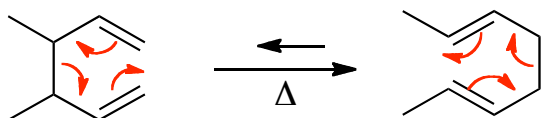
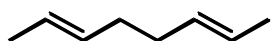


Other Electrocyclic Reactions**Cope Reaction**

This is another pericyclic reaction that, like the Diels-Alder reaction, involves 6 electrons.

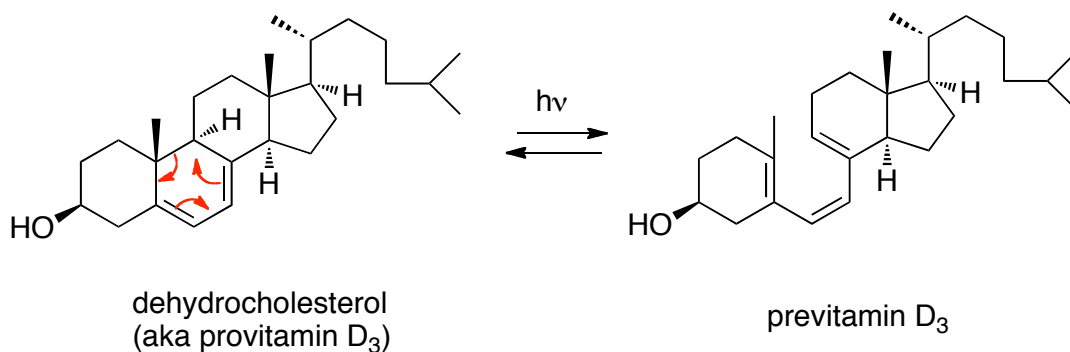


This example favours the less sterically crowded isomer, which can be redrawn as:

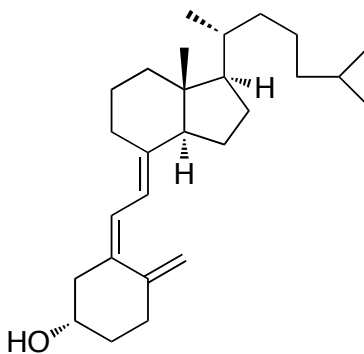


Note the steric interference between the two methyl groups in the first isomer.

This reaction occurs in nature, as shown below:



This goes on to form Vitamin D<sub>3</sub>, whose structure you should be able to recognize.



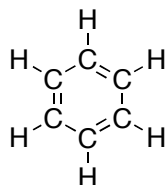
Vitamin D<sub>3</sub>

Deficiency of this is known to cause rickets. This was identified around the year 1650.

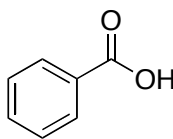
## Aromatic Compounds

### 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.

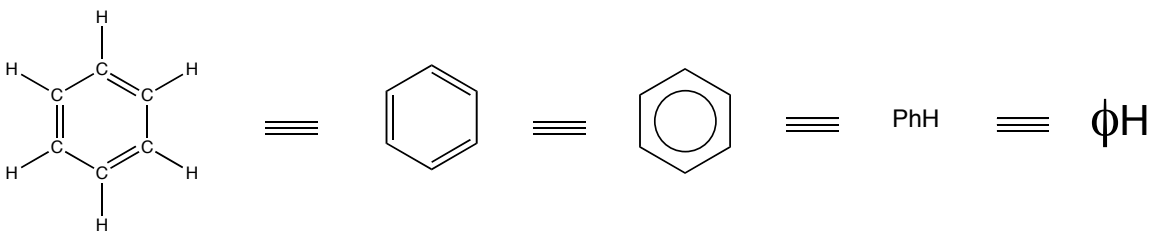


Benzene

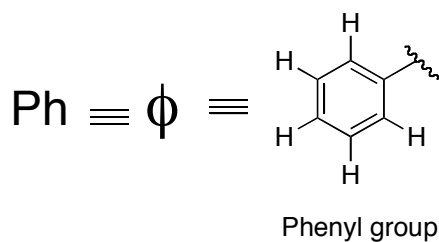


Benzoic acid (from gum benzoin)

There are many representations of benzene, as follows:

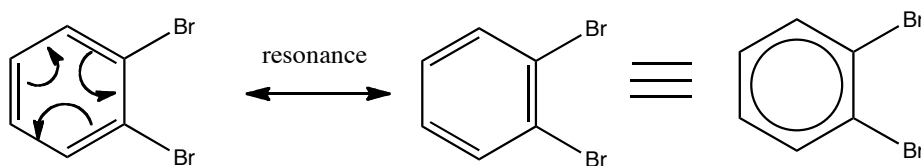


You should know what a phenyl group (note that it is different from phenol)



### Aromaticity

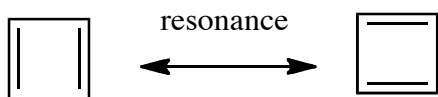
Equivalent resonance forms gives stability to a compound.



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**.



cyclobutadiene

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

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  $4n+2$   $\pi$  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, and it has 6  $\pi$  electrons (where  $n = 1$ ).

### Cyclobutadiene



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

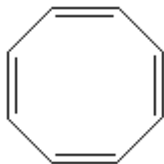
*How many  $\pi$  electrons does it have?*

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

*Is this molecule aromatic?*

Answer: no. It does not fit the  $4n+2$  rule. In fact, it is anti-aromatic and extremely unstable.

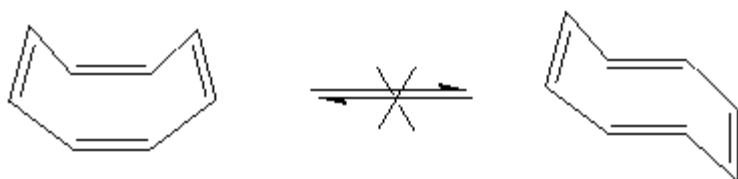
### Cyclooctatetraene



*Is this molecule aromatic?*

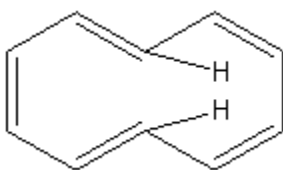
Answer: No. It has 8  $\pi$  electrons, so it does not fit with  $4n+2$  rule. No integer value of  $n$  will give 8.

In addition, the molecule 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  $135^\circ$ , far from the optimum  $sp^2$  value of  $120^\circ$ , hence the tub shape. When the molecule is not planar, the  $p$  orbitals cannot effectively overlap with each other, the  $\pi$  electrons are not delocalized and the molecule becomes unconjugated. Hence, it is not aromatic.



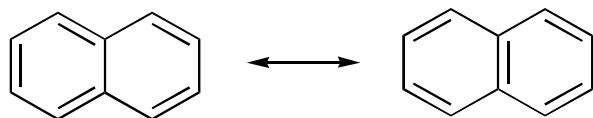
*cis-trans* isomerization does not occur in this molecule, and the *trans* isomer shown above does not exist because there is too much strain (can't have *trans* double bond in small rings).

### Cyclodecapentaene



This molecule has 10  $\pi$  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

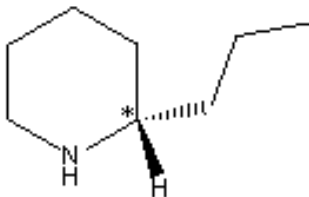


This molecule has 10  $\pi$  electrons. It fits with  $4n+2$  rule ( $n = 2$ ), and the whole molecule is planar. Therefore, naphthalene is aromatic.

### Heterocycles

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:



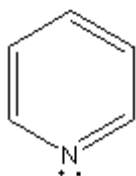
Coniine

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

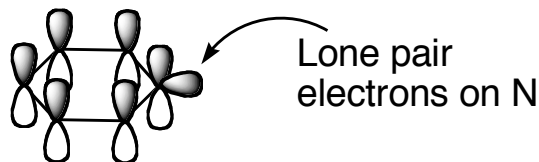
*Is this compound aromatic?*

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

Example:



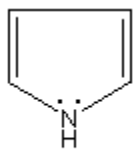
Pyridine



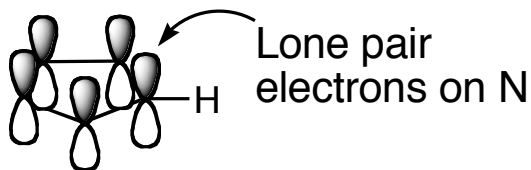
Pyridine is a heterocyclic compound. It is planar, conjugated and has 6  $\pi$  electrons ( $4n + 2$ , where  $n = 1$ ). In the case of pyridine, the lone pair on the nitrogen does not participate in electron delocalization within the ring since there are already 6  $\pi$  electrons. Instead, the lone pair is perpendicular (90 degrees) to the p orbitals ( $\pi$  system) and in the plane of the ring and its hydrogens.

Know the structure of this molecule!

Example:



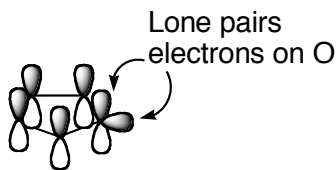
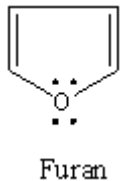
pyrrole



*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  $\pi$  electrons.

Example:

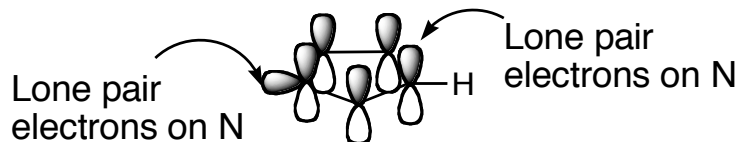
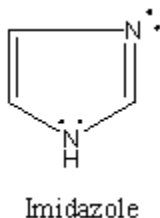


Furan is a heterocyclic compound. It is planar and has conjugated double bonds. Furan is also an aromatic compound.

*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 parallel 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  $\pi$  electrons.

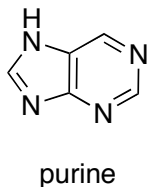
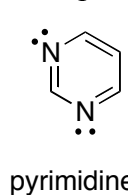
**(Molecules organize themselves and become aromatic if they can, because aromaticity gives extra resonance stabilization).**

Example:



Know this molecule (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 right angles to the  $\pi$  system (as in pyridine).

Example:



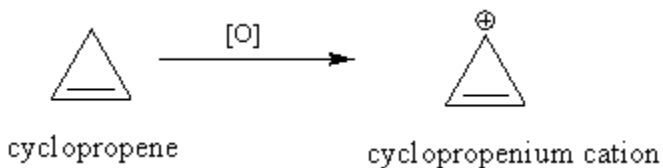
Pyrimidine has 6  $\pi$  electrons, and the two lone pairs of electrons on the N's are on the outside of the ring (i.e., they are not part of the conjugated system). It is an aromatic compound. Compounds like purine are fused heterocyclic aromatic rings and are also aromatic compounds. Only the lone pair on the nitrogen bearing a hydrogen participates in the aromatic system in purine.

**Aromatic intermediates:** Cations and anions

Let's take a look at some anions and cations and radicals, and determine if they are aromatic.

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

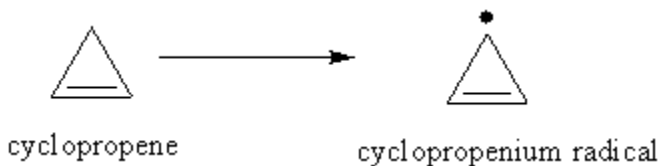
When cyclopropene undergoes oxidation, it forms a cyclopropenium cation.



*Is this cation aromatic?*

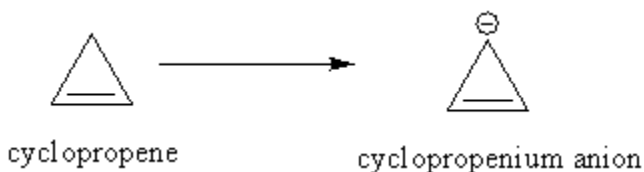
Answer: Yes. This molecule fits the criteria for aromaticity. It is cyclic, planar and conjugated. It has  $4n + 2 \pi$  electrons ( $n = 0$ ).

Compare this to the corresponding radical:



While this is cyclic, planar, and conjugated, it is not aromatic, as it does not fit with  $4n + 2$  rule: there are 3  $\pi$  electrons.

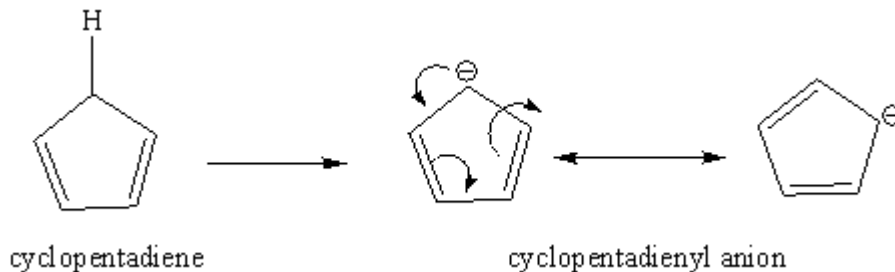
Compare this to the anion:



This has 4  $\pi$  electrons, is cyclic, planar, and conjugated. Therefore it is anti-aromatic like cyclobutadiene.

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

Consider another system:

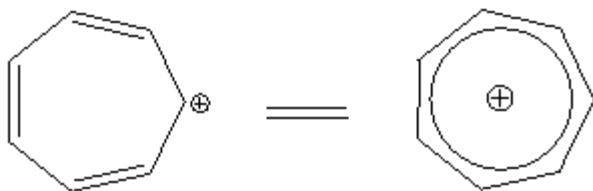


*Is cyclopentadienyl anion aromatic?*

Answer: Yes. It is cyclic, planar, and conjugated. It has 6  $\pi$  electrons (therefore it 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 base).

Another example:



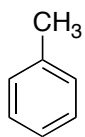
cycloheptatrienyl cation

*Is this cation aromatic?*

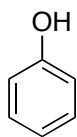
Answer: Yes, it is. The cation is cyclic, planar, fully conjugated, and has 6  $\pi$  electrons. The electrons are delocalized in the ring, and each carbon shares 1/7 positive charge.

## Nomenclature of substituted benzene rings

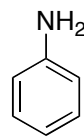
You should know the names of the following structures:



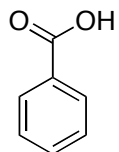
Toluene



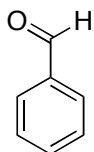
Phenol



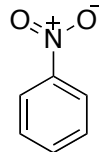
Aniline



Benzoic acid



Benzaldehyde



Nitrobenzene