# **Benzene and Aromaticity**



# Aromaticity and Hückel 4*n*+2 Rule

Benzene is unusually stable

- aromatic
- All carbon–carbon bond lengths of 139 pm
- Resonance hybrid with structure between two Kekulé structures
- Undergoes substitution rather than electrophilic addition

Hückel's rule: a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has  $4n+2\pi$  electrons (n is 0,1,2,3,4)



# Molecular Orbital of Benzene





# **Other Aromatic Ions**



#### Why 4*n* + 2? ψ4<sup>\*</sup>\_\_\_\_ Five p atomic ŧ orbitals <del>1</del> <u></u>+</u> ↓ ÷ <del>1</del> ŧ ŧ What about the MOs for Five cyclopentadienyl Cyclopentadienyl Cyclopentadienyl Cyclopentadienyl cycloheptatrienyl cation, molecular orbitals cation radical anion anion and radical? (five $\pi$ elect (six $\pi$ electrons) four π elec **Polycyclic Aromatic Compounds** 1.42 Å Naphthalene Anthracene Tetracene Phenanthrene (Naphthacene) 39 Å 15-6 Benzolalpyrene Coronen

## Naming Benzene Derivatives



#### Spectroscopic Characteristics of Aromatic Compounds

• Aromatic ring C–H stretching at ca. 3030 cm<sup>-1</sup>;

IR

Peaks at 1450 to 1600 cm<sup>-1</sup> (complex molecular motion of the ring);
Strong absorption from C-H out of plane bending at 690 to 900 cm<sup>-1</sup>.

monosubstited:	690-710 cm <sup>-1</sup>	<i>m</i> -disubstituted:	690-710 cm <sup>-1</sup>
	730-770 cm <sup>-1</sup>		750-850 cm <sup>-1</sup>
o-disubstituted:	735-770 cm <sup>-1</sup>	<i>p</i> -disubstituted:	790-840 cm <sup>-1</sup>





#### NMR Characteristics of Aromatic Compounds



#### Reactions of Benzene: Electrophilic Aromatic Substitution



## **Energetics of Electrophilic Aromatic Substitutions**



# Halogenation of Benzene



# Aromatic Nitration and Sulfonation



# Friedel-Crafts Alkylation



# Limitations of Friedel-Crafts Alkylation







#### Substituent Effects on the Electrophilic Aromatic Substitutions



# Inductive and Resonance Effects











#### Electrophilic Attack on Disubstituted Benzenes

- > When the effects of the directing groups reinforces each other, the situation is straightforward.
- > When the effects of the directing groups oppose each other, the more powerful activating group will dominate.
- > Mixtures of products often results when the directing groups are similar in their directing strength. OH dire

CH<sub>2</sub>O

> Further substitution rarely occurs between two groups in a metadisubstituted compound due to steric hindrance.

CH

C(CH<sub>4</sub>)



the methyl and nitro substituents

direct the incoming substituent to

+ HNO1

H<sub>2</sub>SO<sub>4</sub>

NO

2,4-dinitrotoluene

Ш

OCH<sub>1</sub>

15-27

the indicated positions

CH

NO

p-nitrotoluer



#### Synthetic Strategies toward Substituted Benzenes

- 1. Chemical interconversions of *ortho*, *para* with *meta* directors (nitro  $\Leftrightarrow$  amino or carbonyl  $\Leftrightarrow$  methylene);
- 2. Employment of reversible blocking strategies with sulfonic acid groups (-SO<sub>3</sub>H);
- 3. Additional knowledge about practicality of certain electrophilic substitutions.



# Synthetic Strategies toward Substituted Benzenes



# Reactivity of Polycyclic Benzenoid Hydrocarbons



## Reactivity of Polycyclic Benzenoid Hydrocarbons



## Benzene as an Electrophile: **Nucleophilic Aromatic Substitution**

This reaction goes by an addition/elimination mechanism



