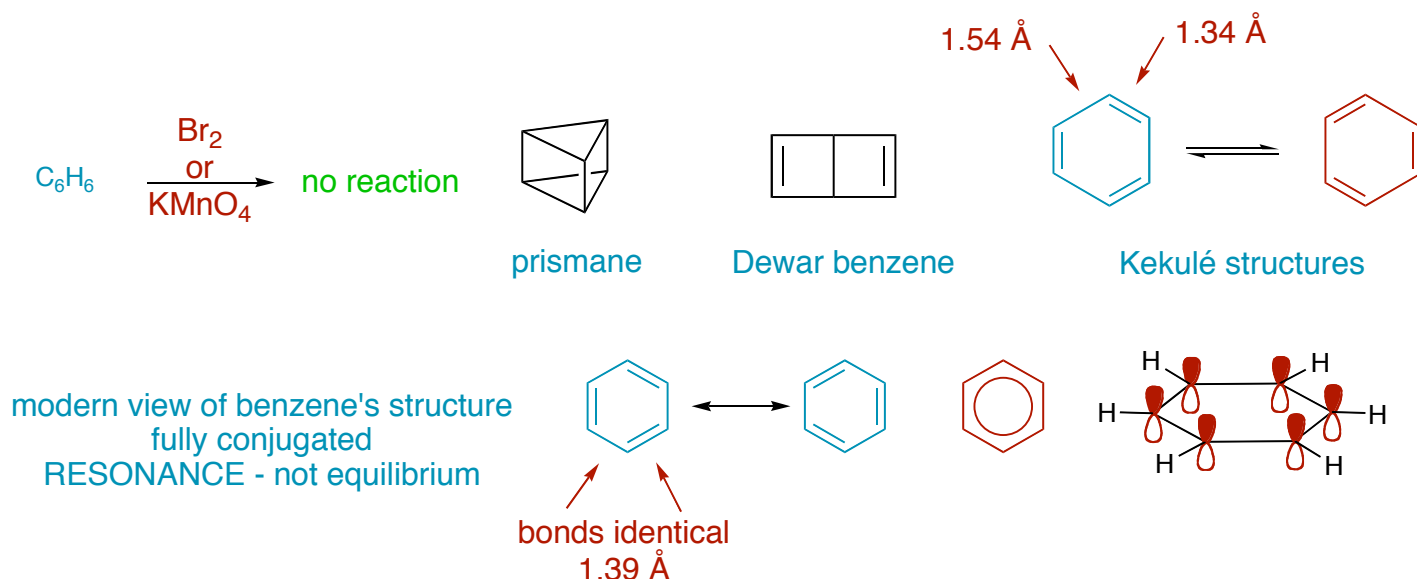


Chapter 15 - Benzene and Aromaticity

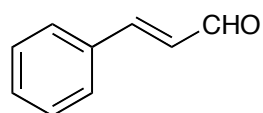
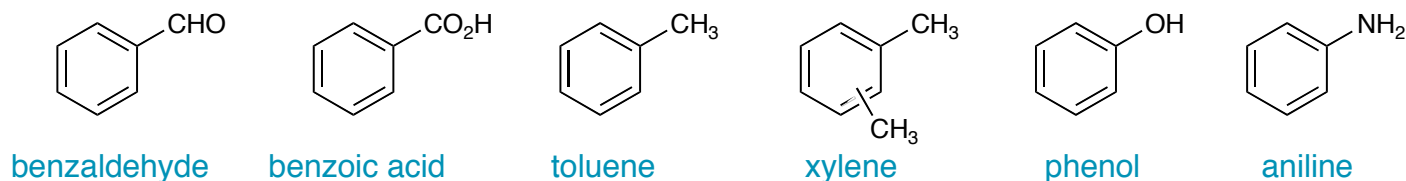
Benzene Structure

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.

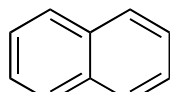


Naming

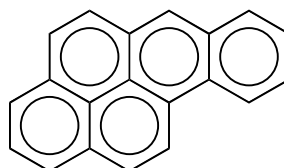
Benzene and its derivatives are termed **Aromatic Compounds** largely due to history. The first aromatic compounds were isolated from natural sources and were very aromatic. For example, benzaldehyde is the distinctive aroma from almonds and is also found in cherries. A number of aromatic compounds have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



cinnamaldehyde



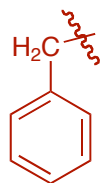
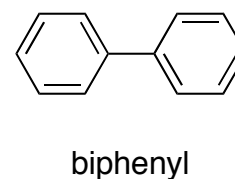
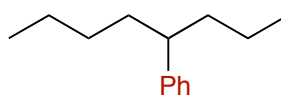
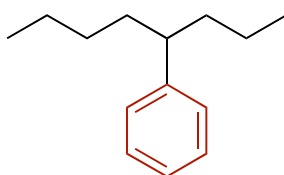
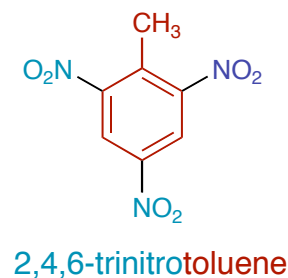
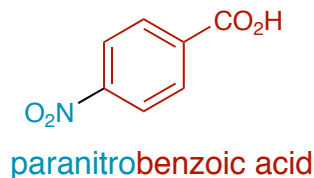
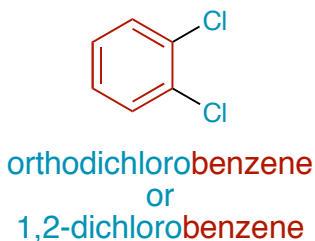
naphthalene



polycyclic aromatic hydrocarbons (PAH's)
 carcinogens formed from combustion
 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).

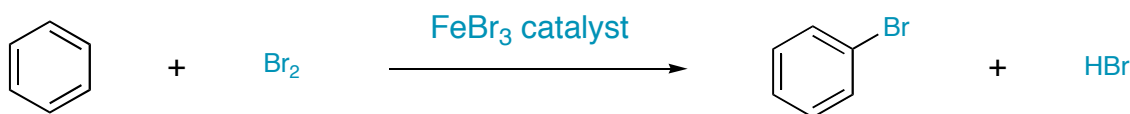


benzyl substituent

Don't confuse a phenyl group with a **benzyl** group. The terminology, benzyl, refers to a benzene ring AND another carbon.

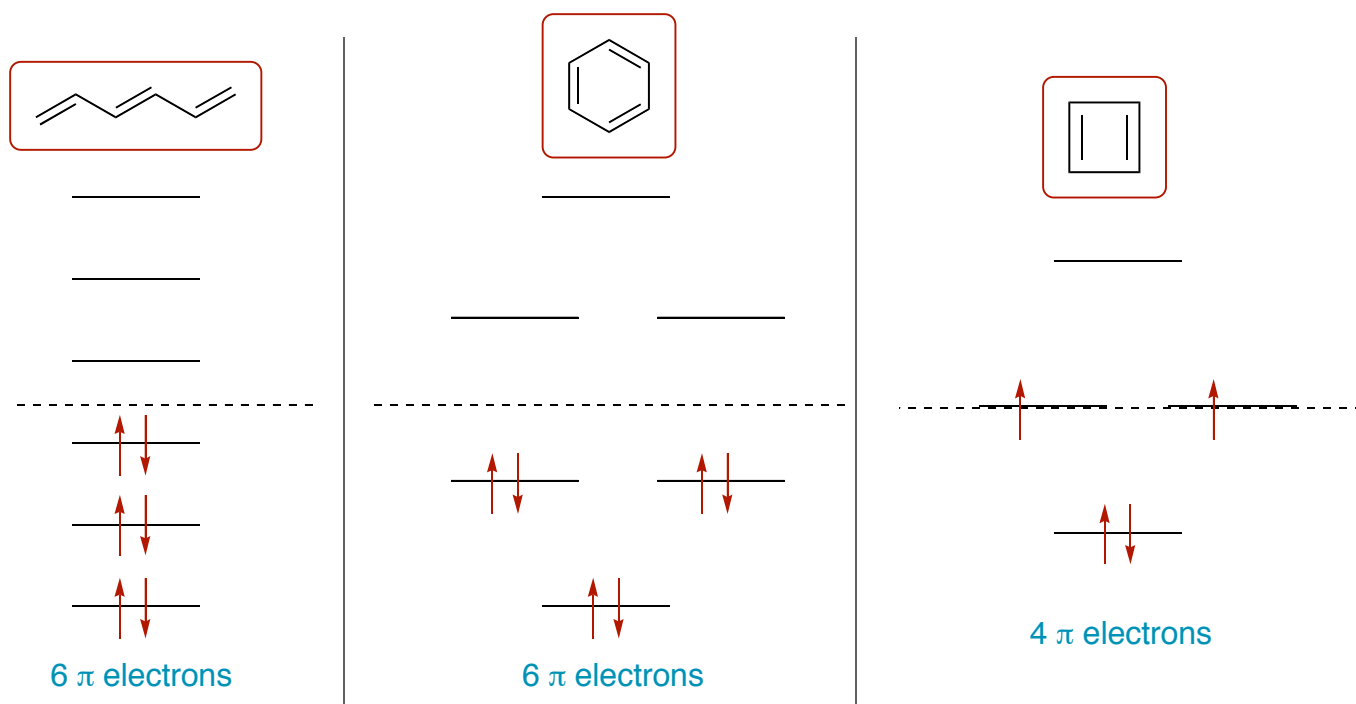
Benzene Stability

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.



To have aromatic stabilization, a molecule must have three things:

- A planar ring
- A fully conjugated pi-system (a p orbital on every atom in the ring)
- Have $4n+2$ number of electrons in the pi-system (Hückel Rule)