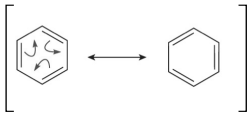
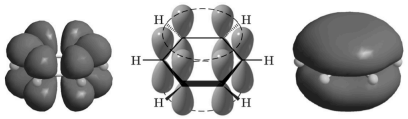
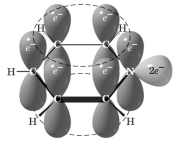
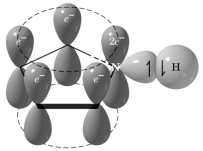




Aromatic Compounds

Chapter 17

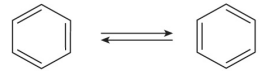




Benzene

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Kekulé suggested the following structure for benzene:

Kekulé description: An equilibrium



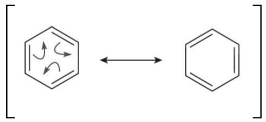
This structure implies that the C–C bonds should have **two different lengths.**

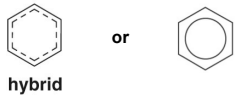
- three short bonds
- three long bonds

Any structure for benzene must account for the following facts:

1. It contains a six-membered ring and three additional degrees of unsaturation.
2. It is planar.
3. All C–C bond lengths are equal.

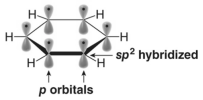
Resonance Hybrid of Benzene





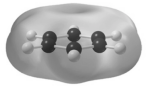
hybrid

The electrons in the π bonds are **delocalized** around the ring.

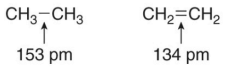


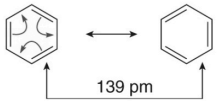
View of the *p* orbital overlap

Electrostatic potential plot



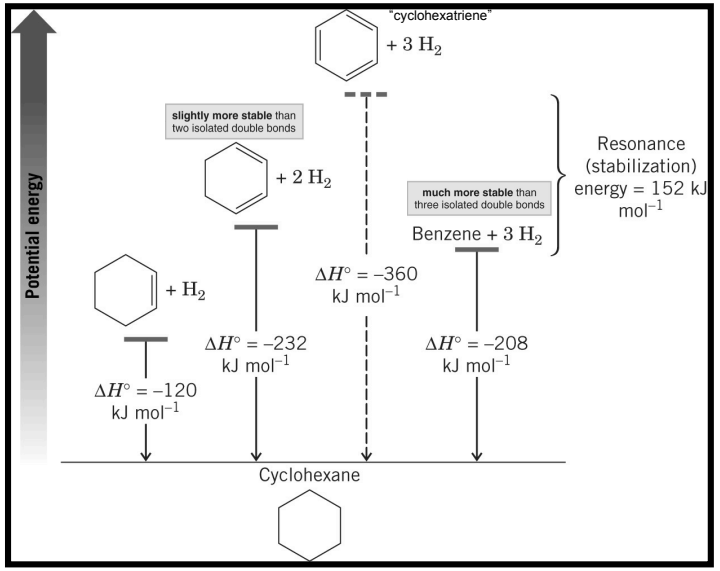
Benzene Bond Lengths





The C–C bonds in benzene are equal and intermediate in length.

Resonance Stabilization Energy of Benzene

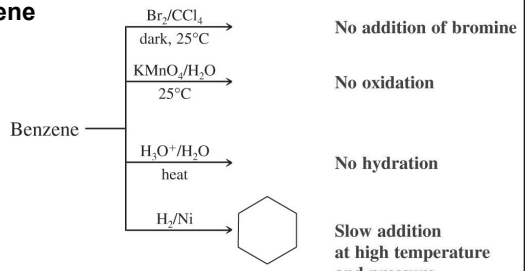


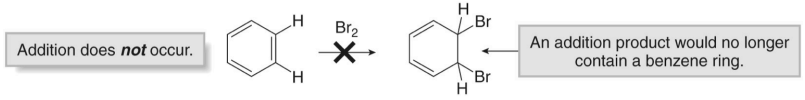
The Stability of Benzene

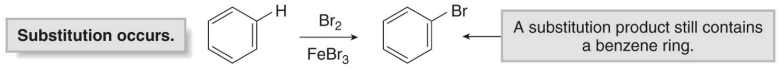
- Benzene is much more stable than would be expected based on calculations for “cyclohexatriene”.
- A reasonable prediction for the heat of hydrogenation of hypothetical cyclohexatriene is -360 kJ mol^{-1} (3 times that of cyclohexene, -120 kJ mol^{-1}).
- The experimentally determined heat of hydrogenation for benzene is -208 kJ mol^{-1}, 152 kJ mol^{-1} more stable than hypothetical cyclohexatriene.
- This difference is the resonance stabilization energy.

Reactivity / Stability of Benzene

- Benzene does not undergo any of the regular reactions of alkenes such as addition or oxidation.
- Benzene can be induced to react with bromine if a Lewis acid catalyst is present however the reaction is a *substitution* and not an addition. ***Aromaticity is conserved.***

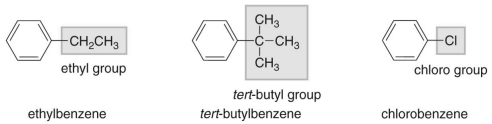




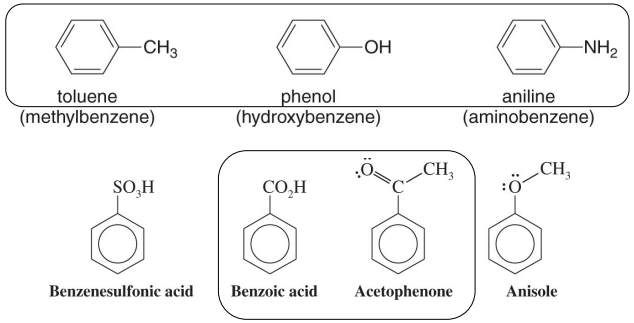


Naming Substituted Benzenes

- To name a benzene ring with one substituent, name the substituent and add the word benzene.

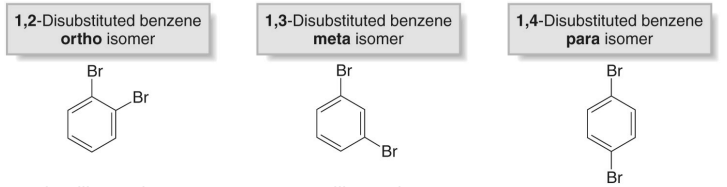


- Many monosubstituted benzenes have common names which you must also learn (know the names and structures for the circled compounds).



Nomenclature of Benzene Derivatives

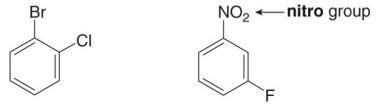
- There are three different ways that two groups can be attached to a benzene ring, so a prefix—ortho, meta, or para—can be used to designate the relative position of the two substituents.



Nomenclature of Benzene Derivatives

- If the two groups on the benzene ring are different, alphabetize the names of the substituents preceding the word *benzene*.
- If one substituent is part of a common root, name the molecule as a derivative of that monosubstituted benzene.

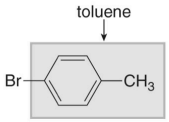
Alphabetize two different substituent names:



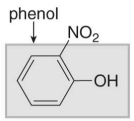
***o*-bromochloro-benzene**

***m*-fluoronitro-benzene**

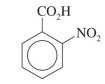
Use a common root name:



***p*-bromo**toluene

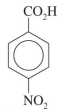


***o*-nitro**phenol

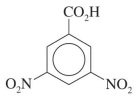


2-Nitrobenzoic acid (*o*-nitrobenzoic acid)

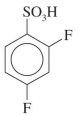
3-Nitrobenzoic acid (*m*-nitrobenzoic acid)



4-Nitrobenzoic acid (*p*-nitrobenzoic acid)



3,5-Dinitrobenzoic acid



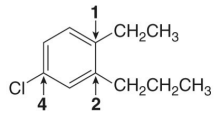
2,4-Difluorobenzenesulfonic acid

Rules for Naming Benzene Derivatives

For three or more substituents on a benzene ring:

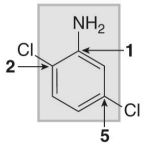
1. Number to give the lowest possible numbers around the ring.
2. Alphabetize the substituent names.
3. When substituents are part of common roots, name the molecule as a derivative of that monosubstituted benzene.
   - The substituent that comprises the common root is located at C1.

Examples of naming polysubstituted benzenes



- Assign the lowest set of numbers.
- Alphabetize the names of all the substituents.

4-chloro-1-ethyl-2-propylbenzene



- Name the molecule as a derivative of the common root **aniline.**
- Designate the position of the NH_2 group as "1," and then assign the lowest possible set of numbers to the other substituents.

2,5-dichloroaniline

Naming Benzene as a Substituent

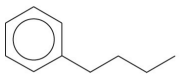
- A benzene substituent is called a phenyl group, and it can be abbreviated in a structure as "Ph-".

phenyl group C_6H_5-

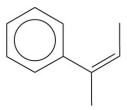
phenol

- A phenyl group (C_6H_5-) is formed by removing one hydrogen from benzene (C_6H_6).

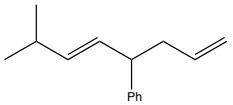
- Benzene as the root compound vs. a substituent:

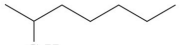


Butylbenzene



(Z)-2-Phenyl-2-butene

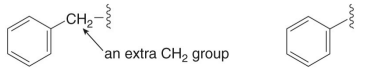




2-Phenylheptane

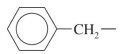
Benzyl and Aryl Groups

- The benzyl group, another common substituent that contains a benzene ring, differs from a phenyl group.

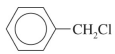


benzyl group $C_6H_5CH_2-$

phenyl group C_6H_5-



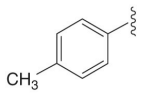
The benzyl group (the phenylmethyl group)

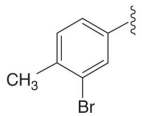


Benzyl chloride (phenylmethyl chloride or BzCl)

- Substituents derived from other substituted aromatic rings are collectively known as aryl groups.

Examples of aryl groups

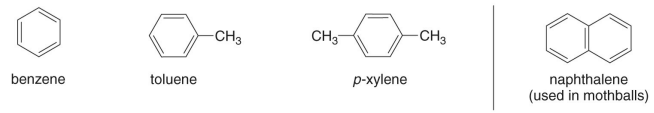




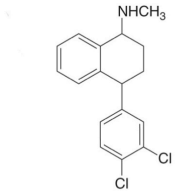
Interesting Aromatic Compounds

- Benzene and toluene, the simplest aromatic hydrocarbons obtained from petroleum refining, are useful starting materials for synthetic polymers.
- They are also two of the components of the BTX mixture added to gasoline to boost octane ratings.
- Compounds containing two or more benzene rings that share carbon–carbon bonds are called polycyclic aromatic hydrocarbons (PAHs).
- Naphthalene, the simplest PAH, is the active ingredient in mothballs.

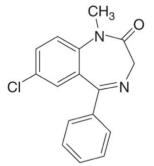
The components of the gasoline additive BTX



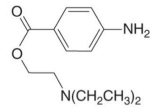
Some Drugs that Contain a Benzene Ring



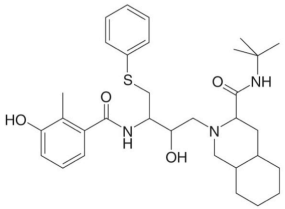
- Trade name: **Zoloft**
- Generic name: **sertraline**
- Use: a psychotherapeutic drug for depression and panic disorders



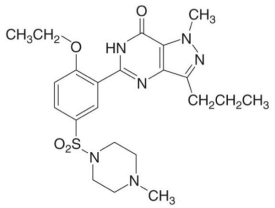
- Trade name: **Valium**
- Generic name: **diazepam**
- Use: a sedative



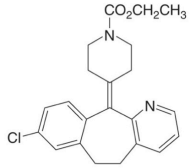
- Trade name: **Novocain**
- Generic name: **procaine**
- Use: a local anesthetic



- Trade name: **Viracept**
- Generic name: **nelfinavir**
- Use: an antiviral drug used to treat HIV



- Trade name: **Viagra**
- Generic name: **sildenafil**
- Use: a drug used to treat erectile dysfunction



- Trade name: **Claritin**
- Generic name: **loratadine**
- Use: an antihistamine for seasonal allergies

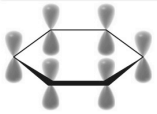
The Criteria for Aromaticity

Four structural criteria must be satisfied for a compound to be aromatic:

1. A molecule must be cyclic.

- To be aromatic, each *p* orbital must overlap with *p* orbitals on adjacent atoms.

Cyclic compound

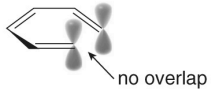


benzene

Every *p* orbital overlaps with two neighboring *p* orbitals.

aromatic

Acyclic compound



1,3,5-hexatriene

There can be no overlap between the *p* orbitals on the two terminal C's.

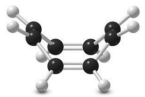
not aromatic

The Criteria for Aromaticity

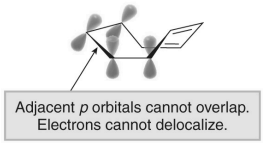
2. A molecule must be planar.

- All adjacent *p* orbitals must be aligned so that the π electron density can be delocalized.

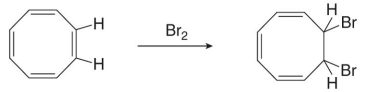
cyclooctatetraene
not aromatic



a tub-shaped, eight-membered ring



- Since cyclooctatetraene is nonplanar and not aromatic, it undergoes addition reactions just like those of other alkenes.



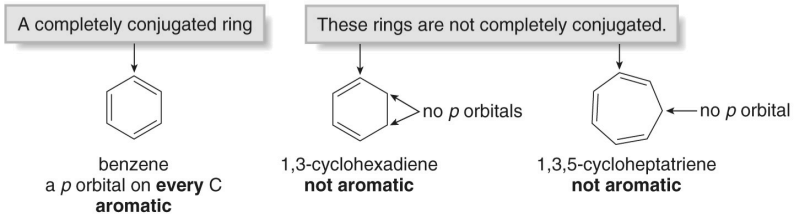
cyclooctatetraene

addition product

The Criteria for Aromaticity

3. A molecule must be completely conjugated.

- Aromatic compounds must have a *p* orbital on every atom.



The Criteria for Aromaticity

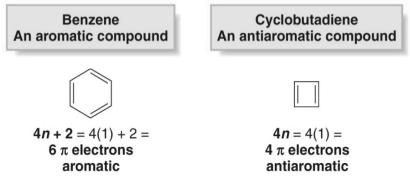
4. A molecule must satisfy Hückel's rule, and contain a particular number of π electrons.

- An aromatic compound must contain $4n + 2$ π electrons (n = 0, 1, 2, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic.*

- Benzene is aromatic and especially stable because it contains 6 π electrons.
- Cyclobutadiene is antiaromatic and especially unstable because it contains 4 π electrons.

The Number of π Electrons That Satisfy Hückel's Rule

n	4*n* + 2
0	2
1	6
2	10
3	14
4, etc.	18



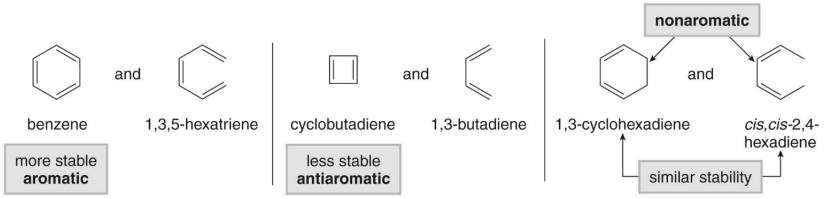
Aromatic, Antiaromatic, and Nonaromatic

- Considering aromaticity, a compound can be classified in one of three ways:

1. **Aromatic** - A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons
2. **Antiaromatic** - A cyclic, planar, completely conjugated compound with $4n$ π electrons
3. **Not aromatic (nonaromatic)** - A compound that lacks one (or more) of the following requirements for aromaticity; being cyclic, planar, and completely conjugated

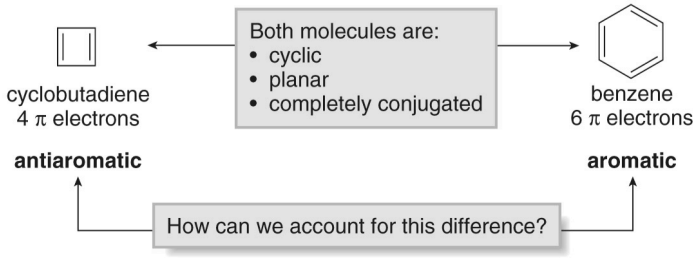
Stability of Aromatics

- An aromatic compound is *more* stable than a similar acyclic compound having the same number of π electrons. Benzene is more stable than 1,3,5-hexatriene.
- An antiaromatic compound is *less* stable than an acyclic compound having the same number of π electrons. Cyclobutadiene is less stable than 1,3-butadiene.
- A compound that is not aromatic is *similar* in stability to an acyclic compound having the same number of π electrons. 1,3-Cyclohexadiene is similar in stability to *cis,cis*-2,4-hexadiene, so it is not aromatic.



The Basis of Hückel's Rule

- Why does the number of π electrons determine whether a compound is aromatic?
- The basis of aromaticity can be better understood by considering orbitals and bonding.

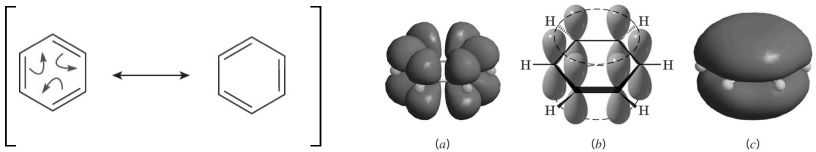


Molecular Orbital Theory

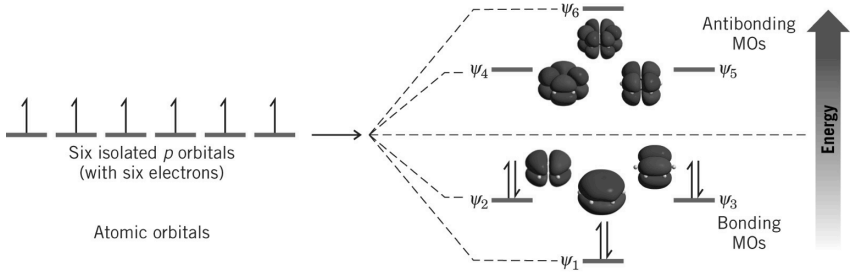
- We have been applying valence bond theory to explain how bonds between atoms are formed in aromatics.
  - However, valence bond theory is inadequate for describing systems with many adjacent *p* orbitals that overlap, as is the case in aromatic compounds.
- Molecular orbital (MO) theory permits a better explanation of bonding in aromatic systems.
  - MO theory describes bonds as the mathematical combination of atomic orbitals that form a new set of orbitals called molecular orbitals (MOs).
  - A molecular orbital occupies a region of space in a molecule where electrons are likely to be found.

MO Theory Explanation of the Structure of Benzene

- Valence Bond (Resonance):



- MO Theory: six π molecular orbitals for benzene.

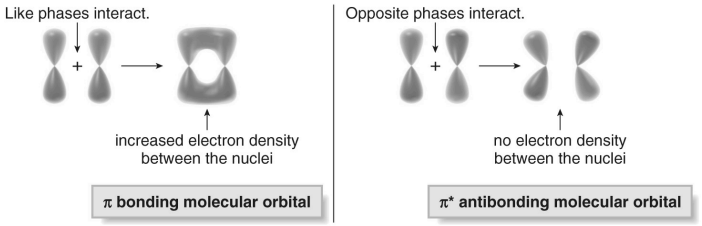


Forming Molecular Orbitals

- When forming molecular orbitals from atomic orbitals, keep in mind that a set of *n* atomic orbitals forms *n* molecular orbitals.
- If two atomic orbitals combine, two molecular orbitals are formed.
- Recall that aromaticity is based on *p* orbital overlap.
- Also note that the two lobes of each *p* orbital are opposite in phase, with a node of electron density at the nucleus.
- When two *p* orbitals combine, two molecular orbitals should form.

Bonding and Antibonding Orbitals

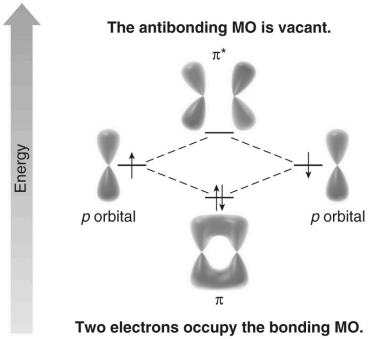
- The combination of two *p* orbitals can be constructive - that is, with like phases interacting - or destructive, that is, with opposite phases interacting.



- When two *p* orbitals of similar phase overlap side-by-side, a π bonding molecular orbital results.
- When two *p* orbitals of opposite phase overlap side-by-side, a π* antibonding orbital results.

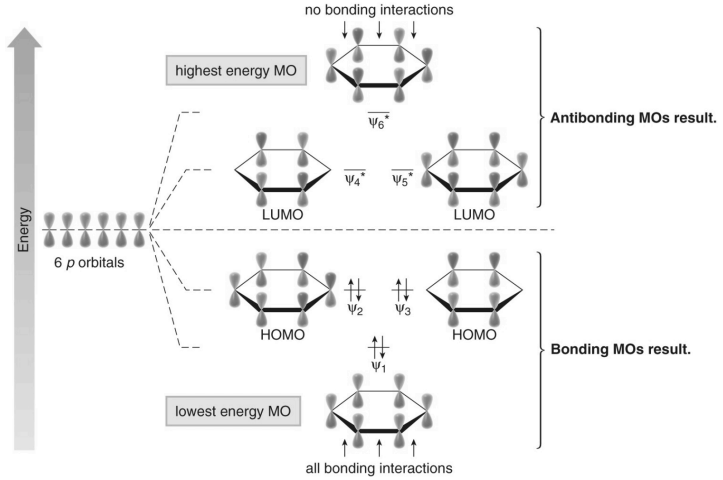
Formation of π and π* Molecular Orbitals

- Two atomic *p* orbitals combine to form two molecular orbitals.
- The bonding π MO is lower in energy than the two *p* orbitals.
- The π* antibonding MO is higher in energy because a destabilizing node results, which pushes nuclei apart when orbitals of opposite phase combine.



π Molecular Orbitals for Benzene

- Since each of the six carbon atoms in benzene has a *p* orbital, six atomic *p* orbitals combine to form six π MOs.



Molecular Orbitals for Benzene

- Some important features of the six benzene MOs:
  - The larger the number of p-orbital bonding interactions, the lower in energy the lowest π MO.
  - The larger the number of nodes, the higher in energy the MO.
  - Two pairs of MOs with the same energy (ψ2 and ψ3; ψ4* and ψ5*) are called degenerate orbitals.
  - The highest energy orbital that contains electrons is called the highest occupied molecular orbital (HOMO).
  - The lowest energy orbital that does not contain electrons is called the lowest unoccupied molecular orbital (LUMO).

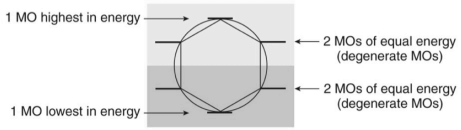
Inscribed Polygon Method of Predicting Aromaticity

How To Use the Inscribed Polygon Method to Determine the Relative Energies of MOs for Cyclic, Completely Conjugated Compounds

Example Plot the relative energies of the MOs of benzene

Step [1] Draw the polygon in question inside a circle with its vertices touching the circle and one of the vertices pointing down. Mark the points at which the polygon intersects the circle.

- Inscribe a hexagon inside a circle for benzene. The six vertices of the hexagon form six points of intersection, corresponding to the six MOs of benzene. The pattern—a single MO having the lowest energy, two degenerate pairs of MOs, and a single highest energy MO—matches that found in Figure 17.9.



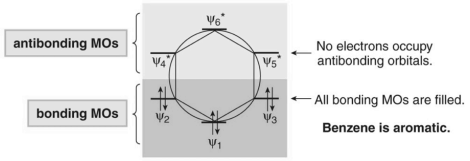
Step [2] Draw a line horizontally through the center of the circle and label MOs as bonding, nonbonding, or antibonding.

- **MOs below this line are bonding,** and lower in energy than the *p* orbitals from which they were formed. Benzene has three bonding MOs.
- **MOs at this line are nonbonding,** and equal in energy to the *p* orbitals from which they were formed. Benzene has no nonbonding MOs.
- **MOs above this line are antibonding,** and higher in energy than the *p* orbitals from which they were formed. Benzene has three antibonding MOs.

Inscribed Polygon Method of Predicting Aromaticity

Step [3] Add the electrons, beginning with the lowest energy MO.

- **All the bonding MOs (and the HOMOs) are completely filled in aromatic compounds. No π electrons occupy antibonding MOs.**
- Benzene is aromatic because it has six π electrons that completely fill the bonding MOs.

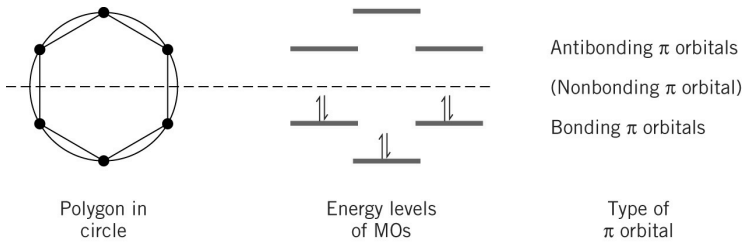


- This method works for all monocyclic completely conjugated systems regardless of ring size.
- The total number of MOs always equals the number of vertices of the polygon.
- The inscribed polygon method is consistent with Hückel's 4*n* + 2 rule—there is always one lowest energy bonding MO that can hold two π electrons and the other bonding MOs come in degenerate pairs that can hold a total of four π electrons.

Predicting Aromaticity (simplified)

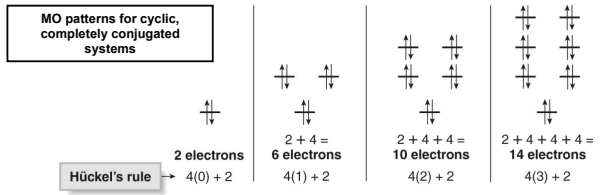
The *polygon-and-circle method* allows the estimation of the relative energies of orbitals of a system with a cyclic, continuous array of *p* orbitals.

1. A polygon corresponding to the ring is inscribed in a circle with one point of the polygon pointing directly down.
2. A horizontal line is drawn where vertices of the polygon touch the circle - each line corresponds to the energy level of the π MOs at those atoms.
3. A dashed horizontal line half way up the circle indicates the separation of bonding and antibonding orbitals.

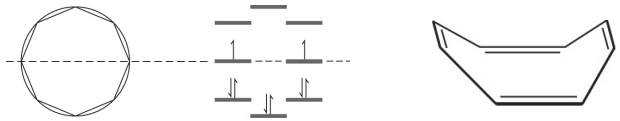


MO Patterns Leading to Aromaticity

- For the compound to be aromatic, these MOs must be completely filled with electrons, so the "magic numbers" for aromaticity fit Hückel's 4*n* + 2 rule.



- Cyclooctatetraene, with 4n electrons has two nonbonding orbitals each with one electron.
- This is an unstable configuration. If it were planar, the compound would be antiaromatic. Instead, cyclooctatetraene adopts a nonplanar conformation with localized p bonds to avoid this instability.

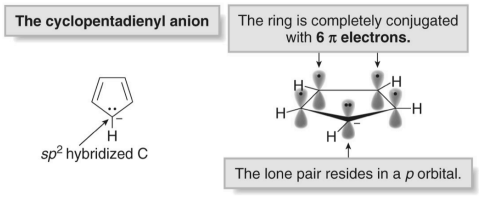


Cyclopentadienyl Anion

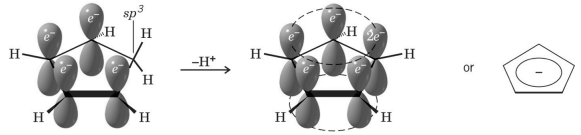
- Cyclopentadiene itself is not aromatic because it is not fully conjugated.
- However, cyclopentadiene is much more acidic (pK_a = 15) than most hydrocarbons because its conjugate base is aromatic and therefore, very stable.
- Loss of a proton causes the cyclopentadienyl anion to become fully conjugated and consequently aromatic.
- Cyclopentadienyl anion has 6 π electrons in a cyclic, continuous π-electron system, and hence follows the 4n + 2 rule for aromaticity.

cyclopentadiene
not aromatic
pK_a = 15

cyclopentadienyl anion
aromatic
a stabilized conjugate base



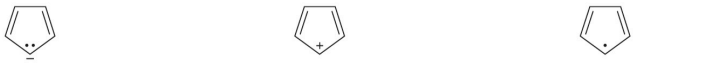
- The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.



Cyclopentadiene Cyclopentadienyl anion

Cyclopentadienyl Compounds

- Having the "right" number of electrons is necessary for a species to be unusually stable due to aromaticity.
- Thus, although five resonance structures can also be drawn for the cyclopentadienyl cation and radical, only the cyclopentadienyl anion has 6 π electrons, a number that satisfies Hückel's rule.



cyclopentadienyl anion
- **6** π electrons
- contains $4n + 2$ π electrons

aromatic

cyclopentadienyl cation
- **4** π electrons
- contains $4n$ π electrons

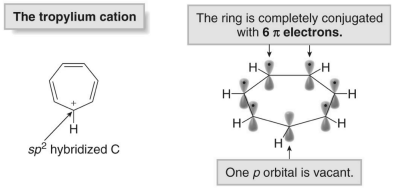
antiaromatic

cyclopentadienyl radical
- **5** π electrons
- does not contain either $4n$ or $4n + 2$ π electrons

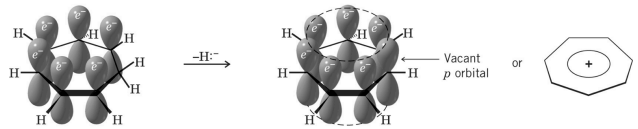
nonaromatic

Tropylium Cation

- The tropylium cation is a planer carbocation with three double bonds and a positive charge contained in a seven-membered ring.
- Because the tropylium cation has three π bonds and no other nonbonded electron pairs, it contains six π electrons and is fully conjugated, thereby satisfying Hückel's rule.

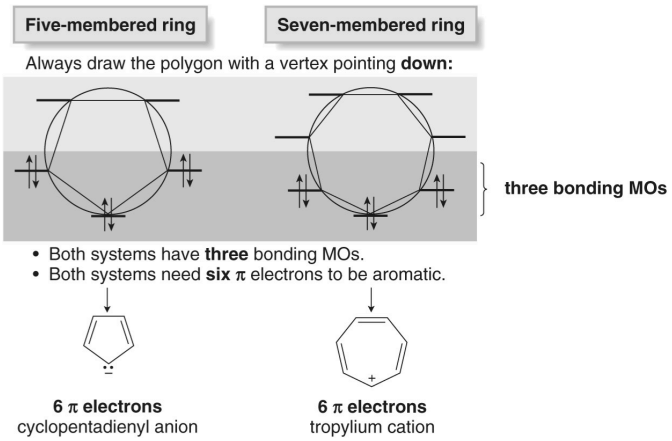


- The tropylium cation is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.



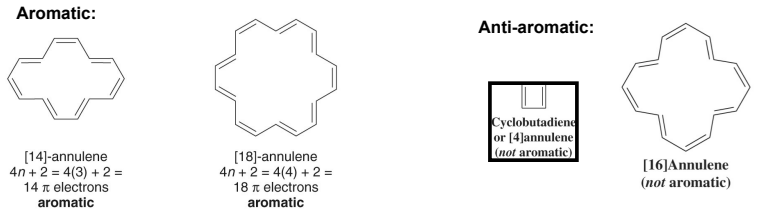
Cycloheptatriene Cycloheptatrienyl cation

Molecular Orbitals & Aromatic Ions

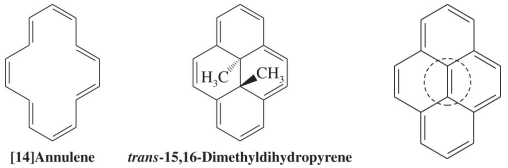


Larger Aromatic Rings

- Completely conjugated rings larger than benzene are also aromatic if they are planar and have $4n + 2$ π electrons.
- Hydrocarbons containing a single ring with alternating double and single bonds are called annulenes.

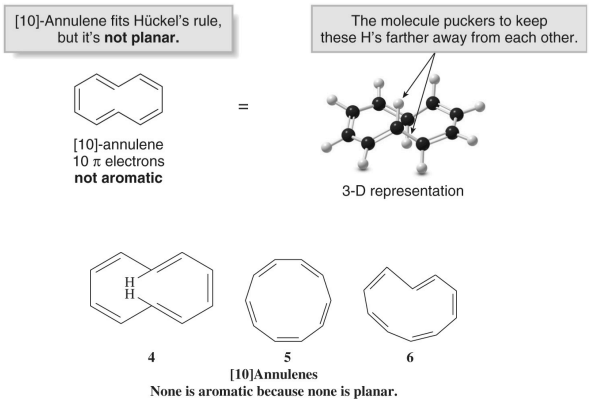


- [14]-annulene analogs:



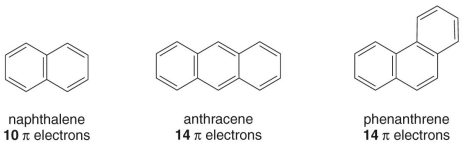
Importance of Planarity

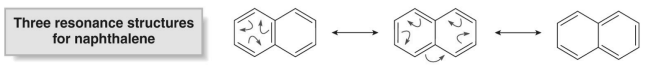
- [10]-Annulene has 10 π electrons, which satisfies Hückel's rule, but a planar molecule would place the two H atoms inside the ring too close to each other.
- Thus, the ring puckers to relieve this strain.
- Since [10]-annulene is not planar, the 10 π electrons cannot delocalize over the entire ring and it is not aromatic.

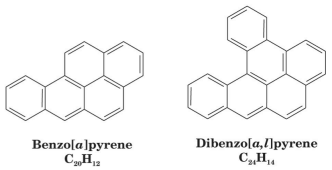


Fused Ring Aromatics

- Two or more six-membered rings with alternating double and single bonds can be fused together to form polycyclic aromatic hydrocarbons (PAH).
- Naphthalene is the simplest PAH.
- There are two different ways to join three rings together, forming anthracene and phenanthrene.

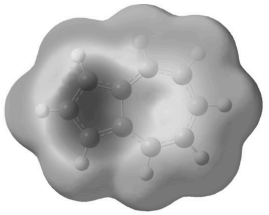


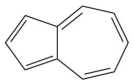




Nonbenzenoid Aromatic Compounds

- Nonbenzenoid aromatic compounds do not contain benzene rings.
- Examples already discussed include the cyclopentadienyl anion and the aromatic annulenes (except [6]-annulene).
- Another possibility is fused ring systems that do not include 6-membered rings, but otherwise fulfill all of the requirements for aromaticity.
- *Example:* **Azulene**
  - It has substantial resonance energy and also substantial separation of charge, as shown in the electrostatic potential map.





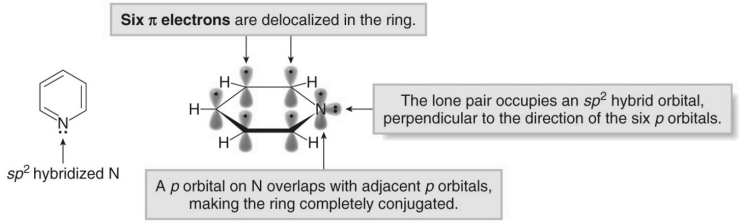
Azulene

Aromatic Heterocyles

- Heterocycles are cyclic, organic compounds containing oxygen, nitrogen, or sulfur, and may or may not also be aromatic.
- An example of an aromatic heterocycle is pyridine.

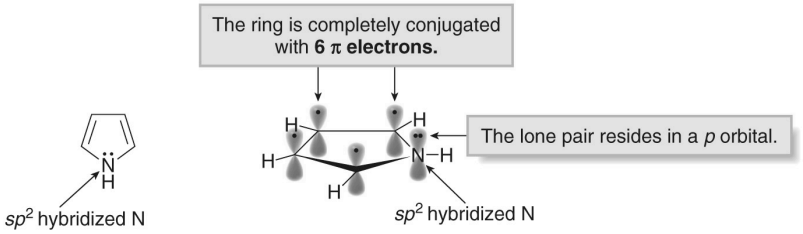
two resonance structures for pyridine
6 π electrons

- Heteroatoms may participate in aromaticity by sharing one electron into the delocalized π system of the compound. In that case, the lone pair(s) of the heteroatom remain localized to that atom.
- Pyridine is aromatic in this way. The N participates in resonance just as a C in benzene does. However instead of having a bond to a H, the nitrogen has a lone pair.
- The lone pair on nitrogen is available to react with protons and so pyridine is basic.

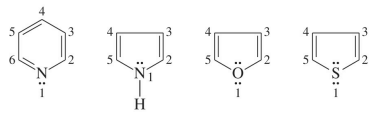


Aromatic Heterocycles

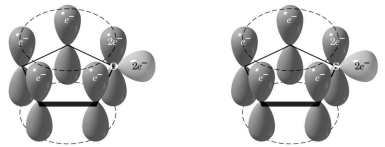
- Pyrrole is another example of an aromatic heterocycle. It contains a five-membered ring with two π bonds and one nitrogen atom.
- Pyrrole has a *p* orbital on every adjacent atom, so it is completely conjugated.
- Pyrrole has six π electrons—four from the π bonds and two from the lone pair.
- Pyrrole is cyclic, planar, completely conjugated, and has $4n + 2$ π electrons, so it is aromatic.
- Pyrrole is isoelectronic to the cyclopentadienyl anion.
- The lone pair of pyrrole is part of the aromatic system and not available for protonation; pyrrole is therefore not basic.



Common Aromatic Heterocycles

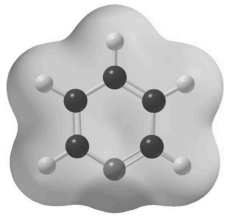


Pyridine **Pyrrole** **Furan** **Thiophene**

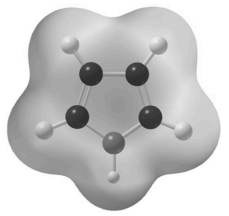


Electrostatic Potential of Aromatic Heterocycles

pyridine

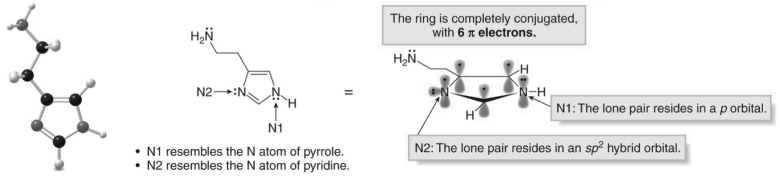


pyrrole



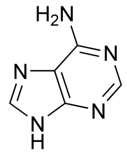
Biologically Heterocycles

- Histamine is a biologically active amine formed in many tissues.
- It is an aromatic heterocycle with two N atoms—one which is similar to the N atom of pyridine, and the other which is similar to the N atom of pyrrole.



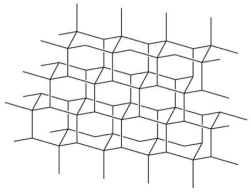
- N1 resembles the N atom of pyrrole.
- N2 resembles the N atom of pyridine.

Adenine

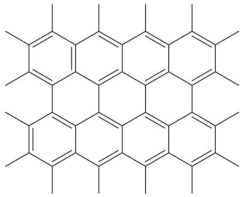


Diamond and Graphite

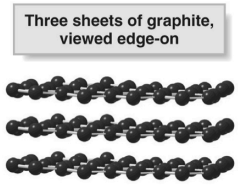
- The two most common elemental forms of carbon are diamond and graphite.
- Their physical characteristics are very different because their molecular structures are very different.
- Carbons in diamods are all sp^3-hybridized. Diamonds are not aromatic (no π-bonds at all).
- Graphite forms planar sheets of interlocking six-membered rings with alternating single and double bonds. Graphite is aromatic.



diamond
an "infinite" array of six-membered rings, covalently bonded in three dimensions



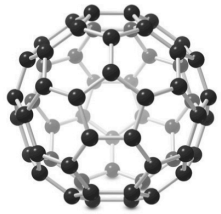
graphite
an "infinite" array of benzene rings, covalently bonded in two dimensions



Graphite exists in planar sheets of benzene rings, held together by weak intermolecular forces.

Buckminsterfullerene - Is it Aromatic?

- Buckminsterfullerene (C_{60}) is a third elemental form of carbon.
- Buckminsterfullerene is completely conjugated, but it is not aromatic since it is not planar.
- It undergoes addition reactions with electrophiles in much the same way as ordinary alkenes.



buckminsterfullerene, C_{60}

20 hexagons + 12 pentagons
of carbon atoms joined together

[The 60 C's of buckminsterfullerene are drawn. Each C also contains a *p* orbital with one electron, which is not drawn.]