

Aromaticity

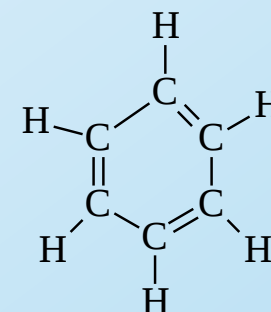
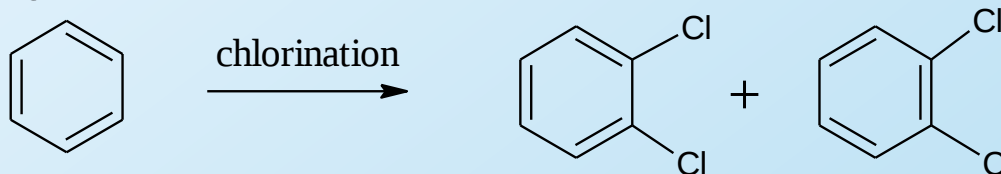
Dr. Sapna Gupta

Discovery of Benzene

- Aromatic class was first used to classify anything that was fragrant (had aroma)
- 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.

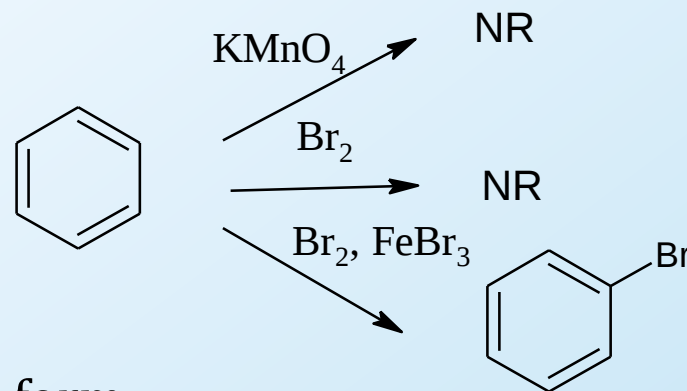
Kekulé Structure

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

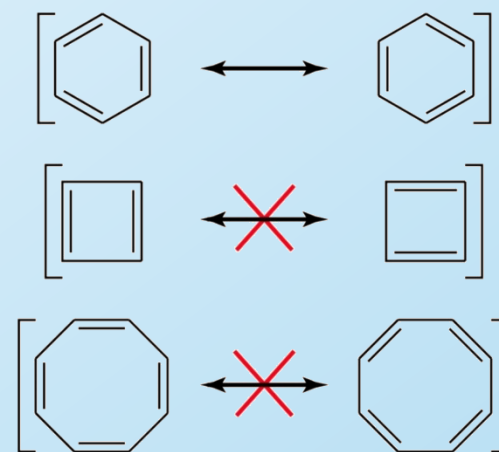


Unusual Reactions

- Alkene + $\text{KMnO}_4 \rightarrow$ diol (addition)
Benzene + $\text{KMnO}_4 \rightarrow$ no reaction
- Alkene + $\text{Br}_2/\text{CCl}_4 \rightarrow$ dibromide (addition)
Benzene + $\text{Br}_2/\text{CCl}_4 \rightarrow$ no reaction
- With FeCl_3 catalyst, Br_2 reacts with benzene to form bromobenzene + HBr (substitution!). Double bonds remain.



- All cyclic conjugated hydrocarbons were proposed to be aromatic.
- However, cyclobutadiene is so reactive that it dimerizes before it can be isolated.
- And cyclooctatetraene adds Br_2 readily like an alkene.

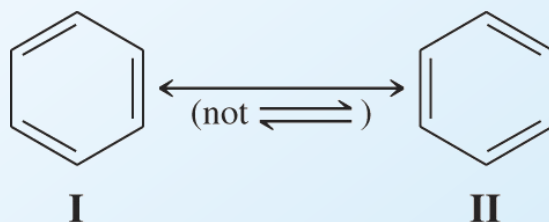


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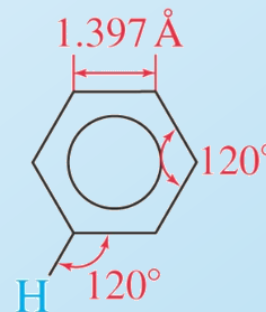
Modern Theory of the Benzene Structure

The Resonance Theory

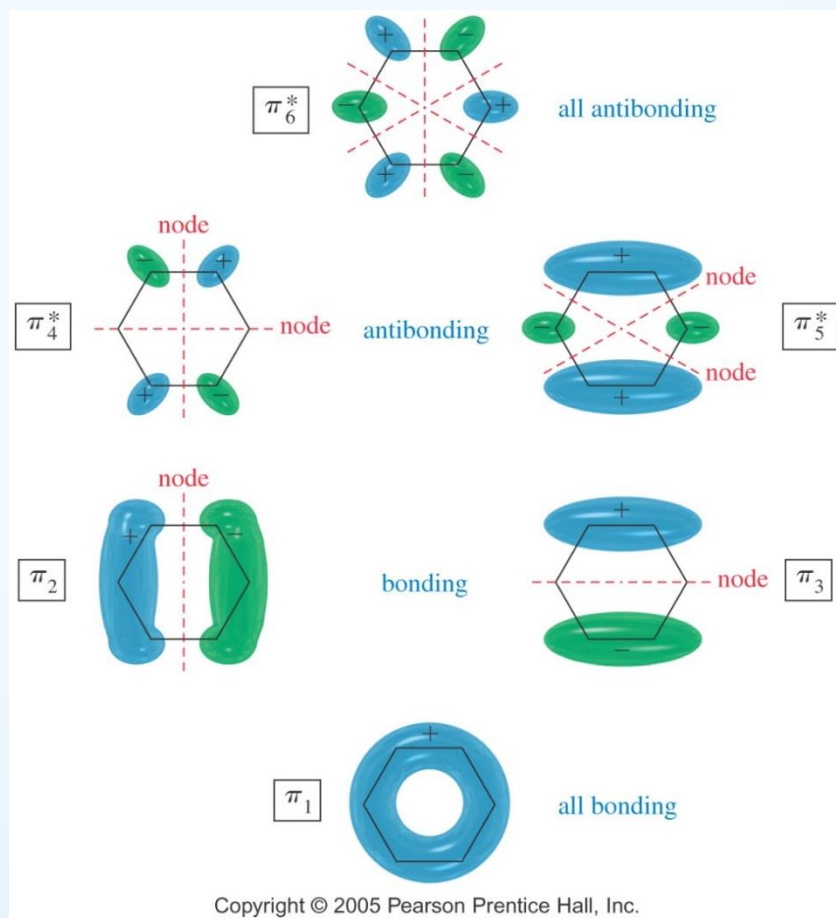
- Structures I and II are equal resonance contributors to the real structure of benzene



- Benzene is particularly stable because it has two equivalent and important resonance structures
- Each carbon-carbon bond is $1.397 \text{ \AA}$, which is between the length of a carbon-carbon single bond between sp^2 carbons ($1.47 \text{ \AA}$) and a carbon-carbon double bond ($1.33 \text{ \AA}$)
- Often the hybrid is represented by a circle in a hexagon (III)

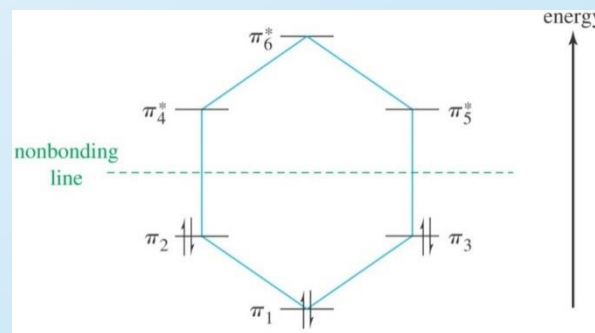


MO Rules for Benzene



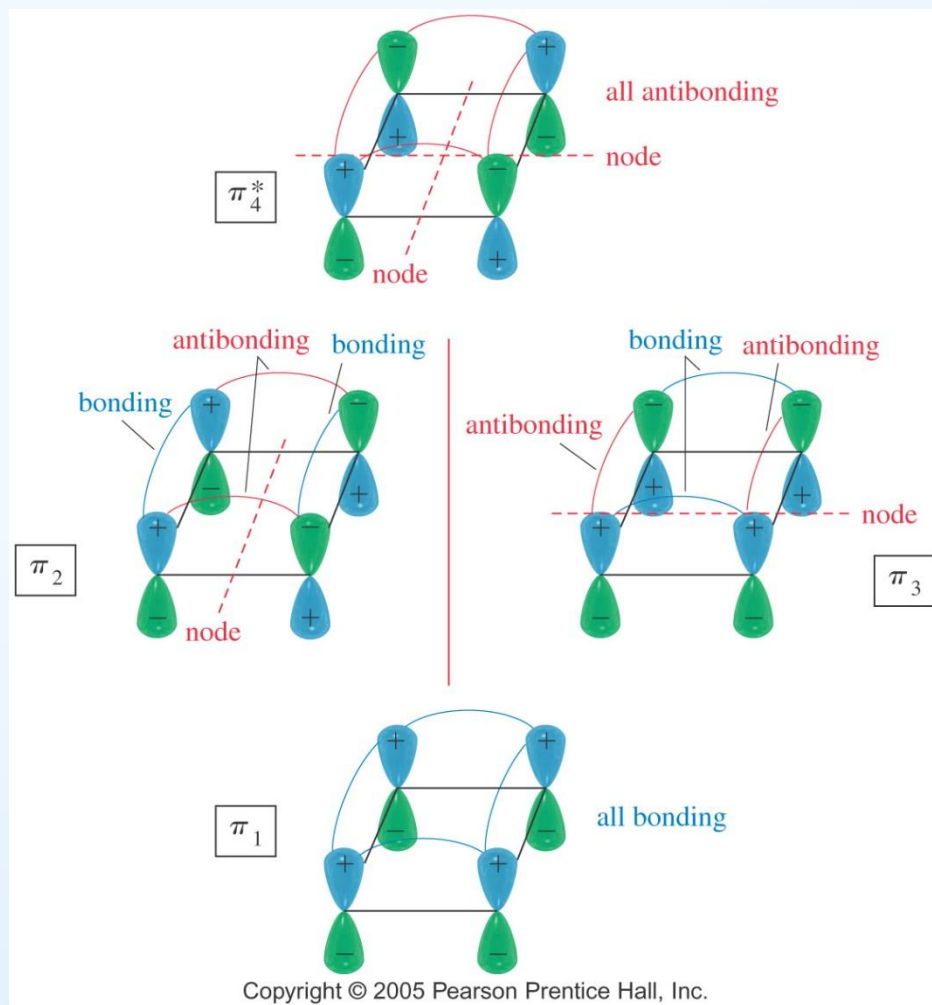
MO diagram

- Six overlapping *p* orbitals must form six molecular orbitals.
- Three will be bonding, three antibonding.
- Lowest energy MO will have all bonding interactions, no nodes.
- As energy of MO increases, the number of nodes increases.

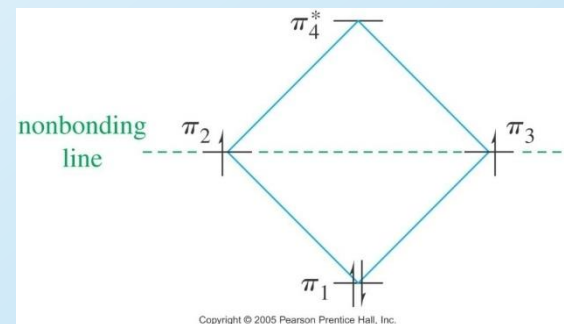


Energy diagram

MO Rules for Cyclobutadiene

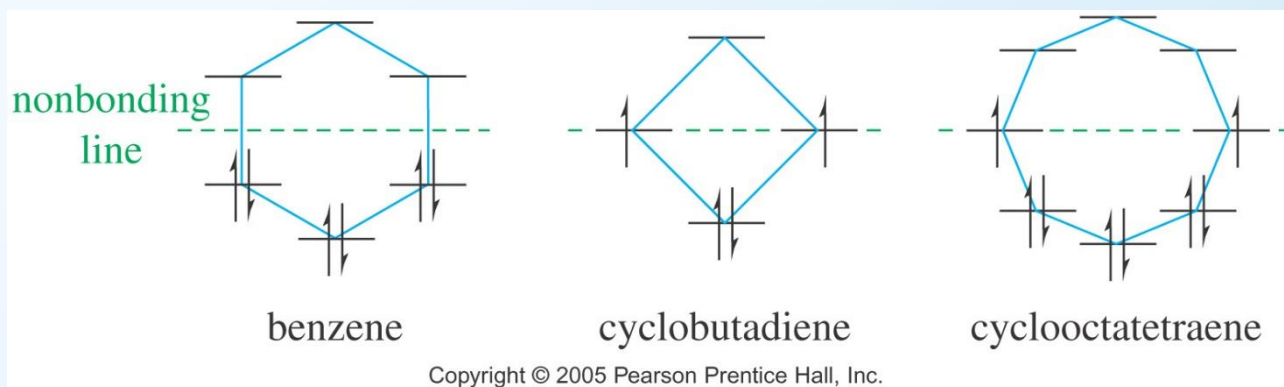


Energy Diagram for Cyclobutadiene



Polygon Rule

The energy diagram for an annulene has the same shape as the cyclic compound with one vertex at the bottom.



Aromaticity, Anti and Non-Aromaticity

Aromatic

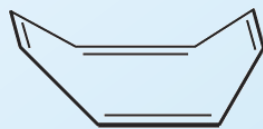
- Structure must be cyclic with conjugated pi bonds.
- Each atom in the ring must have an unhybridized p orbital.
- The p orbitals must overlap continuously around the ring. (Usually planar structure.)
- Follow Huckels number ($4n+2$) (next slide).

Anti and Non Aromaticity

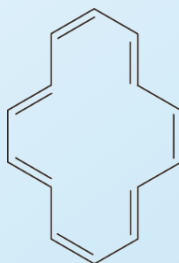
- Antiaromatic compounds are cyclic, conjugated, with overlapping p orbitals around the ring, but do not follow Huckel's number.
- Nonaromatic compounds do not have a continuous ring of overlapping p orbitals and may be nonplanar.

Hückel's Rule

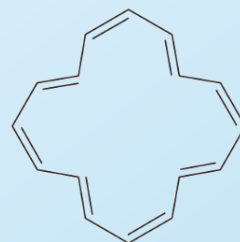
- If the compound has a continuous ring of overlapping p orbitals and has $4n + 2$ electrons (Πe^-), it is aromatic.
- If the compound has a continuous ring of overlapping p orbitals and has $4n$ electrons, it is antiaromatic.
- Examples
- When $n = 0$; πe^- are $4 \times 0 + 2 = 2$ (does not exist)
- When $n = 1$; πe^- are $4 \times 1 + 2 = 6$ (benzene)
- When $n = 2$; πe^- are $4 \times 2 + 2 = 10$ (not aromatic because not planar)
- When $n = 3$; πe^- are $4 \times 3 + 2 = 14$
- 4 and 8 πe^- systems are antiaromatic (both cyclobutadiene and cyclooctatetraene are conjugated but do not have Hückel's number)



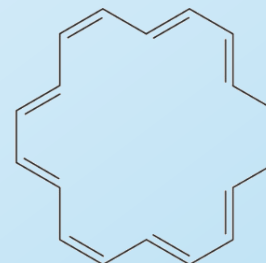
[10] annulene



[14]Annulene
(aromatic)



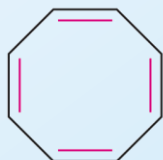
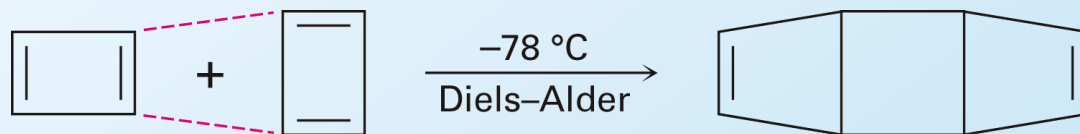
[16]Annulene
(not aromatic)



[18]Annulene
(aromatic)

Anti Aromatic Compounds

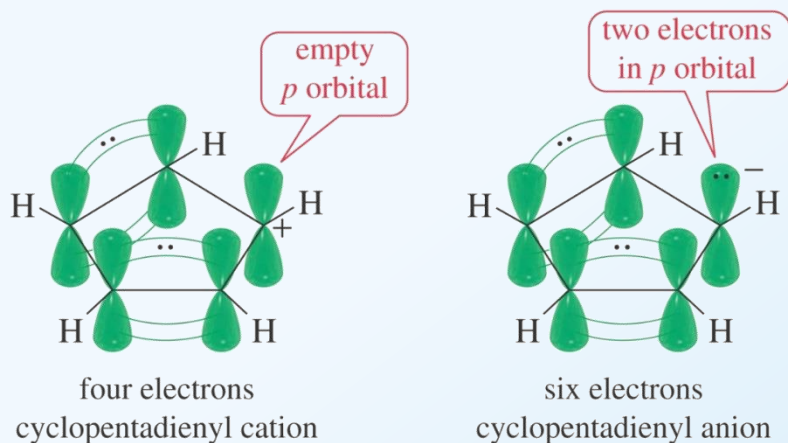
- Planar, cyclic molecules with $4n$ π electrons are much *less* stable than expected (antiaromatic)
- They will distort out of plane and behave like ordinary alkenes
- 4- and 8-electron compounds are not delocalized (single and double bonds)
- **Cyclobutadiene** is so unstable that it dimerizes by a 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

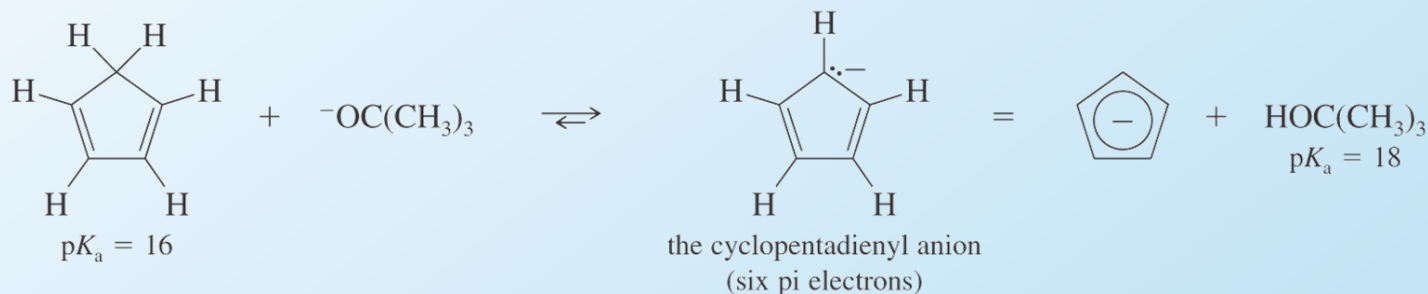
Four double bonds;
eight π electrons

Cyclopentadienyl Ions



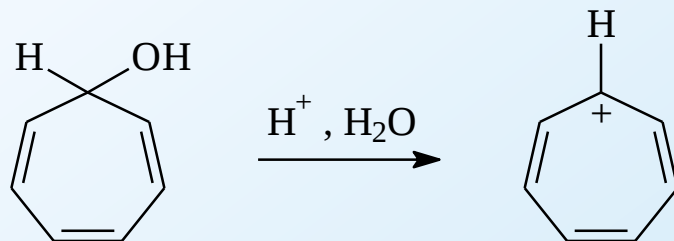
- The cation has an empty *p* orbital, 4 electrons, so antiaromatic.
- The anion has a nonbonding pair of electrons in a *p* orbital, 6 e⁻s, aromatic.

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

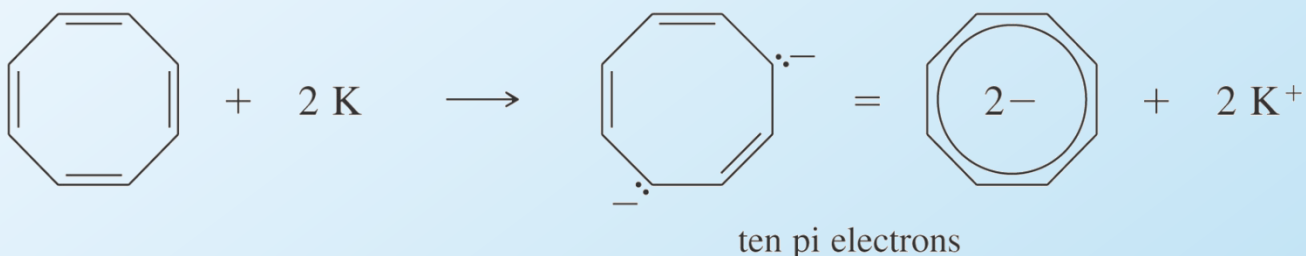


Tropylium Anion and Annulene Dianion

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

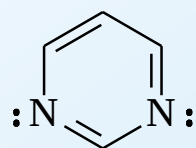
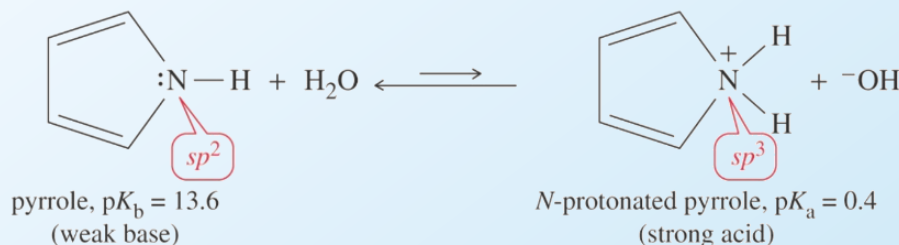
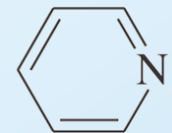


- Cyclooctatetraene easily forms a -2 ion.
- Ten electrons, continuous overlapping p orbitals, so it is aromatic.

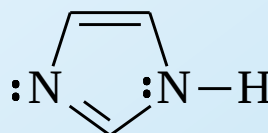


Pyridine and Pyrrole and Basicity of N

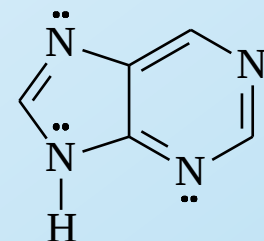
- Heterocyclic aromatic compound.
- Nonbonding pair of electrons in sp^2 orbital, so weak base, $pK_b = 8.8$.
- Pyrrole is also aromatic, but lone pair of electrons is delocalized, so much weaker base.



Pyrimidine has two basic nitrogens.



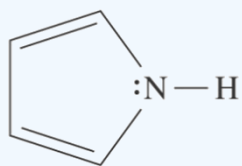
Imidazole has one basic nitrogen and one nonbasic.



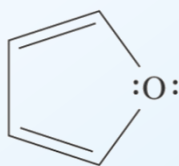
Purine

Other Heterocyclics and Aromatics

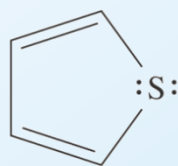
Other Heterocyclics



Pyrrole

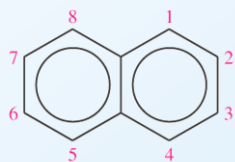


Furan

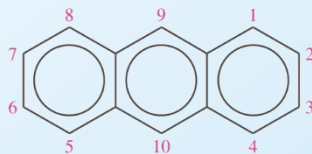


Thiophene

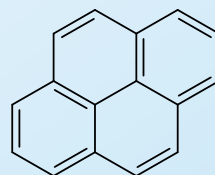
Fused Ring Hydrocarbons



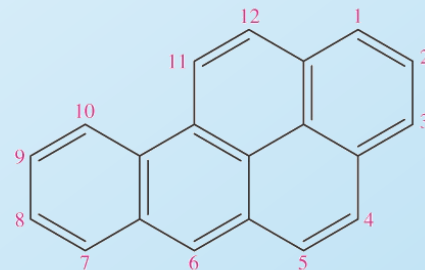
Naphthalene



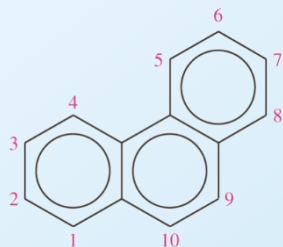
Anthracene



Pyrene



Benzo[a]pyrene



Phenanthrene

Key Concepts

- Why benzene is aromatic.
- MO theory
- Aromatic, non aromatic and anti-aromatic.
- Aromatic ions
- Other compounds that are aromatic.