CHAPTER 15 Benzene and Aromaticity: Electrophilic Aromatic Substitution

15-1 Naming the Benzenes
Proper, IUPAC names for substituted benzene compounds use numbers to indicate relative positions of substituents. When only two substituents are present the terms ortho, meta, and para are commonly used instead.

15-2 Structure and Resonance Energy of Benzene: A First Look at Aromaticity
Were benzene simply cyclohexatriene, it would be expected that reduction would release three times the energy released upon reduction of cyclohexene, or 3 x −28.6 = −85.8. However, the observed value is 49.3 and thus benzene is some 36 kcal/mole more stable that predicted for cyclohexatriene.

15-3 Pi Molecular Orbitals of Benzene
The molecular orbitals of the pi system of benzene are derived by combination of the six p-orbitals on the six carbon atoms. All six molecular orbitals have a nodal plane that includes the carbon atoms as well as the hydrogen atoms. The lowest lying orbital has no other nodes whereas the next two, equal energy orbitals have one additional node. The nodes of these two orbitals are at right angle to each other. These three lowest lying orbitals constitute the bonding molecular orbitals and hold the six-pi electrons of benzene. The relative energies of orbitals of cyclic systems with sp2 atoms can be simply predicted by drawing the polygon of the structure with one atom at the bottom. The vertices of the polygon are then located so as to represent the energy levels of the orbitals.
C₆H₆

C₆H₆

Cl₂ → NR

Cl₂ → AlCl₃

Cl₂ → Cl

Cl₂ → Cl

Cl₂ → Cl

Cl₂ → Cl

?
\[ \Delta H = 28.6 \text{ kcaP/mole} \]

Predict: \[ 3 \times -28.6 = -85.8 \]

Measured: \[ -49.3 \]

\[ \frac{36.5}{36.5} \]
\[ \text{hv} \]
\[ \pi \text{ bonding} \]
\[ \pi \text{ antibonding} \]

171 nm  \[ \text{H}_2\text{C} \equiv \text{CH}_2 \]
217 nm  \[ \text{H}_2\text{C} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_2 \]
263 nm  \[ \text{H}_2\text{C} \equiv 
\text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_2 \]
Base

$pKa = 15$

Diagram of chemical structures.
EAS
(Electrophilic Aromatic Substitution)
Electrophilic Aromatic Substitution
Cl₂ + AlCl₃ → Cl⁻Cl⁻-AlCl₃

Cl⁻ + Cl⁻-AlCl₃ → Cl⁻