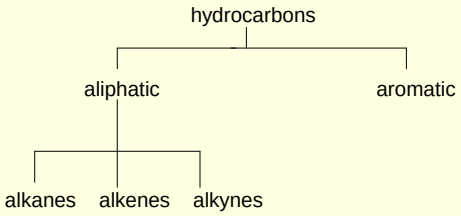
Arenes and Aromaticity



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Arenes and Aromaticity

Aliphatic compounds: open-chain compounds and ring compounds that are chemically similar to open-chain compounds. Alkanes, alkenes, alkynes, dienes, alicyclics, etc.

Aromatic compounds: unsaturated ring compounds that are far more stable than they should be and resist the addition reactions typical of unsaturated aliphatic compounds. Benzene and related compounds.

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Defining Aromatic Compounds

- Historically:
  - organic compounds had an aroma or odour

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Aromatic Compounds

- Unsaturated cyclic hydrocarbons
- Contain single rings or groups of rings
- Simplest aromatic compound is benzene
- Aromatic compounds include benzene or are benzene based and have benzene-like structures and properties.

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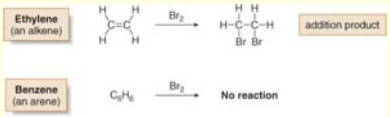
Benzene and Aromatic Compounds

- **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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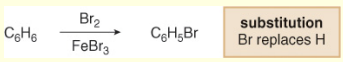
Structure of Benzene

- **Benzene does react with bromine, but only in the presence of $FeBr_3$ (a Lewis acid), and the reaction is a substitution, not an addition.**



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

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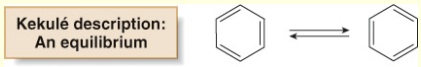
Structure of Benzene

- **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.**



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Structure of Benzene

- 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.
- In the nineteenth century, many other compounds having properties similar to those of benzene were isolated from natural sources. Since these compounds possessed strong and characteristic odors, they were called aromatic compounds. It should be noted, however, that it is their chemical properties, and not their odor, that make them special.

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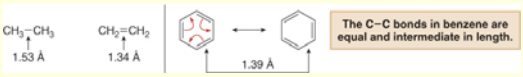
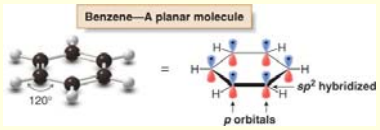
Structure of Benzene

- 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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Structure of Benzene

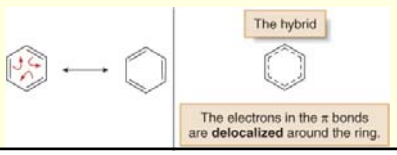
Any structure for benzene must account for the following facts:

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.

Structure 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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MO Rules for Benzene

- Six overlapping *p* orbitals must form six molecular orbitals.
- Three will be bonding, three antibonding.
- Lowest energy MO will have all bonding interactions, no nodes.
- As energy of MO increases, the number of nodes increases.

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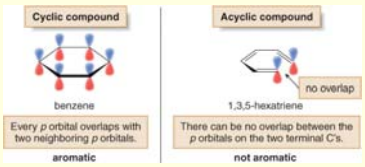
Aromaticity

The Criteria for Aromaticity—Hückel's Rule

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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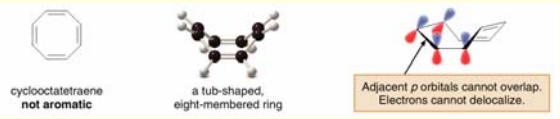
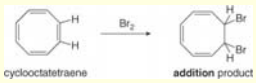
Aromaticity

[2] A molecule must be planar.

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



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



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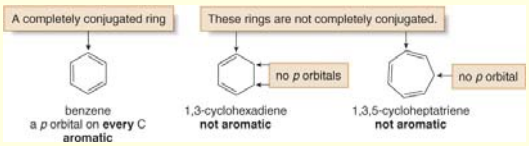
Aromaticity

[3] A molecule must be completely conjugated.

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



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Aromaticity

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

Hückel's rule:

- 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*.

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Aromaticity and the Hückel Rule

The Hückel $4n + 2$ rule

- Theory devised in 1931 by the German physicist Erich Hückel
- A molecule is aromatic only if it has a planar, monocyclic system of conjugation and contains a total of $4n + 2$ π electrons, where n is an integer ($n = 0, 1, 2, 3,\ldots$)
- Only molecules with 2, 6, 10, 14, 18,… π electrons can be aromatic
- Molecules with $4n$ π electrons (4, 8, 12, 16,…) can not be aromatic, said to be *antiaromatic* because delocalization of their π electrons would lead to their *destablization*

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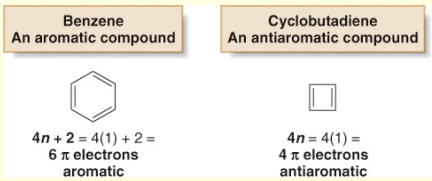
Aromaticity and the Hückel Rule

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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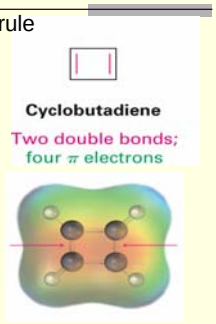
Aromaticity and the Hückel Rule

Examples of the Hückel $4n + 2$ rule

- Cyclobutadiene
  - Contains four π electrons
    - The π electrons are localized into two double bonds rather than delocalized around the ring
  - Antiaromatic
  - Highly reactive
  - Shows none of the properties associated with aromaticity
  - Not prepared until 1965



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Aromaticity and the Hückel Rule

- Benzene
  - Contains six π electrons ($4n + 2 = 6$ when $n = 1$)
  - Aromatic

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Aromaticity and the Hückel Rule

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

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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Aromaticity

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

- **Aromatic**—A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.
- **Antiaromatic**—A cyclic, planar, completely conjugated compound with $4n$ π electrons.
- **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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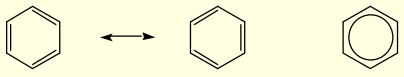
Resonance Structures

- There are two ways to write the structure of benzene
- These are called "resonance structures"
- However, neither of these represents the true structure of benzene since benzene has only one structure, with all C-C bonds being equivalent
- The true structure is a hybrid of the the two resonance structures; this can be represented by drawing the π bonds as a circle
- We use the individual resonance structures when we write reaction mechanisms involving benzene to show more clearly the bond formation and bond breaking in the reaction



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Naming Aromatics

Substituted Benzenes

- Compounds containing substituents (ie alkyl groups, other atoms) in place of one hydrogen atom are named as derivatives of benzene.

Step 1 Identify the branch (alkyl or atom) and write it as the first part of the name.

Step 2 Complete the name with benzene.

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Naming Monosubstituted Benzenes

- Benzene compounds with a single substituent are named by writing the substituent name followed by benzene
- Many of these compounds also have common names that are accepted by IUPAC (you should know those listed here)

Toluene
(methylbenzene)

Phenol
(hydroxybenzene)

Analine
(aminobenzene)

Anisole
(methoxybenzene)

Benzaldehyde
(benzenecarbaldehyde

Benzoic Acid
(benzenecarboxylic acid)

Styrene
(phenylethene)

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Naming Monosubstituted Benzenes

others as substituted benzenes

bromobenzene

nitrobenzene

chlorobenzene

Toluene

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Disubstituted Benzenes

- Some derivatives of benzene have two substituents
- Known as *disubstituted* benzenes.
- Three isomers of disubstituted benzenes exist
- Named according to the location of the substituents on the benzene ring (IUPAC) or with the corresponding prefix (Classical)

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Naming Rules

Step 1 Number the carbons, starting at one of the substituents and numbering in the direction which will give the substituents the lowest number.

Step 2 Write the locations of the branches (IUPAC) or use the appropriate classical prefix.

Step 3 Complete the name with benzene.

Prefix (Classical)	Positions (IUPAC)
ortho- (o)	1,2
meta- (m)	1,3
para- (p)	1,4

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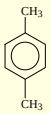
Naming Multisubstituted Benzenes

1,2-dimethylbenzene
ortho-dimethylbenzene
o-dimethylbenzene

1,3-dimethylbenzene
meta-dimethylbenzene
m-dimethylbenzene



1,4-dimethylbenzene
para-dimethylbenzene
p-dimethylbenzene

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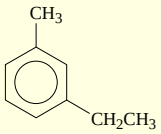
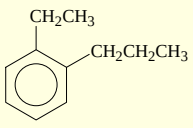
Naming Multisubstituted Benzenes



1-methyl-3-ethylbenzene
m-methylethylbenzene



1-ethyl-2-propylbenzene
o-ethylpropylbenzene

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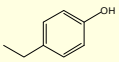
Naming Multisubstituted Benzenes

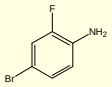
Examples:

meta-dibromobenzene
(1,3-dibromobenzene)

ortho-chlorotoluene
(1-chloro-2-methylbenzene)



para-ethylphenol
(1-hydroxy-4-ethylbenzene)



4-bromo-2-fluoroanaline
(1-amino-4-bromo-2-fluorobenzene)

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Naming Aromatic Compounds

Arenes

- Alkyl-substituted benzenes
- Named depending on the size of the alkyl group
  - Alkyl substituent smaller than the ring (6 or fewer carbons), named as an alkyl substituted benzene
  - Alkyl substituent larger than the ring (7 or more carbons), named as a phenyl-substituted alkane

Phenyl

- Derived from the Greek *pheno* (“I bear light”)
  - Michael Faraday discovered benzene in 1825 from the oily residue left by illuminating gas used in London street lamps
- Used for the $-C_6H_5$ unit when the benzene ring is considered as a substituent

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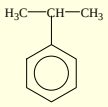
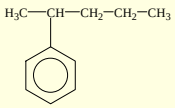
Naming Aromatic Compounds

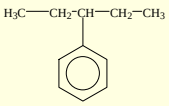
- For larger organic molecules, the benzene is considered a branch or an alkyl group
- *Called phenyl (C_6H_5-)*



2-phenylpropane



2-phenylpentane



3-phenylpentane

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