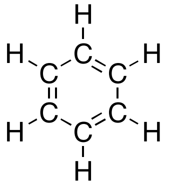
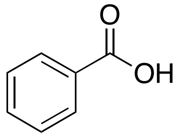
Aromatic Compounds

Benzene

Benzene was first isolated in 1825 by Michael Faraday. The structure was solved by Josef Loschmidt and August Kekule. The name came from benzoic acid, which had been isolated from gum benzoin.

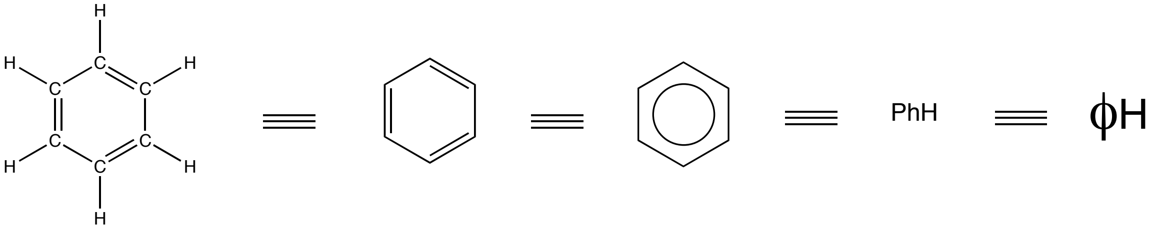


Benzene

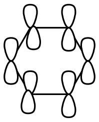


Benzoic acid (from gum benzoin)

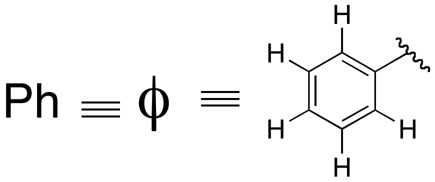
There are many different representations of benzene:



or you can also show the orbitals below:



You should know what a phenyl group is (C_6H_5 - different from phen<u>ol</u>)

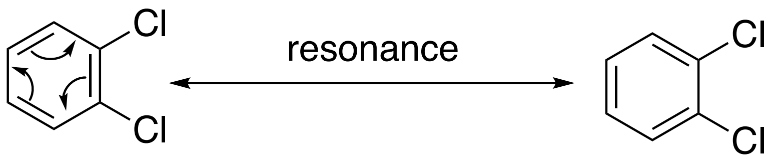


Phenyl group

Aromaticity

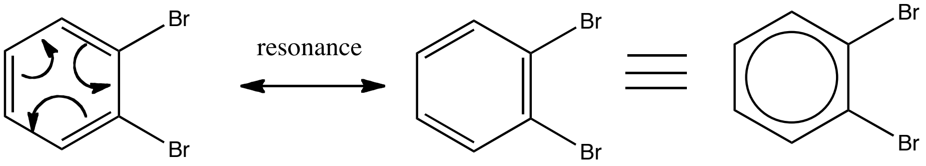
Equivalent resonance forms give stability to a compound.

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



1,2-dichlorobenzene

Another Example:

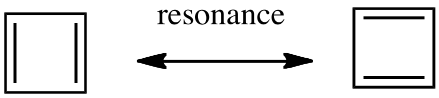


1,2-dibromobenzene

The central circle can be used to represent the resonance within the aromatic ring. The number of conjugated pi electrons plays a key role for **stability**.

Example:
Cyclobutadiene

Cyclobutadiene has four pi electrons (compared to the six pi electrons in benzene), and is **very** unstable.



cyclobutadiene

To be **aromatic** (have aromaticity) a compound or ion must:

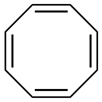
1. Be *cyclic* and *conjugated* around the ring
2. Be *planar*.
3. Have *4n+2 π electrons*, where n = 0, 1, 2, 3, etc.

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

Cyclobutadiene is not aromatic.

Example**:**

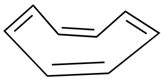
Cyclooctatetraene (or COT)



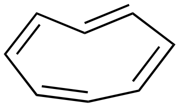
Is this molecule aromatic?

Answer: No. It has 8 π electrons, so it does not fit with 4n+2 rule

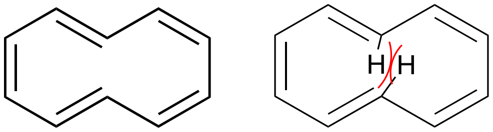
In addition, cyclooctatetraene does not adopt a planar conformation. It is actually tub-shaped. In planar cyclooctatetraene, there is some angle and torsional strain. The angle in regular flat octagon is 135°, far from the optimum *sp*^{2} value of 120°, hence the tub shape.



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

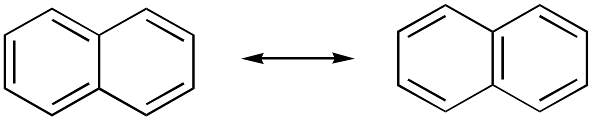


Cyclodecapentaene



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 a planar conformation. Therefore, it is not aromatic.

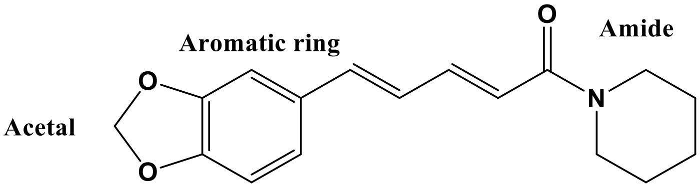
Naphthalene



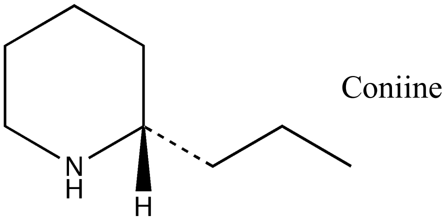
This molecule has 10 π electrons. It fits with 4n+2 rule (n = 2), and the whole molecule is planar. Therefore, naphthalene is aromatic.

Heterocycles (non-carbon atom in the ring)

Heterocycles are cyclic molecules with an atom other than carbon as a member of the ring. Keep in mind that this is a broad term, and it includes lots of molecules that may or may not be aromatic.



Example: **Piperine** from *Piper nigrum*

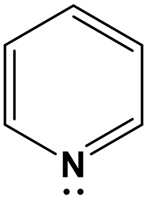


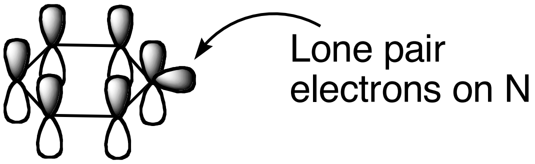
Example: **Coniine** is a heterocycle compound produced by poison hemlock. It is a neurotoxin.

Is this compound aromatic?

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

Example: **Pyridine**

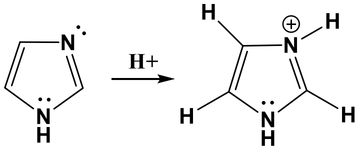


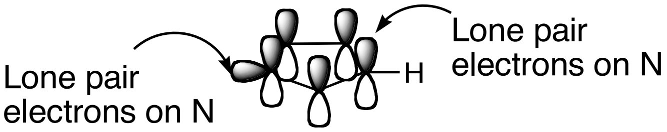


Pyridine is a heterocyclic compound. It is planar, conjugated and has 6 π electrons (4n + 2, where n = 1).

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.

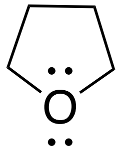
Example: **Imidazole**





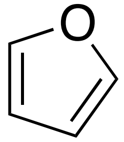
This compound is aromatic. Like pyrrole, the lone pair on the nitrogen bearing a hydrogen participates in the aromatic system. The other nitrogen without the hydrogen has its lone pair at a right angle to the π system (as in pyridine). It is this nitrogen that is more easily protonated because doing so doesn't destroy the aromatic system. Imidazole is part of the amino acid histidine.

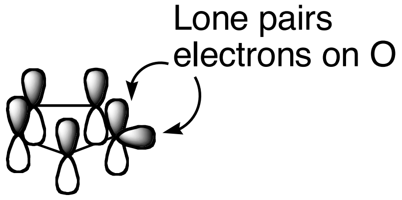
Example: **Tetrahydrofuran**



- Not conjugated, not aromatic

Example: **Furan**

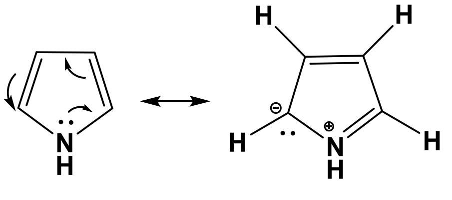


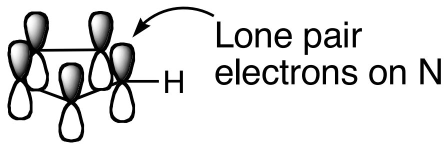


Furan is a heterocyclic compound. It is planar and has conjugated double bonds. Furan is also an aromatic compound.

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 conjugated with one another. The oxygen arranges itself geometrically such that one of the lone pairs on the oxygen is also parallel to 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 conjugated system, there are 6 π electrons.
(Molecules orient themselves to be and be aromatic if they can, because aromaticity gives extra stabilization).

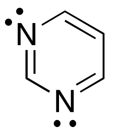
Example: **Pyrrole**



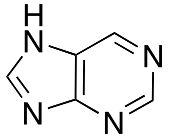


Is the molecule aromatic?
Answer: Yes. Pyrrole, similar to furan, has a lone pair of electrons (on the nitrogen) that participates in conjugation with the double bonds. There are total of 6 π electrons.

Aromatic heterocycles and ions



pyrimidine



purine

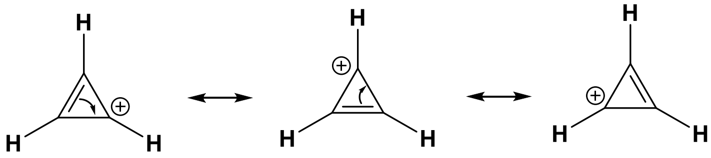
Pyrimidine has 6 π electrons, and the two lone pairs of electrons on the N's are on the outside of the ring (i.e., they are not part of the conjugated system. It is an aromatic compound.

Compounds like purine are fused heterocyclic rings and are also aromatic compounds. Only the lone pair on the nitrogen bearing a hydrogen participates in the aromatic system in purine.

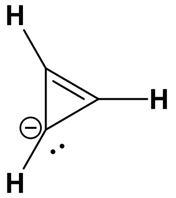
Aromatic Intermediates: Cations and anions

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.

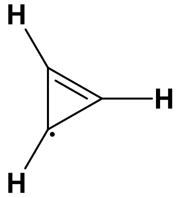
When cyclopropene undergoes oxidation, it forms a cyclopropenium cation.



Aromatic cation: has 2π electrons



Anion: not aromatic (4π electrons)

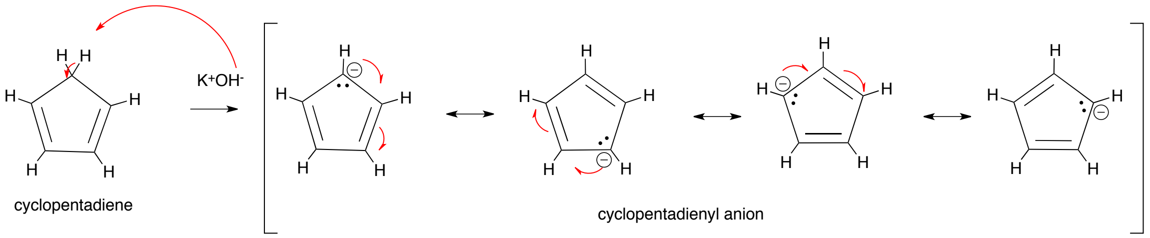


Radical: not aromatic

Is this cation aromatic?

Answer: Yes. This molecule is cyclic, planar, conjugated, has 4n + 2 π electrons (n = 0).

Consider another system:

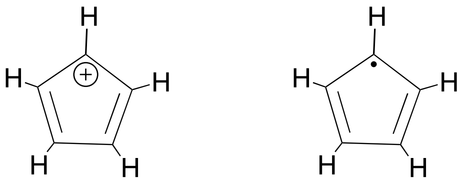


Is cyclopentadienyl anion aromatic?

Answer: Yes. It is cyclic, planar, and conjugated. It has 6 π electrons (therefore it fits the 4n + 2 rule where n = 1).

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.

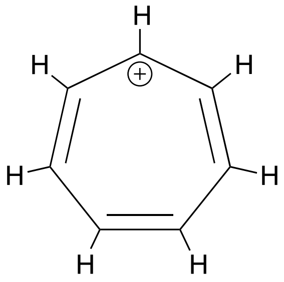
The acidity of the cyclopentadiene hydrogen has been enhanced by 30 orders of magnitude (30 pKa units) due to the extra stability of the cyclopentadienyl anion (recall that the acidity of a molecule depend on the stability of its conjugate base).



Are the cyclopentadienyl cation and radical aromatic?

Answer: No. They are cyclic, planar, conjugated, but do not follow the 4n+2 rule.

Another example:

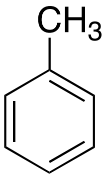


Is this cycloheptatrienyl cation aromatic?

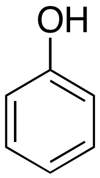
Answer: Yes, it is. The cation is cyclic, planar, fully conjugated, and has 6 π electrons. The electrons are delocalized in the ring, and each carbon shares 1/7 positive charge.

Nomenclature of substituted benzene rings

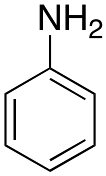
You should know the names of the following structures:



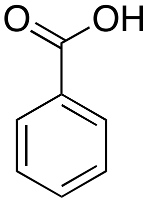
Toluene



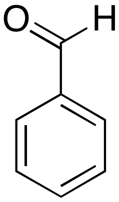
Phenol



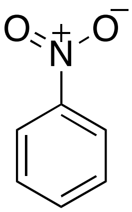
Aniline



Benzoic acid



Benzaldehyde



Nitrobenzene