

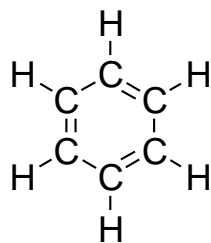
## Aromatic Compounds

Historically, benzene and its first derivatives had pleasant aromas, and were called *aromatic* compounds.

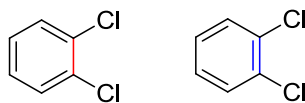
### Structure of Benzene

#### **Kekulé Structure**

Kekulé (1866) bravely proposed that benzene had a *cyclic* structure with three *alternating* C=C double and three C-C single bonds.



Whilst this is reasonably close to accurate, it *cannot* be exactly correct since this would require that 1,2-dichlorobenzene existed as *two* isomeric forms, yet it was known that it did not.

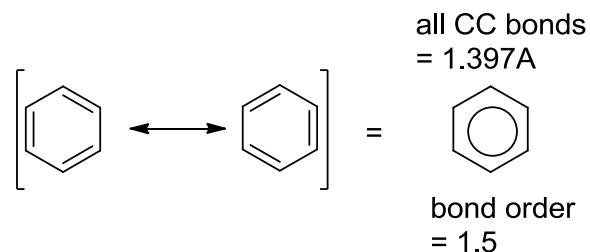


## Resonance Structure

The Kekulé structure would have the single bonds of longer length than the double bonds, and thus an *irregular* hexagonal shape.

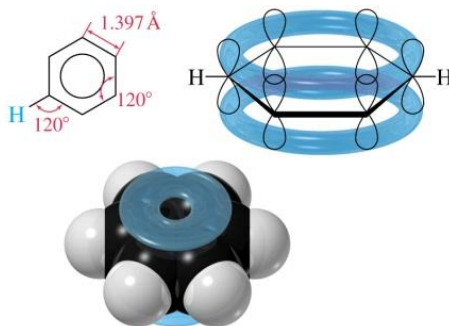
But spectroscopy had shown that benzene had a planar ring, with all the carbon-carbon bond distances the *same* 1.397Å (C-C typically 1.48Å, C=C typically 1.34Å).

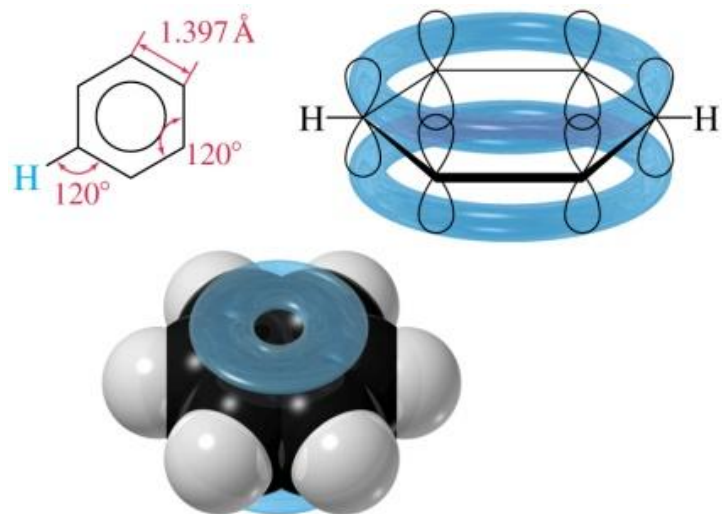
Since the atoms are the same distance apart, and the only difference is the location of the  $\pi$  electrons in the two Kekulé structures, they are in fact *resonance structures* of one another.



This implies that the bond order should be 1.5, and that the  $\pi$  electrons are *delocalized* around the ring.

Because of the delocalization of the  $\pi$  electrons, often the double bonds are represented by a circle in the middle of the hexagon.





This resonance description lets us draw a more *realistic* representation of benzene, with 6  $sp^2$  hybrid carbons, each bonded to one hydrogen atom.

All the carbon-carbon bonds are of equal length, and all the bond angles are  $120^\circ$ .

Each carbon has an unhybridized p orbital, which lies perpendicular to the plane of the ring.

These p orbitals each have 1 electron inside.

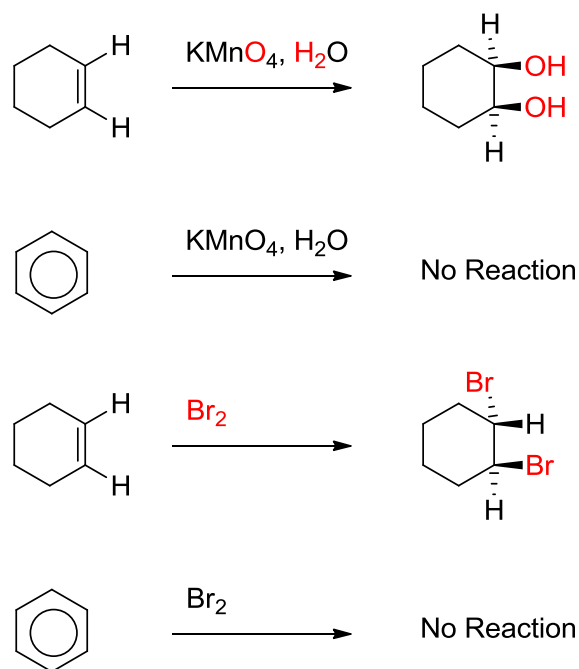
There are therefore 6 electrons in the circle of p orbitals.

(We start to see that *aromatic* compounds are cyclic compounds, containing a certain number of **conjugated** double bonds, and are especially **stable** due to resonance).

## Unusual Behavior of Benzene

Benzene has *much more stability* than predicted by the simple resonance delocalized structure.

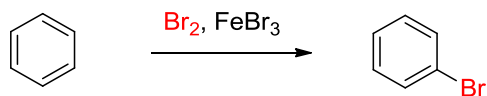
For example, we know alkenes can be oxidized to syn diols ( $\text{KMnO}_4$ ) and undergo electrophilic additions with halogens ( $\text{Br}_2$ ).



Yet the same reactions do not work with benzene.

Benzene does not react - benzene is *more stable* than normal cyclo-alkenes.

When a catalyst is added to the benzene bromination reaction, reaction does occur, but the reaction is not an **addition**, but rather a **substitution** (a ring hydrogen is substituted for a ring bromine).



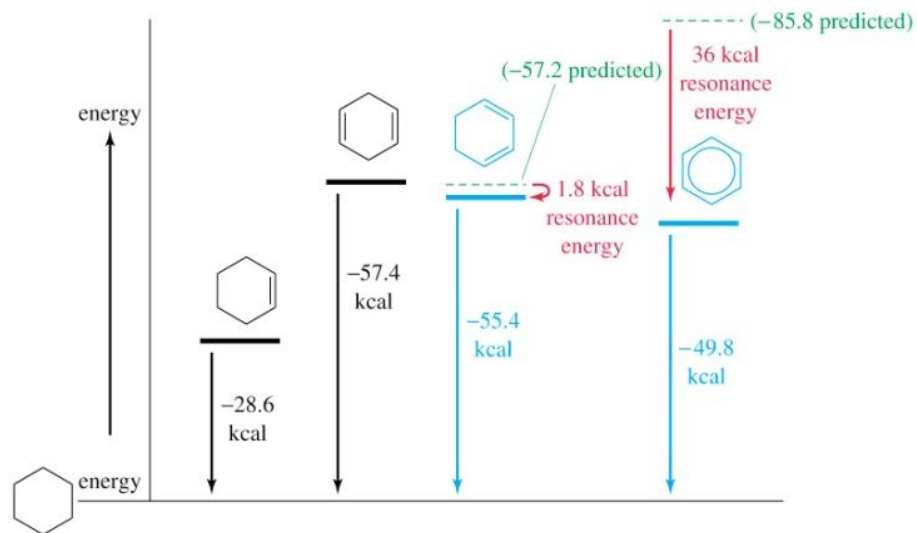
All three double bonds are *retained* in the product.

## The Unusual Stability of Benzene

### Observations/Facts:

- 1) Hydrogenation of cyclohexene is exothermic by 28.6kcal/mol (Isolated double bond).
- 2) Hydrogenation of 1,4-cyclohexadiene is exothermic by 57.4kcal (Two isolated double bonds, no resonance energy).
- 3) Hydrogenation of 1,3-cyclohexadiene is exothermic by 55.4kcal (Conjugated diene, resonance stabilization energy of 1.8kcal).
- 4) Hydrogenation of benzene (which requires much higher pressures of H<sub>2</sub> and a more active catalyst) is exothermic by 49.8kcal (Resonance stabilization of 36kcal/mol compared to three times the value for cyclohexene).

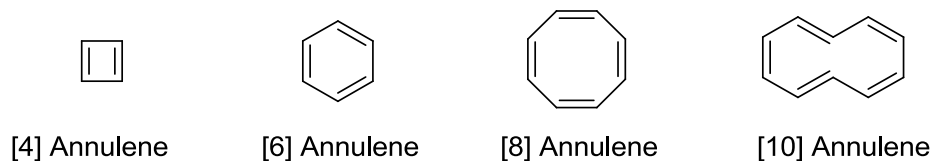
This large amount of stabilization energy *cannot* be explained by resonance effects alone - benzene is exceptionally unreactive.



### Failures of the Resonance Picture for Aromatics

**If** having these identical resonance structures were the sole cause of this pronounced stability, then ALL structures with conjugated systems of alternating double and single bonds **should** show analogous enhanced stabilities.

These cyclic hydrocarbons with alternating double and single carbon carbon bonds are called *Annulenes*.



Benzene is the 6 membered annulene, and is called [6] annulene.

For the double bonds to be totally conjugated, the molecule must be **planar** so that the p orbitals of the  $\pi$  bonds can overlap.

However, molecules like cyclobutadiene and cyclo-octatetraene DO NOT exhibit this increased stability - in fact quite the **opposite!**

Cyclobutadiene has never been isolated and purified because it is so unstable - it reacts with itself to form dimers even at low temperatures.

Cyclo-octatetraene has been shown to **not** exist in a planar structure, but instead it adopts a 'tub' like conformation.

### MO's of Benzene

Benzene's extra stability cannot be explained by resonance alone, and so we must turn to *Molecular Orbital theory* for a fuller answer.

Benzene has 6 planar  $sp^2$  carbons, and therefore each carbon has an unhybridized p orbital.

These p orbitals are perfectly aligned for overlap (i.e. bonding, just like for a  $\pi$  bond). These p orbitals create a continuous ring of orbitals above and below the plane of the carbon atoms.

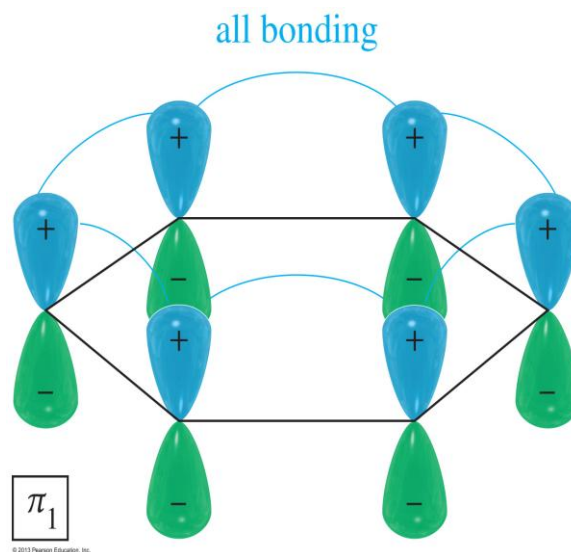
The 6 overlapping p orbitals create a cyclic system of molecular orbitals (i.e. a three dimensional system).

Even though we have only seen two dimensional MO's previously (ethene, allyl systems, the same basic rules apply).

- 1) Six p orbitals are used in the benzene  $\pi$  system, therefore six MO's are created.
- 2) The lowest energy MO is entirely bonding (constructive overlap between all adjacent p orbitals; no nodes).
- 3) The number of nodes increases as the MO's increase in energy.
- 4) The MO's must be divided between bonding and antibonding, with the possibility on non-bonding MO's in some cases.

(The 6 MO's for benzene can be drawn either in 2D or 3D projections).

The lowest energy MO,  $\pi_1$ , is entirely bonding, with zero nodes.

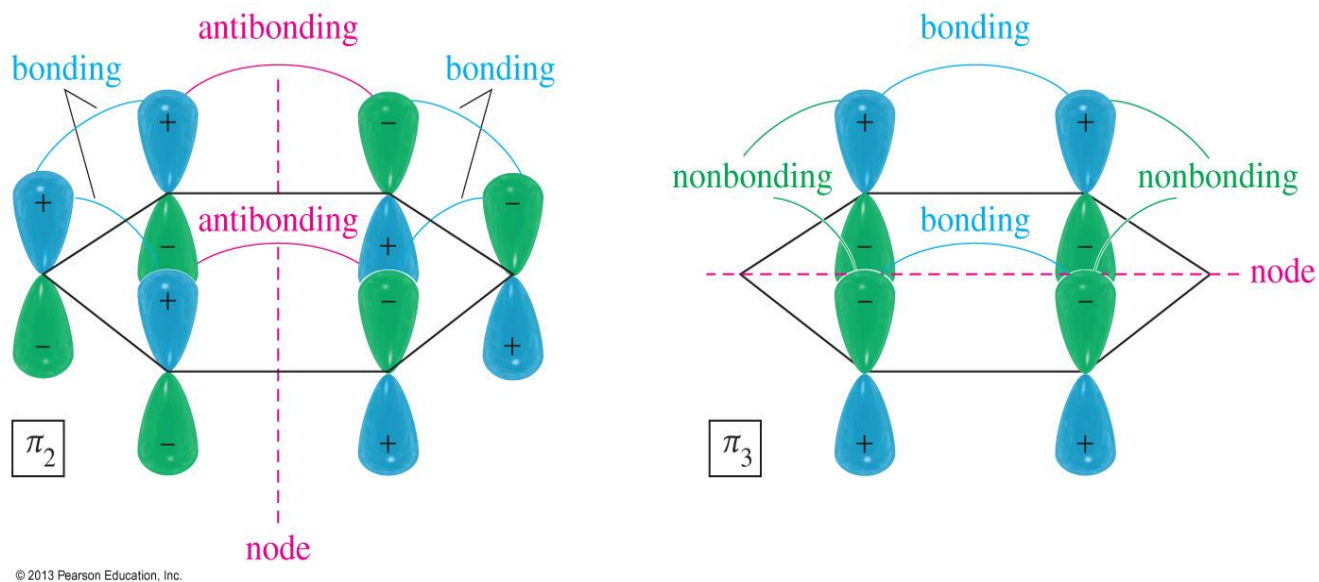


All the lobes above the plane of carbon atoms interfere constructively, as do the lobes below the plane of carbon atoms.

The six p orbitals overlap to form a continuously bonding ring of electron density.

It is of very low energy because of the 6 bonding interactions, and the electrons are delocalized over the six carbons equally.

The MO's of next lowest energy are  $\pi_2$  and  $\pi_3$ .

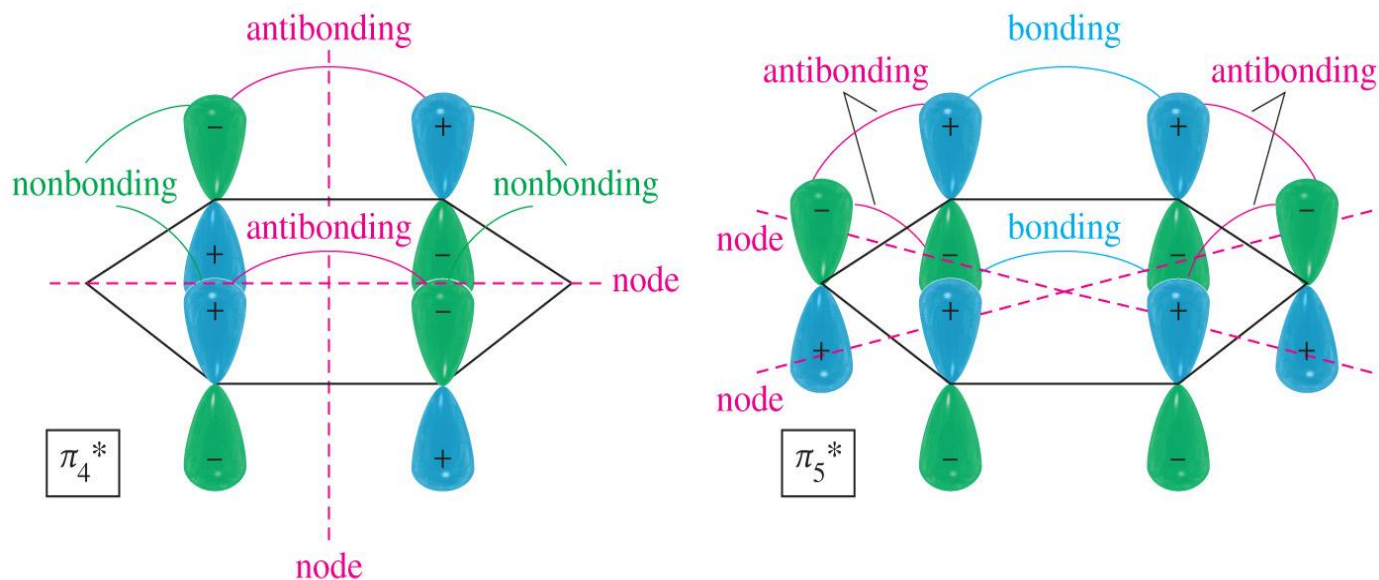


Notice that  $\pi_2$  and  $\pi_3$  are of the same energy (they are said to be **degenerate**).

They both comprise of 4 bonding interactions and two antibonding interactions (and one nodal plane).

They are of the same energy as each other (overall a net two bonding interactions) and are overall bonding, but not as bonding (i.e. of low energy) as  $\pi_1$ .

The next two lowest energy MO's are  $\pi_4^*$  and  $\pi_5^*$ .



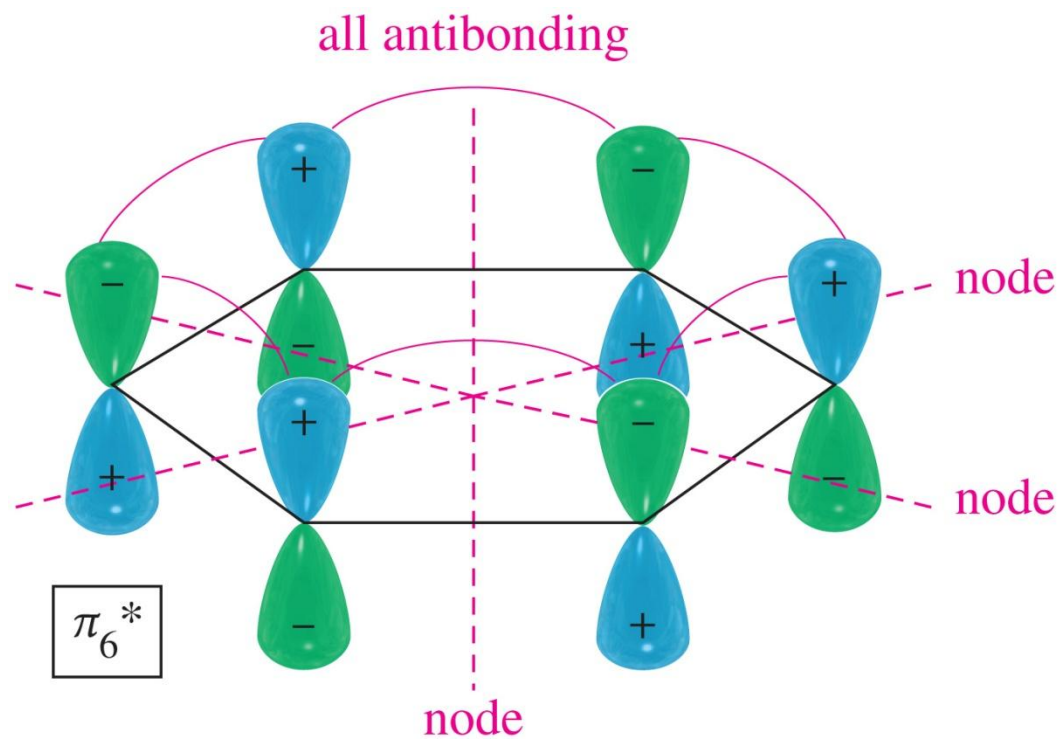
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These are also degenerate orbitals with overall a net two antibonding interaction ( $\pi_4^*$  has two non-bonding interactions, and two anti-bonding interactions;  $\pi_5^*$  has two bonding and 4 anti-bonding interactions).

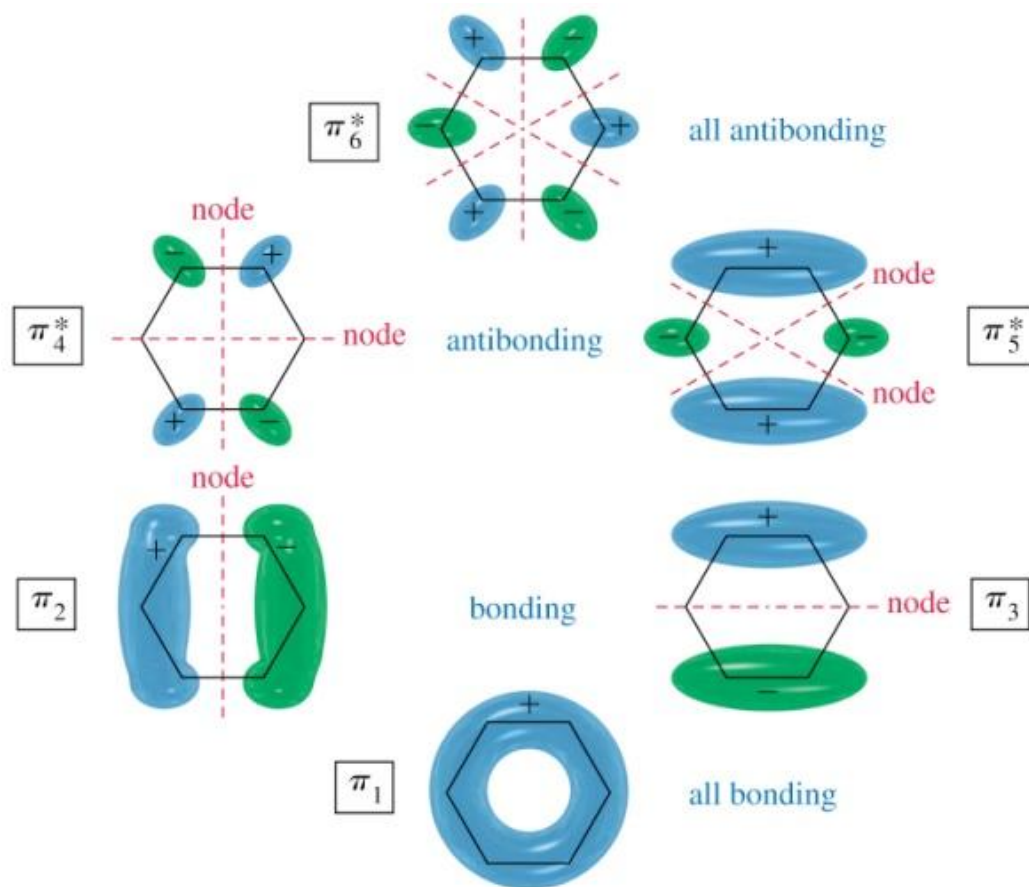
They contain two nodal planes.

The MO's of  $\pi_4^*$  and  $\pi_5^*$  are as antibonding as  $\pi_2$  and  $\pi_3$  are bonding.

The highest energy MO is  $\pi_6^*$  and contains 6 anti-bonding interactions (and three nodal planes).

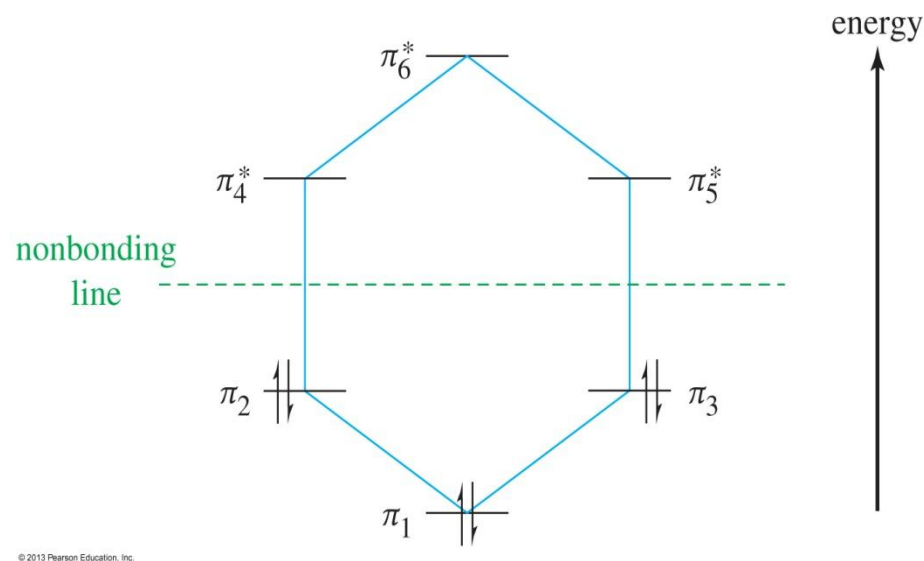


All viewed from above:



## Energy Level Diagram of Benzene

The relative energy levels for the MO's of benzene are shown below.



MO's  $\pi_4^*$ ,  $\pi_5^*$  and  $\pi_6^*$  are all overall *antibonding*, and lie above the level of an isolated p orbital (non-bonding line).

Each p orbital contributes one electron, which means we have 6 electrons to accommodate (this is the same number of electrons as 3 $\pi$  bonds in the Kekulé structure).

The 6 electrons fill the three lowest MO's, which happen to be the bonding MO's.

This electron configuration of all the bonding MO's filled, is a very stable arrangement, and explains the high stability of benzene.

This electron configuration is sometimes referred to as a 'closed bonding shell'.

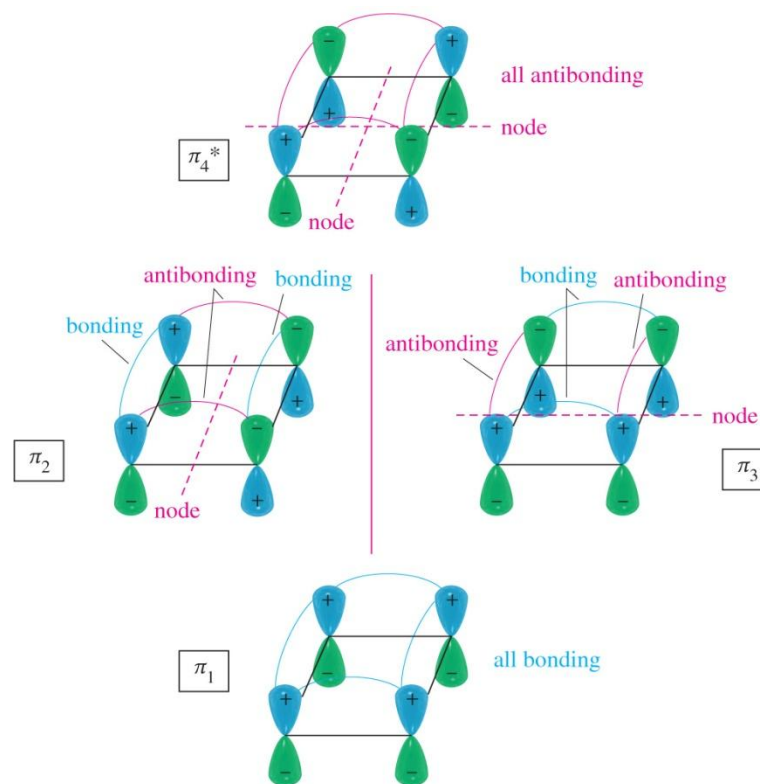
## The MO Picture of Cyclobutadiene

Although it is possible to write resonance structures for cyclobutadiene, experimental evidence indicates that it is very unstable.

Again, MO theory provides an explanation for this (unexpected) **instability**.

Cyclobutadiene contains four  $sp^2$  hybridized carbons, which leaves four p orbitals for the  $\pi$  bonding.

The four p orbitals produce 4 MO's, as shown below.



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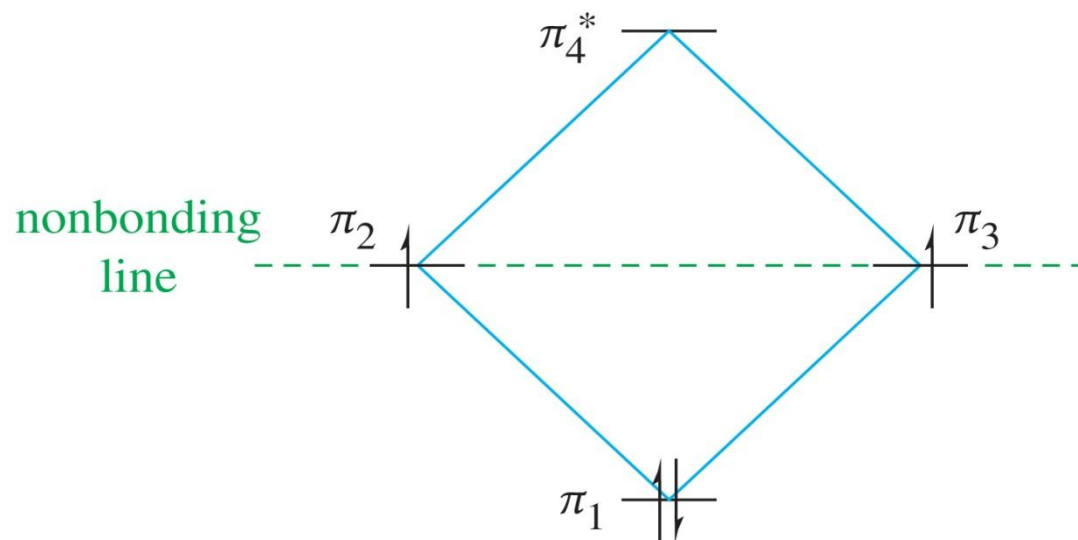
As usual, the lowest energy MO ( $\pi_1$ ) has all bonding interactions between the p orbitals, and zero nodes.

The next highest energy MO's are  $\pi_2$  and  $\pi_3$ . They are degenerate and contain one node.

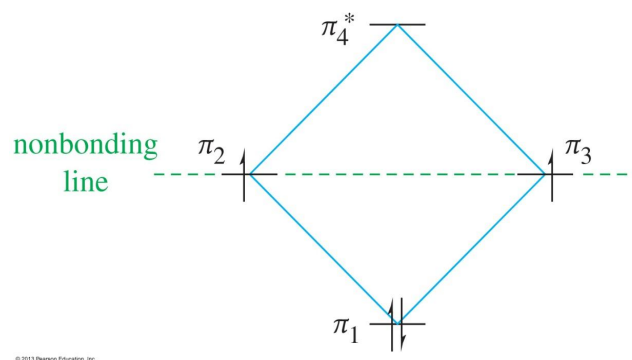
Their overall energy is zero, which is non-bonding ( $\pi_2$  and  $\pi_3$  both have two bonding and two anti-bonding interactions).

The highest energy MO is  $\pi_4$ , and comprises solely of antibonding interactions (and two nodal planes).

The four electrons which have to be accommodated are arranged putting 2 electrons in  $\pi_1$ , and one each in  $\pi_2$  and  $\pi_3$  (Hund's rule Chapter 1).



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This arrangement of electrons is **not** stable.

The MO picture predicts that cyclobutadiene should display diradical character (two unpaired electrons) in its ground state.

This arrangement is **not** a closed bonding shell.

Therefore MO theory correctly predicts that cyclobutadiene should be very **reactive**, and therefore **unstable**.

MO theory offers an explanation for the increased stability of benzene ( $6\pi$  electrons) and the increased instability of cyclobutadiene ( $4\pi$  electrons).

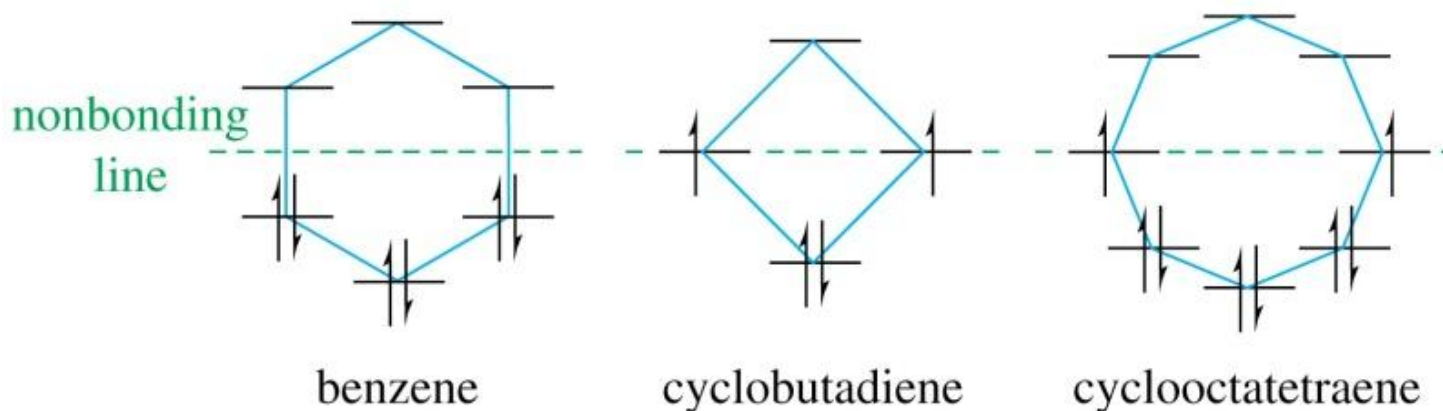
## The Polygon Rule

The patterns of the MO's for benzene and cyclobutadiene are similar to those found for the other annulenes.

In general for an annulene, the MO energy diagram can be predicted by drawing the relevant polygon shape on its *apex*, and drawing MO's at each *vertex*.

The *non-bonding* line passes horizontally through the middle of the polygon.

To obtain the complete MO picture, simply fill the orbitals (according to Hund's Rule) with the appropriate number of electrons.



This is the *polygon rule* for predicting MO's of annulene  $\pi$  systems.

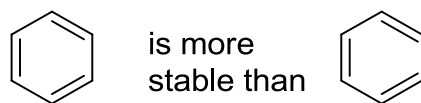
### Aromatic, Antiaromatic and Nonaromatic Compounds

In a more specific, chemical sense, **aromatic** compounds are defined as those which meet the following criteria:

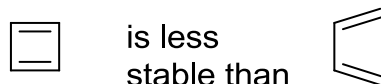
- 1) The structure must be cyclic, and contain some number of conjugated  $\pi$  bonds.
- 2) Each atom in the ring must have an unhybridized p orbital.
- 3) The unhybridized p orbitals must overlap to form a continuous ring of parallel orbitals. This is usually achieved through a planar (or almost planar) arrangement, allowing for the most efficient overlap.
- 4) Delocalization of the  $\pi$  electrons over the ring must result in a **lowering** of the electronic energy.

An antiaromatic compound is one which meets the first three criteria, but delocalization of the  $\pi$  electrons over the ring results in an **increase** of the electronic energy.

**Aromatic** compounds are **more stable** than their open chain counterparts. For example, benzene is more stable than 1,3,5-hexatriene.

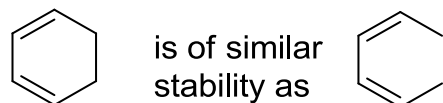


An antiaromatic compound is less stable than its open chain counterpart. For example, cyclobutadiene is less stable than butadiene.



A cyclic compound that does NOT have a continuous, overlapping ring of p orbitals cannot be aromatic or antiaromatic.

The electronic energy is similar to its open chain counterpart. For example 1,3-cyclohexadiene is about as stable as *cis,cis*-2,4-hexadiene.



Such a compound is said to be **nonaromatic** (or **aliphatic**).

### Hückel Aromaticity

Hückel developed a quick way to predict which of the annulenes would be *aromatic*, and which would be *antiaromatic*.

**If** (*and only if*) the molecule in question meets the criteria for being either *aromatic* or *antiaromatic* (i.e. it must have a continuous ring of overlapping p orbitals, arranged in a planar, or almost planar fashion), then Hückel's rule applies.

**Hückel's Rule** states that if the number of  $\pi$  electrons in the cyclic system is equal to  $(4N+2)$ , where N is a whole number integer, then the system is **aromatic**.

If the number of  $\pi$  electrons in the cyclic system is equal to  $4N$ , where N is a whole number integer, then the system is **antiaromatic**.

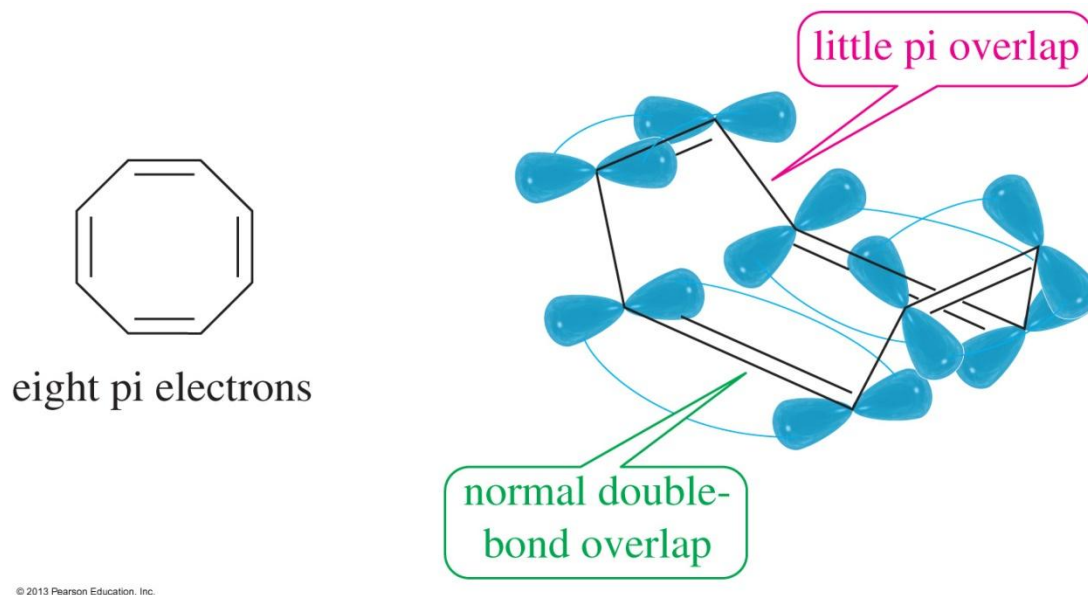
Thus systems with 2, 6, 10, 14, ...  $\pi$  electrons are *aromatic*.

Systems with 4, 8, 12, ...  $\pi$  electrons are *antiaromatic*.

## Exceptions

There are **no** exceptions to the Hückel rule, although there are situations where planarity cannot be achieved, thus preventing (anti-)aromaticity to exist (i.e. making the rule irrelevant).

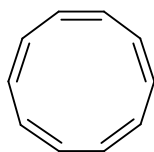
For example, if cyclo-octatetraene was planar, it would be antiaromatic, but it is flexible enough to exist in a tub-like geometry, and therefore is not antiaromatic.



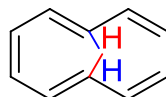
Since it is not planar, it does not meet the necessary criteria for the Hückel rule to be applied.

This also applies larger  $4N$  annulenes, which adopt nonplanar geometries to avoid being antiaromatic. Sometimes, molecules with  $(4N+2)$   $\pi$  electrons **cannot** adopt a planar arrangement, and are therefore non-aromatic.

Examples of this are the all-cis [10] annulene (too strained) and the [10] annulene with two trans double bonds (transannular steric hindrance).

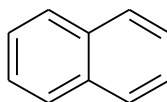


all cis  
non-aromatic  
(too strained  
being planar)



two trans  
non-aromatic  
(too sterically  
crowded to be planar)

However, if the two offending hydrogens are replaced with a C-C single bond ( $\rightarrow$  naphthalene), then aromaticity is observed.



naphthalene  
aromatic

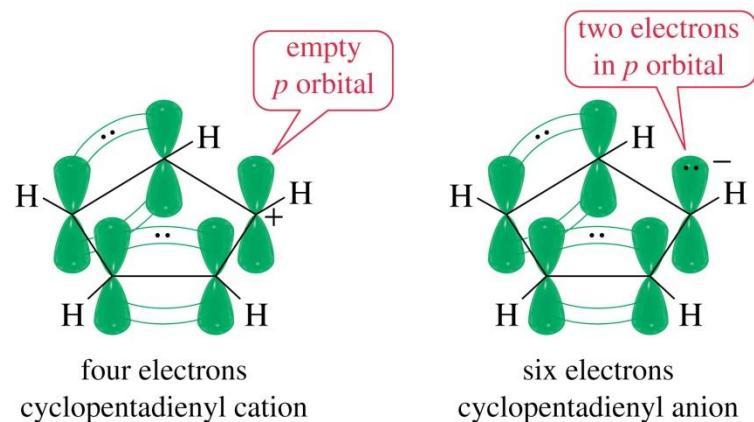
Most of the larger  $4N+2$  annulenes can adopt planar structures, and are therefore aromatic.

## Aromatic Ions and Heteroaromatics

So far we have only considered aromaticity of annulenes. However, it may be extended to cover charged species (e.g. cyclopentadienides), and heteroaromatic species (e.g. pyridine).

### Cyclopentadienyl Ions

If 5  $sp^2$  carbons are joined in a planar ring, then the 5 unhybridized p orbitals could be lined up to form a continuous ring.



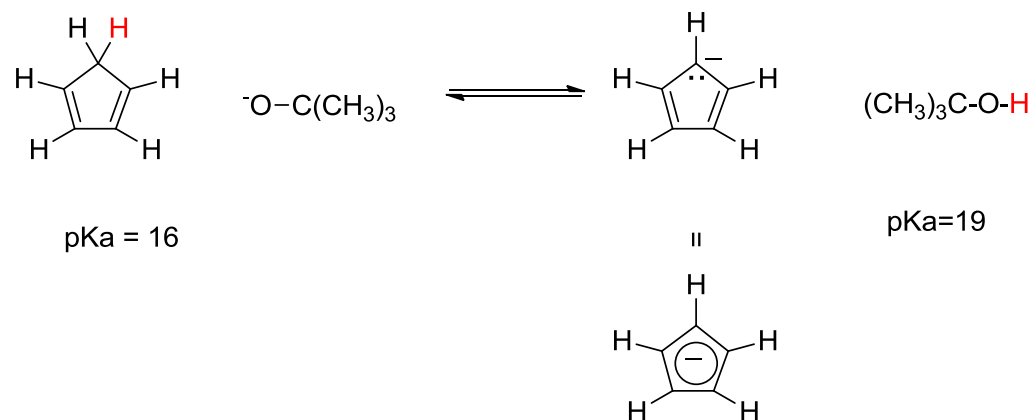
The five  $\pi$  electrons would make this system a **neutral** free radical species.

If we removed an electron to form a cation ( $4\pi$  electrons), then Hückel's rule implies that it would be antiaromatic.

If we added an electron to the radical to produce an anion ( $6\pi$  electrons), then Hückel's rule implies this would be aromatic.

Indeed, the cyclopentadienyl anion (cyclopentadienide) is found to be aromatic, and is therefore unusually **stable** relative to other anions.

Cyclopentadiene **can** be deprotonated (unusual for an alkene) to degenerate cyclopentadienide,  $pK_a = 16$  for cyclopentadiene, whereas cyclohexene has  $pK_a = 46$ .

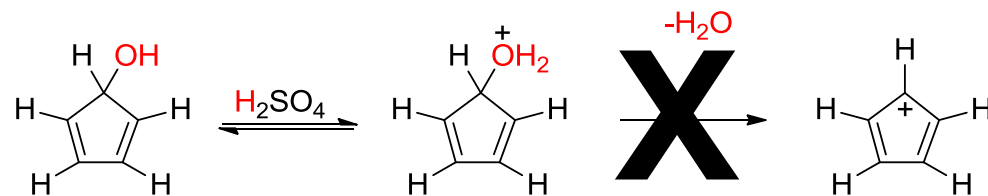


Even though cyclopentadienide is aromatic, that does not necessarily mean that it is as stable as benzene. Cyclopentadienide is still fairly reactive (and reacts with a variety of electrophiles), but it is much more stable than its open chain counterpart.

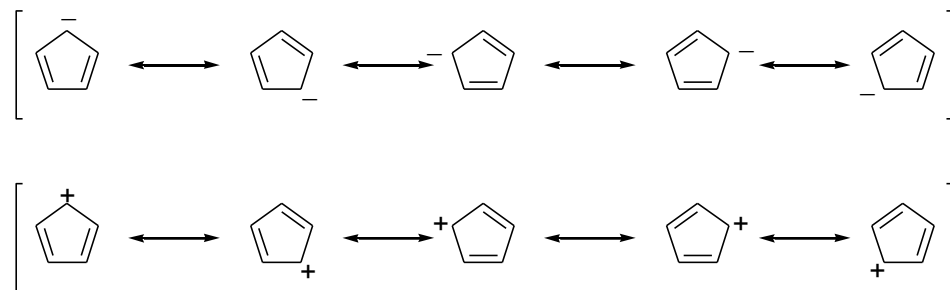


Hückel's rule predicts that the cyclopentadienyl cation would be **antiaromatic**, and indeed it cannot be (easily) formed.

E.g.



A simple resonance approach to the stability of the cyclopentadienyl cation and anion would be misleading, since both have 5 resonance structures, and should therefore be very stable.



This is clearly not the case, and for conjugated cyclic systems, MO theory gives a better prediction of stability.

### Cycloheptatrienyl Ions

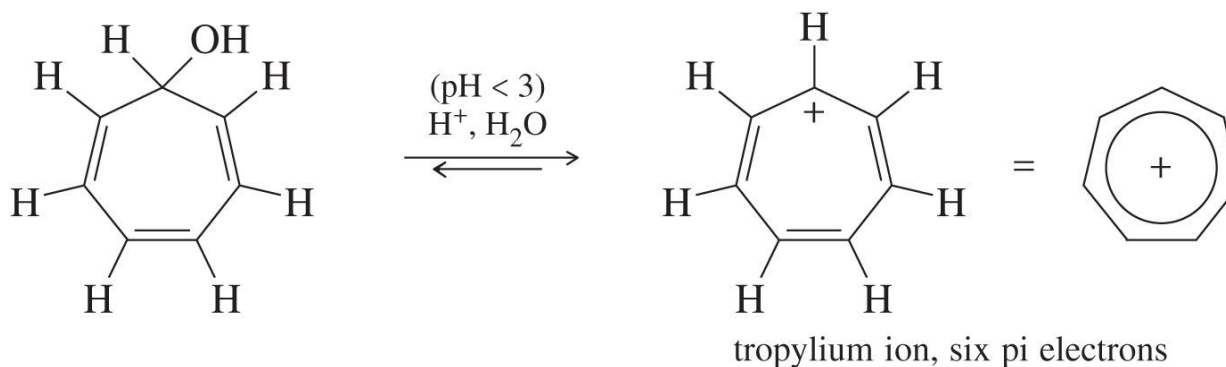
Now if we consider seven  $sp^2$  carbons aligned in a planar ring, this gives us 7  $\pi$  electrons.

So the cycloheptatrienyl anion has 8 electrons, and the cycloheptatrienyl cation has 6 electrons.

Therefore the cycloheptatrienyl anion ( $4N$ ,  $N=2$ ) is antiaromatic (if it were to stay planar), and the cycloheptatrienyl cation ( $4N+2$ ,  $N=1$ ) is aromatic.

Again, it is MO theory that predicts the stability of the cation, and the instability of the anion, whereas resonance structures would lead us to believe that both were very stable.

The cycloheptatrienyl cation is easily formed, and is often called the *tropylium* ion.



It is an *aromatic* carbocation, and therefore less reactive than normal carbocations.

It is, of course, more stable than its open chain analogue.

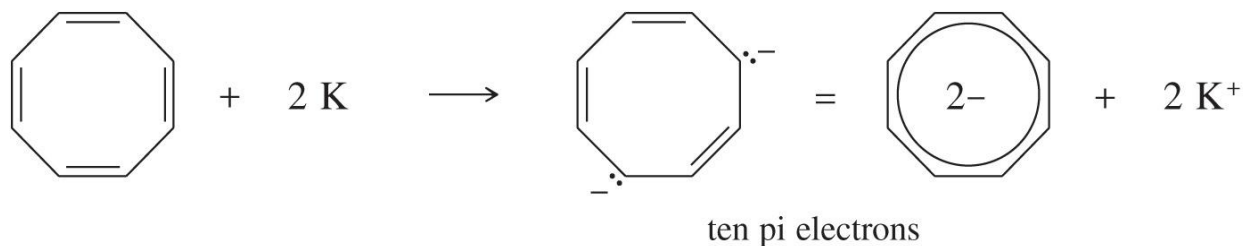
### The Cyclooctatetraene Dianion

Dianions of hydrocarbons are very rare, but since we have seen that aromatic stabilization can lead to stable hydrocarbon ions, what about some aromatic **dianions**?

In fact, it is possible.

Cyclooctatetraene has 8  $\pi$  electrons (4N antiaromatic), but if two electrons were added, the dianion would have 10  $\pi$  electrons, which is (4N+2) aromatic.

Reaction of cyclooctatetraene with potassium metal (a good electron donor,  $K \rightarrow K^+ + e^-$ ), easily generates an aromatic dianion.



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The dianion has a planar, regular octagonal structure, with C-C bond lengths of 1.40Å (c.f. benzene of 1.397Å).

## Summary of Annulenes and Their Ions

### *2 $\pi$ electron systems (aromatic)*



cyclopropenyl cation (cyclopropenium ion)

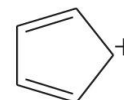
### *4 $\pi$ electron systems (antiaromatic)*



cyclobutadiene



cyclopropenyl anion



cyclopentadienyl cation

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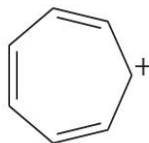
### *6 $\pi$ electron systems (aromatic)*



benzene

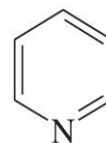


cyclopentadienyl anion  
(cyclopentadienide ion)



cycloheptatrienyl cation  
(tropylium ion)

### *Heterocyclic 6 $\pi$ systems (aromatic)*



pyridine



pyrrole

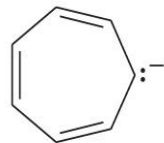


furan

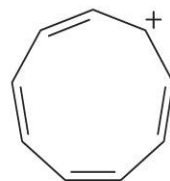
### *8 $\pi$ electron systems (antiaromatic if planar)*



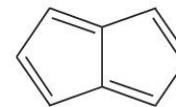
cyclooctatetraene  
(not planar)



cycloheptatrienyl  
anion



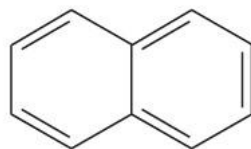
cyclononatetraenyl  
cation



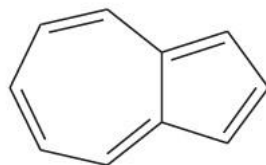
pentalene

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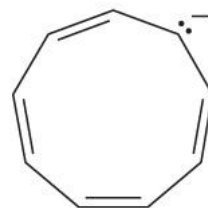
*10  $\pi$  electron systems (aromatic)*



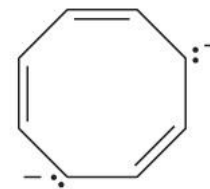
naphthalene



azulene

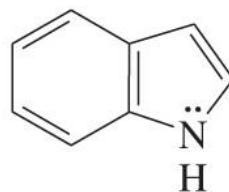


cyclononatetraenyl  
anion

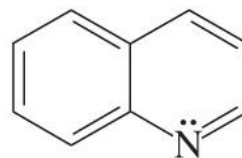


cyclooctatetraenyl  
dianion

*Heterocyclic 10  $\pi$  systems  
(aromatic)*

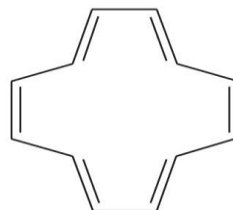


indole

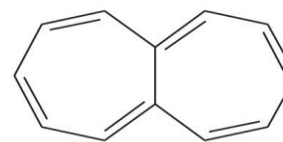


quinoline

*12  $\pi$  electron systems (antiaromatic if planar)*



[12]annulene  
(not planar)



heptalene

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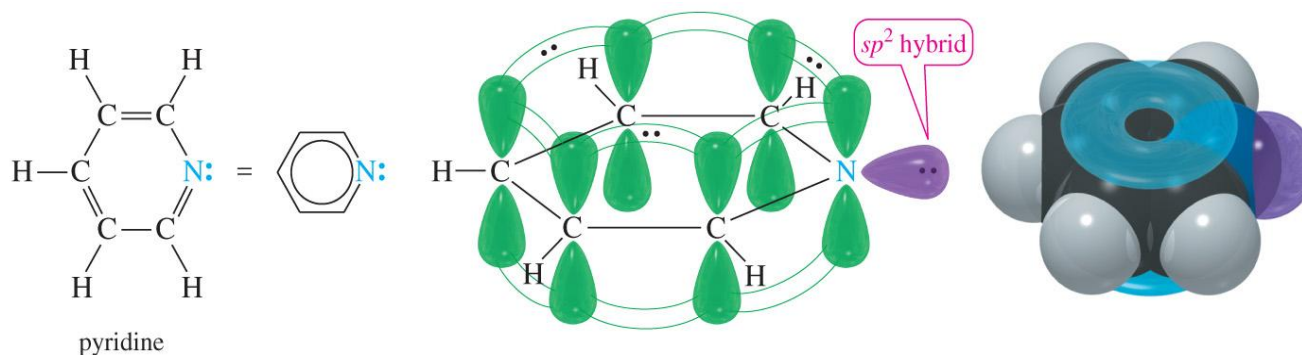
## Heterocyclic Aromatic Compounds

Nitrogen, oxygen and Sulfur are the most common **heteroatoms** found in aromatic compounds.

### Pyridine

Hückel's rule requires a ring of atoms with unhybridized p orbitals, and nitrogen is capable of doing this.

Replacing a C-H in benzene with a Nitrogen produces Pyridine.



Pyridine is a nitrogen containing aromatic analogue of benzene.

The N in pyridine is sigma bonded to two atoms and has a lone pair, and is therefore  $sp^2$  hybridized.

This leaves one electron in an unhybridized p orbital, which contributes to the  $\pi$  system, making a total of 6, and therefore an aromatic molecule (5 x C-H contribute 5 electrons, N contributes 1, = 6,  $4N+2$ ).

The lone pair on the N is in an  $sp^2$  orbital, which means it is directed away from the ring but in the same plane.

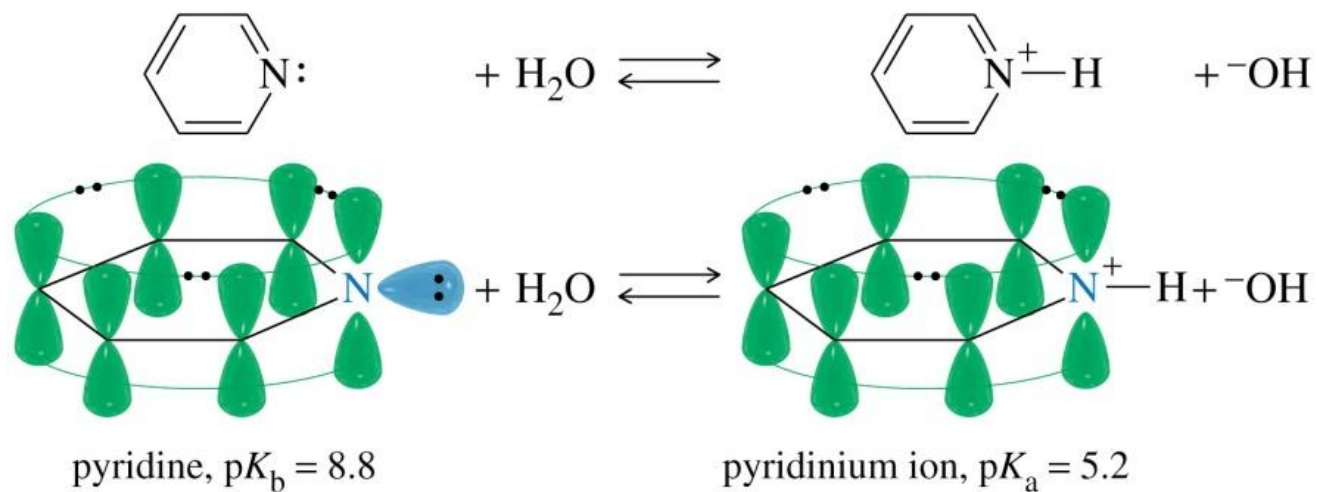
The lone pair of electrons are **not** involved in the aromatic system, and stick out away from the molecule. Pyridine is aromatic, and displays aromatic characteristics such as high resonance energy (27kcal/mol), and undergoes *substitution* as opposed to addition.

The additional lone pair also adds new characteristics to pyridine.

The lone pair makes pyridine capable of acting as a *base*.

In the presence of acids, pyridine will become protonated, generating the *pyridinium ion*.

The pyridinium ion is still aromatic, the lone pair was not involved in the aromatic  $6\pi$  system. The proton is attached to the lone pair of the nitrogen.

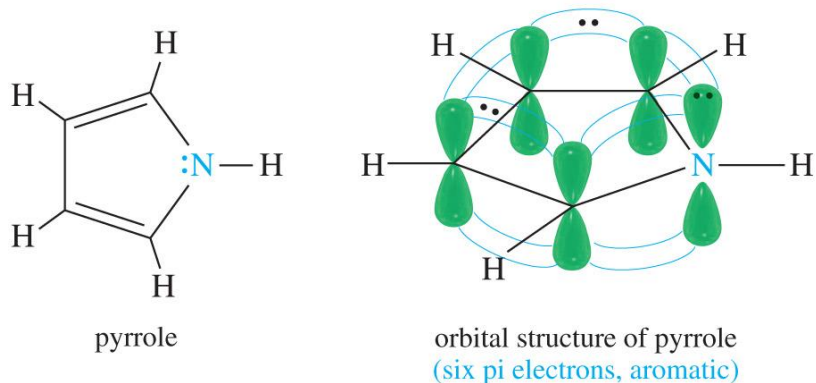


## Pyrrole

Pyrrole is a 5 membered heterocycle which is also aromatic.

It contains an N-H unit and 4 C-H units, with 2 double bonds.

At first look, it may seem that pyrrole only has  $4\pi$  electrons, but the Nitrogen can contribute its lone pair (2 electrons) to the  $\pi$  system, and thus create an aromatic  $6\pi$  system.



This is an (actually another) exception to the hybridization rule.

The Nitrogen is bound to 3 atoms and has a lone pair, it should be  $sp^3$ , but this would not allow for a p orbital to partake in the ring of p orbitals required for aromaticity.

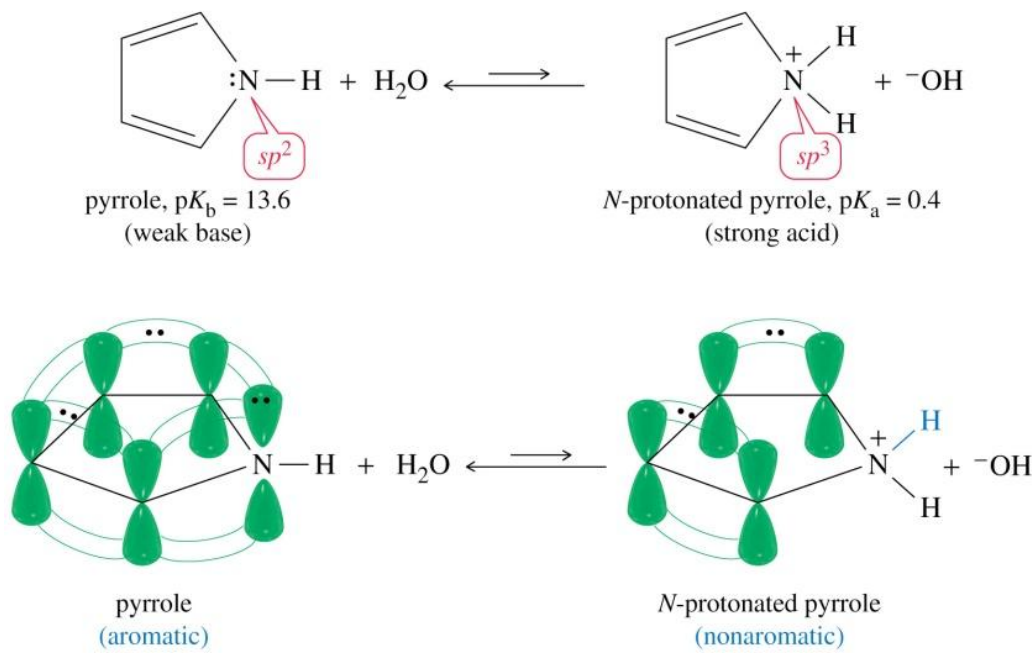
Therefore, N adopts an  $sp^2$  hybridization (for the three bonds to atoms), and puts the lone pair into the remaining p orbital.

This p orbital becomes part of the  $\pi$  system, and contributes the necessary two electrons to make the ring  $4N+2$  aromatic.

In pyrrole, the lone pair of N *is* used in the  $\pi$  system.

Pyrrole is 6  $\pi$  aromatic, and has a resonance energy of 22kcal/mol.

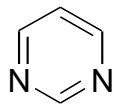
Since the lone pair of N in pyrrole is tied up in the  $\pi$  system, it is much *less available* to act as a base, and therefore pyrrole is a much *weaker base* than pyridine ( $pK_b = 13.6$  for pyrrole, and 8.8 for pyridine).



The protonated pyrrole would no longer be aromatic, because there would no longer be 6 $\pi$  electrons, and also the N would have to be  $sp^3$  (4 bonds) and so have no p orbital for the required ring of p orbitals for aromaticity.

## Pyrimidine and Imidazole

**Pyrimidine** is a six membered heterocycle with two nitrogen atoms in a 1,3 arrangement.

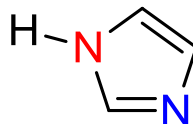


pyrimidine

Both nitrogen atoms behave like pyridine nitrogens. (Each has the lone pair in an  $sp^2$  orbital, with 1 electron in a p orbital for the  $\pi$  system).

These lone pairs are not used in the  $\pi$  system, and are therefore basic.

**Imidazole** is a 5 membered ring with 2 nitrogens which is also aromatic.



imidazole

One **nitrogen** (the one without a H bonded) behaves like a pyridine Nitrogen with its lone pair in an  $sp^2$  orbital, which is not involved in the  $\pi$  bonding.

The other **nitrogen** (N-H) is like a pyrrole nitrogen, and uses an  $sp^2$  to bond to H, and puts its lone pair in a p orbital to contribute 2 electrons to the  $\pi$  system.

This **nitrogen** is therefore not basic.

### Furan and Thiophene

Furan is an aromatic 5 membered ring that is similar to pyrrole, but has an oxygen in place of the N-H.



Furan

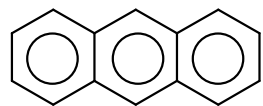


Thiophene

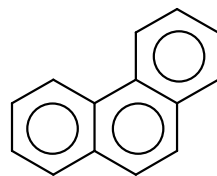
Thiophene is the sulfur analogue.

### Polynuclear Aromatic Hydrocarbons

These compounds (often called PAH's or PNA's) are composed of two or more **fused** benzene rings. (Recall that fused rings share two carbons and the bond between them).

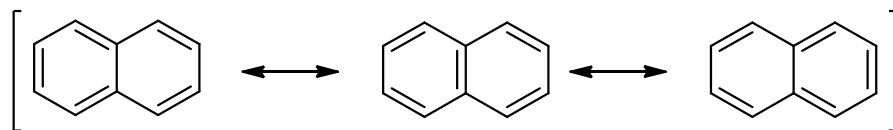


Anthracene

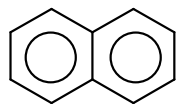


Phenanthrene

Naphthalene is the simplest fused aromatic compound, and is comprised of two fused benzene rings.



Naphthalene can be represented by 3 different Kekulé structures, but is more commonly drawn with the circle notation.

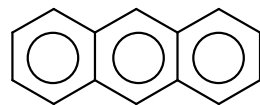


The aromatic system contains 10  $\pi$  electrons, and it has 60kcal/mol resonance energy.

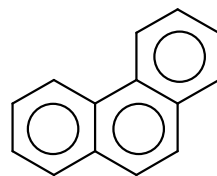
This is less than 2 x the amount for benzene (36kcal/mol) since this is a 10 $\pi$  system (not 12  $\pi$ ).

#### Anthracene and Phenanthrene

These tricyclic fused compounds both have 14  $\pi$  electrons, and are therefore aromatic.



Anthracene

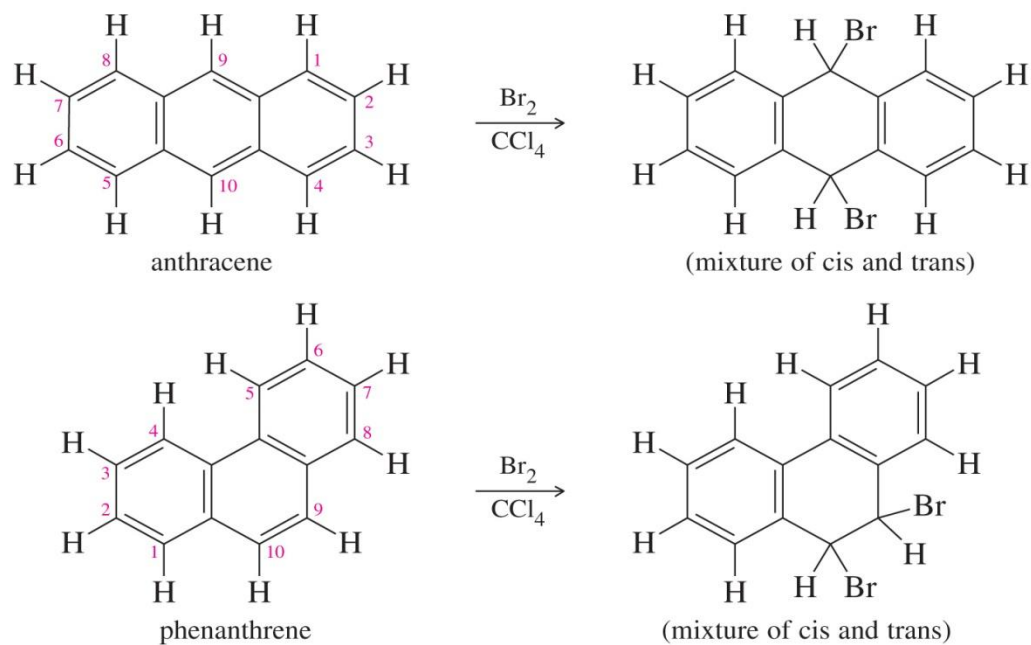


Phenanthrene

Their resonance energies are 84kcal/mol and 91kcal/mol respectively.

As the number of aromatic rings increases, the resonance energy per ring decreases, this means the larger compounds have less aromatic stability, and as a result they start to display more (alkene) reactivity.

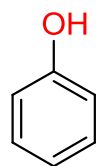
E.g.



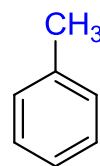
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## Nomenclature of Benzene Derivatives

Aromatic compounds have been widely used for the last hundred years, and most are referred to almost exclusively by their common names.

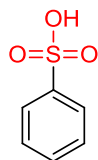


Phenol

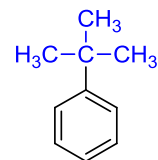


Toluene

Some are referred to as simple derivatives of benzene.



benzenesulfonic acid

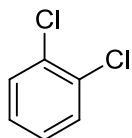


<sup>t</sup>Butylbenzene

*Disubstituted* benzenes are commonly named using *ortho*, *meta* and *para* prefixes. These are often shorted to o-, m- and p-.

However, these are **non-IUPAC**, and *numbers* have to be given to the substituents.

E.g.

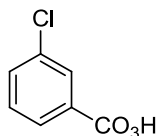


**common:** ortho-dichlorobenzene

**IUPAC:** 1,2-dichlorobenzene

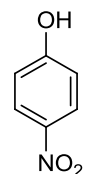
In certain cases, the functional group defines the base name, and this also defines C-1.

E.g.



**(m-cpba)**

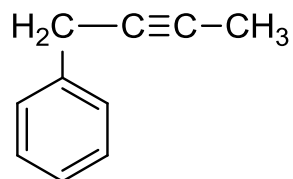
3-chloroperoxybenzoic acid



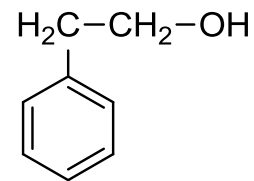
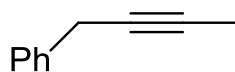
**(p-nitrophenol)**

4-nitrophenol

When the benzene group is simply a *substituent*, it is called a *Phenyl* group, and is often abbreviated to *Ph-* or  $\phi$ .



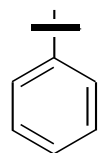
1-phenyl-2-butyne



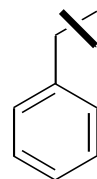
$\text{PhCH}_2\text{CH}_2\text{OH}$

2-phenylethanol

Do not confuse the *benzyl* group with the *phenyl* group.



Phenyl-



Benzyl-

Just as any alkyl group can be written as **R-**, any aryl (aromatic) group is represented by **Ar-**.