

Chapter 15: Aromaticity, Reactions of Benzene

Learning Objectives:

1. Recognize and distinguish between aromatic and antiaromatic compounds by their structures.
2. Know the properties of aromatic and antiaromatic compounds, and the chemical consequences of aromaticity.
3. Recognize and be able to write the mechanism of electrophilic aromatic substitution
4. Be able to outline the completed electrophilic aromatic substitution reactions of the following types: halogenation, nitration, sulfonation, and Friedel-Crafts acylation & alkylation

Sections:

- 15.1 Criteria for Aromaticity*
- 15.2 Aromatic Hydrocarbons
- 15.3 Aromatic Heterocyclic Compounds
- 15.4 Some Chemical Consequences of Aromaticity*
- 15.5 Antiaromaticity
- 15.6 A Molecular Orbital Description of Aromaticity and Antiaromaticity
- 15.7 Nomenclature of Monosubstituted Benzenes
- 15.8 How Benzene Reacts*
- 15.9 General Mechanism for Electrophilic Aromatic Substitution Reactions*
- 15.10 Halogenation of Benzene*
- 15.11 Nitration of Benzene*
- 15.12 Sulfonation of Benzene*
- 15.13 Friedel-Crafts Acylation of Benzene*
- 15.14 Friedel-Crafts Alkylation of Benzene*
- 15.15 Alkylation of Benzene by Acylation-Reduction*

* Sections that will be focused

Sections that will be skipped

Recommended additional problems

15.25 – 15.40

Class Note

15.1 Criteria for Aromaticity and 15.5 Antiaromaticity

A. Cyclic molecule

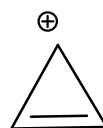
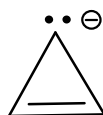
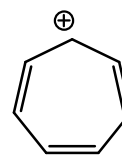
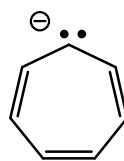
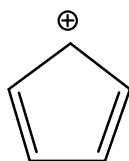
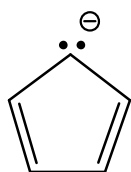
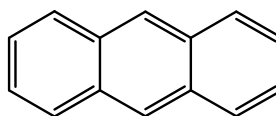
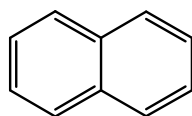
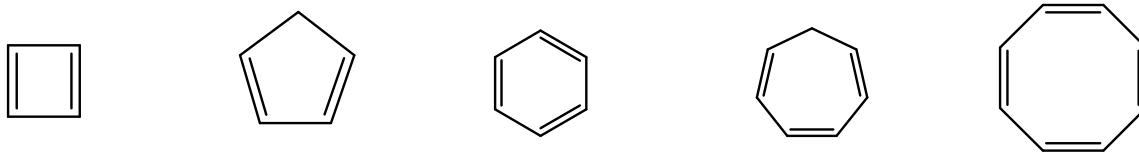
B. Every atom has p orbital

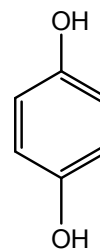
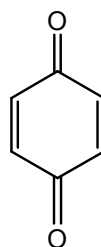
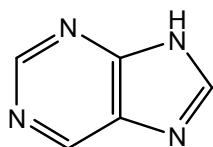
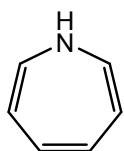
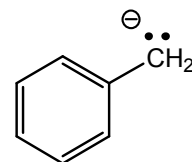
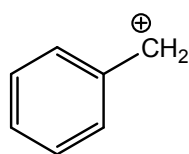
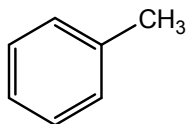
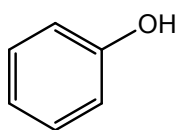
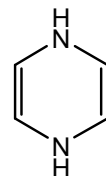
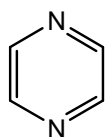
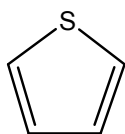
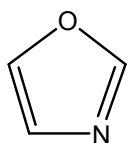
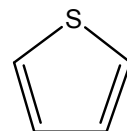
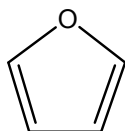
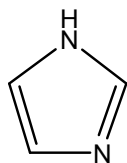
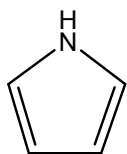
C. Planar molecule

D. Comply with $4n+2$ rule (as compared with $4n$ rule)

E. Consequence of aromaticity

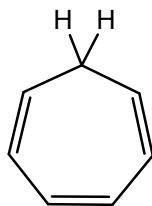
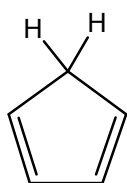
15.2 Aromatic Hydrocarbons and 15.3 Aromatic Heterocyclic Compounds



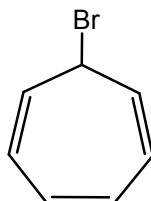
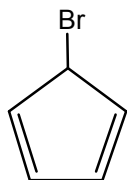


15.4 Some Chemical Consequences of Aromaticity

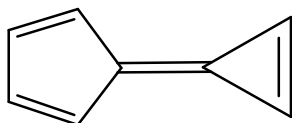
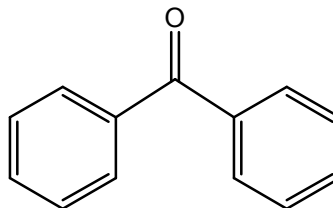
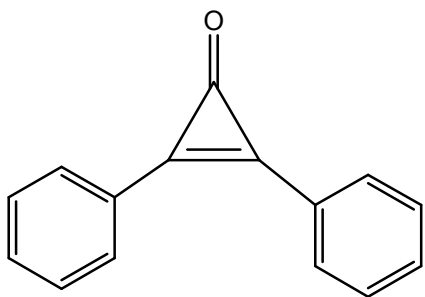
A. Acidity of protons



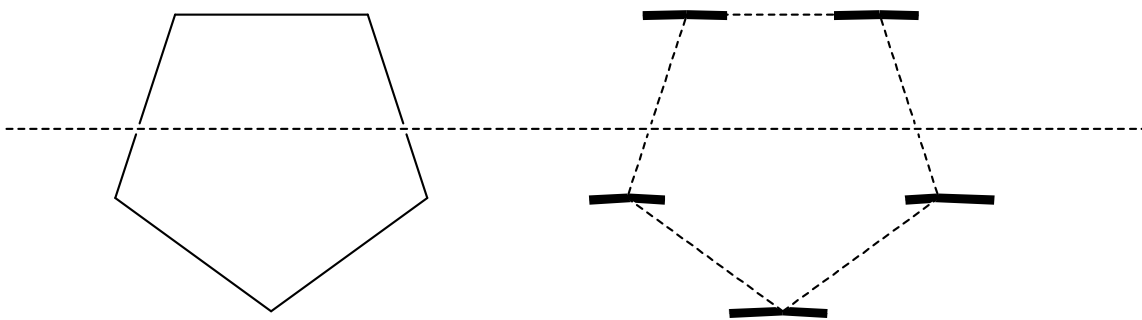
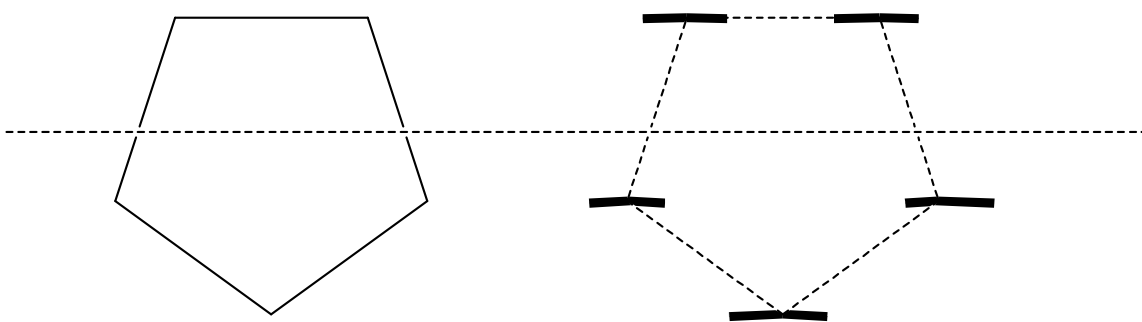
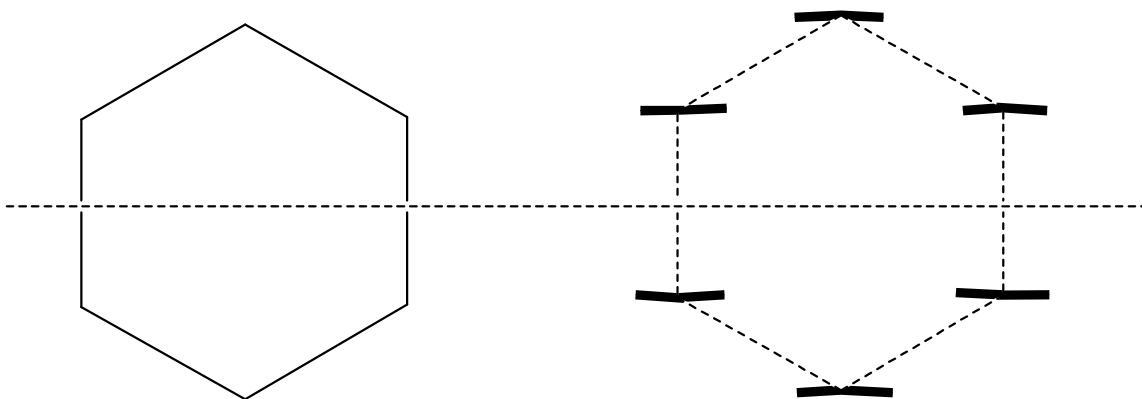
B. Aromaticity on leaving group



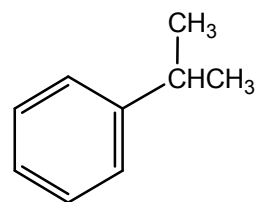
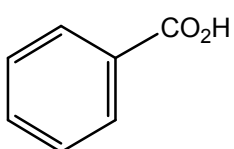
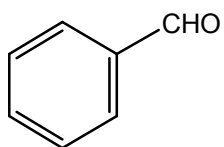
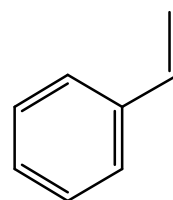
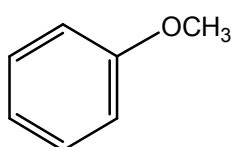
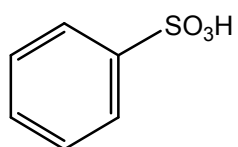
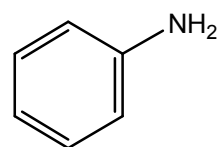
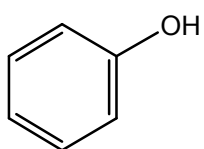
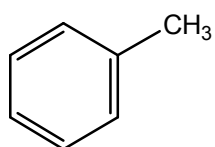
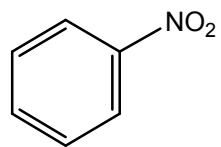
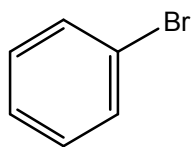
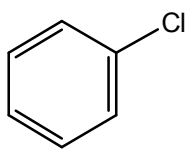
C. Aromaticity on dipole moment (polarity)



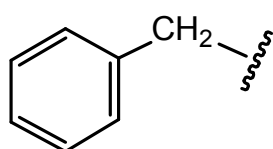
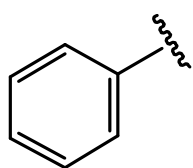
15.6 A Molecular Orbital Description of Aromaticity and Antiaromaticity



15.7 Nomenclature of Monosubstituted Benzenes



As substituent:



15.8 How Benzene Reacts and 15.9 General Mechanism for Electrophilic Aromatic Substitution Reactions

Addition vs. Substitution

Electrophilic Aromatic Substitution vs. Nucleophilic Aromatic Substitution

A. General Mechanism of Electrophilic Aromatic Substitution

B. Reaction coordinate diagram

15.10 Halogenation of Benzene

15.11 Nitration of Benzene

15.12 Sulfonation of Benzene

15.13 Friedel-Crafts Acylation of Benzene

15.14 Friedel-Crafts Alkylation of Benzene

Result from carbocation migration

15.15 Alkylation of Benzene by Acylation-Reduction

A. Clemmensen reduction

B. Wolff-Kishner reduction

C. Skip Stille and Suzuki reaction