's rule

Benzene and Aromatic Compounds

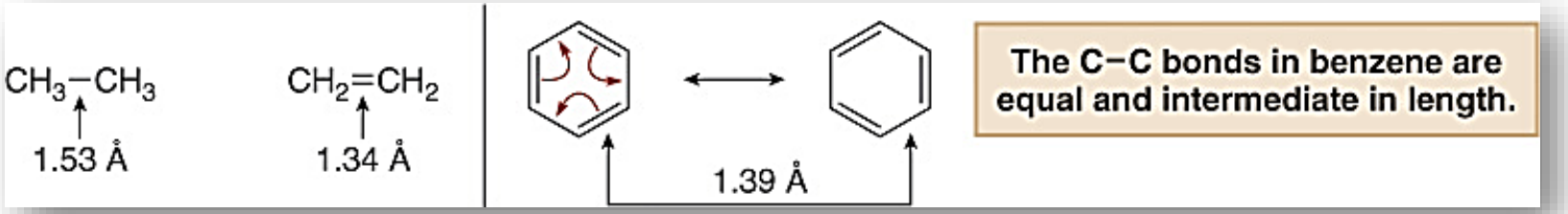
Background

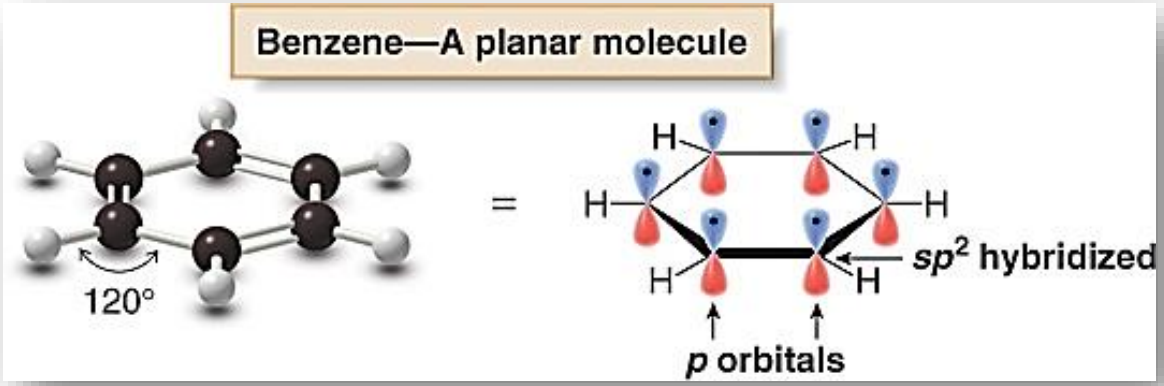
- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Benzene has four degrees of unsaturation, making it a highly unsaturated hydrocarbon.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not.



The Structure of Benzene

- In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon single bond (1.53 Å) and the carbon—carbon double bond (1.34 Å).





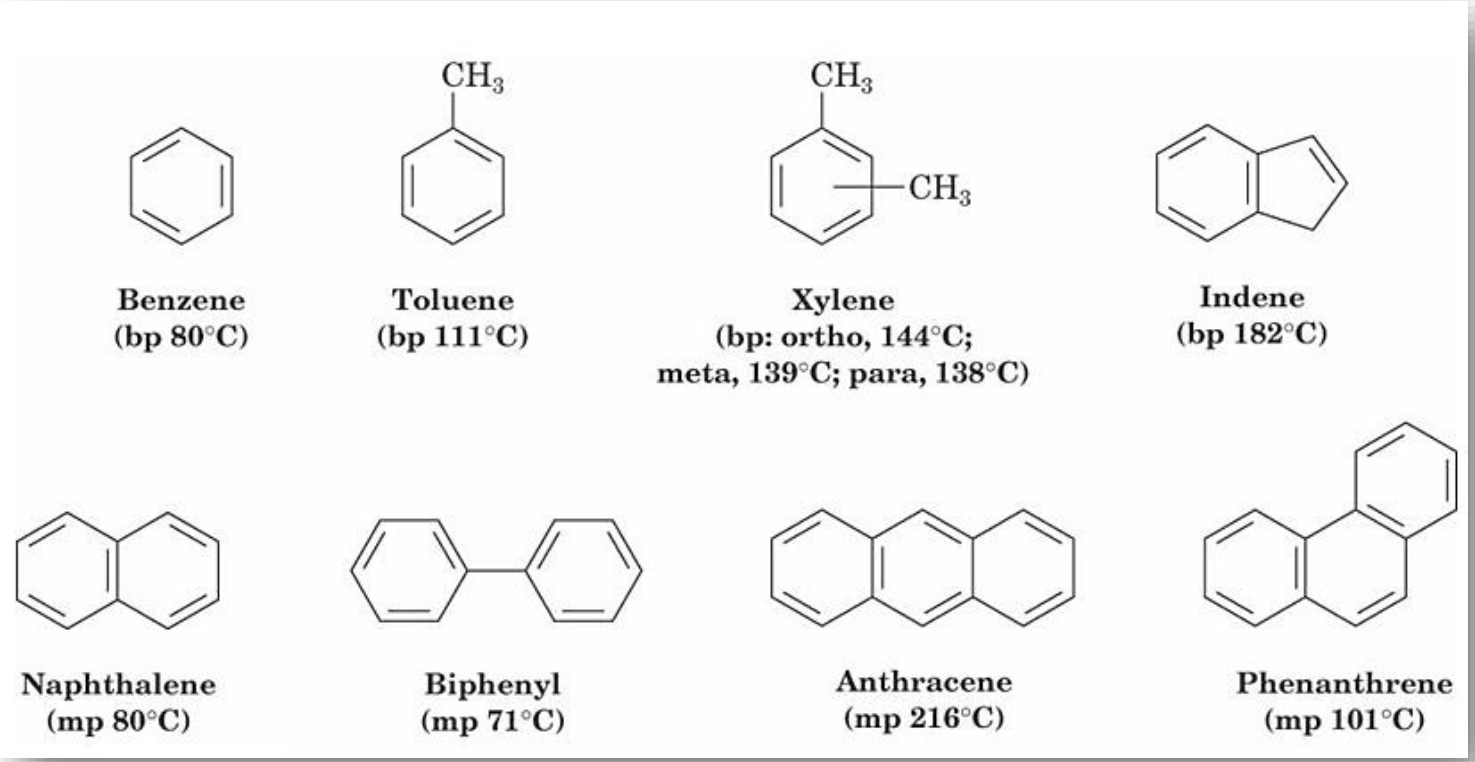
Source of Aromatic Hydrocarbons

- There are two main sources of simple aromatic hydrocarbons:

  i. coal
  ii. petroleum

i. High temperature distillation of coal tar

– Coal is a mixture of benzene-like rings joined together. Under high temperature, it produces coal tar which, upon fractional distillation, yields:

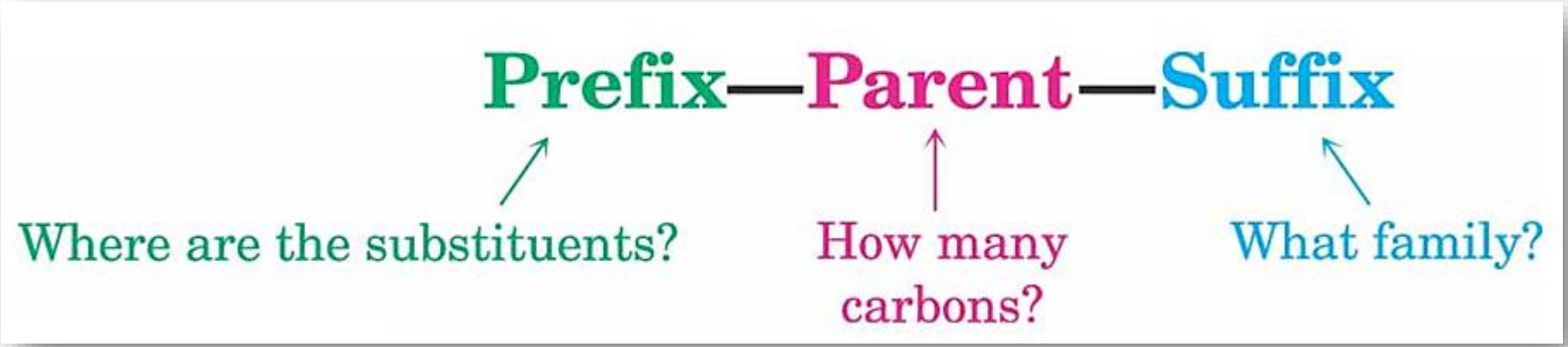


ii. Heating petroleum at high temperature under high pressure over a catalyst

– Petroleum consists mainly of alkanes which, at high temperature under pressure over a catalyst, convert into aromatic compounds.

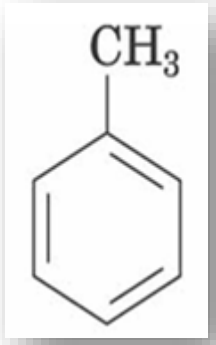
Naming Aromatic Compounds

- Aromatic compounds are named according to the system devised by the **I**nternational **U**nion of **P**ure and **A**pplied **C**hemistry (**IUPAC**).

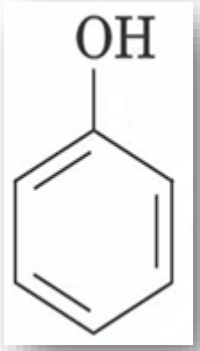


- Aromatic compounds have many common names that have been accepted by IUPAC:

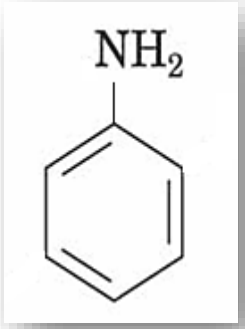
- ***Toluene*** = methylbenzene
- ***Phenol*** = hydroxybenzene
- ***Aniline*** = aminobenzene



Toluene



Phenol



Aniline

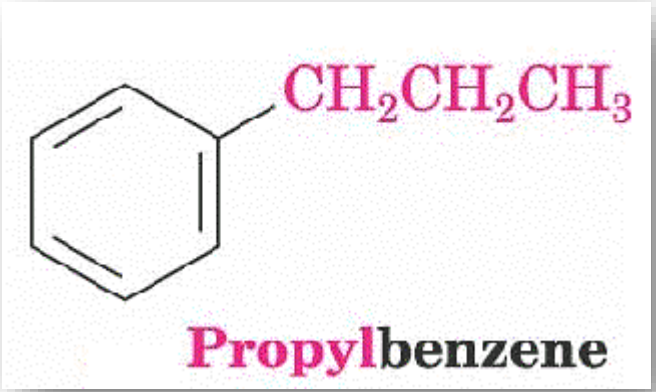
Monosubstituted benzenes

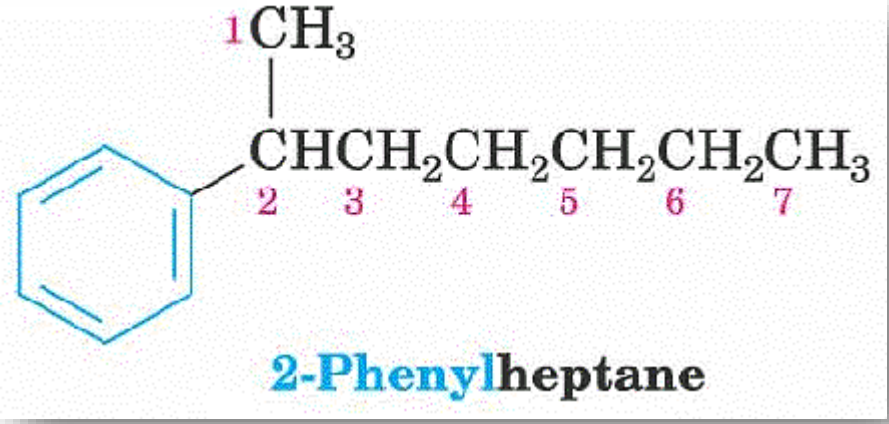
- Monosubstituted benzenes, like hydrocarbons, are systematically named with –*benzene* as the parent name

C_6H_5Br $C_6H_5NO_2$ $C_6H_5CH_2CH_2CH_3$

Arenes

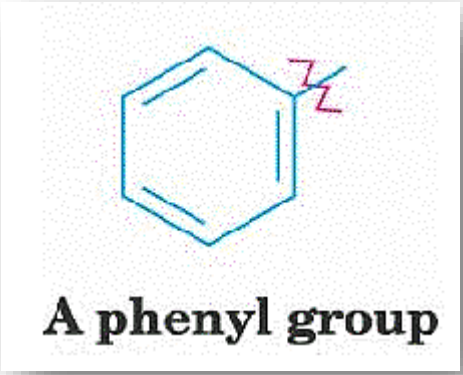
- Arenes are alkyl-substituted benzenes
  - If # $C_{substituent}$ < or = 6, then the arene is named as an alkyl-substituted benzene
  - If # $C_{substituent}$ > 6, then the arene is named as a phenyl-substituted alkane



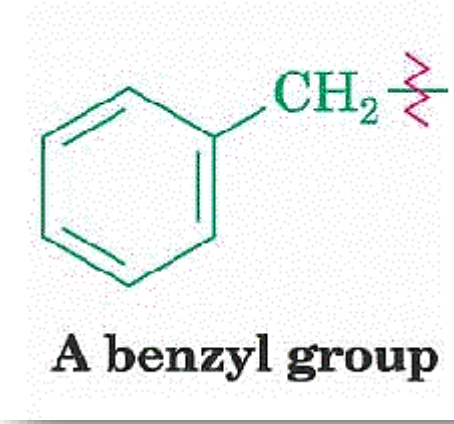


Aryl groups

- "**Phenyl**" refers to "C_6H_5 "
  - It is used when a benzene ring is a substituent
  - "Ph" or "ϕ" can also be in place of "C_6H_5"
- "**Benzyl**" refers to "$C_6H_5CH_2$ "



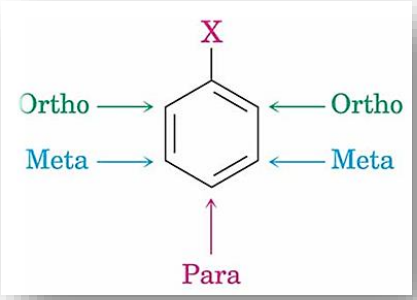
A phenyl group

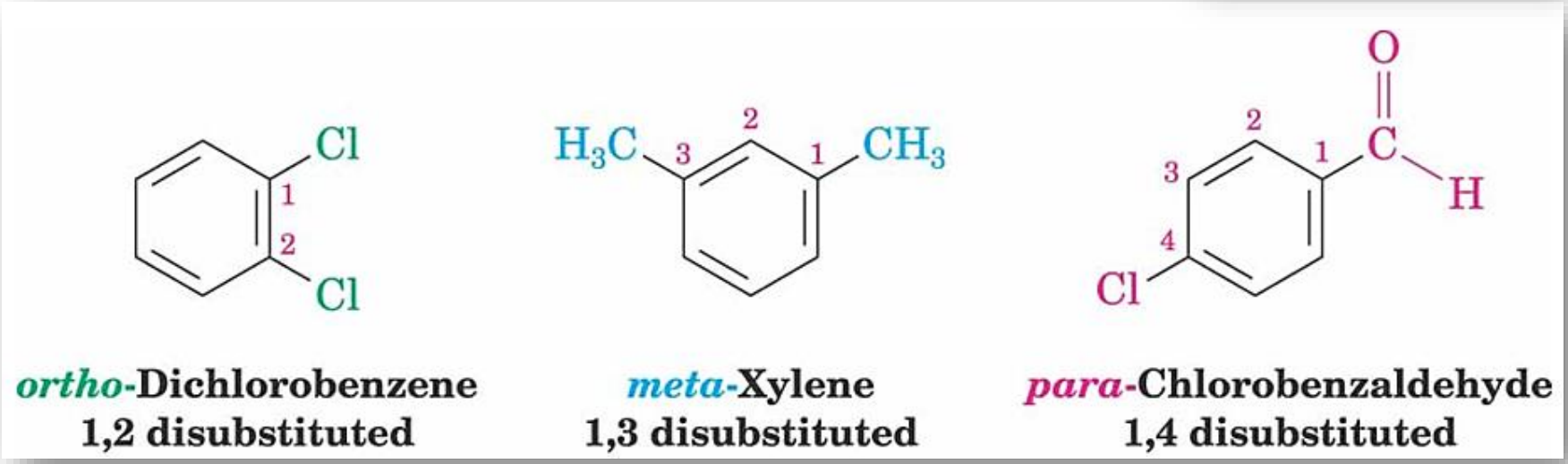


A benzyl group

Disubstituted benzenes

- Relative positions on a disubstituted benzene ring:
  - ***ortho- (o)*** on adjacent carbons **(1,2 disubstituted)**
  - ***meta- (m)*** separated by one carbon **(1,3 disubstituted)**
  - ***para- (p)*** separated by two carbons **(1,4 disubstituted)**

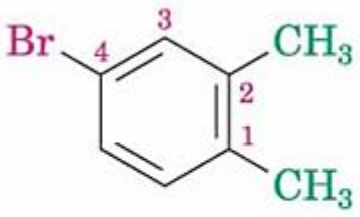




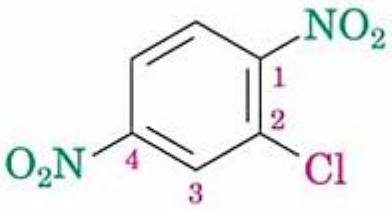
1,2-dichlorobezene | 1,3-dimethylbenzene | 4-chlorobenzaldehyde

Multisubstituted benzenes

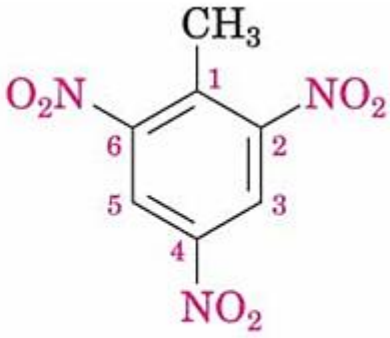
- Multisubstituted benzenes (more than two substituents) are named as follows:
  - Choose the sequence when the substituents have the lowest possible number
  - List substituents alphabetically with hyphenated numbers
  - Use common names, such as “toluene”, as parent name (as in TNT)



4-Bromo-1,2-dimethylbenzene



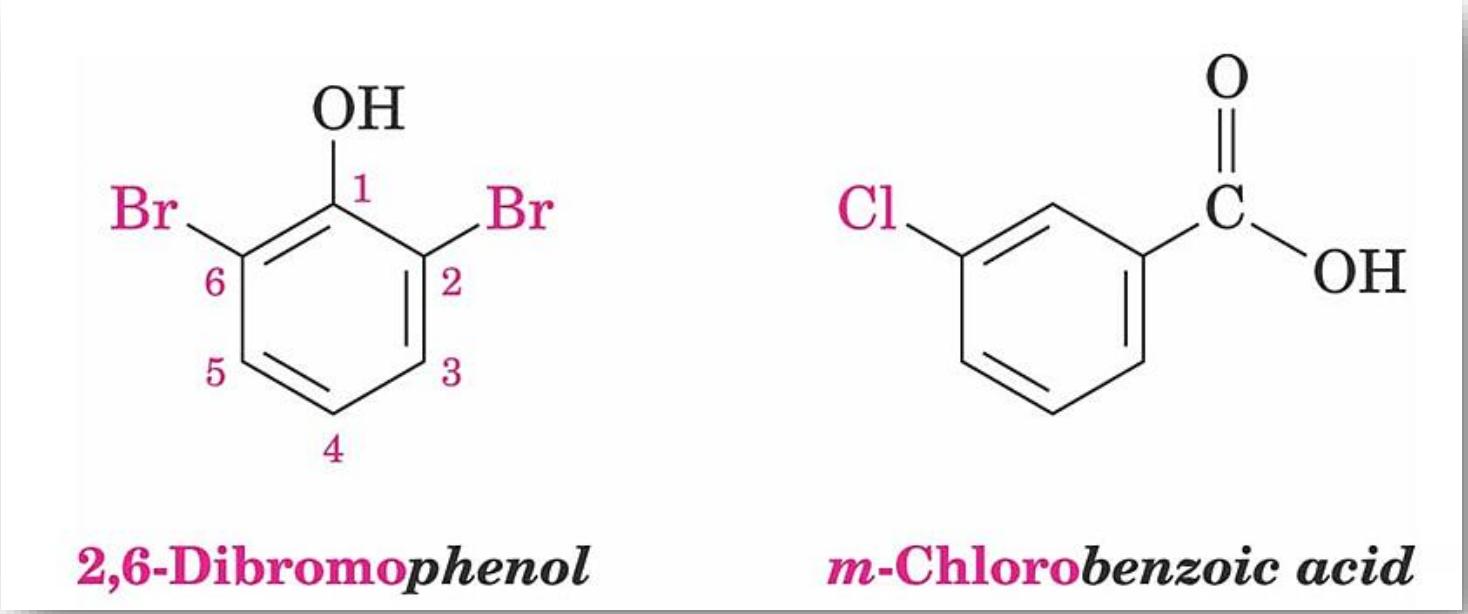
2-Chloro-1,4-dinitrobenzene



2,4,6-Trinitrotoluene (TNT)

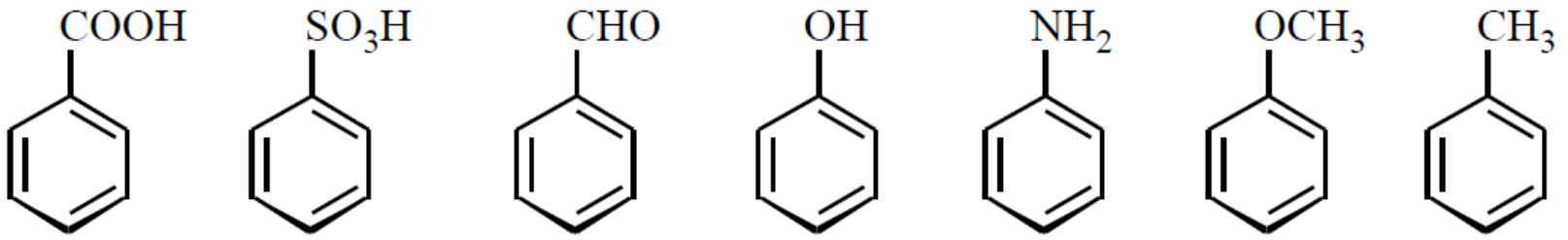
– Use common names, such as “**phenol**” & “**benzoic acid**”, as parent name

- The principal substituent is assumed to be on C1



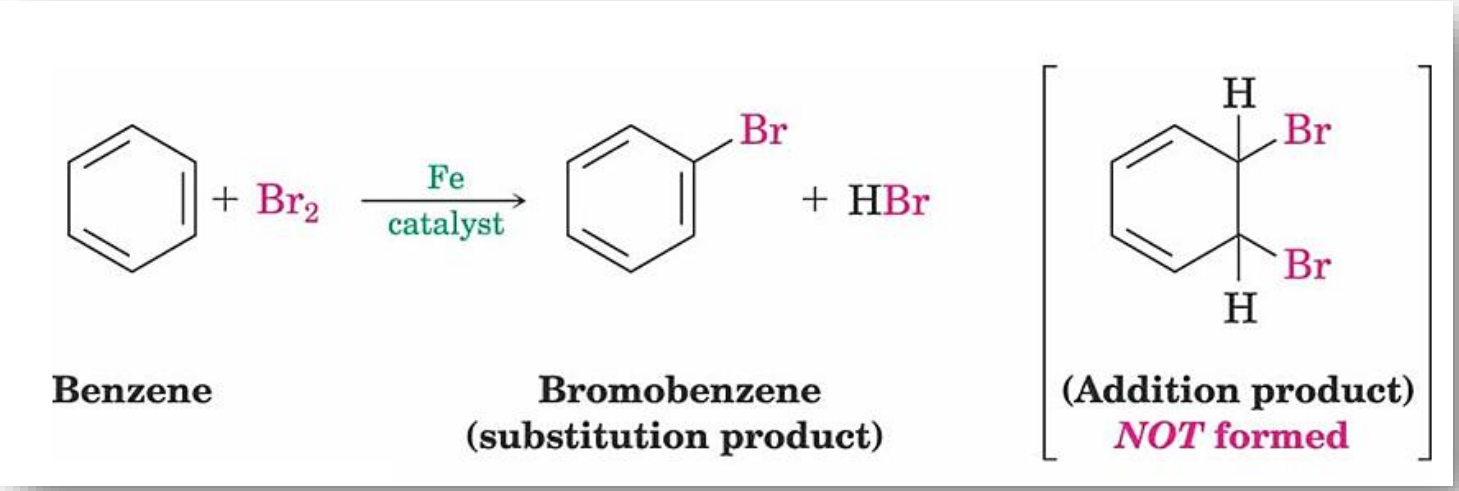
OR 3-chlorobenzoic acid

Some common substituents change the root name of the ring. IUPAC accepts these as root names, listed here in decreasing priority:



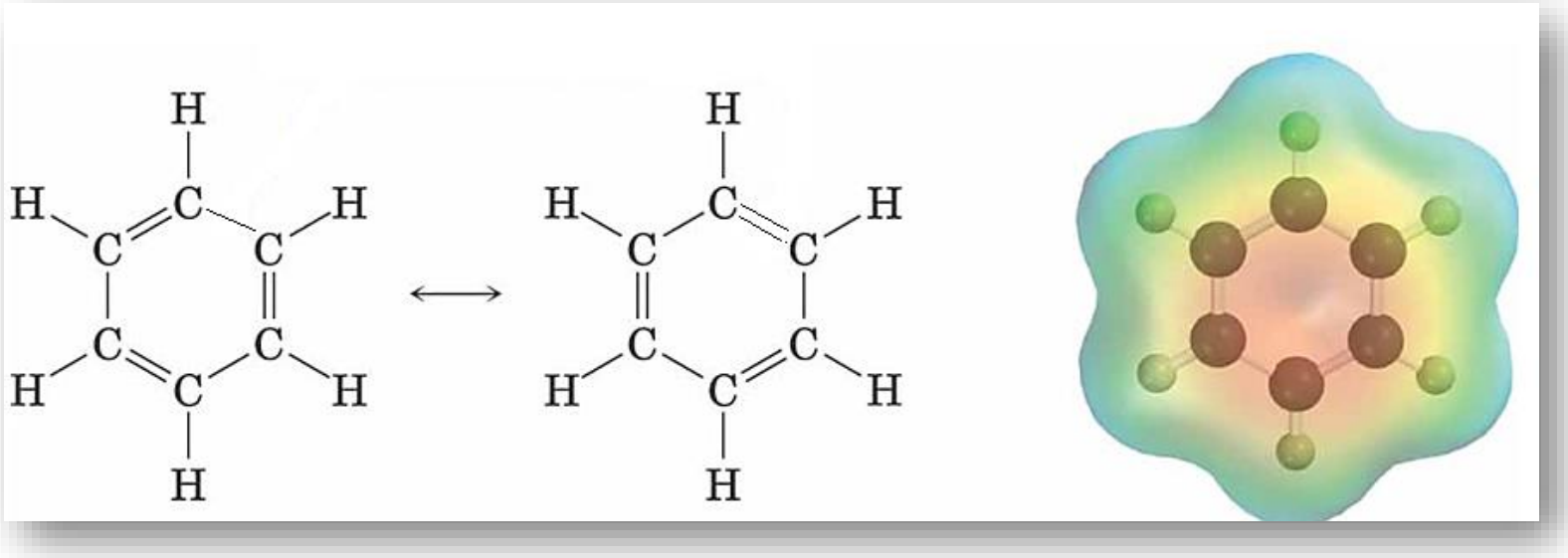
Structure and Stability of Benzene

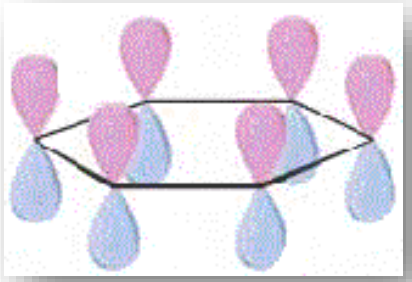
- Benzene is very stable
  - It **undergoes substitution** rather than the rapid addition reaction common to compounds with C=C, suggesting that in benzene there is a higher barrier
  - *Example:* Benzene reacts slowly with Br_2 to give bromobenzene (where Br replaces H)



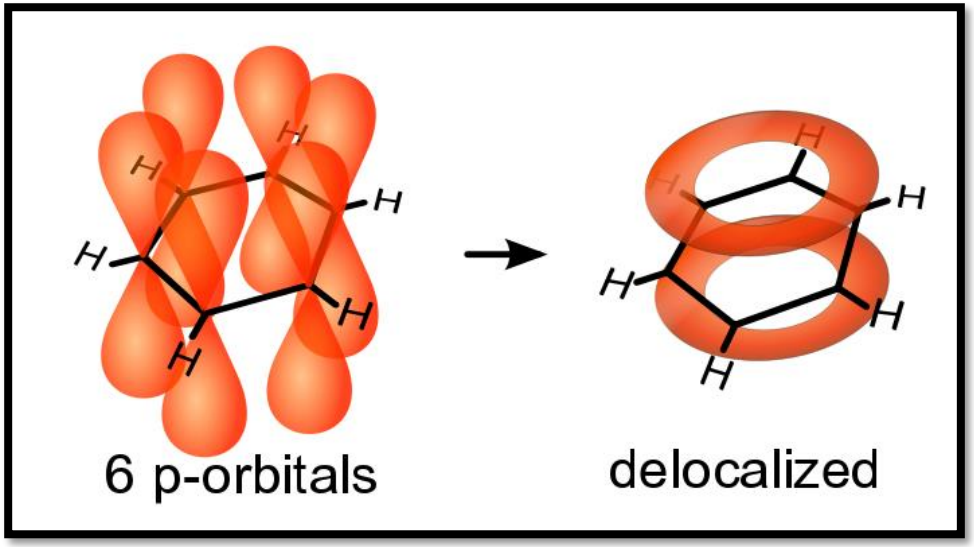
Benzene's Unusual Structure

- All its C-C bonds are the same length: 1.39 Aº — between single (1.54) Aº and double (1.34) Aº bonds
- Electron density in all six C-C bonds is identical





- Structure is planar, hexagonal
- All C–C–C bond angles are 120°
- Each C is sp^2-hybridized and has a *p* orbital perpendicular to the plane of the six-membered ring



Recall: Key Ideas on Benzene

- Benzene is a cyclic conjugated molecule
- Benzene is unusually stable - $DH_{hydrogenation}$ = 150 kJ/mol less negative than a cyclic triene
- Benzene is planar hexagon: bond angles are 120°; carbon–carbon bond lengths, 1.39 Aº
- Benzene undergoes substitution rather than electrophilic addition
- Benzene is a resonance hybrid with structure between two line-bond structures
- Benzene has 6 p electrons, delocalized over the ring

Aromaticity and the Hückel 4n + 2 Rule

The Hückel 4n + 2 rule:

- was devised by Eric Hückel in 1931
- states that planar, monocyclic conjugated systems with a total of 4n + 2 π electrons where n is an integer (n = 0, 1, 2, 3,…) are aromatic

Criteria for Aromaticity:

1. An aromatic compound should have cyclic and planar.
2. Each atom of aromatic system should have p orbital, must parallel and overlap to the ring.
3. The cyclic system of π molecular orbital must follow the Huckel's rule $(4n+2)\pi$ electrons.

The Number of π Electrons That Satisfy Hückel's Rule

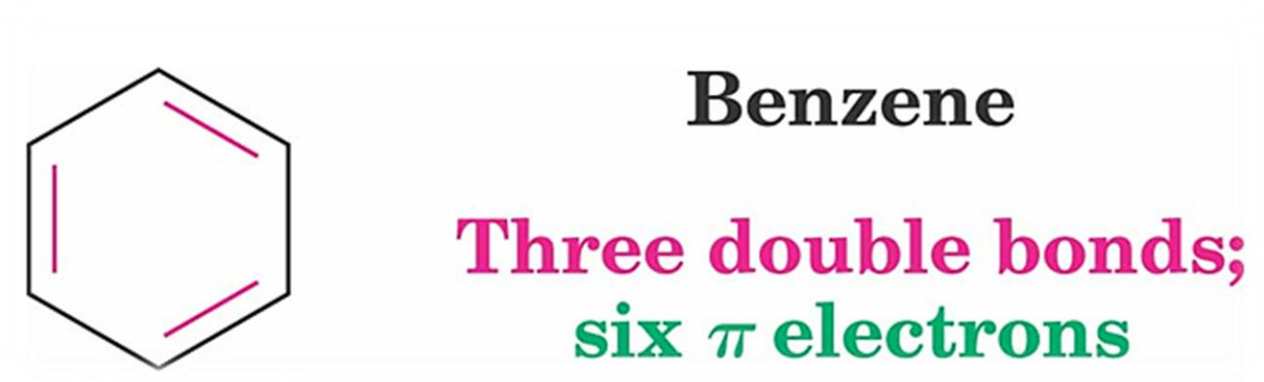
n	4*n* + 2
0	2
1	6
2	10
3	14
4, etc.	18

Considering aromaticity, a compound can be classified in one of three ways:

1. **Aromatic**-A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.
2. **Antiaromatic**-A cyclic, planar, completely conjugated compound with $4n$ π electrons.
3. **Not aromatic (nonaromatic)-**A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.

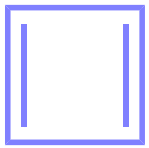
Aromatic compounds with 4n + 2 p electrons

- Benzene
  - It has 6 π electrons: 4n + 2 = 6, thus n = 1
  - It is aromatic: it is stable and the electrons are delocalized

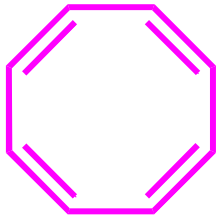


Compounds with 4n π electrons are NOT aromatic

- Planar, cyclic conjugated molecules with 4n π electrons are **antiaromatic**
  - They are much less stable than expected
  - They will distort out of plane and behave like ordinary alkenes



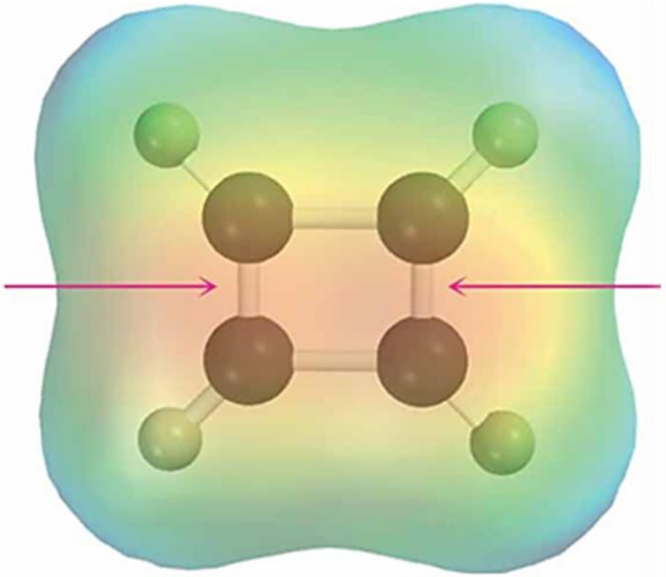
cyclobutadiene



cyclooctatetraene

Which of the above is antiaromatic?

- Cyclobutadiene
  - It has 4 π electrons: 4n + 2 = 4, thus n = ½ (not an integer)
  - It is antiaromatic: The π electrons are localized into two double bonds

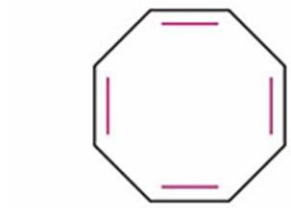


localized π electrons

Cyclobutadiene

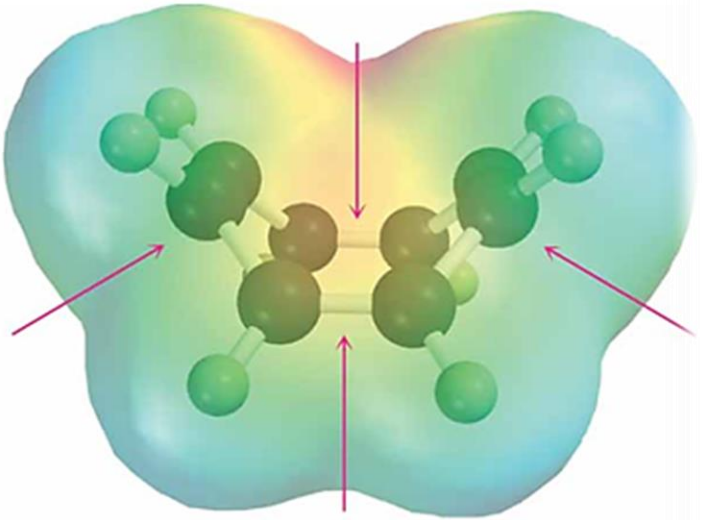
Two double bonds;
four π electrons

- Cyclooctatetraene
  - It has 8 π electrons: 4n + 2 = 8, thus n = 3/2 (not an integer)
  - It is nonaromatic:
    - the π electrons are localized into four double bonds
    - it is tub-shaped not planar
    - it 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



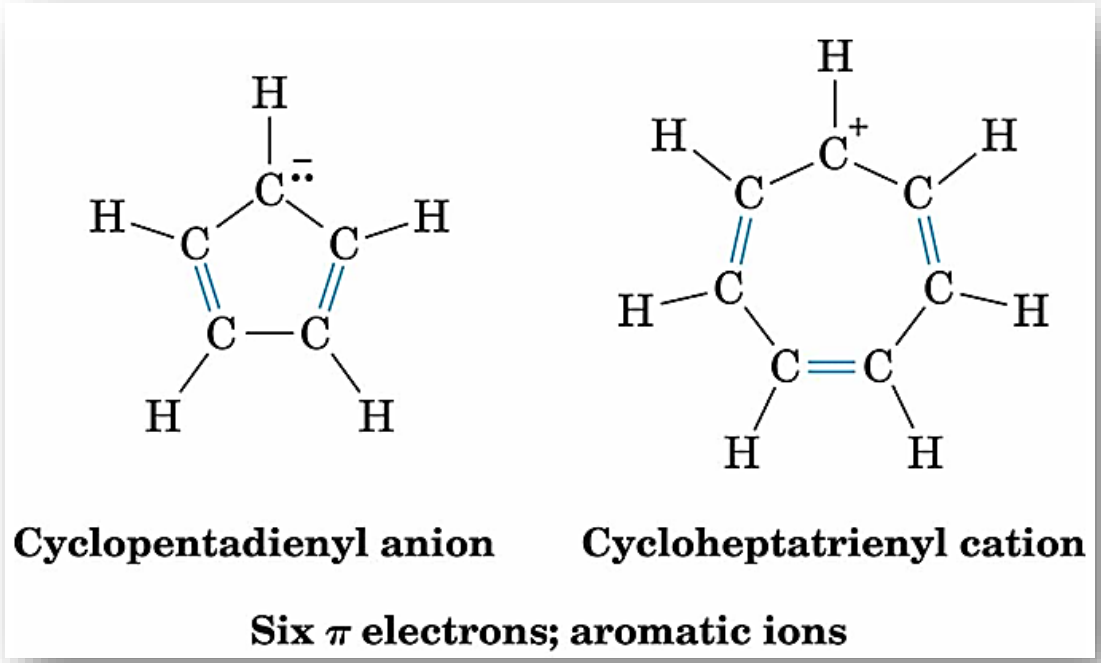
p orbitals not parallel for overlap

Aromatic Ions

- The Hückel $4n + 2$ rule applies to ions as well as to neutral species:
  - To be aromatic, a molecule must be planar, cyclic conjugated system with $4n + 2$ π electrons
  - *Example:* Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic.

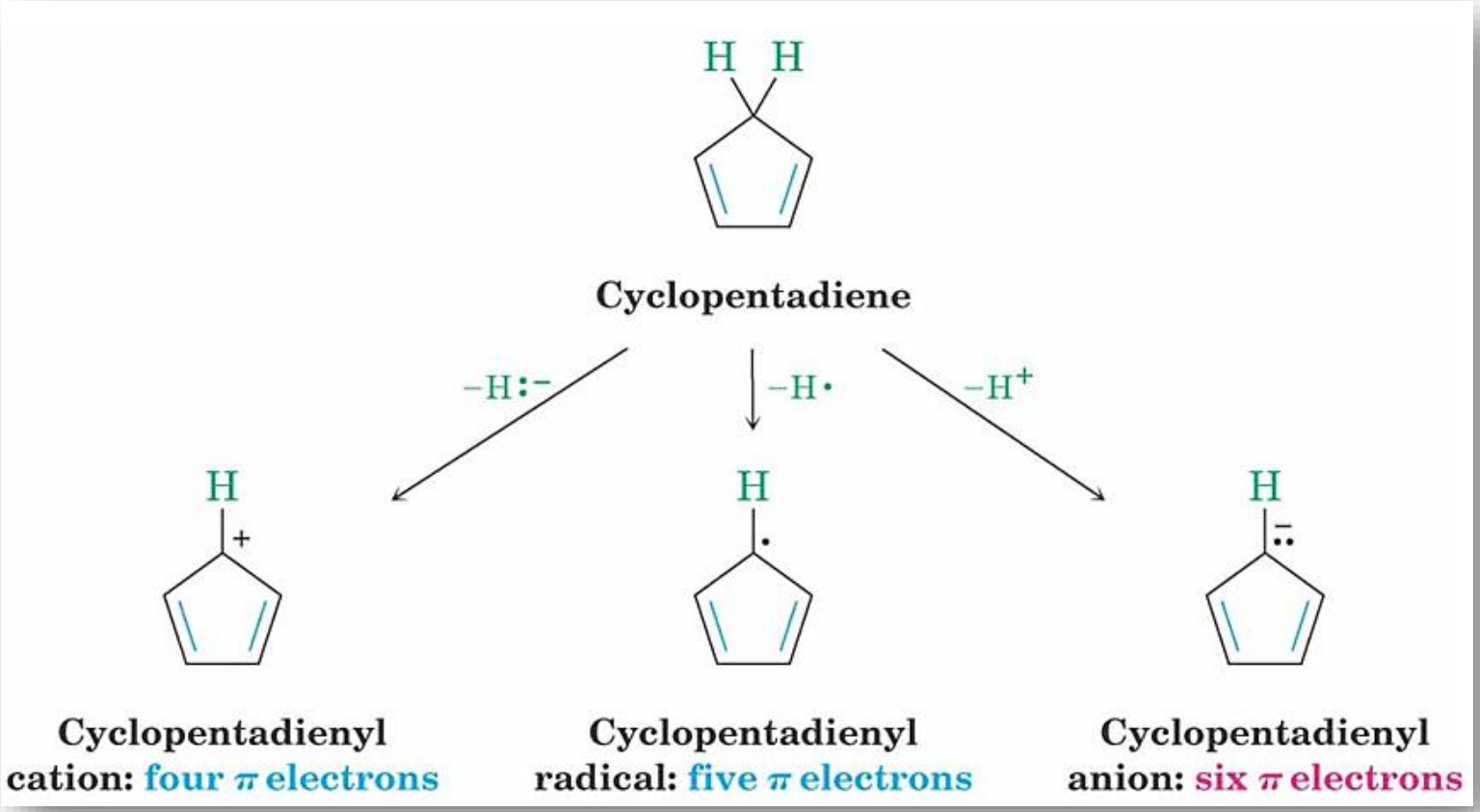
- *Example:* Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic.

  The key feature of both is that they contain 6 π electrons in a ring of continuous p orbitals



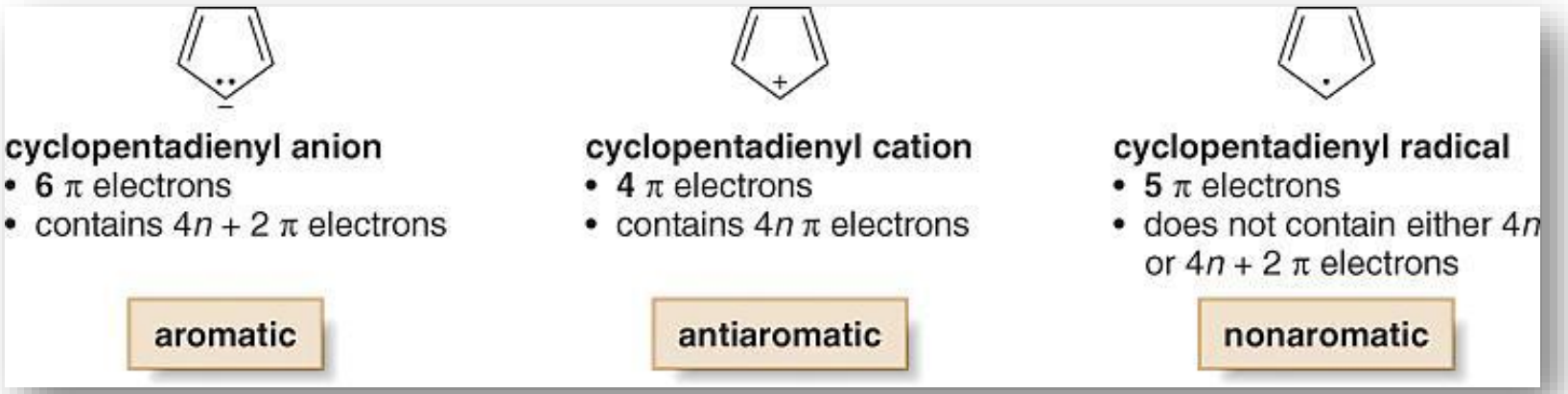
Aromaticity of the Cyclopentadienyl Anion

Not fully conjugated and not aromatic



Unstable and anti and nonaromatic

Stable and aromatic

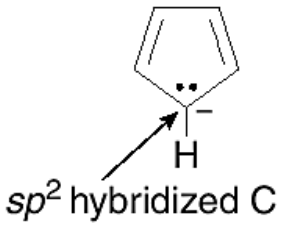


We can draw five equivalent resonance structures for the cyclopentadienyl anion.

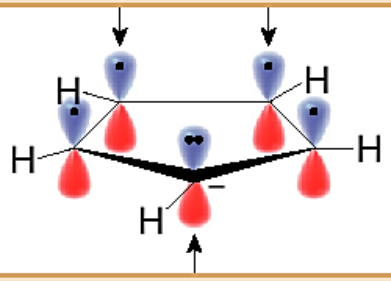
Examples of Aromatic Rings

Both negatively and positively charged ions can be aromatic if they possess all the necessary elements.

The cyclopentadienyl anion



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

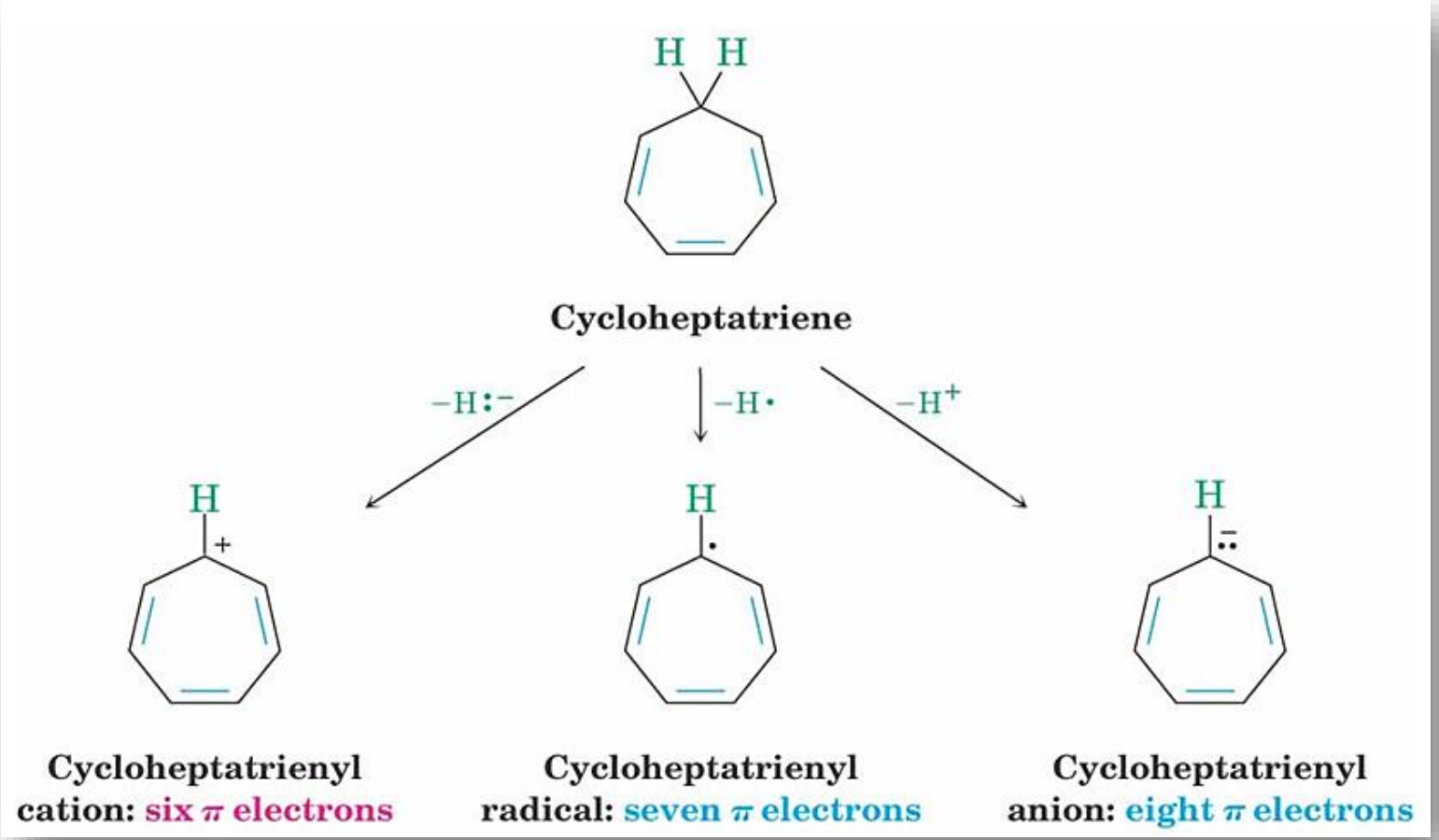


The lone pair resides in a *p* orbital.

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

Aromaticity of the Cycloheptatrienyl Cation

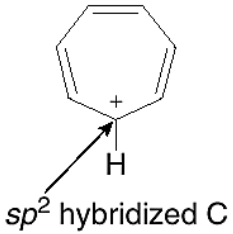
Not fully conjugated and not aromatic



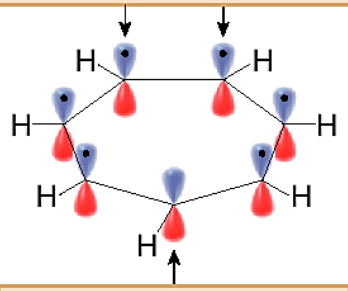
Stable and aromatic

Unstable and nonaromatic

The tropylium cation

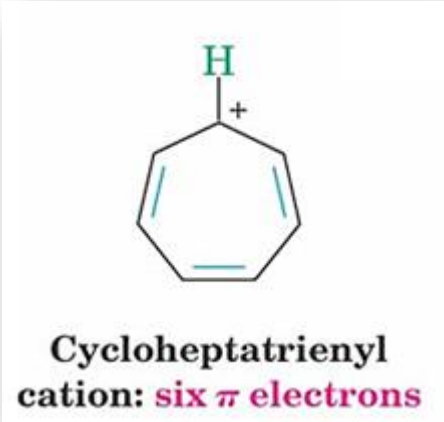


The ring is completely conjugated with **6 π electrons**.



One *p* orbital is vacant.

- 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.

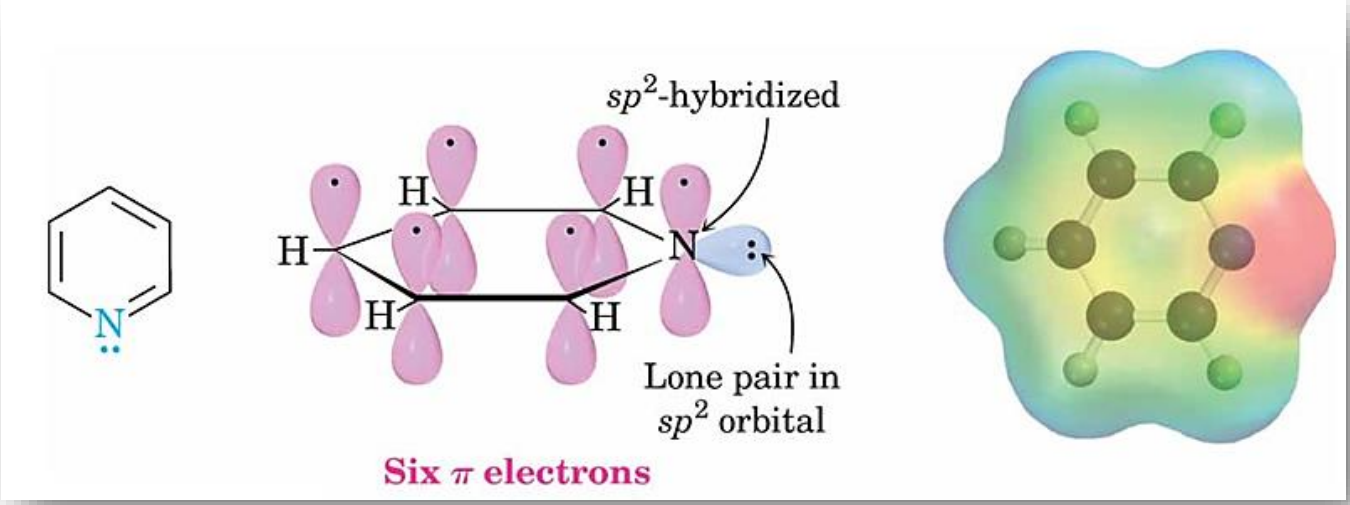


Aromatic Heterocycles: Pyridine and Pyrrole

- A heterocycle is a cyclic compound that contains an atom or atoms other than carbon in its ring, such as N, O, S, P
  - 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
  - *Example:* Pyridine and Pyrrole

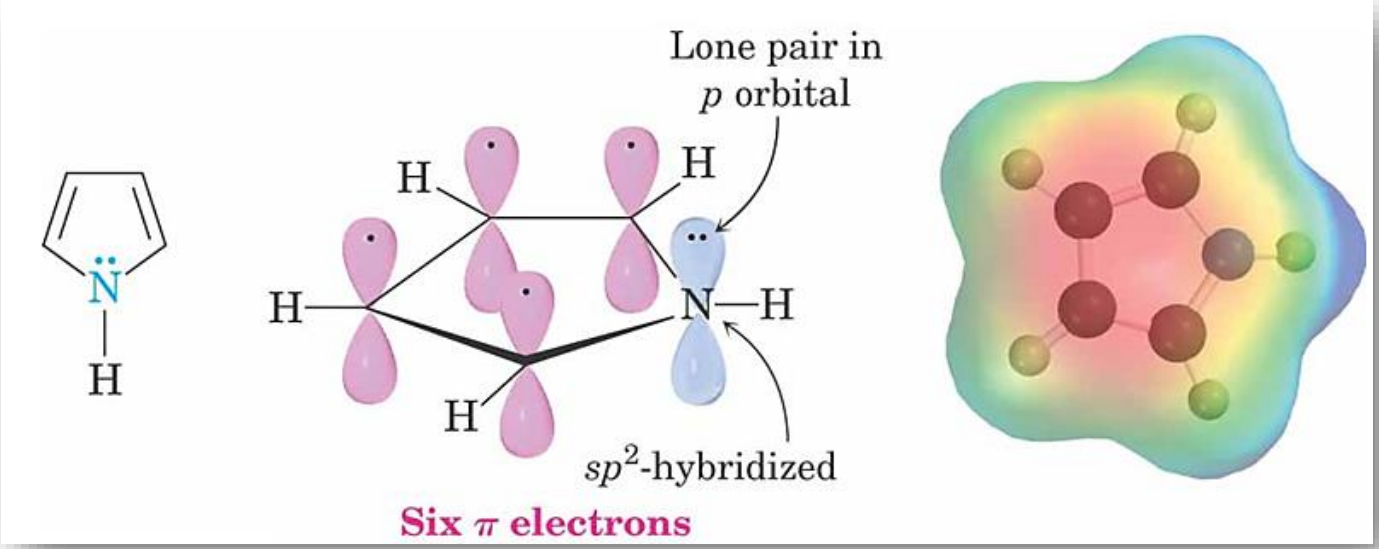
Pyridine

- Pyridine is a six-membered heterocycle with a nitrogen atom in its ring
  - π electron structure resembles benzene (6 electrons)
  - The nitrogen lone pair electrons are in sp^2 orbital, not part of the p aromatic system (perpendicular orbital)
  - Pyridine is a relatively weak base compared to normal amines but protonation does not affect aromaticity



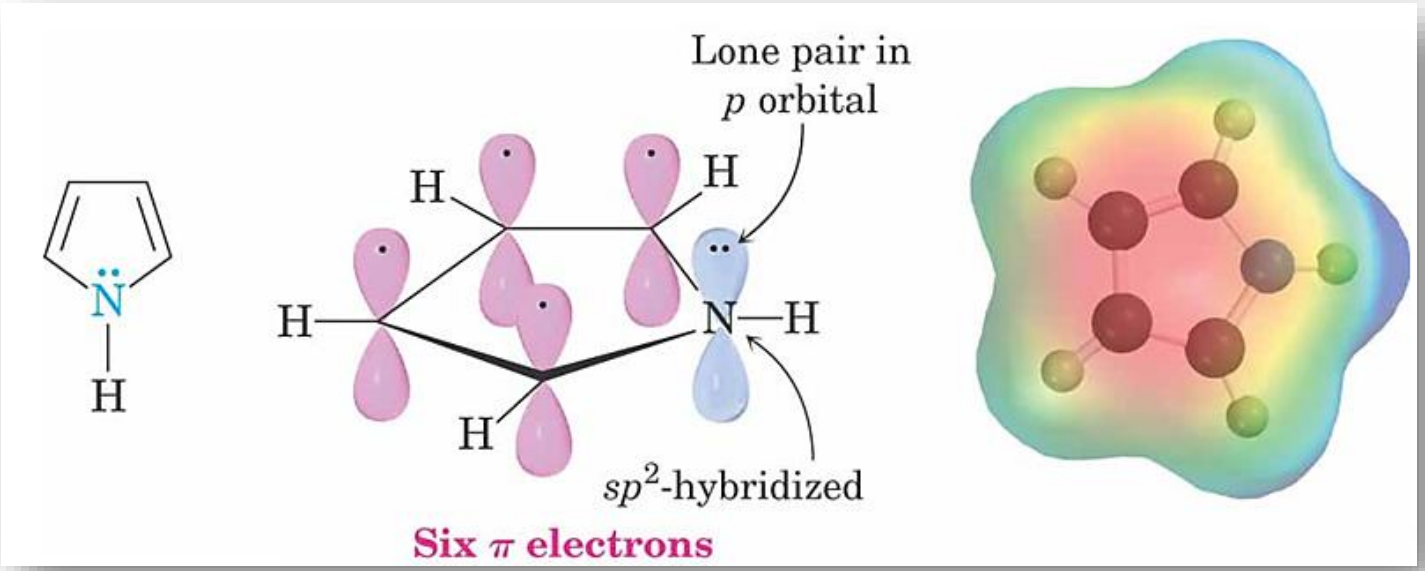
Pyrrole

- Pyrrole is a five-membered heterocycle with a nitrogen atom in its ring
  - π electron system is similar to that of cyclopentadienyl anion
  - Four sp^2-hybridized carbons with 4 *p* orbitals perpendicular to the ring and 4 p electrons



Pyrrole

- 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

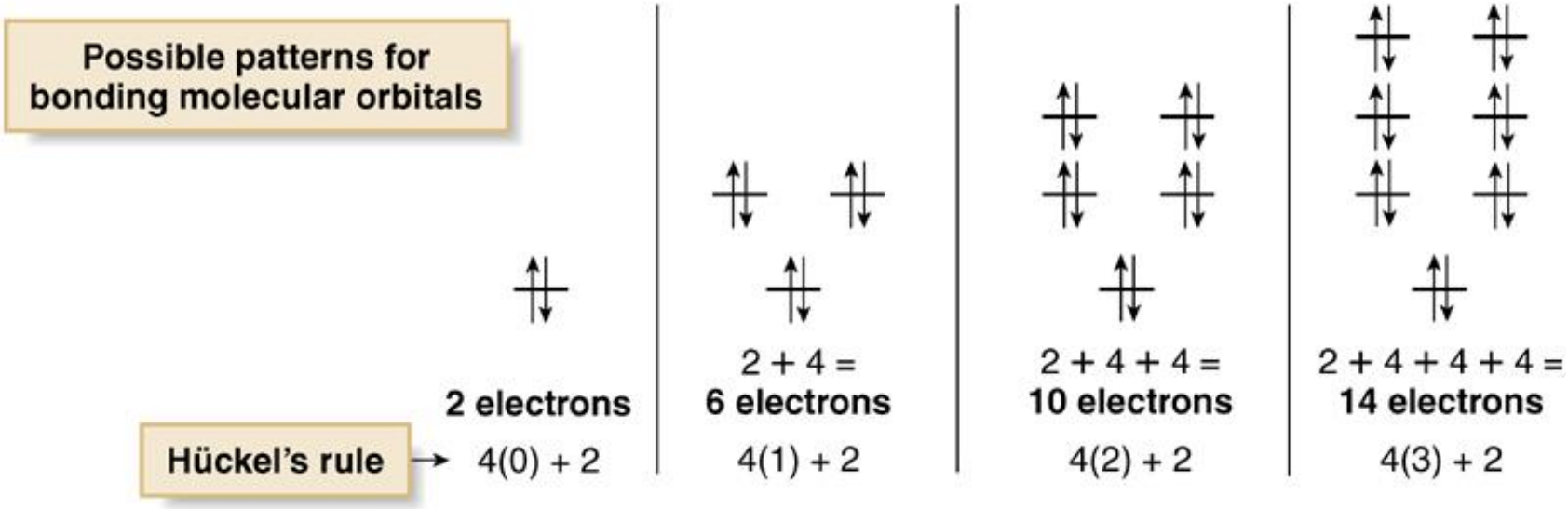


Benzene and Aromatic Compounds

The Inscribed Polygon Method of Predicting Aromaticity

- **For the compound to be aromatic, these MOs must be completely filled with electrons, so the "magic numbers" for aromaticity fit Hückel's 4*n* + 2 rule.**

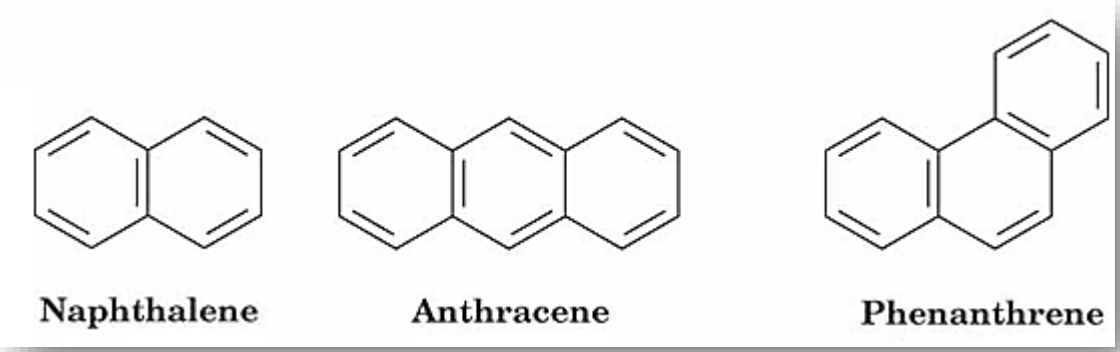
MO patterns for cyclic, completely conjugated systems



Polycyclic Aromatic Compounds:

Naphthalene

- Polycyclic aromatic compounds are
  - aromatic compounds with rings that share a set of carbon atoms (fused rings)
  - compounds from fused benzene or aromatic heterocycle rings

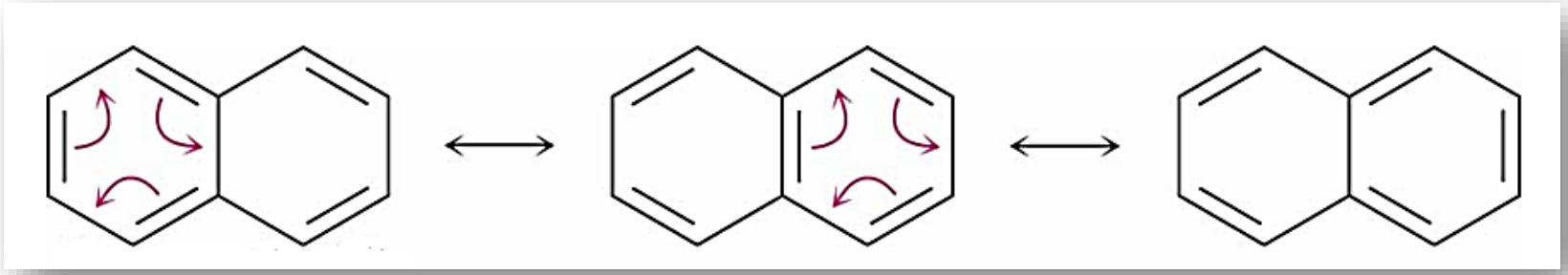


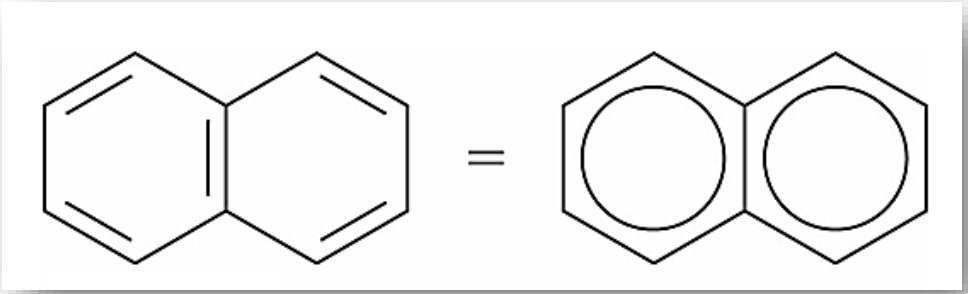
Characteristics of Polycyclic Aromatic Compounds

- They are cyclic, planar and conjugated molecules
- They are unusually stable
- They react with electrophiles to give substitution products, in which cyclic conjugation is retained, rather than electrophilic addition products
- They can be represented by different resonance forms
- They have $4n + 2$ π electrons, delocalized over the ring

Naphthalene

- Naphthalene has three resonance forms





Naphthalene

- Naphthalene is a cyclic, conjugated π electron system, with p orbital overlap both around the ten-carbon periphery of the molecule and across the central bond
  - It has *ten* delocalized π electrons (Hückel number)