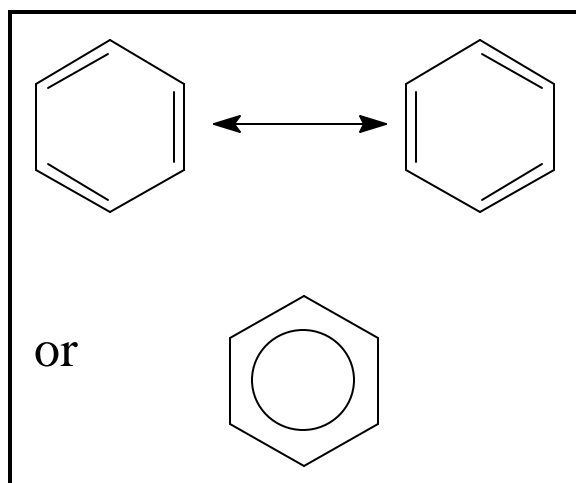


BENZENE - AROMATIC COMPOUNDS

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_6H_6 , and other unsaturated compounds that resemble it in chemical behavior. The aromatic properties of benzene are those that distinguish it from aliphatic hydrocarbons.



Benzene

What are these properties?

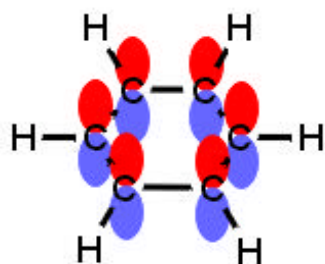
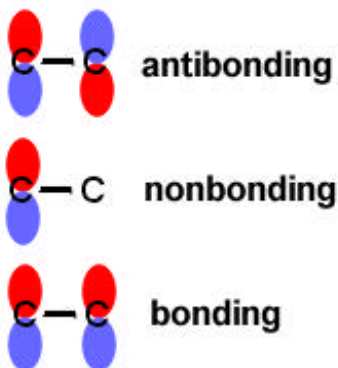
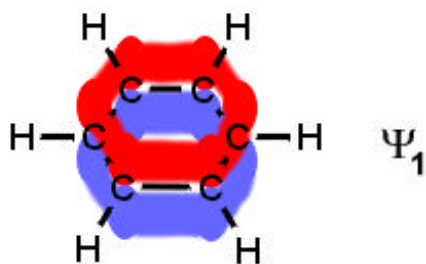
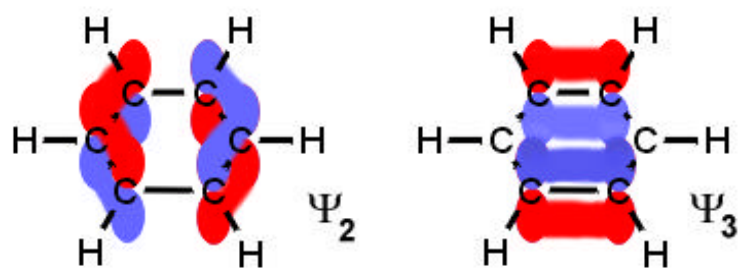
Properties of Aromatic Compounds —

- ☞ Cyclic and each atom in the ring is a π -center (uses a p atomic orbital to form π -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.

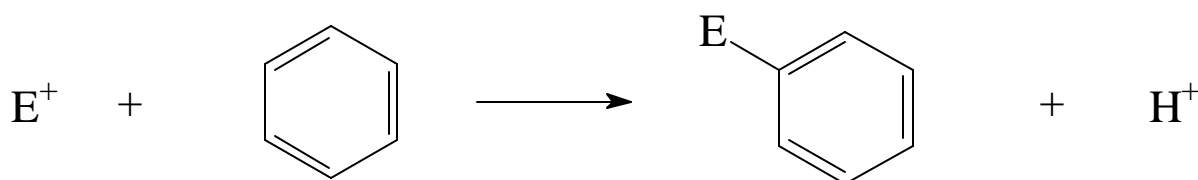
π -Electron Delocalization – Benzene

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, Ψ_1 through Ψ_6 . Ψ_1 through Ψ_3 are bonding orbitals; Ψ_4 through Ψ_6 are antibonding. It turns out that Ψ_1 is the lowest energy orbital. Ψ_2 and Ψ_3 are *degenerate*, *i.e.* they have the same energy, and it is higher than the energy of Ψ_1 . **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 p 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 π -orbitals.

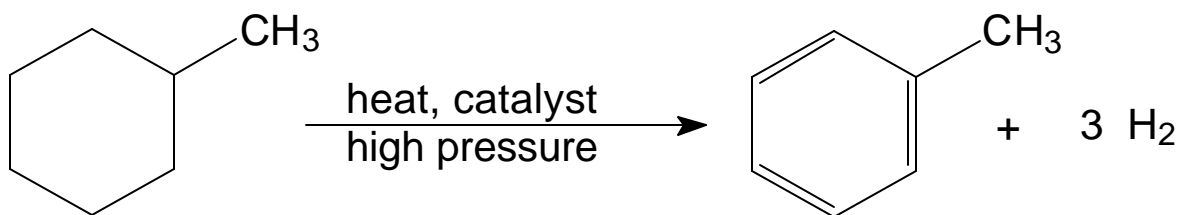
Because of the π -electrons, benzene, and other aromatic compounds, frequently act as Lewis bases or nucleophiles; thus, they are susceptible to *electrophilic attack*. Because of the stability associated with the delocalized electrons, this feature tends to be retained in the products; consequently, these reactions are usually *substitutions, not additions*.



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



3) coal tar and coal gas.

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

plants → peat → lignite → bituminous (soft) coal →
→ 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.]

