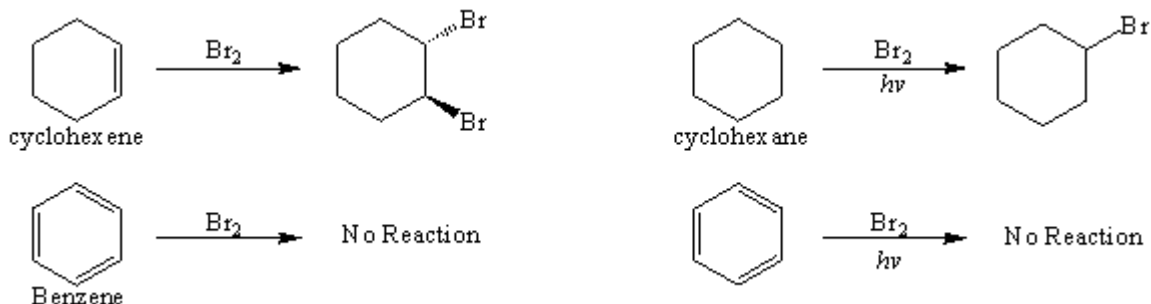


Aromatic Compounds

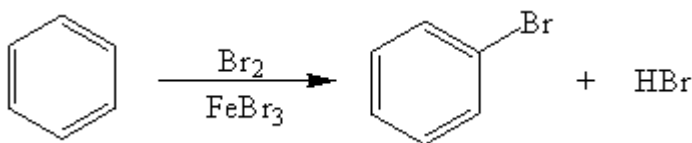
Benzene appears to be remarkably stable and unreactive compared to an alkene such as cyclohexene or an alkane such as cyclohexane.



When cyclohexene is allowed to react with bromine (an addition reaction), a di-brominated product is formed. However, when benzene is allowed to react with bromine in the absence of catalyst, nothing occurs. It is much less reactive.

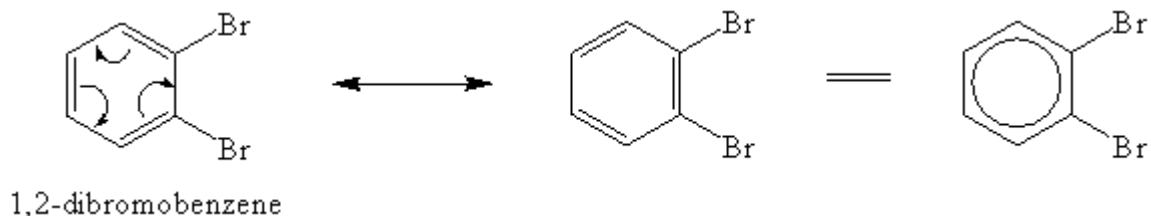
In the case of the alkane, cyclohexane, light ($h\nu$) is required for the bromination to occur (this is a substitution). For benzene, there is still no reaction under these conditions.

However, this is not to say that benzene is completely unreactive. Under certain conditions, benzene can be forced to react.



This is an Aromatic Electrophilic Substitution. We will learn more about this in later lectures.

Now let's look at 1,2-dibromobenzene.



There are two equally good resonance forms of 1,2-dibromobenzene, one with a double bond between the carbons attached to bromine, another with a single bond between. These are different pictures of the same compound. The electrons of the double bonds are

delocalized in the ring (since a given bond can be depicted as single or double depend on the resonance form drawn), this is why we can write the benzene ring as a circle inscribed inside the ring.

Each C-H sigma (σ) bond is made by overlapping an s orbital of hydrogen and sp^2 orbital of carbon. The C-C σ bond of the benzene ring is made by overlapping sp^2 hybridized orbitals. The 6 p orbitals overlap to form the π bonds. At the lowest energy, electrons are delocalized across the 6 carbon atoms (they share electrons in π orbitals that have density above and below the ring).

Benzene is **AROMATIC**

Aromatic compounds are especially stable. For benzene, the delocalization energy (stability) is 36 kcal/mol relative to that expected for cyclohexatriene.

To be **aromatic** (have aromaticity):

1. The molecule is *cyclic*.
2. The molecule is *fully conjugated*.
3. The molecule is *planar*.
4. The molecule contains $4n+2$ π electrons, where $n = 0, 1, 2, 3 \dots$

Benzene fulfills all the above criteria. It is conjugated (has three pairs of alternating double and single bonds). It is cyclic and planar. It has 6 π electrons (where $n = 1$).

Now let's look at some other conjugated cyclic compounds.

Cyclobutadiene



This molecule is cyclic, apparently fully conjugated, and planar.

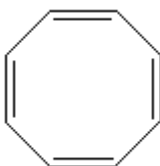
How many π electrons does it have?

Answer: 4 (a double bond is made of 2 π electrons. There are two double bonds, therefore, 4 π electrons)

Is this molecule aromatic?

Answer: no. It did not fit the $4n+2$ rule. It is in fact anti-aromatic, extremely unstable and behaves like alkenes.

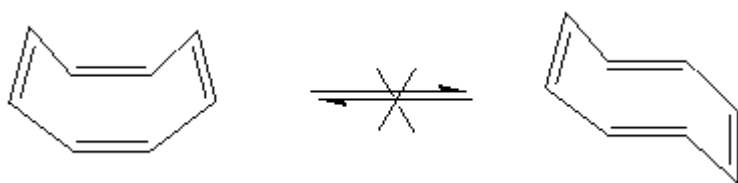
Cyclooctatetraene



Is this molecule aromatic?

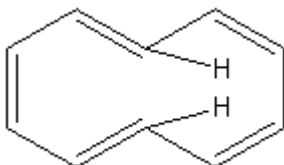
Answer: No. It has 8 π electrons, but it does not fit with $4n+2$ rule. No integer value of n will give 8. Therefore, it will behave like an alkene.

In addition, the molecule does not adopt planar conformation. It is actually tub-shaped. In planar cyclooctatetraene, there is some angle and torsional strain. The angle in regular flat octagon is 135° , far from the optimum sp^2 value of 120° , hence the tub shape. When the molecule is not planar, the p orbitals cannot effectively overlap with each other, the π electrons are not delocalized and the molecule becomes unconjugated. Hence, it is not aromatic.



cis-trans isomerization does not occur in this molecule, and the *trans* isomer shown above does not exist because there is too much strain (can't have *trans* double bond in small rings).

Cyclodecapentaene

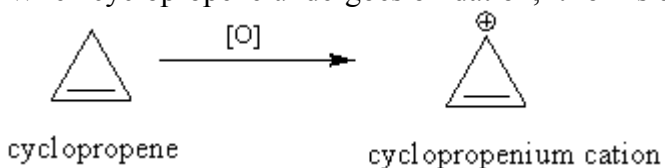


This molecule has 10 π electrons. It fits with $4n+2$ rule ($n = 2$). Although it seems to be aromatic, the hydrogens shown in the figure interfere with one another, and the molecule cannot adopt planar conformation. Therefore, it is not aromatic.

Let's take look at some anions and cations, and ask yourself are they aromatic and if they are stable.

Cyclopropane and cyclopropene are extremely reactive compounds due to angle strain. The normal preferred angle of an alkane is 109° and for a double bond is 120° . In both of these molecules, the internal angle is 60° . They are highly strained.

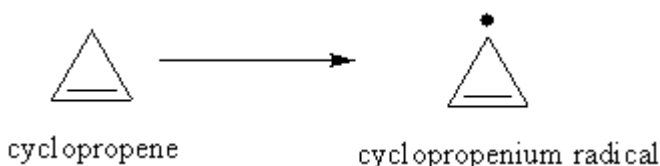
When cyclopropene undergoes oxidation, it forms cyclopropenium cation.



Is this cation aromatic?

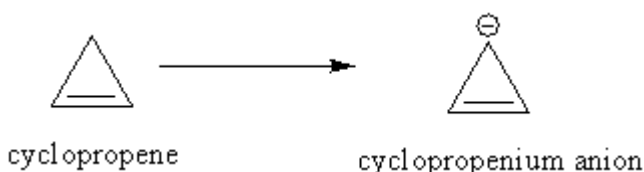
Answer: Yes. This molecule fits the criteria for aromaticity. It is cyclic, planar and conjugated. It has $4n+2$ π electrons ($n = 0$).

Now that we saw cyclopropenium cation is aromatic, we can ask ourselves if the radical is aromatic.



Answer: No. It does not fit with $4n+2$ rule. There are 3 π electrons.

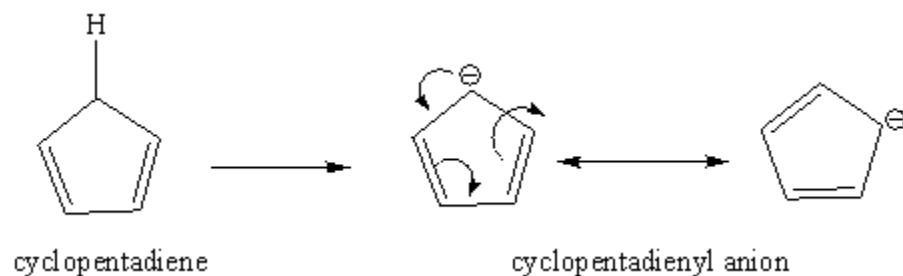
What about the anion?



Answer: No. It has 4 π electrons, and it is anti-aromatic like cyclobutadiene.

In cyclopropene system, the cation is easily formed since it is more stable (aromatic), where as radicals and anions are hard to make.

Let's look at another system.



Is cyclopentadienyl anion Aromatic?

Answer: Yes. It is cyclic. It is planar. It is conjugated (the anion has alternating single and double bonds). It has 6 π electrons (therefore fits the $4n+2$ rule).

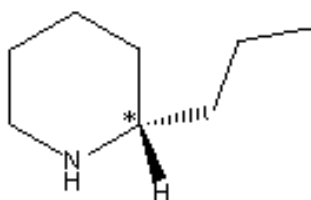
The pKa of the hydrogen shown on the parent cyclopentadiene on the above figure is around 16. A normal alkane hydrogen pKa is around 45. The acidity of the cyclopentadiene hydrogen has been enhanced by 30 orders of magnitude (30 pKa units)

due to the extra stability of the cyclopentadienyl anion (recall that the acidity of a molecule depend on the stability of its conjugate anion).

Heterocycles

Heterocycles have rings with atoms other than carbon. Keep in mind that this is a broad term, includes lots of molecules that may or may not be aromatic.

Example:



Cornine

Cornine is a heterocycle produced by the poison hemlock. It is a neurotoxin (which was once used to end Socrates' life).

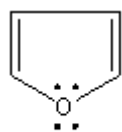
Is this compound chiral?

Answer: Yes. It has a stereogenic center (marked by the asterisk). An interesting thing to note is that if the stereochemistry of the chiral center is changed, the compound is not toxic anymore.

Is this compound aromatic?

Answer: No. It is not conjugated since there is no double bond present in the molecule.

Example:



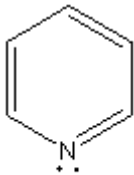
Furan

Furan is a heterocyclic compound. It is planar and has conjugated double bonds. Now ask yourself if this compound is aromatic. The answer is yes. Furan is an aromatic compound.

How? One of the lone pairs of electrons on the oxygen is conjugated into the ring system. The p orbitals of the double bonds are in parallel with one another. The oxygen arranges itself geometrically such that one of the lone pairs on the oxygen is also in parallel with the p orbital of the double bonds, and the electrons are conjugated. The other lone pair will stick out of the ring like the hydrogens on the double bonds. Within the ring, there would be total of 6 π electrons.

(Molecules organize themselves and become aromatic if they can since aromaticity gives extra resonance stabilization).

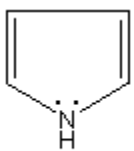
Example:



Pyridine

Pyridine is a heterocyclic compound. It is planar, conjugated and has 6 π electrons. In the case of pyridine, the lone pair on the nitrogen does not participate in electron delocalization within the ring since there are already 6 π electrons. Instead, the lone pair is perpendicular (90 degrees) to the p orbitals (π system) and in the plane of the ring and its hydrogens.

Example:

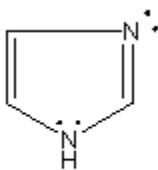


pyrrole

Is the molecule aromatic?

Answer: Yes. Similar to furan, the lone pair on the nitrogen participates in conjugation with the double bonds. There are total of 6 π electrons.

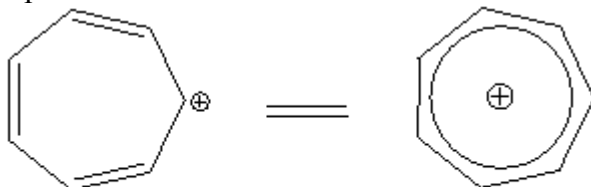
Example:



Imidazole

This compound is aromatic. Like pyrrole, the lone pair on the nitrogen bearing a hydrogen participates in making the aromatic system. The other nitrogen without the hydrogen has its lone pair at right angles to the π system (as in pyridine).

Example:



cycloheptatrienyl cation

Is this cation aromatic?

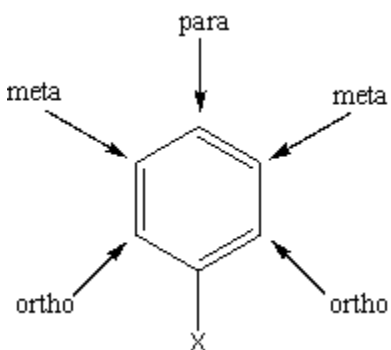
Answer: Yes, it is. The cation is cyclic, planar, fully conjugated with the double bonds, and has 6 π electrons. The electrons are delocalized in the ring, and each carbon shares 1/7 positive charge.

Benzene Derivatives

Nomenclature of substituted benzene rings

Review the substituted benzene structures from the last lecture, including toluene, phenol, aniline, benzoic acid and benzaldehyde (will be tested on exams).

When you have two substituents on a benzene ring, *ortho*, *meta*, and *para* are used to tell where the second substitution is relative to the first one.

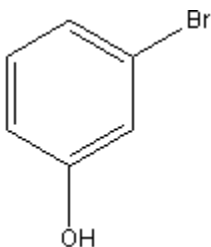


Ortho refers to 1,2-substitution

Meta refers to 1,3-substitution

Para refers to 1,4-substitution

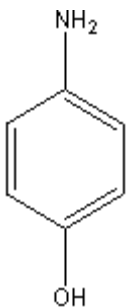
Example:



Name: *m*-bromophenol or meta-bromophenol

In this compound, the -OH (hydroxy) and -Br are in the 1 and 3 positions, so they are *meta* (or abbreviated *m*) to each other. The parent structure is phenol (phenol is a benzene with a hydroxyl group directly attached, not to be confused with phenyl which means just a benzene ring), so we call this meta-bromophenol.

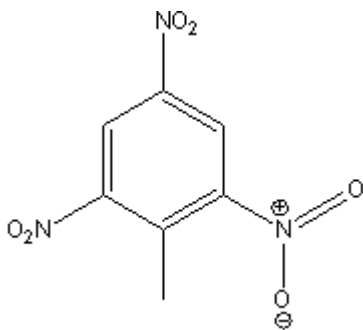
Example:



Nomenclature: *p*-hydroxyaniline or *p*-aminophenol.

The amine and hydroxyl group are in 1 and 4 positions, so they are *para* to each other. The parent structure in this molecule can be either aniline or phenol. For this course, it doesn't matter which parent structure you pick in the nomenclature with these substituents. Usually when naming the substituents, the atomic number takes priority.

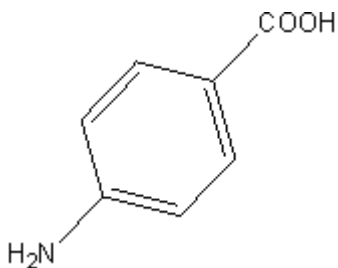
Example:



Nomenclature: 2,4,6-trinitrotoluene (TNT)

It is the main gradient in many military explosives.

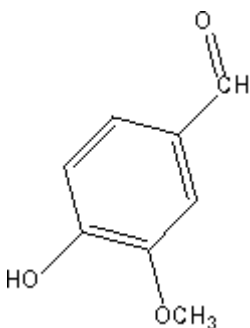
Example:



Nomenclature: *p*-aminobenzoic acid or para-aminobenzoic acid

Note: although there are two parent structures (aniline or benzoic acid), the carbon substituent gets priority as parent structure. Therefore, this is a substituted benzoic acid.

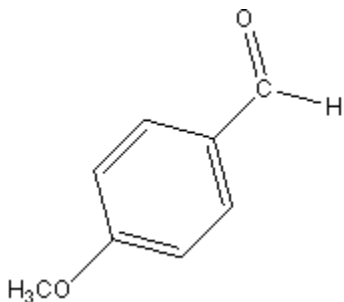
Example:



Nomenclature: 4-hydroxy-3-methoxybenzaldehyde (or vanillin from vanilla extract). The carbon substituent (and aldehyde group) gets priority.

Note: we number the ring in a way such that the substituents have the lowest numbers (so it's not 4-hydroxy-5-methoxy-, but 4-hydroxy-3-methoxy-)

Example:



Nomenclature: *p*-methoxybenzaldehyde (also known as anisaldehyde) (comes from anise, dill and related plants)