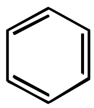
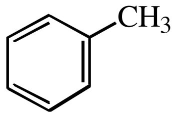
CHAPTER 15 - BENZENE AND AROMATICITY

"Aromatic" referred to compounds that were fragrant such as benzaldehyde and toluene. It now refers to a class of organic compounds that have a particular chemical behavior.

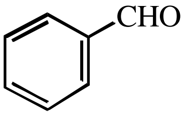
"Aromatic" refers to benzene and its structural relatives.



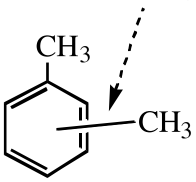
Benzene



Toluene



Benzaldehyde

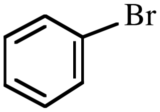


The CH_3 could
be attached to any
of the 3 ring positions

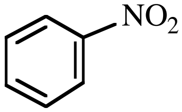
Xylene(s)

The rings occur in natural products and many synthetic drugs also contain these rings, often as part of a more complicated fused system. See your text for examples of these structures.

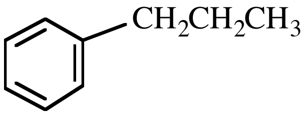
Many of these systems are products of fractional distillation and cracking processes of petroleum.



Bromobenzene



Nitrotbenzene

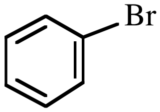


Propylbenzene

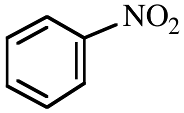
Nomenclature

Some simple substituted benzene derivatives have common names. The ones listed in Table 15.1 in your text should be memorized.

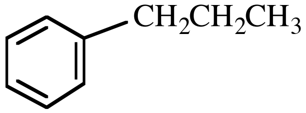
Others are named as substituted benzenes with ---*benzene* as the parent name.



Bromobenzene

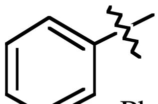


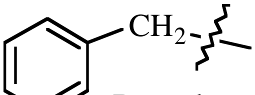
Nirotbenzene



Propylbenzene

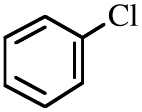
Alkyl-substituted benzenes are called **arenes** and are named differently depending on the size of the alkyl chain. If the chain has fewer than six carbons they are named as substituted benzenes. If the chain has more than six carbons they are named as **phenyl-substitued alkanes**


Phenyl

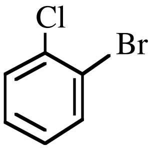


Benzyl

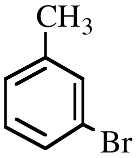
Disubstituted benzenes are names using *ortho*- (1,2 relationship), *meta*- (1,3 relationship) and *para*- (1,4 relationship) prefixes. .



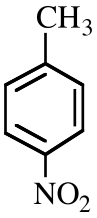
Chlorobenzene



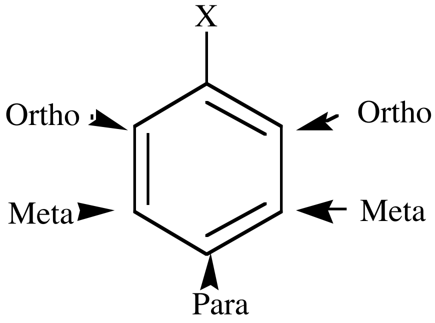
ortho-bromochlorobenzene
2-chloro-1-bromobenzene



meta-bromotoluene
3-bromotoluene



These prefixes cannot be used for tri- or higher substituted benzenes. The terms are useful for describing relative substitution positions in reactions



More than two substituents require numbering of the ring... lowest numbers, listed alphabetically.

If one of the common names is used in the name (e.g. toluene), the # 1 position on the ring is the substituent that is part of the name.

Structure of Benzene:

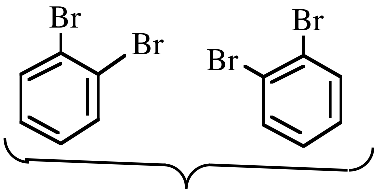
By 1850's knew that the molecular formula was C_6H_6. Knew something about the chemistry of benzene

Benzene gives substitution product with Br_2 in the presence of iron (Fe). Only one monosubstitution product was known - no isomers.

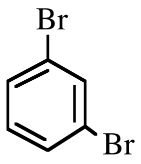
$$C_6H_6 + Br_2 \xrightarrow{Fe} C_6H_5Br + HBr$$

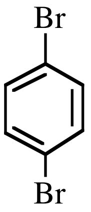
Substitution product not addition product. Need iron or $FeBr_3$ to react

Also only three disubstitution products.



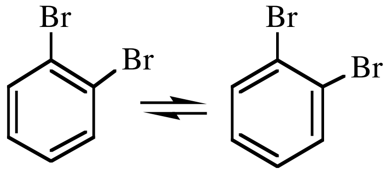
Are there two ortho products?



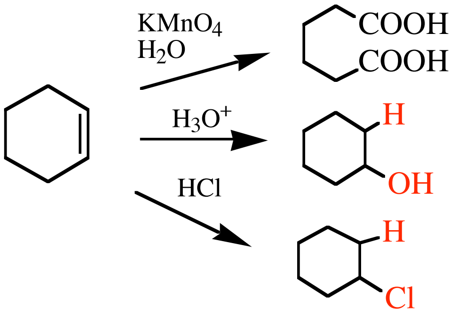


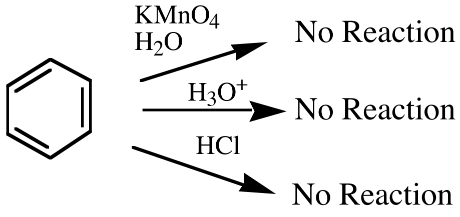
(August) Kekule proposed that structure was a ring that was equivalent to 1,3,5-cyclohexatriene. Would account for only one <u>mono</u>substitution product as all C and all H are equivalent. But should there be two 1,2-disubstitution products?

Kekule proposed that there was rapid oscillation between the two positions. Two isomers cannot be separated because they interconvert too rapidly.



Structure still does not answer why is benzene unreactive compared to other alkenes -and why substitution products and not addition products?





Benzene does not undergo electrophilic **addition** reactions.

If we examine heat of hydrogenation of benzene we find that there is a difference of 150kJ/mol **<u>less heat</u>** (36kcal/mol) given off than we would expect if the structure were indeed cyclohexatriene.

Also find that all carbon-carbon bonds are the same length - between C-C (1.54Å) and C=C (1.34Å), measuring 1.39Å.

Ways to explain this….

Resonance approach -

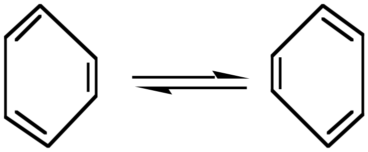
Remember...
1. Resonance forms are imaginary - not real.

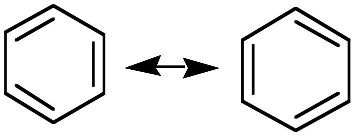
2. Resonance structures differ only in the positions of their electrons

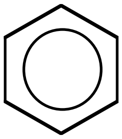
3. Different forms don't have to be equivalent.

4. The more resonance forms there are, the more stable the molecule.

Kekule's representation is not quite a resonance explanation because he still considered double and single bonds and not something in between.

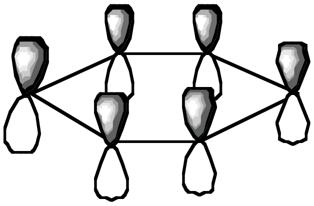

Kekule


Resonance

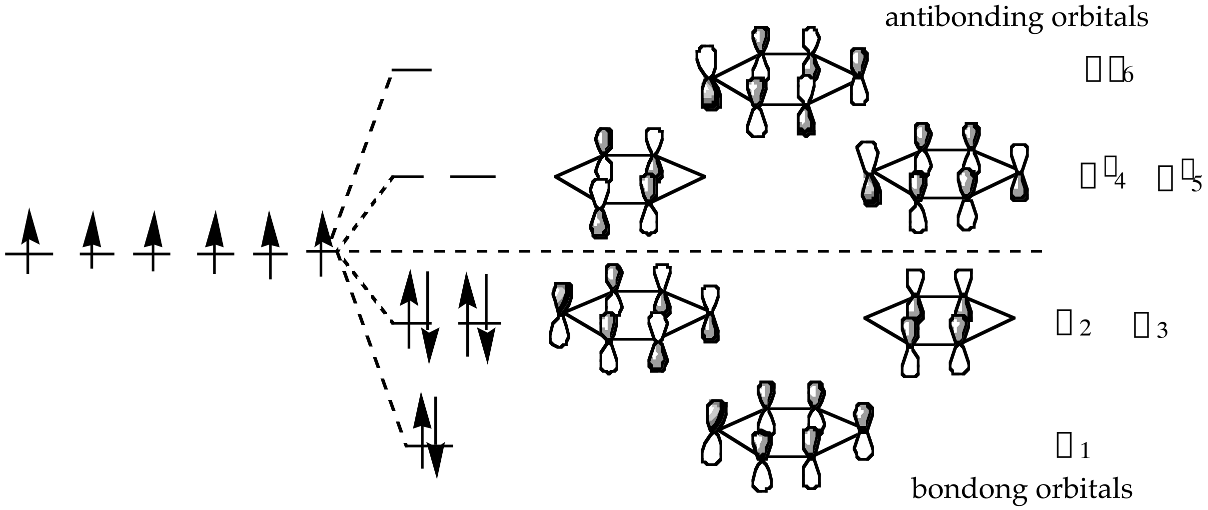


Molecular Orbital explanation -

Benzene is a planar molecule - all six C's are sp^2 hybridized & each carbon has a p-orbital that is perpendicular to the plane of the ring.



When we construct molecular orbital diagram we get that below. All electrons (6) involved in the pi system are in bonding orbitals



Aromaticity and the Hückel 4*n* + 2 Rule

Review

1. Benzene is a cyclic conjugated molecule

2. Benzene is unusually stable - 150 kJ/mol than expected for cyclohexatirene

3.Benzene is planar, regular hexagon. All bond angles 120° and all bond lengthe are 1.39Å.

4.Benene undergoes substitution rather than addition that would destroy the conjugation.

5.Benzene is a resonance hybrid.

But there are other aromatic molecules. What makes them aromatic.

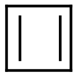
HÜCKEL 4n + 2 π ELECTRON RULE

(Erich) Hückel devised a theory.

A molecule is aromatic if it is a **planar**, mono**cyclic** system with a **p orbital on each atom** (sp2 hybrid) in the ring and if the **π orbital system contains 4n + 2 π electrons** where n is an integer 0, 1, 2, 3, 4...............

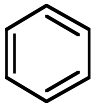
Examine

Cyclobutadiene



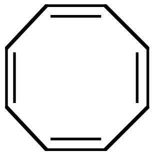
Cyclic, planar, all sp^2, but not 4n + 2 π electrons, thus ANTIAROMATIC

Benzene



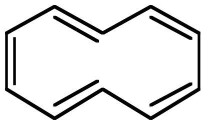
We have already examined this.! AROMATIC

Cycloocatetraene



Cyclic, all sp^2, but not 4n + 2 π electrons AND <u>not planar.</u> ANTIAROMATIC

What about?....

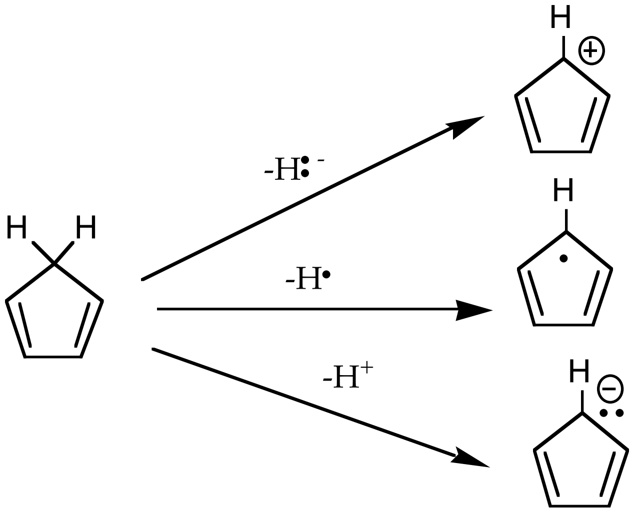


Cyclic, all sp^2, 10 p electrons, but not planar

Aromatic Ions

Nothing in the definition of and requirements for aromaticity says that the number of p orbiltals and the number of electrons involved has to be the same (such as 6 carbons and six electrons in benzene). In fact, there are organic ions that are aromatic.

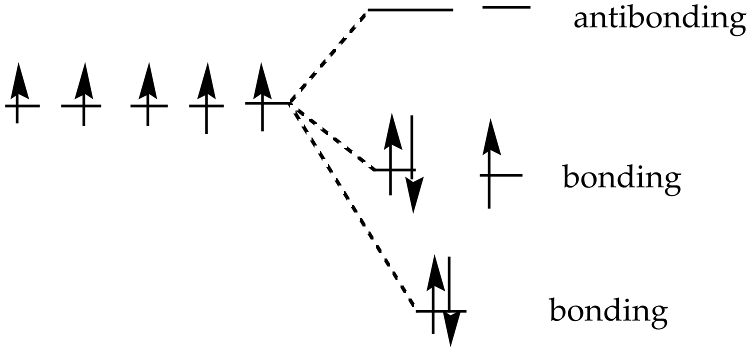
Examine cyclopentadiene



Three ways of removing the H from the sp^3 carbon.... to yield a carbocation, a carbon radical or a carbanion.

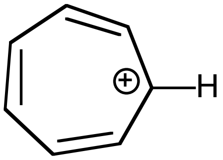
The anion should be aromatic because of the number of electrons.

Examine the molecular orbitals

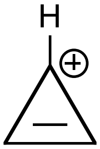


Shown is that of the radical. If we consider the anion there is one more electron and so we now have all electrons paired and all in bonding orbitals. Stable situation.

We can see the same sort of analysis for cycloheptatrienyl CATION. All atoms are sp^2 hybridized, six □ electrons, (remember the carbocation is sp^2).



The small ring, cyclopropenyl cation is also aromatic



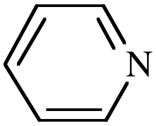
Heterocyclic Aromatics

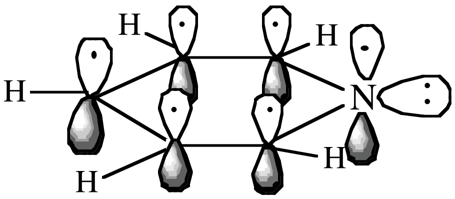
Heterocyclic compounds are ring compounds that contain at least one atom other than carbon in the ring. This hetero atom is very often S, N. or O.

Examples:

Some of these are aromatic

Pyridine:

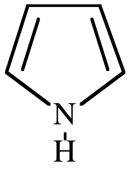


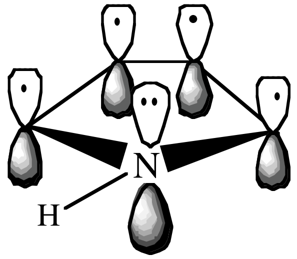


The lone pair of electrons on nitrogen is in an sp2 orbital in the pl;ane of the ring as are the hydrogens

Pyridine is aromatic. The six pi electrons come from each of the atoms in the ring including the nitrogen.

Pyrrole:

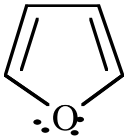




The lone pair of electons on nitrogen is part of the aromite pi system.

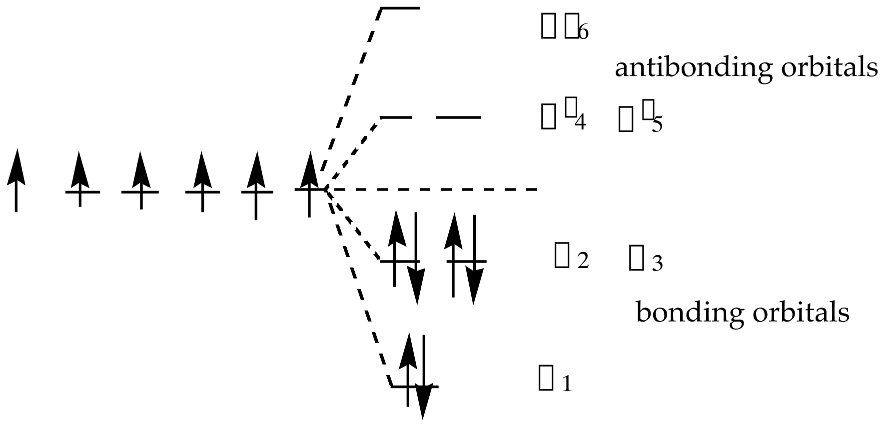
In pyrrole, the lone pair of electrons on nitrogen is part of the pi system

What about furan?



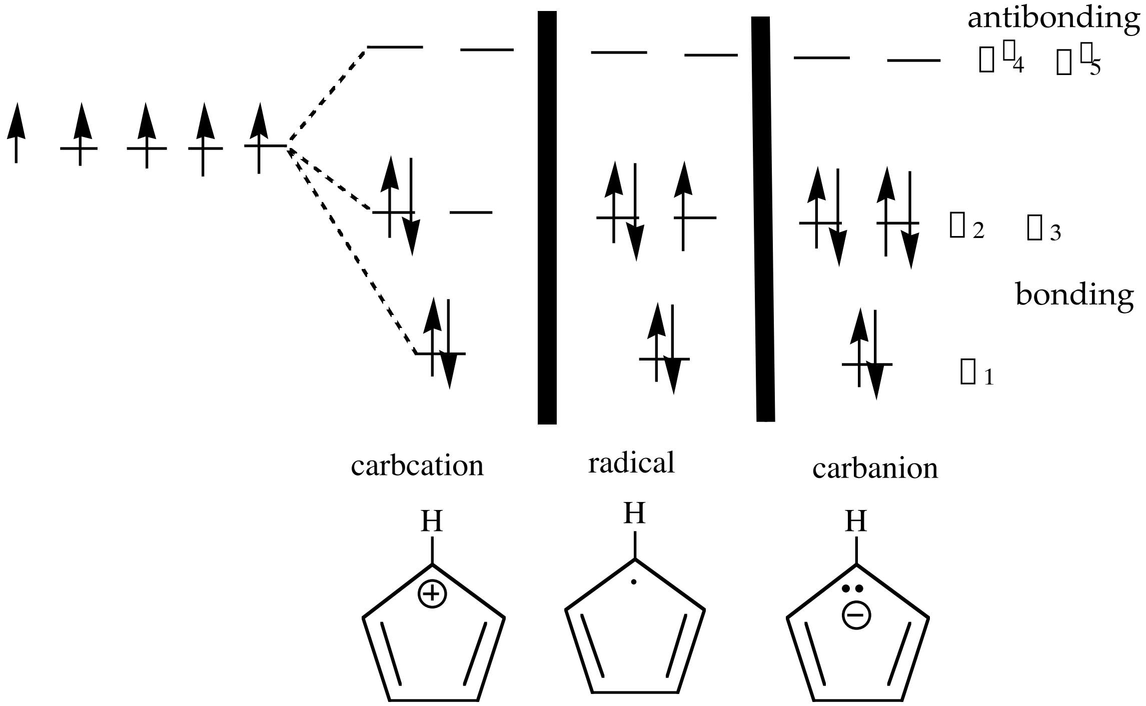
Why 4n + 2 ?????

Let's look at the M.O. diagram for benzene.



All electrons in the pi system are in bonding orbitals and all are paired. This is a stable situation.

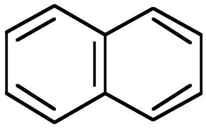
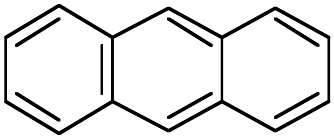
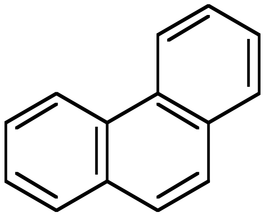
When we look at the cyclopentadienyl cation, radical and anion we can see a stable situation.



In the carbanion only are all of the pi electrons paired.

Polycyclic aromatics

Naphthalene, anthracene and phenanthrene are examples of polycyclic aromatics.

There are three resonance forms of naphthalene. See text for these.

Try drawing the resonance forms for anthracene and phenanthrene.

Omit Section 15.10 Spectroscopy of Aromatic Compounds