**BENZENE - AROMATIC COMPOUNDS**

*Aliphatic Compounds:* Open chain (acyclic) and those cyclic compounds with similar chemical properties. A typical reaction type of unsaturated aliphatic compounds: electrophilic addition.

*Aromatic Compounds:* Benzene, C\(_6\)H\(_6\), and other unsaturated compounds that resemble it in chemical behavior. The aromatic properties of benzene are those that distinguish it from aliphatic hydrocarbons.

What are these properties?

*Properties of Aromatic Compounds —*

- Cyclic and each atom in the ring is a \(\pi\)-center (uses a p atomic orbital to form \(\pi\)-type bonds), *ie*, sp\(^2\) or sp.
- Ring is flat or nearly so.
High degree of unsaturation but resistant to addition reactions — generally undergo electrophilic substitution (an electrophilic reagent replaces a hydrogen [usually] attached to the ring).

Unusually stable.

π-Electrons delocalized above and below plane of ring.

π-Electron Delocalization – Benzene

Each carbon "starts" with a p atomic orbital containing one electron. These orbitals are perpendicular to the ring, but parallel to each other. These atomic orbitals are shown in the figure below. Each p orbital interacts ("overlaps") with two neighbors. This gives rise to six π-type orbitals, Ψ₁ through Ψ₆. Ψ₁ through Ψ₃ are bonding orbitals; Ψ₄ through Ψ₆ are antibonding. It turns out that Ψ₁ is the lowest energy orbital. Ψ₂ and Ψ₃ are degenerate, i.e. they have the same energy, and it is higher than the energy of Ψ₁. The electrons in the three occupied bonding orbitals give rise to one doughnut of electron density above the ring and one below, containing a total of 6 π electrons. This aromatic electronic delocalization results in considerable stabilization — more than is observed in the case of conjugated aliphatic compounds.
Atomic p-orbitals: basis orbitals for benzene $\pi$-orbitals.
Because of the $\pi$-electrons, benzene, and other aromatic compounds, frequently act as Lewis bases or nucleophiles; thus, they are susceptible to *electrophilic attack*. Because of the stability associated with the delocalized electrons, this feature tends to be retained in the products; consequently, these reactions are usually *substitutions, not additions*.

\[
E^+ + \text{C}_6\text{H}_6 \rightarrow \text{ECH}_3 + H^+ 
\]

**Sources of Aromatic Compounds**

Aromatic hydrocarbons may be obtained from —

1) petroleum – not rich in aromatics, but has some.

2) reforming cycloalkanes from petroleum, *eg*

\[
\text{CH}_3
\begin{array}{c}
\text{heat, catalyst} \\
\text{high pressure}
\end{array}
\rightarrow \text{CH}_3
\]

\[
\begin{array}{c}
+ 3 \text{ H}_2
\end{array}
\]
3) coal tar and coal gas.

Coal derives from plants which have suffered partial decay and been subjected to heat and pressure.

plants $\rightarrow$ peat $\rightarrow$ lignite $\rightarrow$ bituminous (soft) coal $\rightarrow$ $\rightarrow$ anthracite (hard)

Bituminous coal is a good source of aromatic compounds. Destructive distillation of it forms coal gas, coal tar, and coke. Coal tar is rich in aromatic hydrocarbons, bases (eg, pyridine), and phenolic (Ar-OH) compounds. [Ar- is shorthand for an aromatic ring, just as R- is shorthand for an alkyl group.]