Organic Chemistry, *Fourth Edition*

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Chapter 17
Lecture Outline

Prepared by Layne A. Morsch
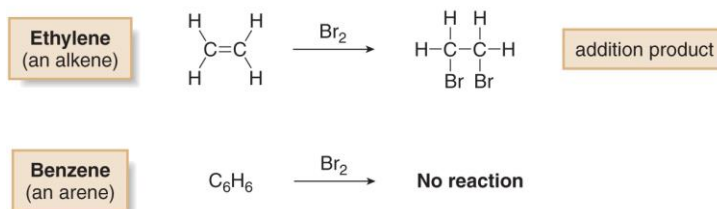**The University of Illinois - Springfield**

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Benzene

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Benzene has four degrees of unsaturation, making it a highly unsaturated hydrocarbon.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes, and dienes readily undergo addition reactions, benzene does not.
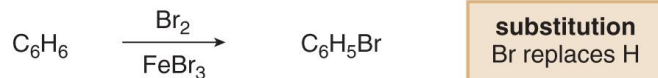
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Reactivity of Benzene

- **Benzene does react with bromine, but only in the presence of FeBr$_3$ (a Lewis acid), and results in substitution, not addition.**

$$C_6H_6 \xrightarrow[\text{FeBr}_3]{\text{Br}_2} C_6H_5Br$$

substitution
Br replaces H

- **Proposed structures of benzene must account for its high degree of unsaturation and its lack of reactivity towards electrophilic addition.**

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Benzene Background

- **August Kekulé proposed that benzene was a rapidly equilibrating mixture of two compounds, each containing a six-membered ring with three alternating π bonds.**
- **In the Kekulé description, the bond between any two carbon atoms is sometimes a single bond and sometimes a double bond.**
- **These structures are known as Kekulé structures.**

**Kekulé description:
An equilibrium**

- **Although benzene is still drawn as a six-membered ring with alternating π bonds, in reality there is no equilibrium between the two different kinds of benzene molecules.**
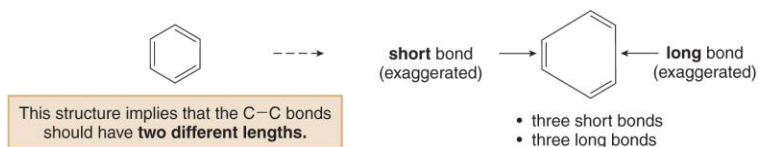- **Current descriptions of benzene are based on resonance and electron delocalization due to orbital overlap.**

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Structure of Benzene

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.**

- **The Kekulé structures satisfy the first two criteria but not the third, because having three alternating π bonds means that benzene should have three short double bonds alternating with three longer single bonds.**

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short bond (exaggerated)   long bond (exaggerated)

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

- three short bonds
- three long bonds

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Resonance Hybrid of Benzene

- **The resonance description of benzene consists of two equivalent Lewis structures, each with three double bonds that alternate with three single bonds.**
- **The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds.**
- **We will use one of the two Lewis structures and not the hybrid in drawing benzene. This will make it easier to keep track of the electron pairs in the π bonds (the π electrons).**

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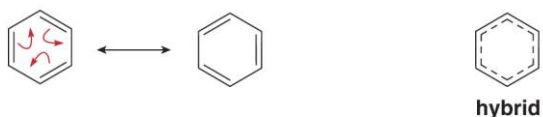
The electrons in the π bonds are **delocalized** around the ring.

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Representations of Benzene

- Because each π bond has two electrons, benzene has six π electrons.

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Some texts draw benzene as a hexagon with an inner circle:

The circle represents the **six π electrons,** distributed over the six atoms of the ring.

- In benzene, the actual bond length (1.39 Å) is intermediate between the carbon–carbon single bond (1.53 Å) and the carbon–carbon double bond (1.34 Å).

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CH_3-CH_3
153 pm

$CH_2=CH_2$
134 pm
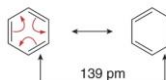
The C–C bonds in benzene are equal and intermediate in length.

139 pm

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Benzene Bond Lengths

- Each carbon atom in a benzene ring is surrounded by three atoms and no lone pairs of electrons, making it sp^2 hybridized.
- Each carbon is then trigonal planar with 120º bond angles.
- Each carbon also has a *p* orbital with one electron that extends above and below the plane of the molecule.

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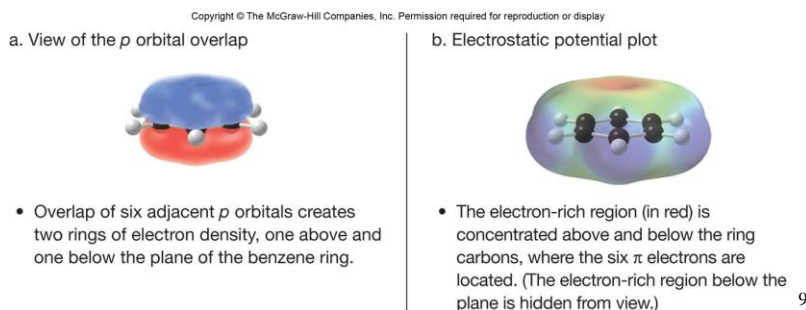
Benzene—A planar molecule

120°

sp^2 hybridized

p orbitals

8

4
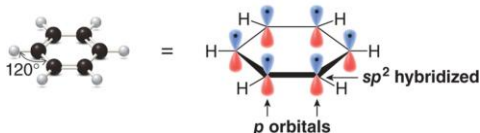
Electron Density in Benzene

- **Overlap of six adjacent *p* orbitals creates two rings of e-density, one above and one below the plane of the benzene ring.**
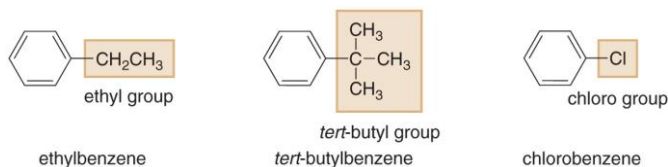- **These π electrons make benzene electron-rich and reactive with strong electrophiles.**

Figure 17.1

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a. View of the *p* orbital overlap

b. Electrostatic potential plot

- Overlap of six adjacent *p* orbitals creates two rings of electron density, one above and one below the plane of the benzene ring.

- The electron-rich region (in red) is concentrated above and below the ring carbons, where the six π electrons are located. (The electron-rich region below the plane is hidden from view.)
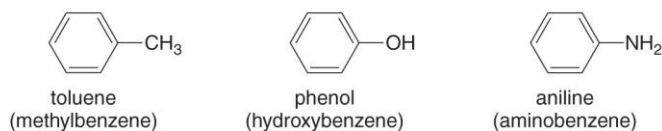
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Naming Substituted Benzenes

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

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$-CH_2CH_3$
ethyl group

ethylbenzene

CH_3
$-C-CH_3$
CH_3
tert-butyl group

tert-butylbenzene

$-Cl$
chloro group

chlorobenzene

- **Many monosubstituted benzenes have common names which you must also learn.**

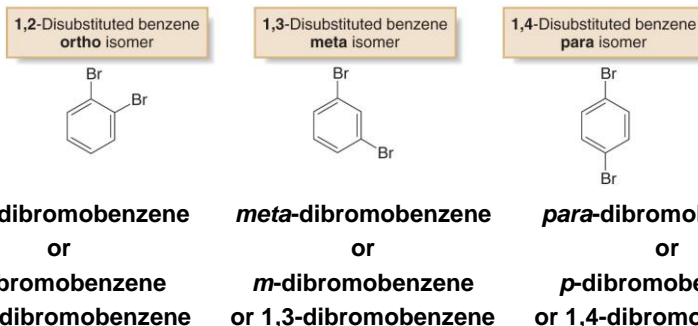Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display

$-CH_3$
toluene
(methylbenzene)

$-OH$
phenol
(hydroxybenzene)

$-NH_2$
aniline
(aminobenzene)

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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.**

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1,2-Disubstituted benzene **ortho** isomer	1,3-Disubstituted benzene **meta** isomer	1,4-Disubstituted benzene **para** isomer

ortho-dibromobenzene
or
o-dibromobenzene
or 1,2-dibromobenzene

meta-dibromobenzene
or
m-dibromobenzene
or 1,3-dibromobenzene

para-dibromobenzene
or
p-dibromobenzene
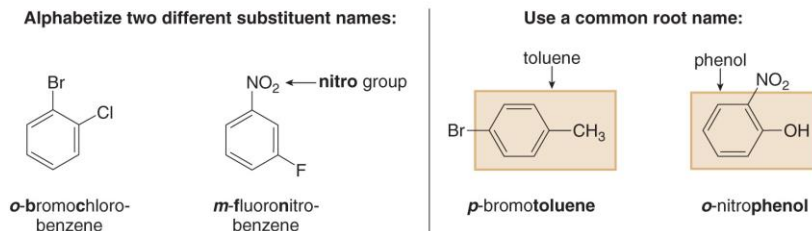or 1,4-dibromobenzene

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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.**

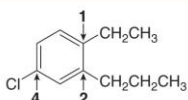Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display

Alphabetize two different substituent names:

NO_2 ← **nitro** group

o-**b**romo**c**hloro-benzene

m-fluoro**n**itro-benzene

Use a common root name:

toluene

phenol

p-bromo**toluene**

o-nitro**phenol**

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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.**
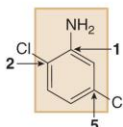   - **The substituent that comprises the common root is located at C1.**

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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.
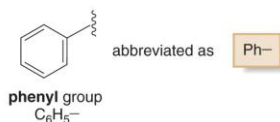
2,5-dichloroaniline

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Naming Benzene as a Substituent

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

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abbreviated as   Ph—

phenyl group
C$_6$H$_5$—

- A phenyl group (C$_6$H$_5$−) is formed by removing one hydrogen from benzene (C$_6$H$_6$).

- **Therefore, benzene can be represented as PhH, and phenol would be PhOH.**

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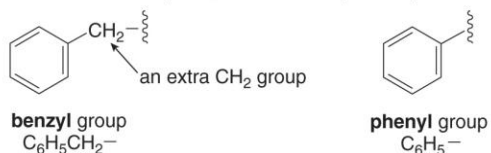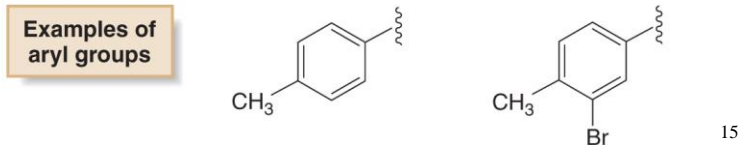
benzene   =   C$_6$H$_5$−H
                PhH

phenol   =   C$_6$H$_5$−OH
               PhOH

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Benzyl and Aryl Groups

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

an extra CH_2 group

benzyl group
$C_6H_5CH_2-$

phenyl group
C_6H_5-

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

Examples of aryl groups

CH_3 CH_3 Br

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Table 17.1 Characteristic Spectroscopic Absorptions of Benzene Derivatives

Type of spectroscopy	Type of C, H	Absorption
IR absorptions	$C_{sp^2}-H$ C=C (arene)	3150–3000 cm^{-1} 1600, 1500 cm^{-1}
^{1}H NMR absorptions	(aryl H)	6.5–8 ppm (highly deshielded protons)
	$-CH_2-$ (benzylic H)	1.5–2.5 ppm (somewhat deshielded $C_{sp^3}-H$)
^{13}C NMR absorption	C_{sp^2} of arenes	120–150 ppm

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^{13}C NMR Absorptions of Dibromobenzenes
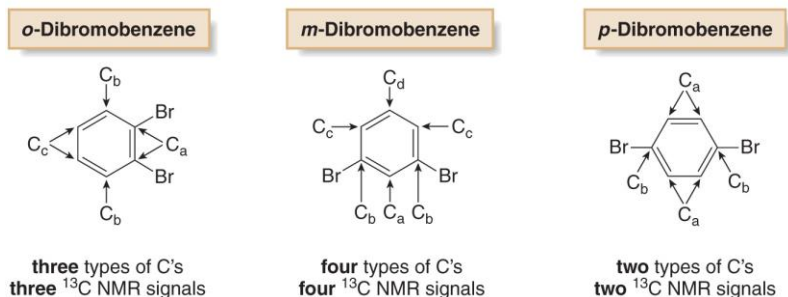
- The number of signals (lines) in the ^{13}C NMR spectrum of a disubstituted benzene with two identical groups indicates whether they are ortho, meta, or para to each other.

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.**
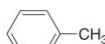
Benzo[a]pyrene, a Common PAH

- **Benzo[a]pyrene, produced by the incomplete oxidation of organic compounds in tobacco, is found in cigarette smoke.**
- **When ingested or inhaled, benzo[a]pyrene and other similar PAHs are oxidized to carcinogenic products.**

Figure 17.3

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benzo[a]pyrene
(a polycyclic aromatic hydrocarbon)

tobacco plant
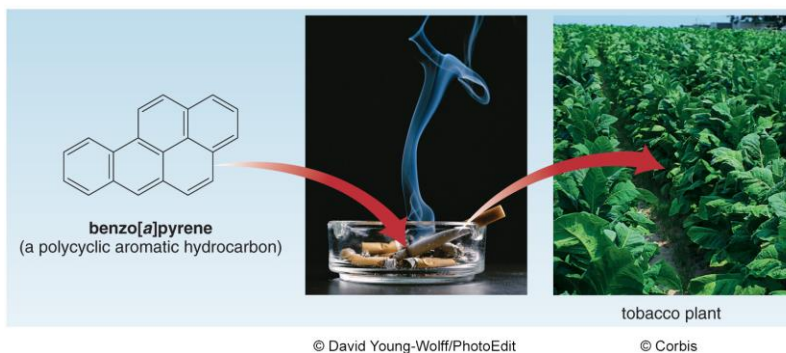
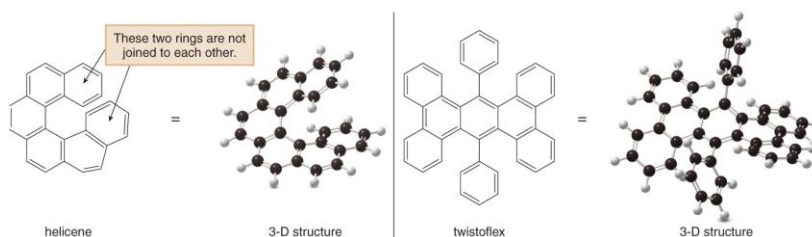© David Young-Wolff/PhotoEdit   © Corbis   19

Synthetic PAHs

Figure 17.4   Helicene and twistoflex—Two synthetic polycyclic aromatic hydrocarbons

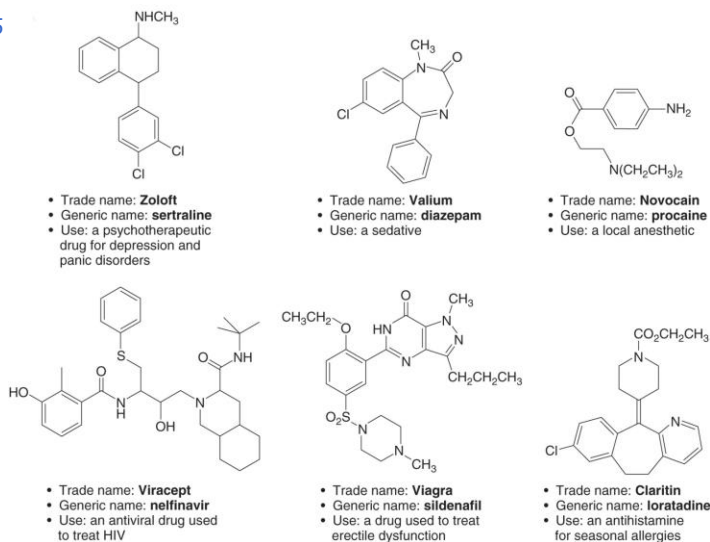Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display

These two rings are not joined to each other.

helicene   3-D structure   twistoflex   3-D structure

- **In helicene all the rings twist slightly creating a rigid helical shape that prevents the hydrogens on both ends from colliding.**
- **Twistoflex is also non-planar to reduce steric interactions.**
- **Both of these molecules are examples of chiral molecules that do not contain stereogenic centers.**

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Drugs that Contain a Benzene Ring

Figure 17.5

- 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**
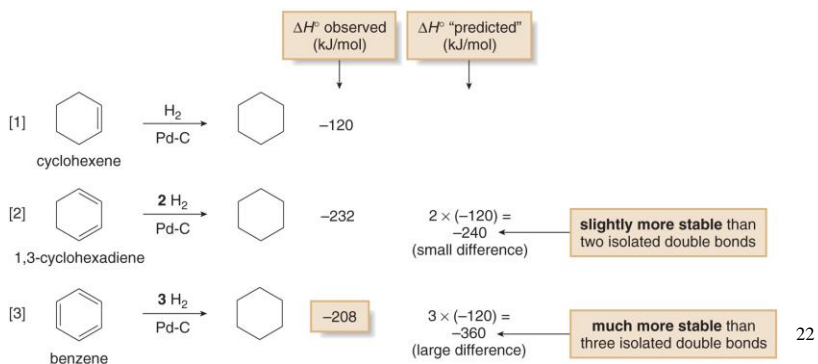- Use: an antihistamine for seasonal allergies

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Stability of Benzene

- **Consider the heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene and benzene:**
  - **All three give cyclohexane when treated with excess hydrogen in the presence of a metal catalyst.**
  - **However, the ΔH^o for benzene is much less than predicted.**

		ΔH^o observed (kJ/mol)	ΔH^o "predicted" (kJ/mol)	
[1] cyclohexene	$\xrightarrow{\text{H}_2}{\text{Pd-C}}$	−120		
[2] 1,3-cyclohexadiene	$\xrightarrow{\text{2 H}_2}{\text{Pd-C}}$	−232	$2 \times (-120) =$ −240 (small difference)	**slightly more stable than** two isolated double bonds
[3] benzene	$\xrightarrow{\text{3 H}_2}{\text{Pd-C}}$	−208	$3 \times (-120) =$ −360 (large difference)	**much more stable than** three isolated double bonds

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Heats of Hydrogenation for Benzene

Figure 17.6
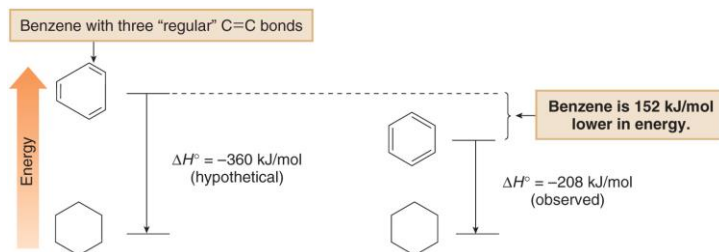
- **The huge difference between the hypothetical and observed heats of hydrogenation for benzene cannot be explained solely on the basis of resonance and conjugation.**
- **The low heat of hydrogenation of benzene means that benzene is especially stable—even more so than conjugated polyenes.**
- **This unusual stability is characteristic of aromatic compounds.**

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Unusual Reactivity of Benzene

- **Benzene's unusual behavior is not limited to hydrogenation.**
- **Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.**
- **Benzene does not react with Br_2 to yield an addition product.**
- **Instead, in the presence of a Lewis acid, bromine substitutes for a hydrogen atom, yielding a product that retains the benzene ring.**
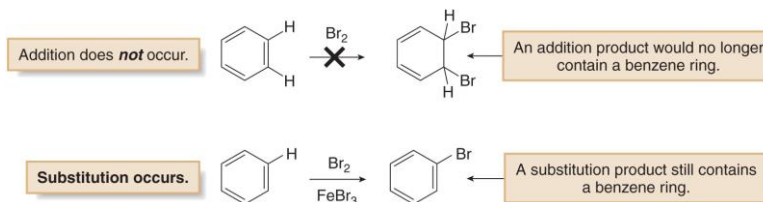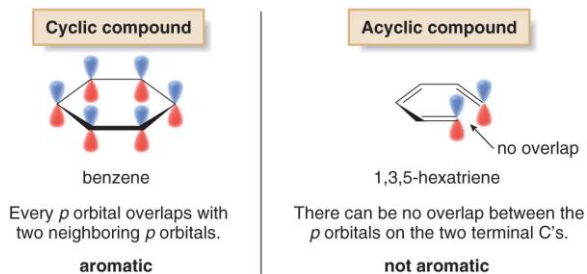

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The Criteria for Aromaticity

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.**

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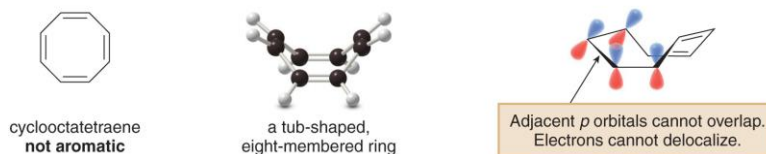
Cyclic compound	Acyclic compound
benzene	1,3,5-hexatriene — no overlap
Every *p* orbital overlaps with two neighboring *p* orbitals.	There can be no overlap between the *p* orbitals on the two terminal C's.
aromatic	**not aromatic**

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The Criteria for Aromaticity
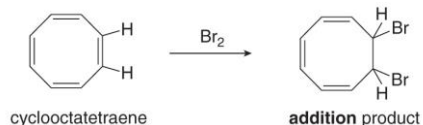
2. A molecule must be planar.

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

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cyclooctatetraene
not aromatic

a tub-shaped, eight-membered ring

Adjacent *p* orbitals cannot overlap. Electrons cannot delocalize.

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

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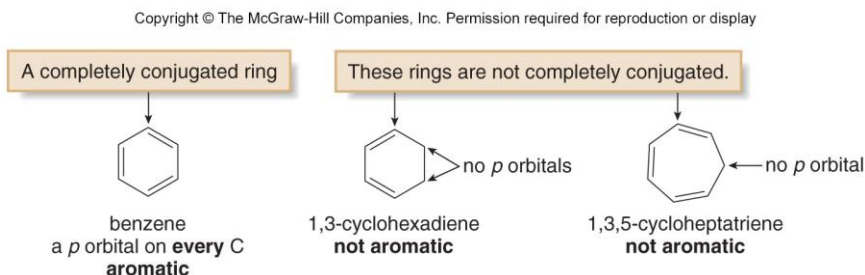
cyclooctatetraene $\xrightarrow{Br_2}$ **addition** product

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The Criteria for Aromaticity

3. A molecule must be completely conjugated.

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

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| A completely conjugated ring | These rings are not completely conjugated. |

benzene
a *p* orbital on **every** C
aromatic

←no *p* orbitals
1,3-cyclohexadiene
not aromatic

←no *p* orbital
1,3,5-cycloheptatriene
not aromatic

The Criteria for Aromaticity

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

Hückel's rule:

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• 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.**

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| Benzene
An aromatic compound | Cyclobutadiene
An antiaromatic compound |

$4n + 2 = 4(1) + 2 =$
6 π electrons
aromatic

$4n = 4(1) =$
4 π electrons
antiaromatic
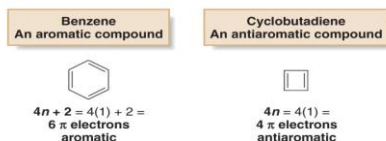
Hückel's Rule and Number of π Electrons

- **Hückel's rule refers to the number of π electrons, not the number of atoms in a particular ring.**

Table 17.2 The Number of π Electrons That Satisfy Hückel's Rule

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

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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**

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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.
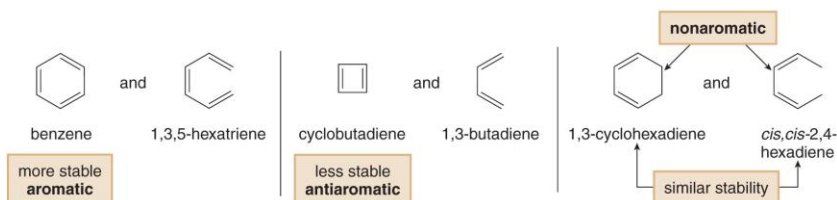
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NMR and Aromaticity

- ^{1}H NMR spectroscopy readily indicates whether a compound is aromatic.
- The protons on sp^2 hybridized carbons in aromatic hydrocarbons are highly deshielded and absorb at 6.5–8 ppm, whereas hydrocarbons that are not aromatic absorb at 4.5–6 ppm.
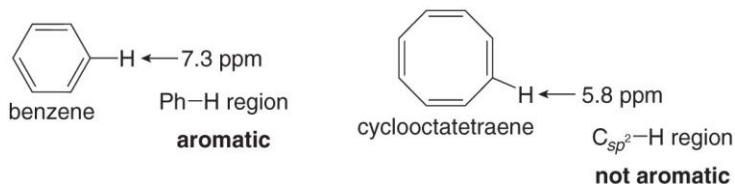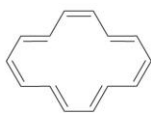
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Larger Aromatic Rings

- 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.
- To name an annulene, indicate the number of atoms in the ring in brackets and add the word *annulene*.

[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic

[18]-annulene
$4n + 2 = 4(4) + 2 =$
18 π electrons
aromatic

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Hückel's Rule and Number of π Electrons

- [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.
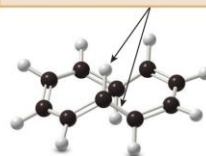
[10]-Annulene fits Hückel's rule, but it's **not planar.**

The molecule puckers to keep these H's farther away from each other.

[10]-annulene
10 π electrons
not aromatic

=

3-D representation

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Fused Ring Aromatics

- **Two or more six-membered rings with alternating double and single bonds can be fused together to form PAHs.**
- **There are two different ways to join three rings together, forming anthracene and phenanthrene.**

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naphthalene
10 π electrons

anthracene
14 π electrons

phenanthrene
14 π electrons
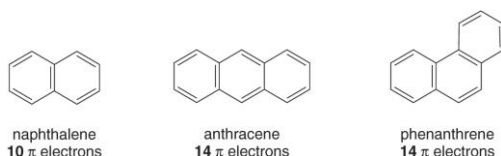
Resonance Structures of Fused Ring Aromatics

- **As the number of fused rings increases, the number of resonance structures increases.**
- **Naphthalene is a hybrid of three resonance structures whereas benzene is a hybrid of two.**

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Three resonance structures for naphthalene
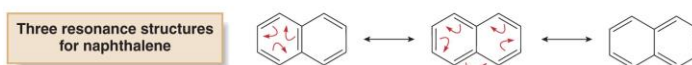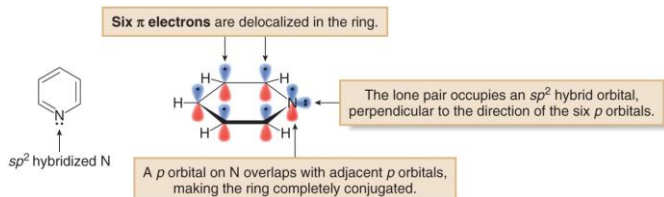
Heterocyles

- **Heterocycles containing oxygen, nitrogen or sulfur, can also be aromatic.**
- **With heteroatoms, we must determine whether the lone pair is localized on the heteroatom or part of the delocalized π system.**
- **An example of an aromatic heterocycle is pyridine.**

two resonance structures for pyridine
6 π electrons

Six π electrons are delocalized in the ring.

The lone pair occupies an sp^2 hybrid orbital, perpendicular to the direction of the six p orbitals.

A p orbital on N overlaps with adjacent p orbitals, making the ring completely conjugated.
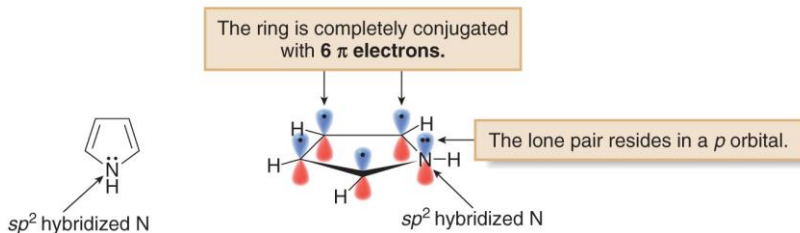
sp^2 hybridized N

37

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.**

The ring is completely conjugated with **6 π electrons.**

The lone pair resides in a p orbital.

sp^2 hybridized N

sp^2 hybridized N

- **Pyrrole is cyclic, planar, completely conjugated, and has $4n + 2$ π electrons, so it is aromatic.**
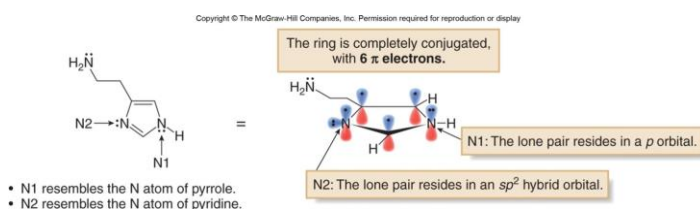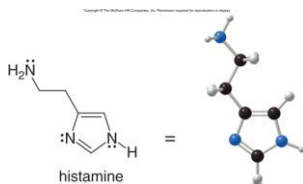
38

Electrostatic Potential of Aromatic Heterocycles

- **In pyridine, the nonbonded electron pair is localized on the N atom in an *sp2* hybridized orbital**
  - **This can be seen by the region of high electron density on N.**
- **In pyrrole, the nonbonded electron pair is in a *p* orbital and is delocalized over the ring.**
  - **The entire ring is electron rich.**

Figure 17.7

pyridine

pyrrole

39
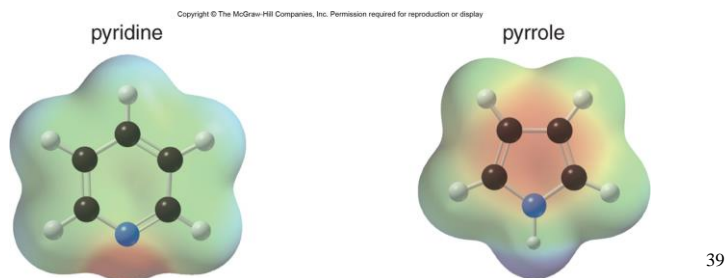
Biologically Active Heterocycles

- **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.**
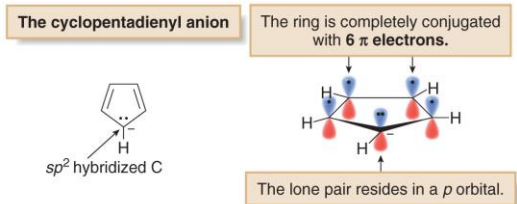

histamine

The ring is completely conjugated, with **6 π electrons.**

N1: The lone pair resides in a *p* orbital.

N2: The lone pair resides in an *sp²* hybrid orbital.

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

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Ionic Aromatic Compounds

- **Both negatively and positively charged ions can be aromatic if they possess all the necessary elements.**

The cyclopentadienyl anion

The ring is completely conjugated with **6 π electrons.**

sp^2 hybridized C

The lone pair resides in a *p* orbital.

- The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.
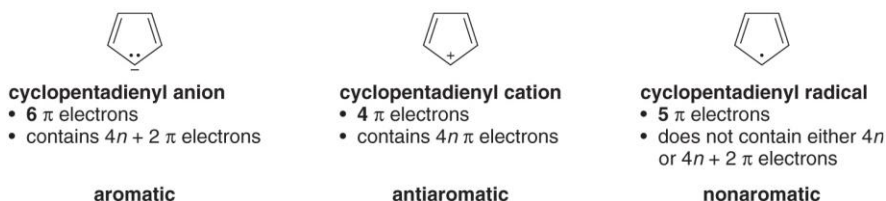
- **We can draw five equivalent resonance structures for the cyclopentadienyl anion.**

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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	cyclopentadienyl cation	cyclopentadienyl radical
• **6 π** electrons	• **4 π** electrons	• **5 π** electrons
• contains $4n + 2$ π electrons	• contains $4n$ π electrons	• does not contain either $4n$ or $4n + 2$ π electrons
aromatic	**antiaromatic**	**nonaromatic**

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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.**

no p orbital

H H   :B   →

cyclopentadiene
not aromatic
pK_a = 15

+   H—B$^+$

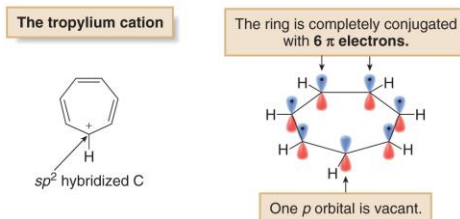cyclopentadienyl anion
aromatic
a stabilized conjugate base
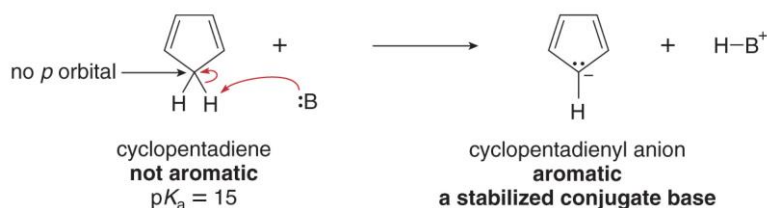
43

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

The ring is completely conjugated
with **6 π electrons.**

sp^2 hybridized C

One p orbital is vacant.

- 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.

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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.
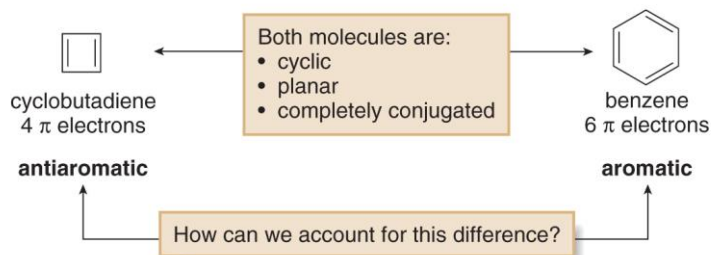
Molecular Orbital Theory

- Thus far, we have used "valence bond theory" to explain how bonds between atoms are formed.
  - 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.
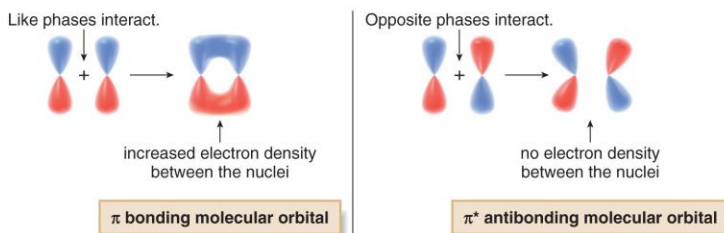
Forming Molecular Orbitals

- **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.**

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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.**

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Like phases interact.

increased electron density between the nuclei

π bonding molecular orbital

Opposite phases interact.

no electron density between the nuclei

π* antibonding molecular orbital

- **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.**
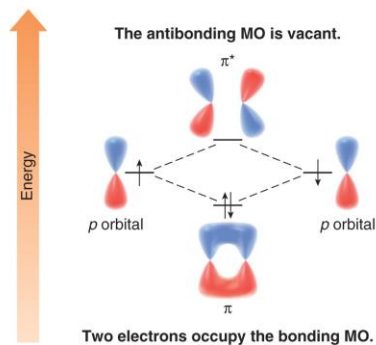
48

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.**
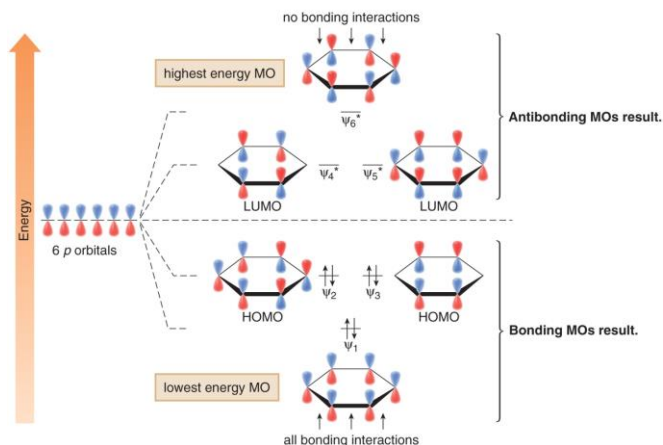
Figure 17.8

49

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.**

Figure 17.9

50

Molecular Orbitals for Benzene

- **The molecular orbital description of benzene is much more complex than the two MOs formed in Figure 17.8.**

- **Since each of the six carbon atoms of benzene has a *p* orbital, six atomic *p* orbitals combine to form six π molecular orbitals as shown in Figure 17.9.**

    - **The six MOs are labeled $\psi 1$ to $\psi 6$, with $\psi 1$ being the lowest energy and $\psi 6$ being the highest.**

    - **There are three bonding orbitals $\psi 1$, $\psi 2$, and $\psi 3$.**

    - **There are three antibonding orbitals $\psi 4^*$, $\psi 5^*$, and $\psi 6^*$.**

51

Molecular Orbitals for Benzene

- **The most important features of the six benzene MOs:**

    - **The larger the number of bonding interactions, the lower in energy the MO.**

    - **The larger the number of nodes, the higher in energy the MO.**

    - **Two pairs of MOs with the same energy ($\psi 2$ and $\psi 3$; $\psi 4^*$ and $\psi 5^*$) 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).**

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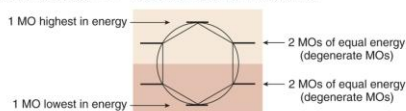
Step [2] Draw a line horizontally through the center of the circle and label MOs as bonding, nonbonding, or antibonding.

- **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.

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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 $4n + 2$ 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.** 54
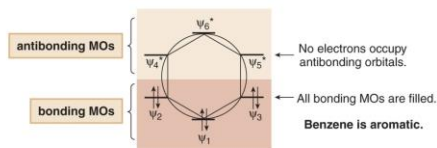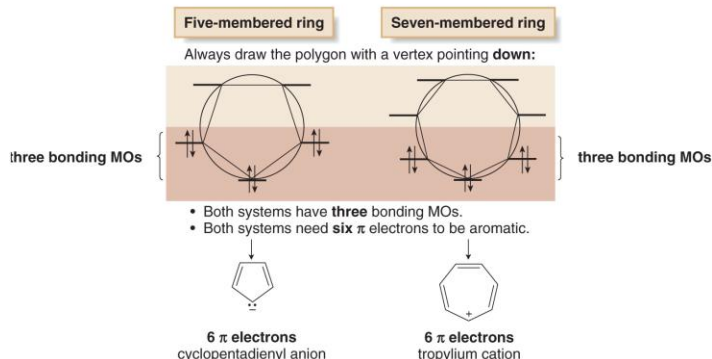
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Inscribed Polygon Method of Predicting Aromaticity

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Five-membered ring   **Seven-membered ring**

Always draw the polygon with a vertex pointing **down:**

three bonding MOs   three bonding MOs

- Both systems have **three** bonding MOs.
- Both systems need **six** π electrons to be aromatic.

6 π electrons
cyclopentadienyl anion   **6 π electrons**
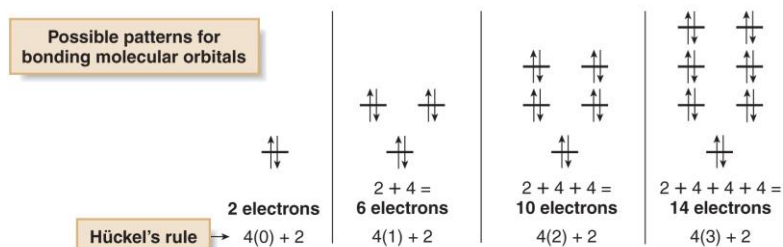tropylium cation

55

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 $4n + 2$ rule.**

MO patterns for cyclic,
completely conjugated systems

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Possible patterns for bonding molecular orbitals

	2 electrons	2 + 4 = 6 electrons	2 + 4 + 4 = 10 electrons	2 + 4 + 4 + 4 = 14 electrons
Hückel's rule →	$4(0) + 2$	$4(1) + 2$	$4(2) + 2$	$4(3) + 2$

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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.**

Three sheets of graphite, viewed edge-on
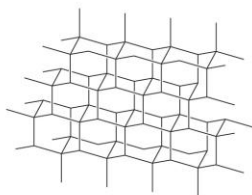
diamond
an "infinite" array of six-membered rings, covalently bonded in three dimensions
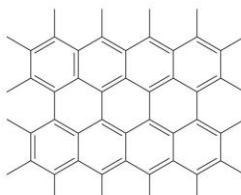
graphite
an "infinite" array of benzene rings, covalently bonded in two dimensions

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

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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.

58