

Aromatic Compounds

2 - Aromaticity

Dr. Sapna Gupta

Discovery of Benzene

The aromatic name was first used to classify anything that was fragrant (had aroma).

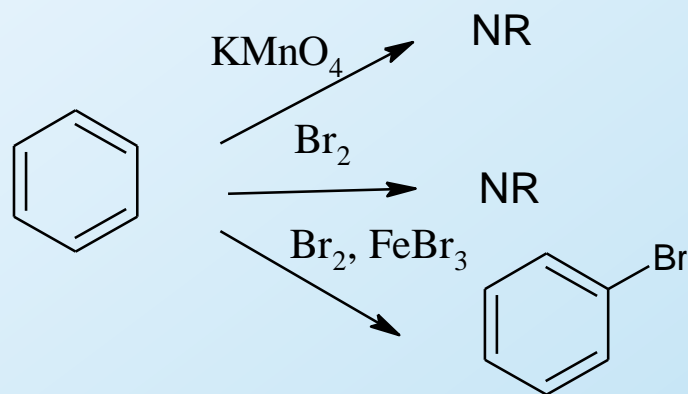
- Benzene was first isolated in 1825 by Michael Faraday who determined C:H ratio to be 1:1, a highly unsaturated compound.
- Benzene was first synthesized in 1834 by Eilhard Mitscherlich who determined molecular formula to be C_6H_6 , a compound with 4 degrees of unsaturation.
- Other related compounds with low C:H ratios had a pleasant smell, so they were classified as aromatic.

Unusual Reactions

Since benzene had such a high unsaturation index it was proposed that it should react like an alkene.

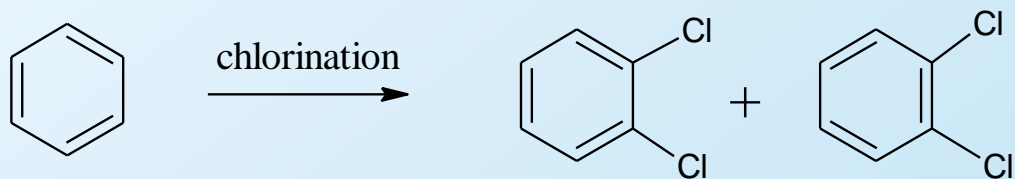
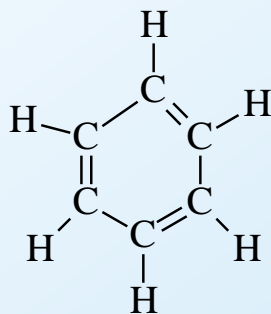
Several alkene reactions were carried out on benzene but to no results.

- 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 , a substitution product and the double bonds remain.



Kekule's Structure

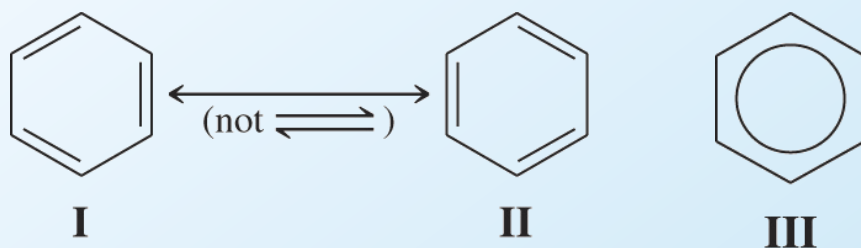
Friedrich Kekulé, in 1866, first proposed a cyclic structures shown on the right. He suggested multiple bonds in the structure. But he failed to explain the existence of only one isomer when benzene was chlorinated.



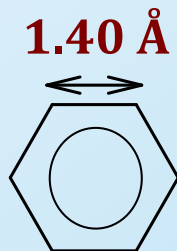
Resonance in Benzene Ring

Benzene is unusually stable. It does not undergo any addition reactions. What leads to the stability?

It was proposed that benzene has resonance, which leads to stability. Structures I and II are equal resonance contributors to the real structure of benzene and structure III would be the hybrid representation.



The resonance structure can be verified by the bond length. All carbon-carbon bond lengths are 1.40 \AA , which is between the length of a carbon-carbon single bond (1.54 \AA) and a carbon-carbon double bond (1.34 \AA).



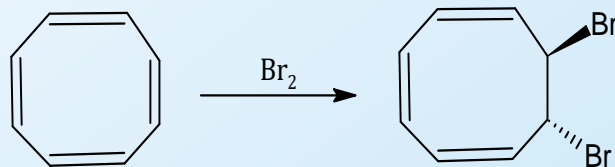
Conjugation in Benzene Ring

Another proposal was that conjugation gave it stability. If this is the case, then other cyclic conjugated systems should also be similar to benzene.

- However, cyclobutadiene is so reactive that it dimerizes before it can be isolated.



- Willstatter synthesized cyclooctatetraene in 1905, to study its reactive properties. Cyclooctatetraene, however, adds Br_2 readily like an alkene.



- All this led to the thinking that there was something else making the benzene stable.
- Huckel proposed his theory of aromaticity to help understand the reactivity and stability of benzene, and other cyclic conjugated compounds.

Hückel's Rules of Aromaticity

There are four rules that Huckel proposed to help determine if a compound is aromatic, nonaromatic or antiaromatic (conjugated but carries out addition reactions).

- 1) Structure should be cyclic.
- 2) Each atom in the ring must have an unhybridized p orbital. Compound should have alternated single and double bonds or lone pair of electrons.
- 3) Structure should be planar so all pi or nonbonding electrons can overlap.
- 4) The structure should have Huckel's number, $4n + 2$. of pi electrons.
 - When $n = 0$; πe^- are $4 \times 0 + 2 = 2 \pi e^-$ (does not exist)
 - When $n = 1$; πe^- are $4 \times 1 + 2 = 6 \pi e^-$ (benzene)
 - When $n = 2$; πe^- are $4 \times 2 + 2 = 10 \pi e^-$ (not aromatic because not planar)
 - When $n = 3$; πe^- are $4 \times 3 + 2 = 14 \pi e^-$

Following Huckel's rules 4 and 8 πe^- systems are classified as antiaromatic. Both cyclobutadiene and cyclooctatetraene are conjugated but do not have Huckel's number of pi electrons.

Aromatic, Antiaromatic and Nonaromatic

Aromatic (follow all 4 of Huckel's Rules)

1. Structure must be cyclic with conjugated pi bonds.
2. Each atom in the ring must have an unhybridized p orbital.
3. Structure should be planar to have pi orbital overlap.
4. Follow Huckels number ($4n+2$).

Antiaromatic

- Antiaromatic compounds are cyclic, conjugated, with overlapping p orbitals around the ring, but do not follow Huckel's number of πe^- . (Follow rules 1, 2 and 3 but not 4)

Nonaromatic

- Nonaromatic compounds do not have a continuous ring of overlapping p orbitals and may be nonplanar. (May not follow any of the rules 1-3 in addition to 4).

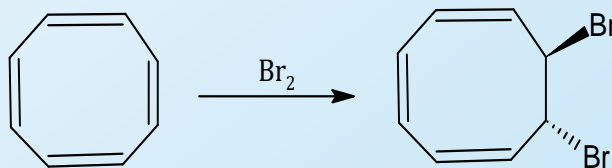
Anti Aromatic Compounds

Anti aromatic compounds are planar, cyclic molecules with $4n$ π electrons are much *less* stable than expected. They tend to distort out of plane and behave like ordinary alkenes

- 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



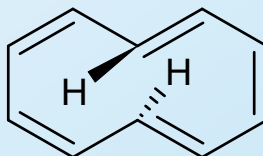
Exceptions: Huckel's πe^- but not Aromatic

Looking at Huckel's rules it should be simple to assign aromaticity. But there are two exceptions – the $2 \pi e^-$ and $10 \pi e^-$ systems.

It is easy to see why the $2 \pi e^-$ system is not aromatic – there is no conjugation.

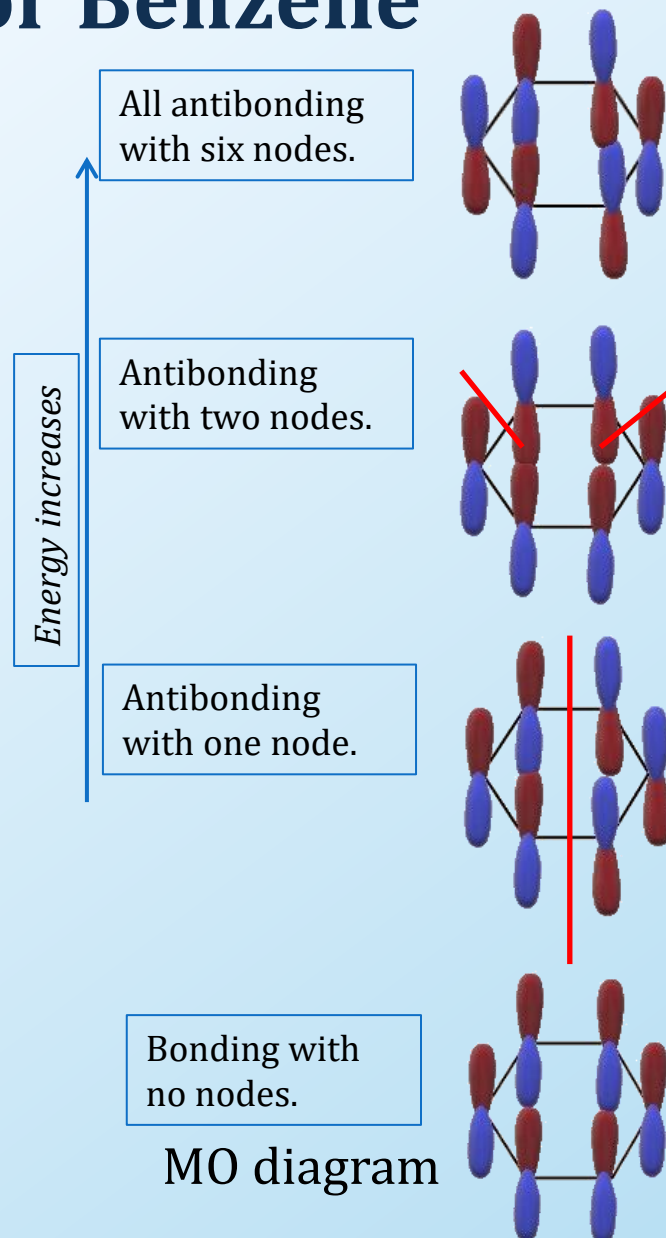
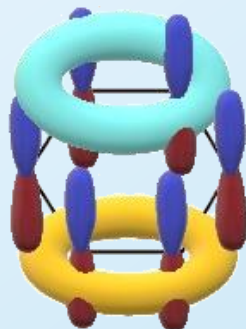


The $10 \pi e^-$ system is harder to visualize. The ring is structured in such a way that it is out of plane because of the steric hinderance of the two hydrogens in the middle of the ring. When the ring is not planar the electrons cannot overlap thus one of Huckel's rules is not followed in this $10 \pi e^-$ system.



Stability Using MO Rules for Benzene

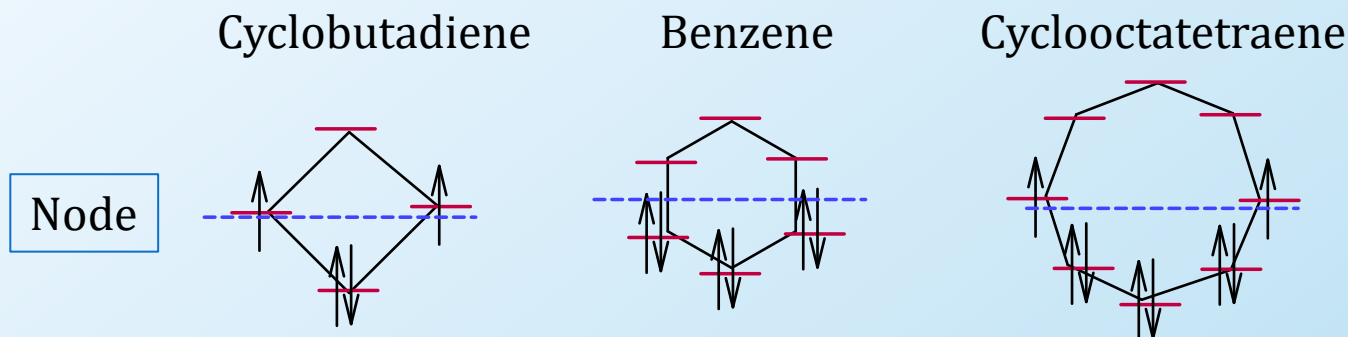
- Six overlapping p orbitals must form six molecular orbitals: three bonding and three antibonding.
- Lowest energy MO will have all bonding interactions, no nodes.
- As energy of MO increases, the number of nodes increases.
- The structure below shows the delocalization of pi bonds (yeah those yellow and light blue rings) above and below the benzene. This also explains how we can write a circle inside the benzene ring to show resonance.



Polygon Rule – Frost Circles

An easy way to see the MO theory is by filling electrons in an energy diagram for an annulene that has the same shape as the cyclic compound with one vertex at the bottom. These are Frost circles and easy to see how bonding electrons will occupy the lower bonding molecular orbitals.

Electrons found in the nodes in the middle of the circles, causes the ring to be more reactive as seen in cyclobutadiene. As we can see from the MO electron distribution, benzene's 6 pi electrons are all found below the node.



Cyclopentadienyl Ions

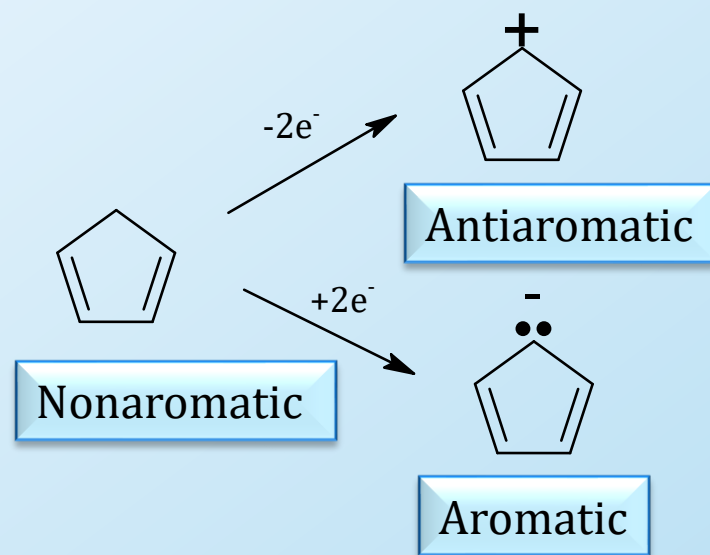
Ions can also be aromatic or not depending on how many electrons they have. Cations means they have lost an electron, creating an empty orbital for resonance. Anions have extra electrons thus can provide more electrons in case needed for aromaticity.

Cyclopentadiene is a nonaromatic compound since it does not have complete conjugation (*presence of sp^3 C in the middle*).

The cation of cyclopentadiene has an empty p orbital, which allows for conjugation, but the cation does not follow Huckel's number of πe^- ($4 \pi e^-$) so antiaromatic.

The anion has a nonbonding pair of electrons in a p orbital, $6 \pi e^-$, Huckel's number, thus aromatic.

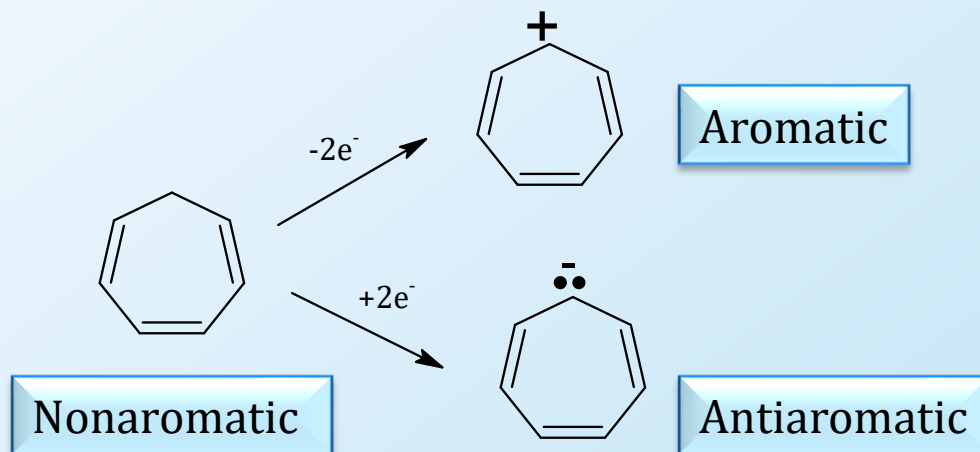
Acidity of Cyclopentadiene: pK_a of cyclopentadiene is 16, much more acidic than other hydrocarbons since it leads to aromatic anion.



Tropylium Anion

The cycloheptatriene ring is nonaromatic. However, adding or removing electrons can change the properties.

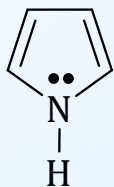
- The cycloheptatrienyl cation has $6 \pi e^-$ and an empty p orbital allowing for resonance and thus conjugation. The cation becomes aromatic.
- The anion is now $8 \pi e^-$ system, all conjugated. This is conjugated system but does not follow Huckel's number of πe^- .



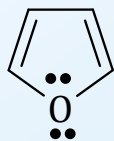
Heterocyclic Aromatic Rings

Heterocyclic compounds have one atom other than C in their ring. Heterocyclic rings can be aromatic or not, depending on if there is a lone pair of electrons on the heteroatom contributing to the conjugated/aromatic system.

The compounds shown below are all aromatic. The **N** of pyrrole, **O** of furan and **S** of thiophene contribute one lone pair of electron to aromaticity.



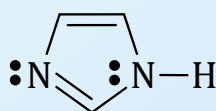
pyrrole



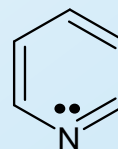
furan



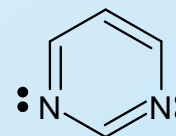
thiophene



imidazole



pyridine

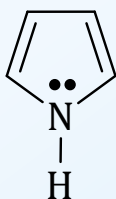


pyrimidine

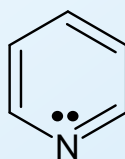
In pyridine and pyrimidine, the lone pair of electrons are not required for aromaticity.

Basicity of N of Heterocyclic Rings

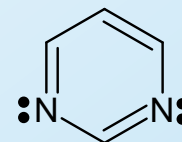
Nitrogen compounds are generally Lewis bases. Depending on the availability of the lone pair of electrons on N, the N can be basic or not. If the lone pair of electron is involved in aromaticity, then they are unavailable for reaction. This happens in pyrrole. In pyridine the lone pair of electrons are not required for aromaticity, so pyridine is a weak base.



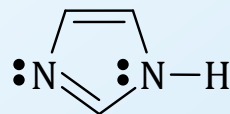
Pyrrole has no basic N.
Electrons are involved in aromaticity.



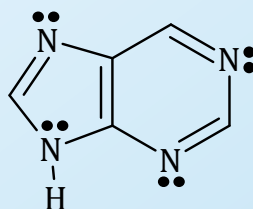
Pyridine N is basic because the ring is already aromatic.



Pyrimidine has two basic nitrogens.



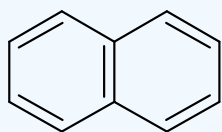
Imidazole has one basic nitrogen and one nonbasic.



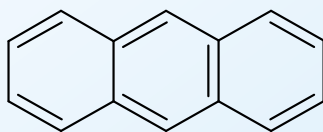
Purine: the only N involved in aromaticity is the one with the H.

Polynuclear Aromatics

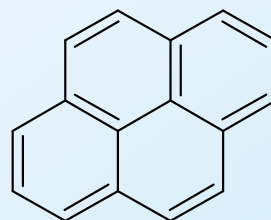
Compounds made from fusion of benzene rings are by default aromatic.



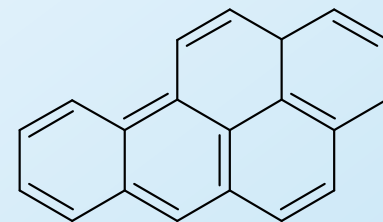
Naphthalene



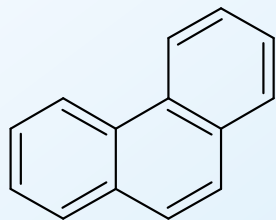
Anthracene



Pyrene

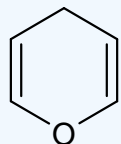
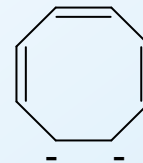
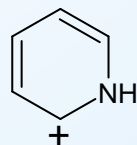
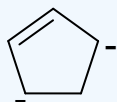
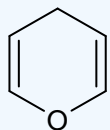


Benzo[a]pyrene

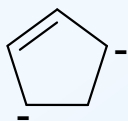


Phenanthrene

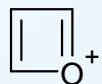
Solved Problem: Classify the following as aromatic, nonaromatic or antiaromatic.



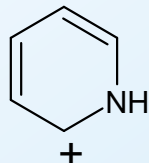
Non – the CH_2/sp^3 carbon on the top prevents full conjugation.



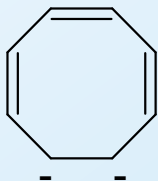
Non – the CH_2/sp^3 carbon between the two carbonanions prevent full conjugation.



Anti – there is conjugation but no Huckel's number of πe^- .



Aromatic – there is conjugation and Huckel's number of πe^- , $6 \pi e^-$.



Aromatic – there is conjugation and Huckel's number of πe^- , $10 \pi e^-$.

Key Concepts

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