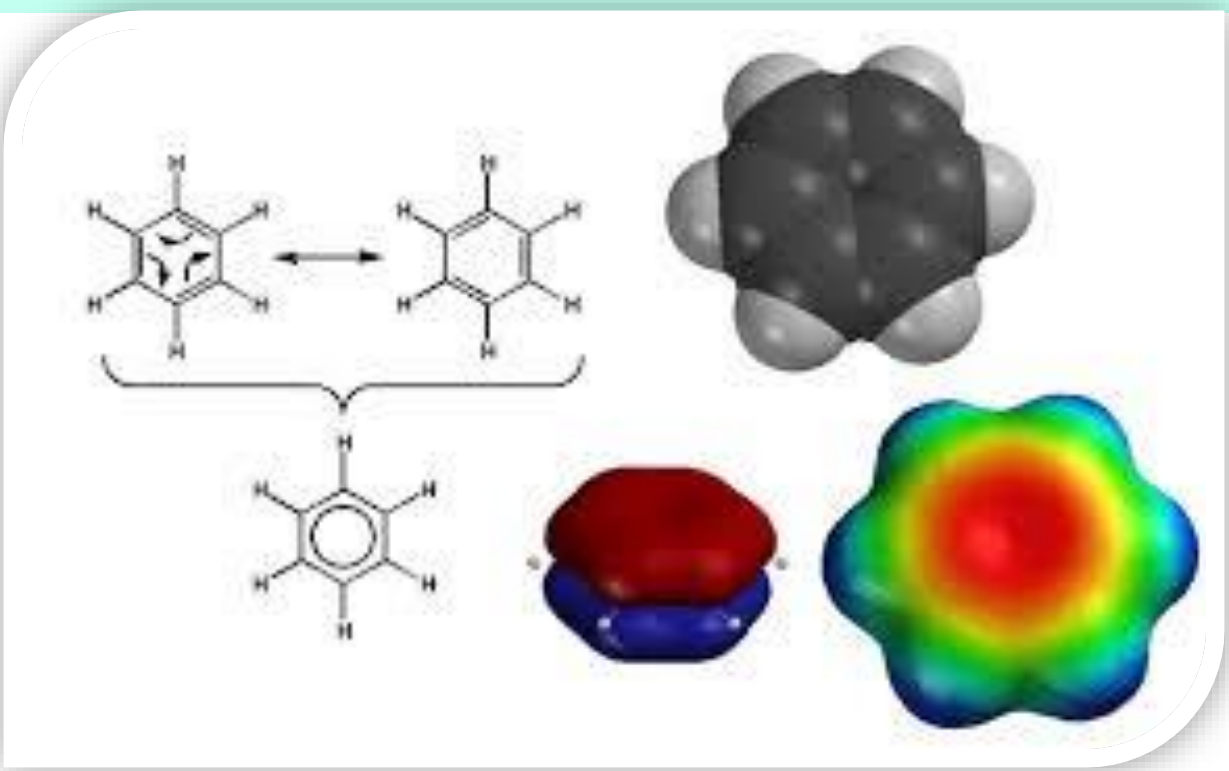
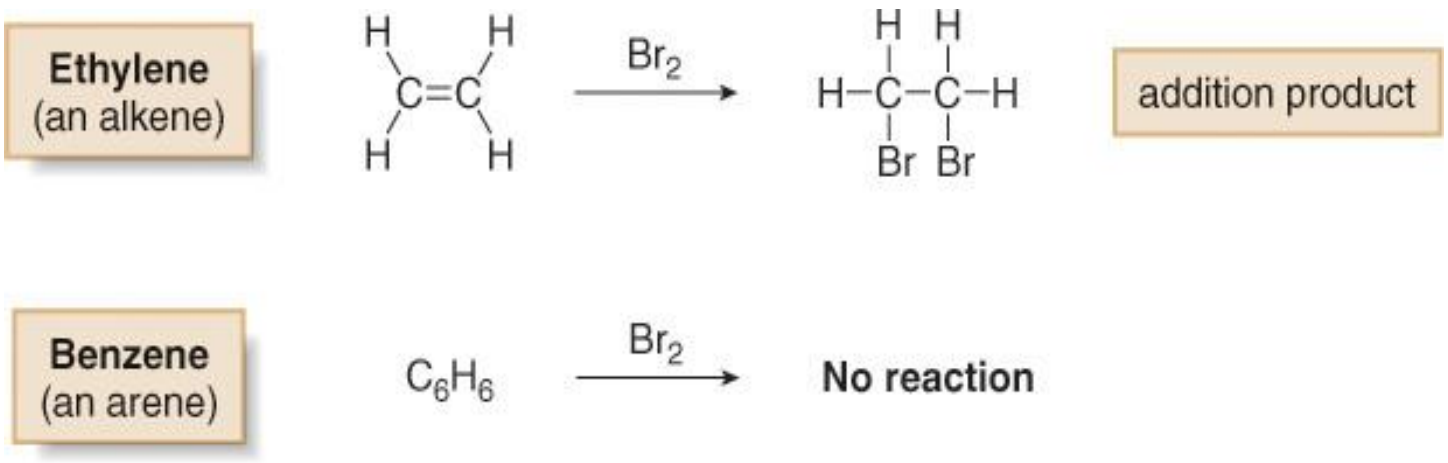
Benzene and Aromatic Compounds

- Based on McMurry's *Organic Chemistry*, 7th edition
- Assistant Lecturer. Jalal Hasan Mohammed

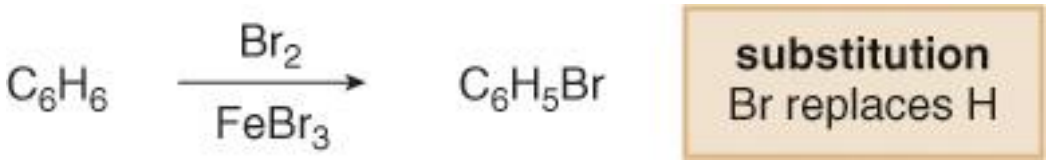


Benzene and Aromatic Compounds

- **Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).**
- **Benzene has three 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.**

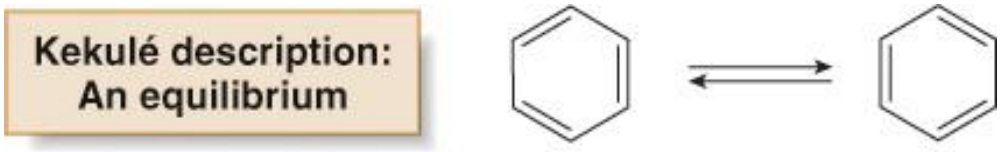


- **Benzene does react with bromine, but only in the presence of $FeBr_3$ (a Lewis acid), and the reaction is a substitution, not an addition.**



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

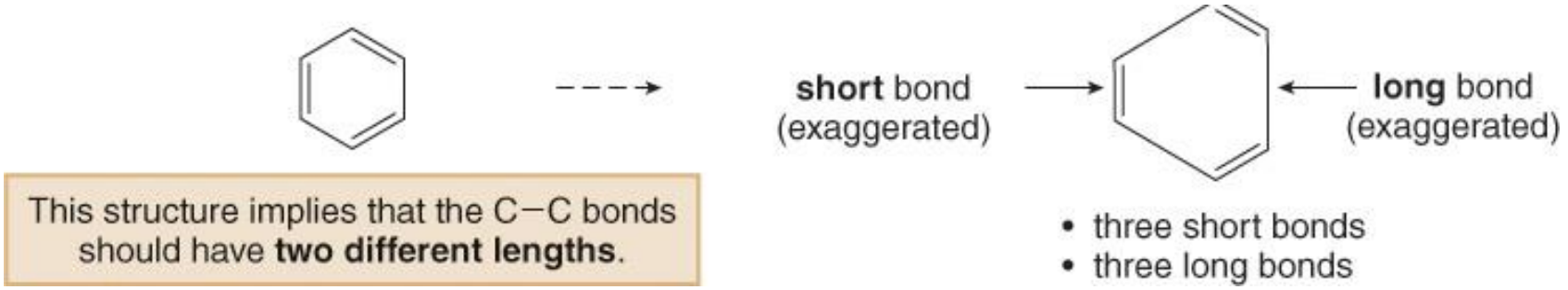


- **Although benzene is still drawn as a six-membered ring with alternating π bonds, in reality there is no equilibrium between the two different kinds of benzene molecules.**
- **Current descriptions of benzene are based on resonance and electron delocalization due to orbital overlap.**
- **In the nineteenth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

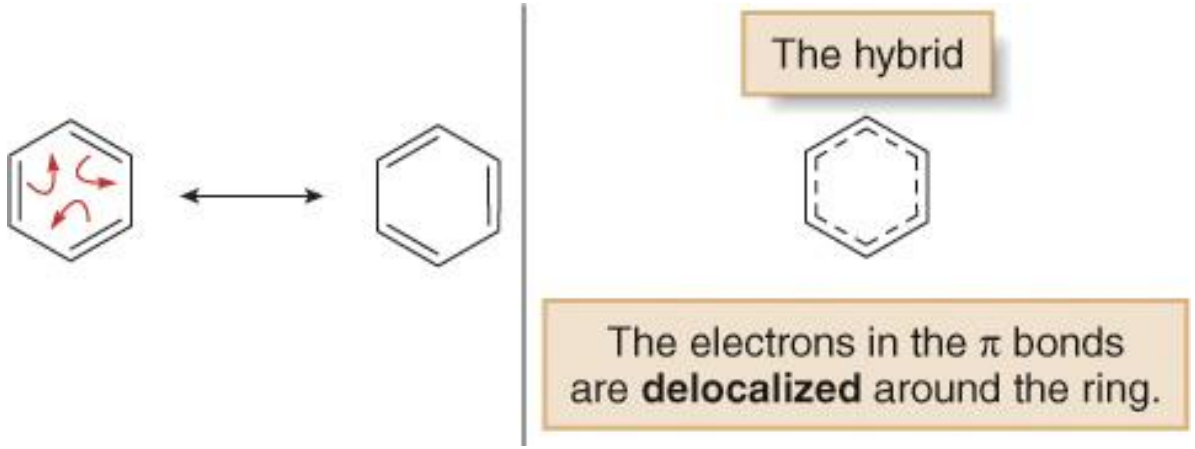
Any structure for benzene must account for the following facts:

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.

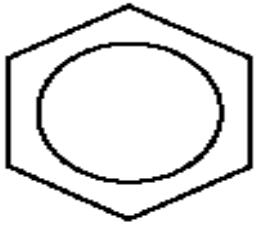


- **The resonance description of benzene consists of two equivalent Lewis structures, each with three double bonds that alternate with three single bonds.**
- **The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position 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).**



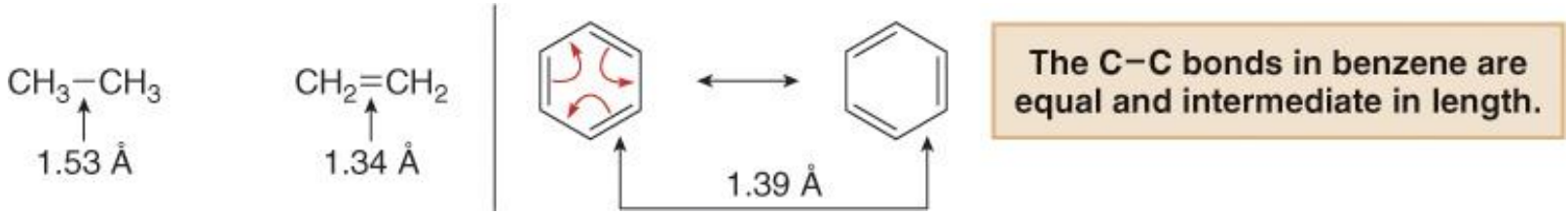
- **Because each π bond has two electrons, benzene has six π electrons.**

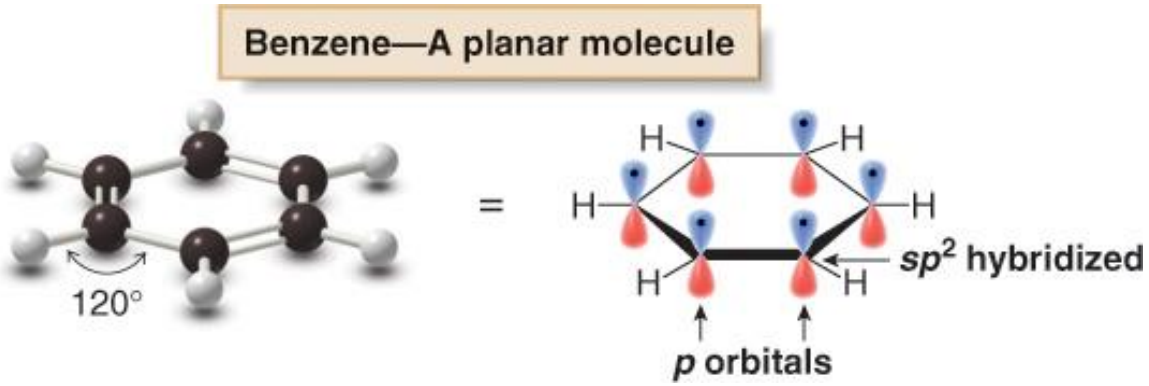
Some texts draw benzene as a hexagon with an inner circle:



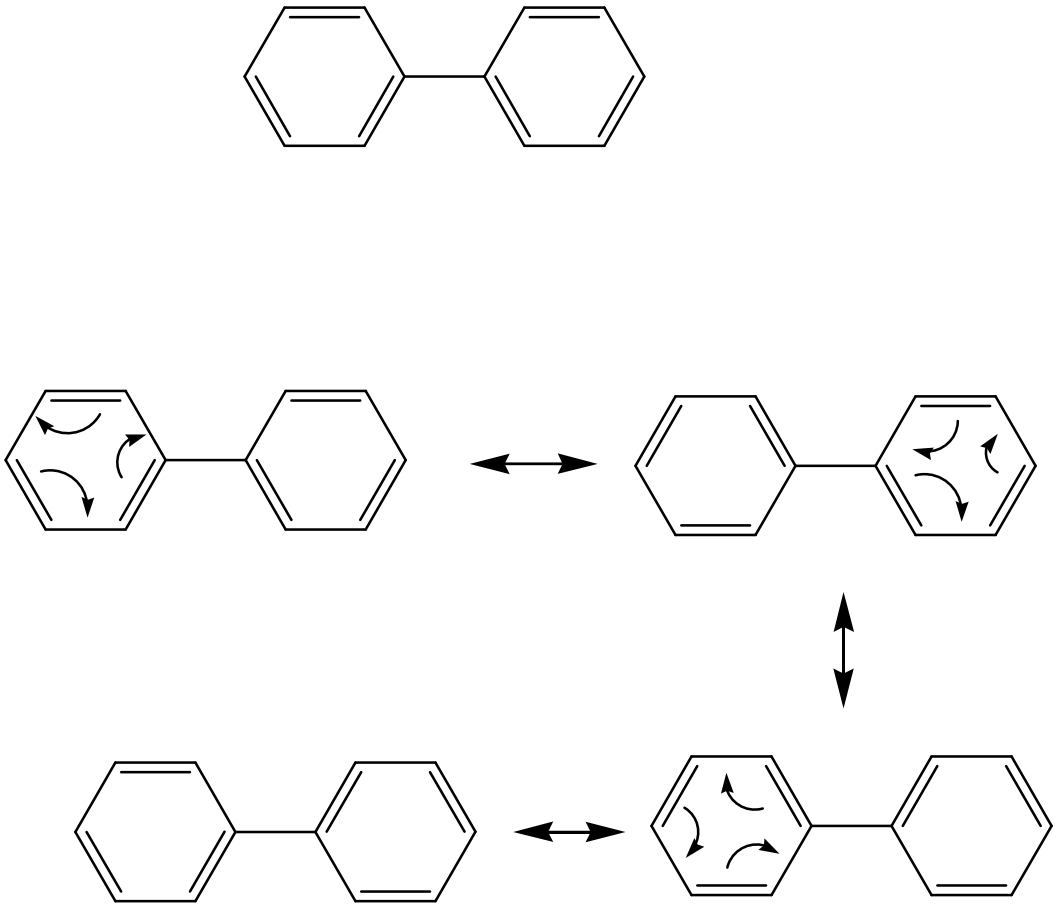
The circle represents the **six π electrons,** distributed over the six atoms of the ring.

- **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).**



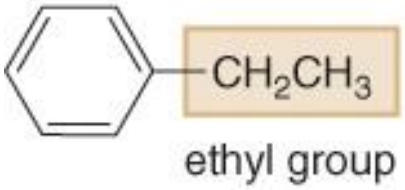


Draw all possible resonance structures for biphenyl?



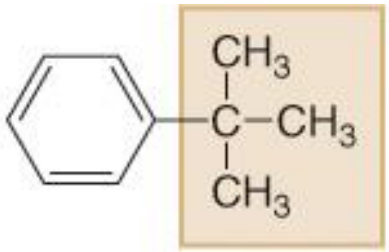
Nomenclature of Benzene Derivatives

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



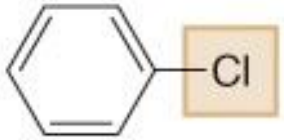
ethyl group

ethylbenzene



tert-butyl group

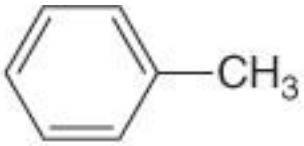
tert-butylbenzene



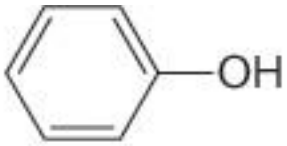
chloro group

chlorobenzene

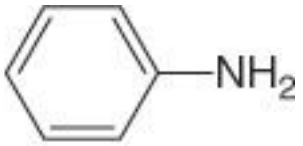
- **Many monosubstituted benzenes have common names which you must also learn.**



toluene
(methylbenzene)



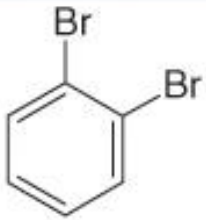
phenol
(hydroxybenzene)



aniline
(aminobenzene)

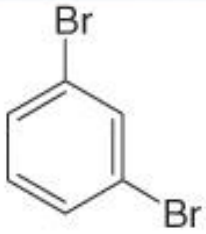
- **There are three different ways that two groups can be attached to a benzene ring, so a prefix—ortho, meta, or para—can be used to designate the relative position of the two substituents.**

1,2-disubstituted benzene
ortho isomer



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

1,3-disubstituted benzene
meta isomer



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

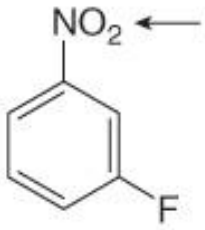
1,4-disubstituted benzene
para isomer

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

- **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.**

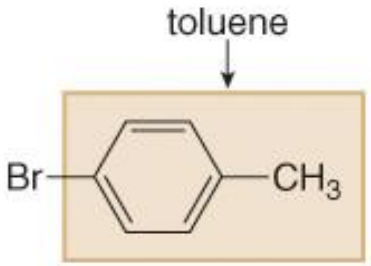
Alphabetize two different substituent names:

***o*-bromochloro-benzene**

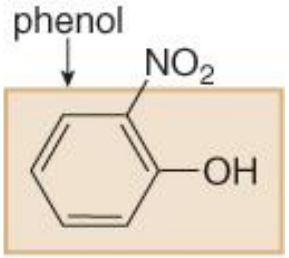


***m*-fluoronitro-benzene**

Use a common root name:



***p*-bromotoluene**



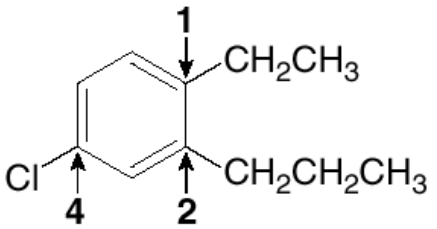
***o*-nitrophenol**

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

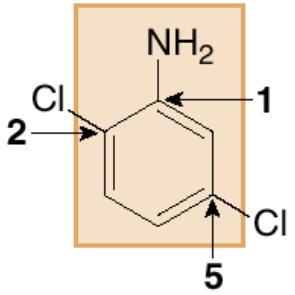
[1]



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

4-chloro-1-ethyl-2-propylbenzene

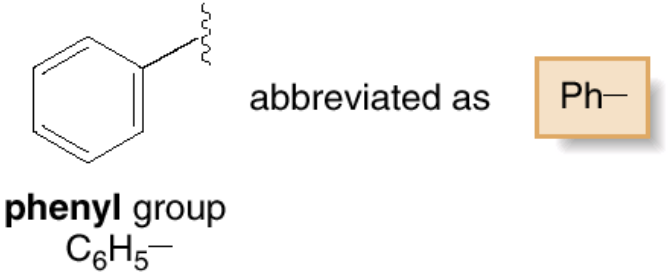
[2]



- 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.

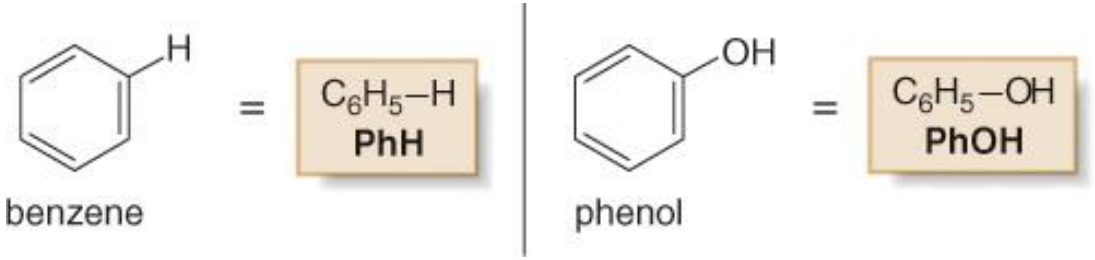
2,5-dichloroaniline

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

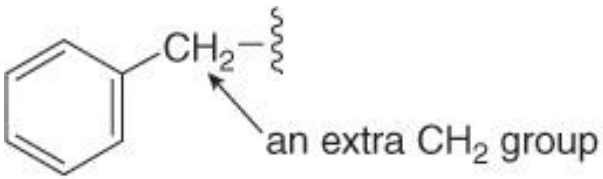


- A phenyl group (C_6H_5–) is formed by removing one hydrogen from benzene (C_6H_6).

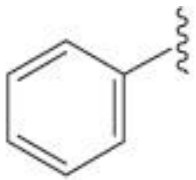
- **Therefore, benzene can be represented as PhH, and phenol would be PhOH.**



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



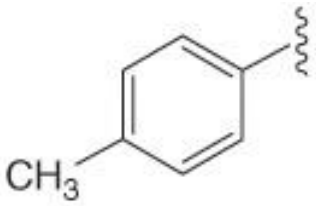
benzyl group
$C_6H_5CH_2-$

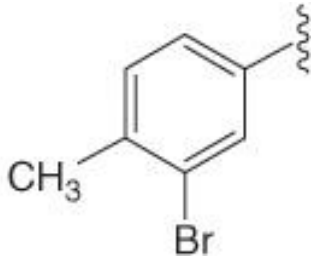


phenyl group
C_6H_5-

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

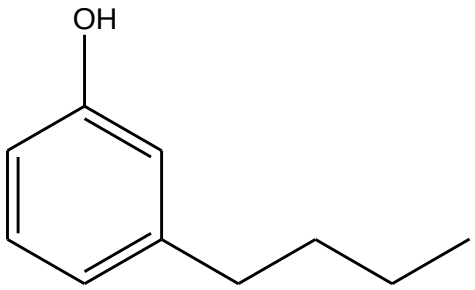
Examples of aryl groups



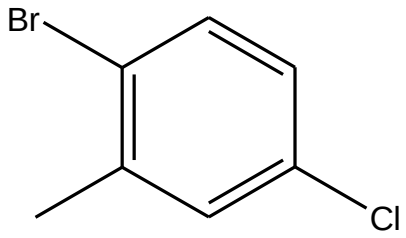


Give the IUPAC name for each compound.

$PhCH(CH_3)_2$ **isopropylbenzene**



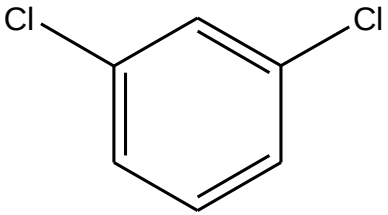
m-butylphenol



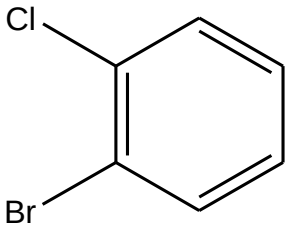
2-bromo-5-chlorotoluene

Which structure matches the given name?

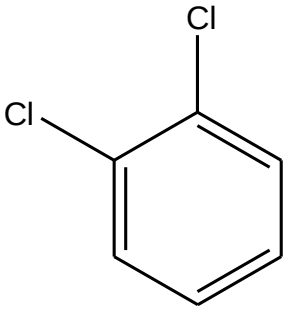
o-dichlorobenzene



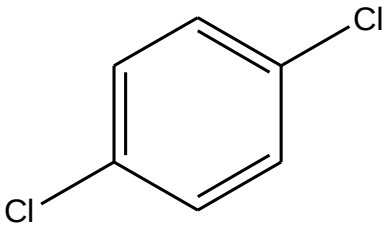
A



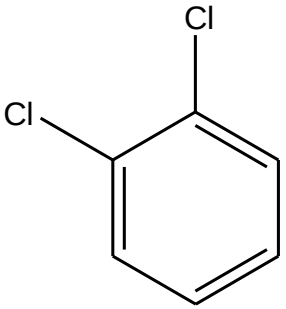
B



C

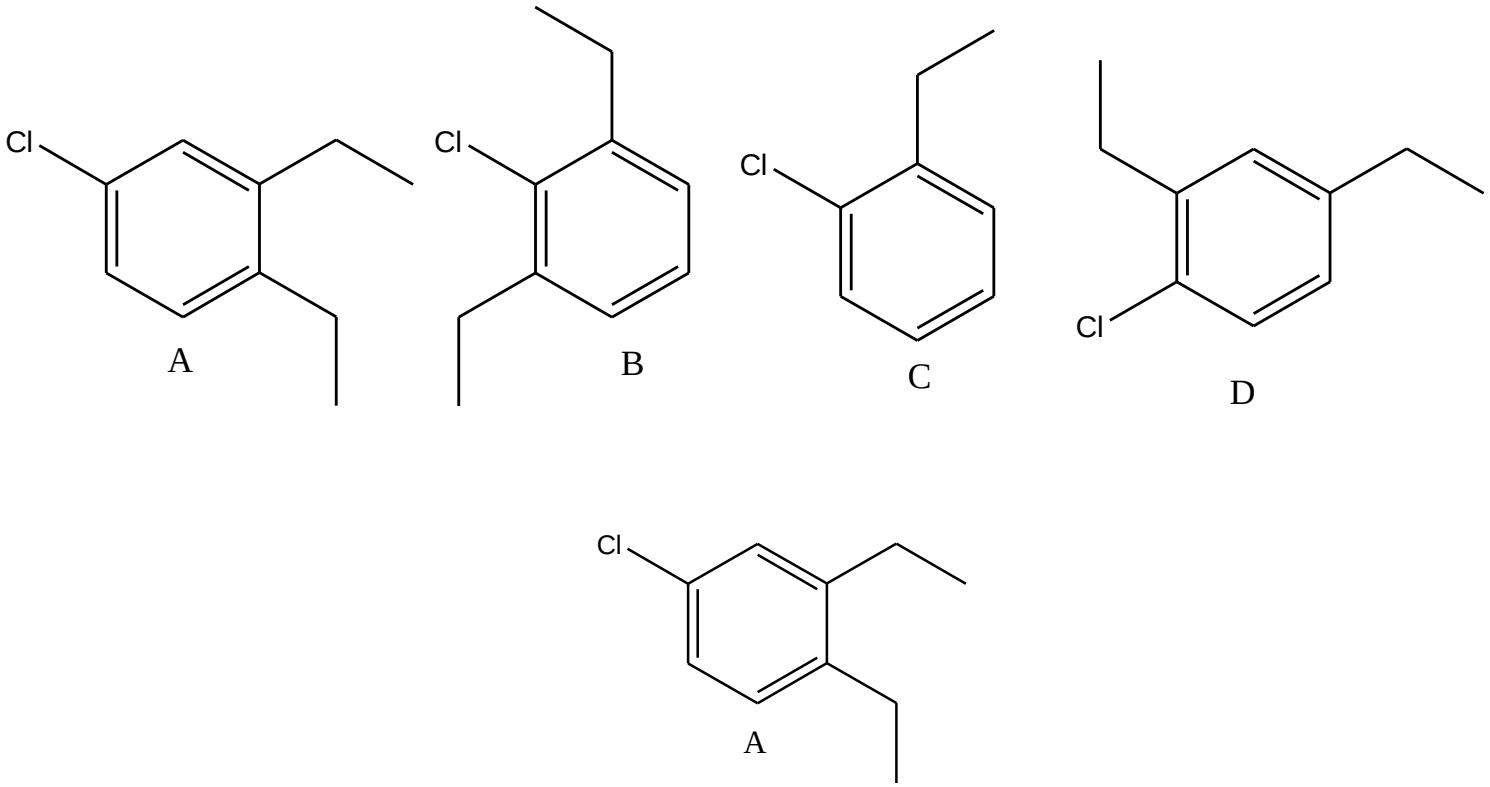


D



C

4-chloro-1,2-diethylbenzene



Stability of Benzene

- **Consider the heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene and benzene, all of which give cyclohexane when treated with excess hydrogen in the presence of a metal catalyst.**

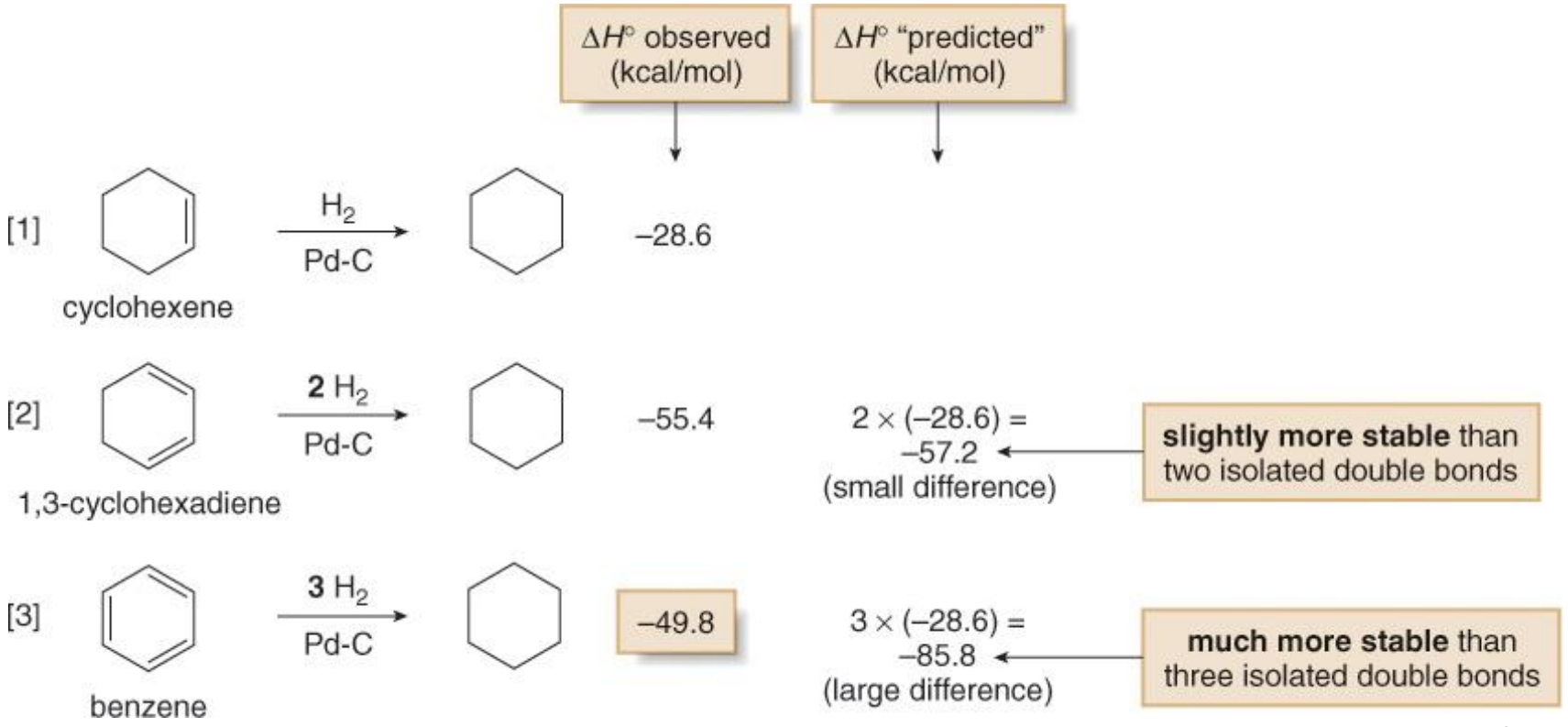
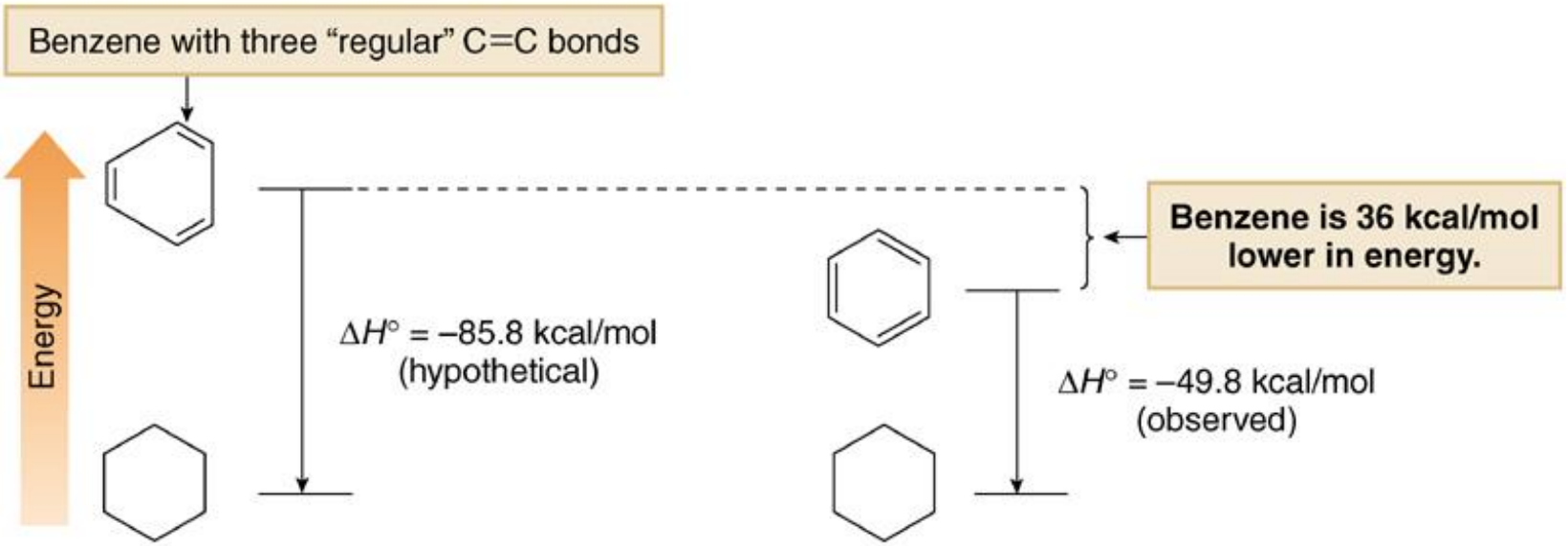


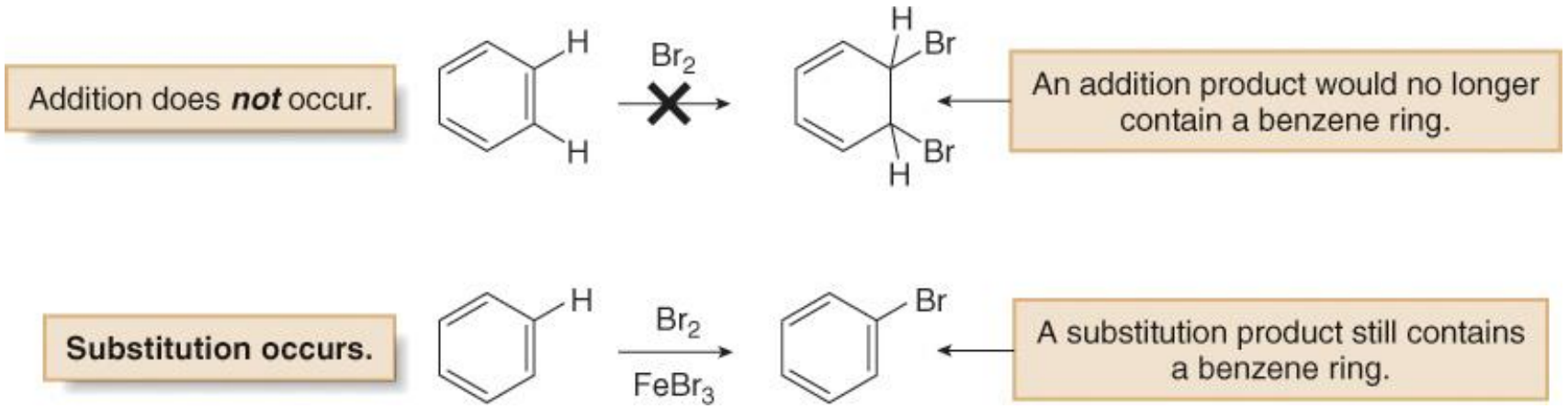
Figure 17.6 compares the hypothetical and observed heats of hydrogenation for benzene.

Figure 17.6
A comparison between the observed and hypothetical heats of hydrogenation for benzene



The huge difference between the hypothetical and observed heats of hydrogenation for benzene cannot be explained solely on the basis of resonance and conjugation.

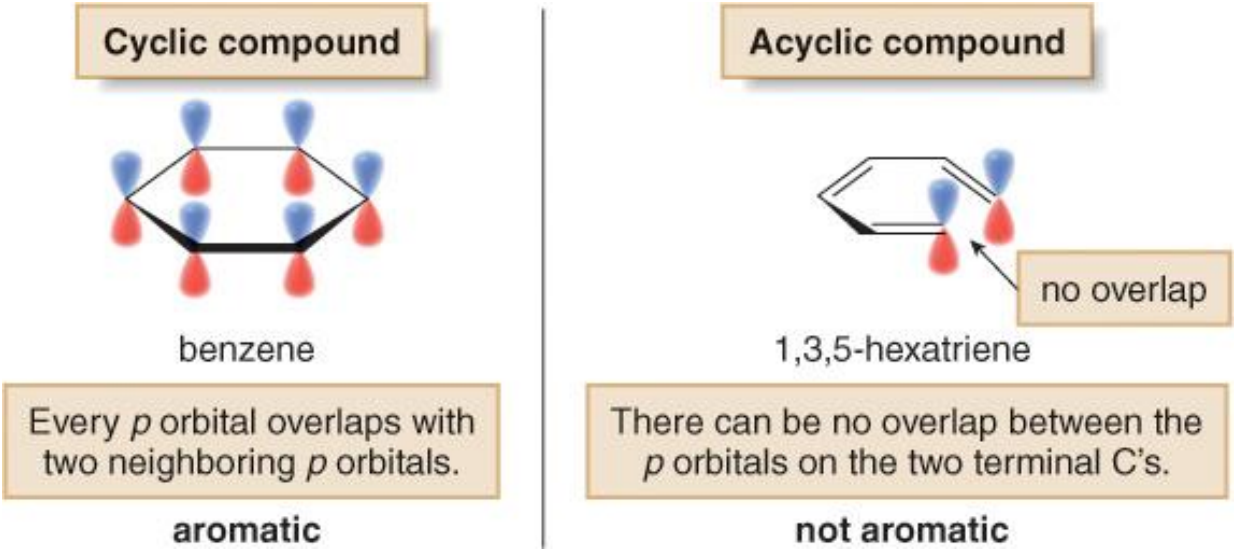
- **The low heat of hydrogenation of benzene means that benzene is especially stable—even more so than conjugated polyenes. This unusual stability is characteristic of aromatic compounds.**
- **Benzene's unusual behavior is not limited to hydrogenation. Benzene does not undergo addition reactions typical 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.**



The Criteria for Aromaticity—Hückel's Rule

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

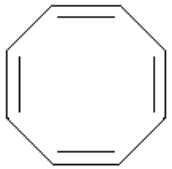
[1] A molecule must be cyclic.



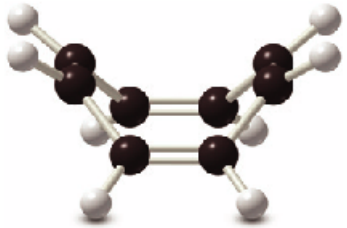
To be aromatic, each *p* orbital must overlap with *p* orbitals on adjacent atoms.

[2] A molecule must be planar.

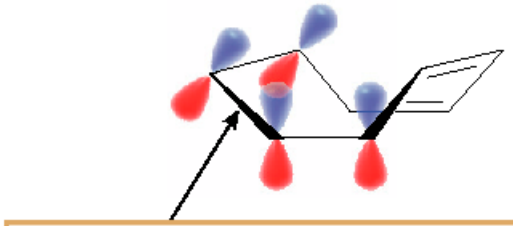
All adjacent *p* orbitals must be aligned so that the π electron density can be delocalized.



cyclooctatetraene
not aromatic

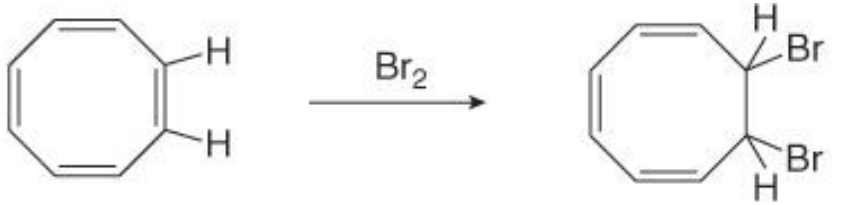


a tub-shaped,
eight-membered ring



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

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

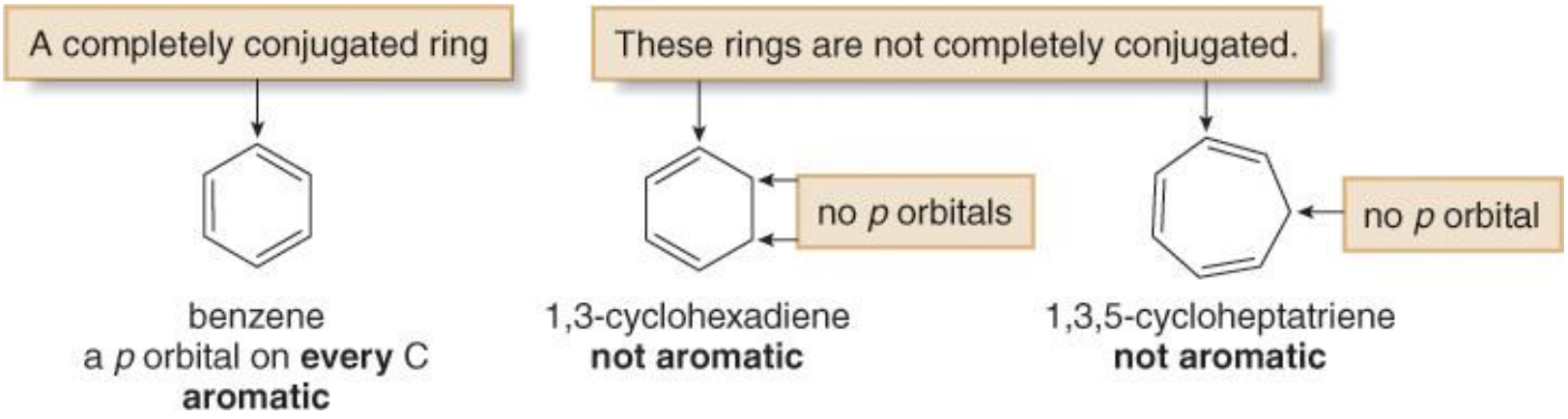


cyclooctatetraene

addition product

[3] A molecule must be completely conjugated.

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



[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.*

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

Benzene An aromatic compound	Cyclobutadiene An antiaromatic compound
	
$4n + 2 = 4(1) + 2 =$ 6 π electrons aromatic	$4n = 4(1) =$ 4 π electrons antiaromatic

Note that 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

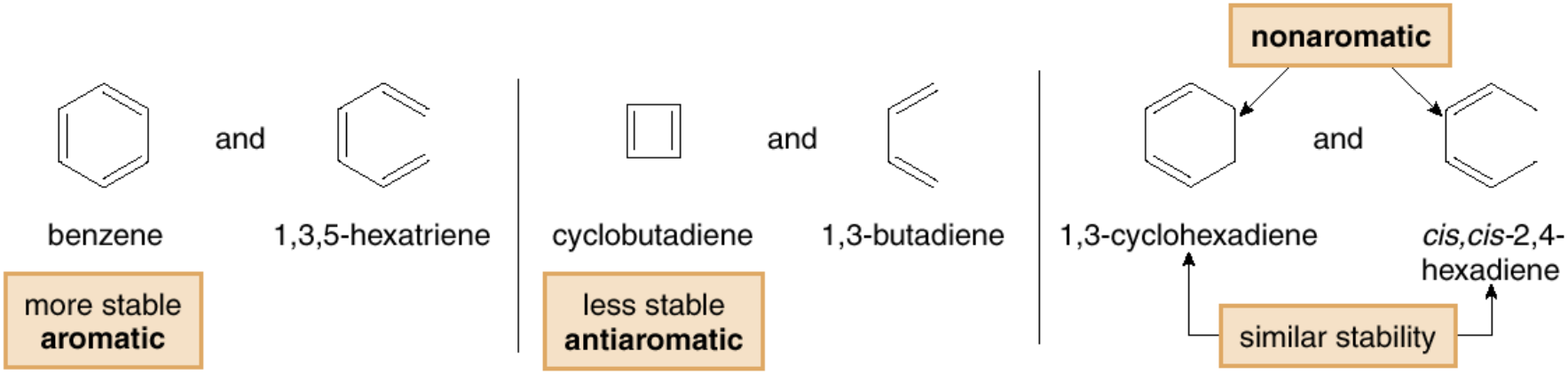
n	4*n* + 2
0	2
1	6
2	10
3	14
4, etc.	18

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.**

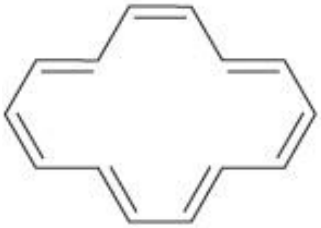
Note the relationship between each compound type and a similar open-chained molecule having the same number of π electrons.

- 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.

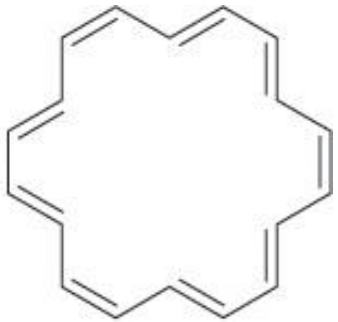


Examples of Aromatic Rings

- **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.**



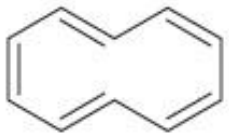
[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic



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

- **[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 can't delocalize over the entire ring and it is not aromatic.**

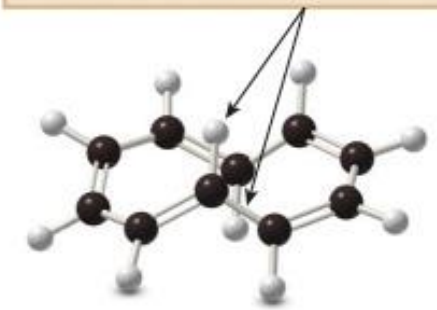
[10]-Annulene fits Hückel's rule, but it's **not planar**.



[10]-annulene
10 π electrons
not aromatic

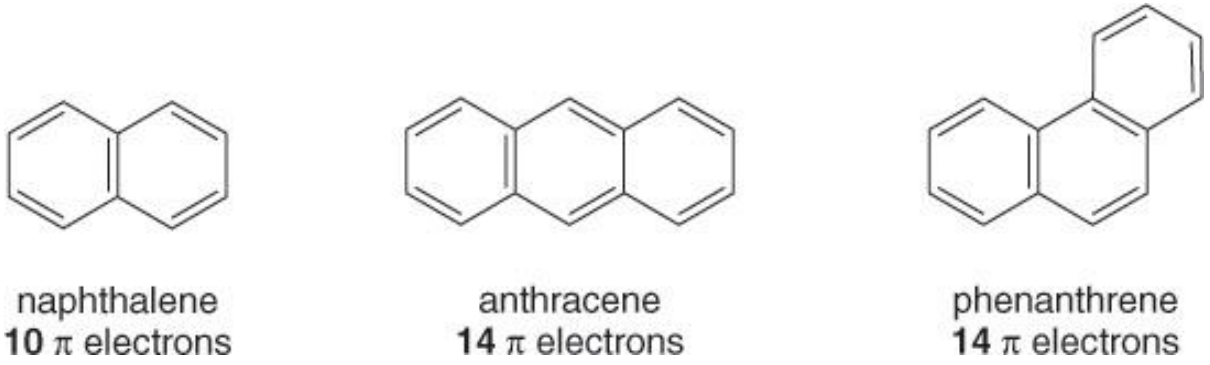
=

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



3-D representation

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



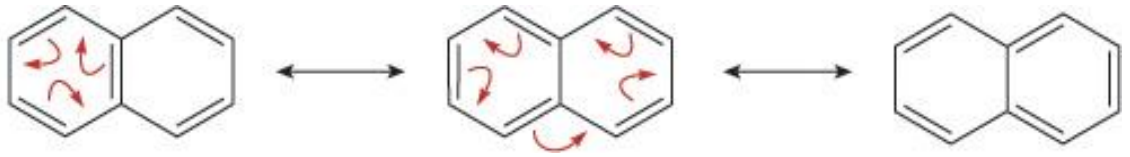
naphthalene
10 π electrons

anthracene
14 π electrons

phenanthrene
14 π electrons

- **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.**

Three resonance structures for naphthalene



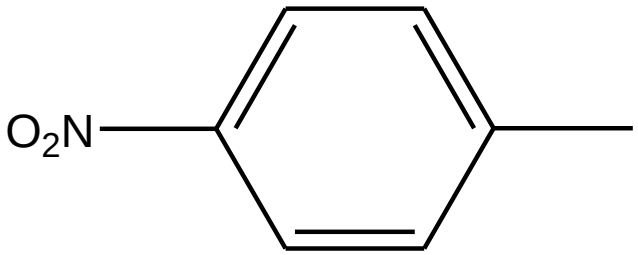
What is the correct name for this compound?

A) 3-Nitrotoluene

B) 4-Nitromethylbenzene

C) *p*-Nitrotoluene

D) (4,1)-Methylnitrobenzene



C) *p*-Nitrotoluene

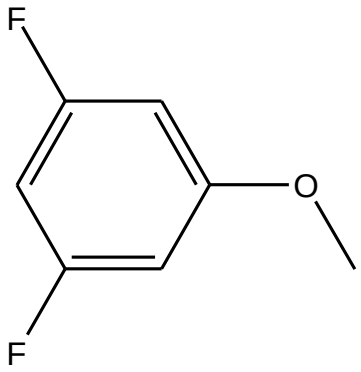
What is the correct name for this compound?

A) 3,5-difluoroanisole

B) Difluoromethoxybenzene

C) 1,5-difluoro-3-methoxybenzene

D) 1,3-difluoro-5-methyl-O-benzene



3,5-difluoroanisole

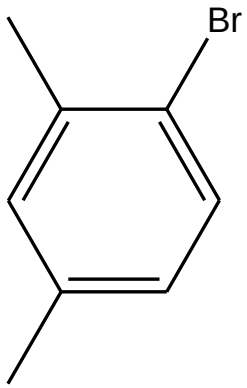
What is the correct name for this compound?

A) 4-bromo-*m*-xylene.

B) 1-bromo-2,4-dimethylbenzene.

C) *p*-bromo-*m*-methyltoluene.

D) *o*-bromo-*m*-methyltoluene.



B) 1-bromo-2,4-dimethylbenzene.

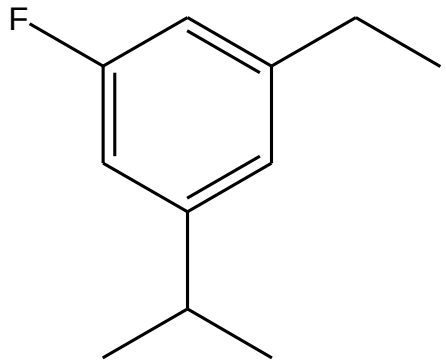
What is the correct name?

A) 1-fluoro-3-isopropyl-5-ethylbenzene

B) 1-ethyl-3-isopropyl-5-fluorobenzene

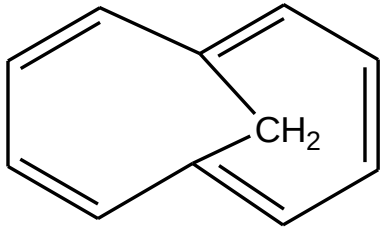
C) 1-ethyl-3-fluoro-5-isopropylbenzene

D) 1-isopropyl-3-fluoro-5-ethylbenzene

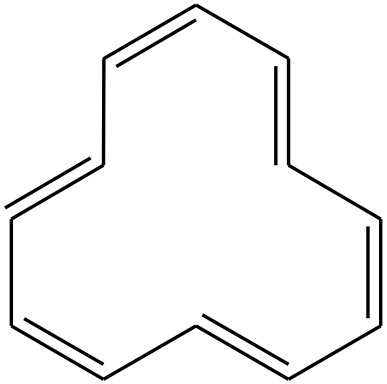


C) 1-ethyl-3-fluoro-5-isopropylbenzene

Which of these is aromatic?



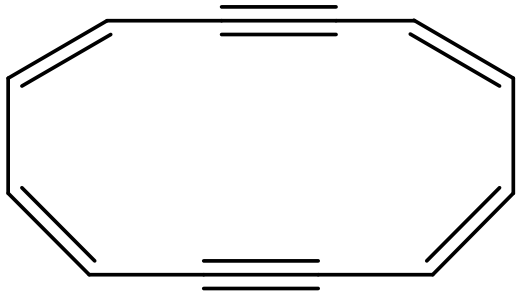
A



B

A) Is aromatic. Count the number of pi bonds in the outer ring. A has 5 which means 10 pi electrons, 4(2)+2=10. While B has 6 pi bonds and 12 pi electrons, 4(3)=12. Doesn't meet the Huckel rule requirements for aromaticity.

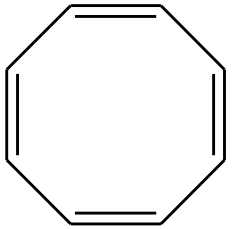
Is this compound aromatic or antiaromatic?



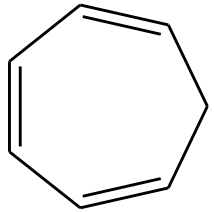
Antiaromatic – cyclic, planar, conjugated , but does not meet Huckel's rule.

4 doulbe bonds and 2 triple bonds so 4(2) + 2(4)=16 pi electons. 4n+2 or 4n? 4(4)=16

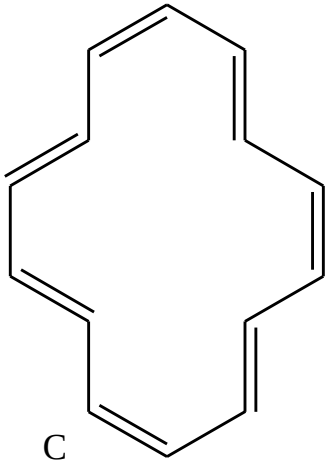
Indicate which of the following are aromatic and antiaromatic?



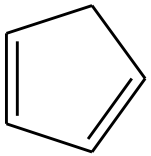
A



B



C



D

C is aromatic 4(3)+2=14

A is antiaromatic 4(2)=8

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.**