Chem 342 Organic Chem II

Lecture Summary 13
11 Feb 2002

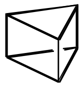
These notes can be obtained at: http://www.ndsu.nodak.edu/instruct/grcook/chem342/notes.shtml

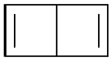
Chapter 15: Benzene and Aromaticity

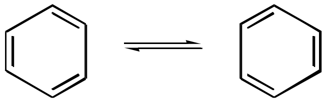
Benzene Structure

Benzene was first isolated from whale oil in 1825 by Michael Faraday. It was found to be highly unsaturated, but did not show positive chemical tests for unsaturation. A number of structures were postulated to explain the unsaturation and reactivity of benzene. In 1865, Kekulé came up with the idea of a 6-membered ring with three alternating double bonds. His vision was not completely correct as he saw these double bonds moving and the structure as two equilibrating molecules. Today the structure is much better understood by resonance theory which explains why all the C-C bonds are equivalent. The molecule is flat and has a completely conjugated pi-system.

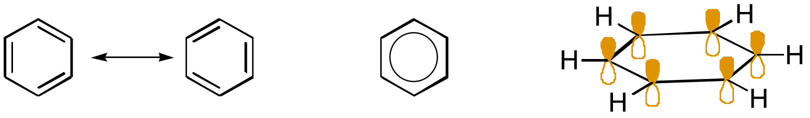
$$C_6H_6 \xrightarrow[KMnO_4]{Br_2 \text{ or}} \text{no reaction}$$


prismane


Dewar benzene

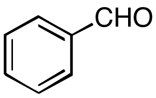

Kekulé structures

modern view of benzene's structure

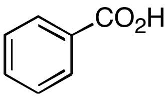


Nomenclature

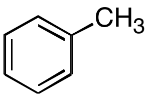
Benzene and its derivatives are termed Aromatic Compounds largely due to history. The first aromatic compounds were isolated from natural sources and were very aromatic. For example, benzaldehyde is the distinctive aroma from almonds and is also found in cherries. A number of aromatic compounds have common names that are in use today and are worth learning.



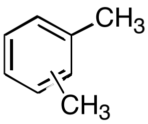
benzaldehyde



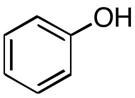
benzoic acid



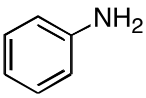
toluene



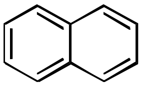
xylene

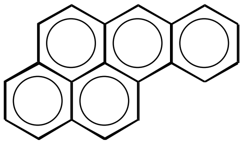


phenol



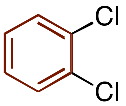
aniline


naphthalene

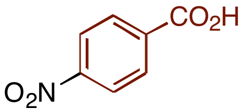

polyaromatic hydrocarbons (PAH's)
carcinogens formed from burning organic material
This PAH is the main carcinogen found in Tobacco smoke (so quit for goodness sake!)

Aromatic compounds are named with benzene as the parent. If there is a common derivative with a common name, that may be used as the parent name as well. For benzene derivatives that have two substituents, the terms ortho, meta, and para are used to refer to the groups being in the 1,2- 1,3- and 1,4-positions, respectively. More than two substituents are always numbered using the lowest possible numbers.

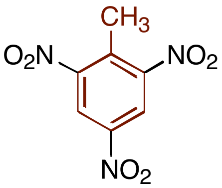
A benzene ring as a substituent to a larger molecule is called a phenyl group. This is often abbreviated as Ph in structure drawings. Phenyl may also be used in some common names (eg. biphenyl).



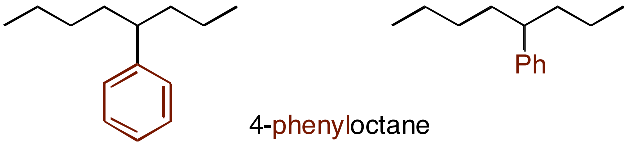
orthodichlorobenzene
or
1,2-dichlorobenzene



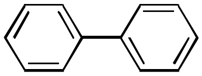
paranitrobenzoic acid



2,4,6-trinitrotoluene



4-phenyloctane

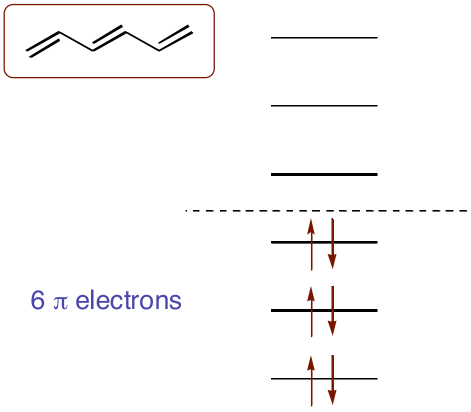


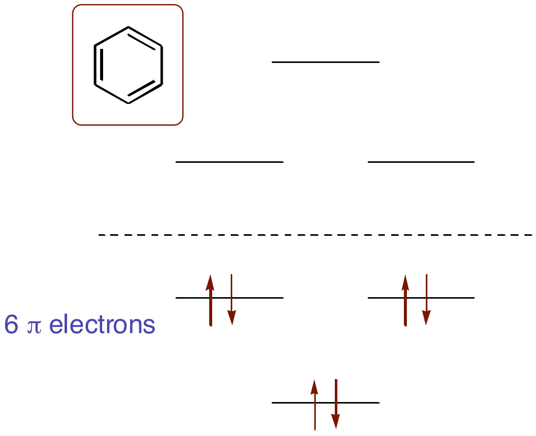
biphenyl

Benzene Stability

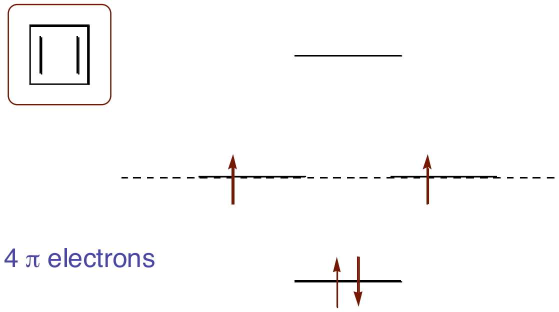
Benzene is much more stable than would be predicted from just the energy of the double bonds, even more stable than conjugated double bonds. It does not undergo chemistry that is typical of alkenes. It will, however, react with very reactive electrophiles to do substitution reactions leaving the aromatic ring intact.

Molecular orbital theory explains aromatic stability quite well. If a conjugated molecule is a ring, some of the molecular orbitals become degenerate in energy due to the symmetry of the ring. Compare 1,3,5-hexatriene and benzene. The benzene pi-electrons are overall lower in energy due to the degenerate orbitals.





Other conjugated ring systems may or may not be aromatic. For example, cyclobutadiene would be expected to NOT be stable. If the molecular orbitals are filled with electrons, there would be unpaired electrons. This molecule is very reactive and not stable.



In order to be aromatic, three requirements must be met:

A fully conjugated pi-system

A planar ring

Must have 4n+2 electrons in the pi-bonds (n = any integer) (Huc̈kel’s Rule)