

Bonding

Problems (Hoffman chap 1: 3, 5, 6, 8, 15; chapter 3: 2, 4, 7; C&S Chap 1: 2, 3, 4, 6, 10, 11, 15, 18, 20)

Stabilization of Electrons; Octet Rule

Ionic Bonding

Covalent Bonding

Number of Bonds from Electron Count

Hybridization of atomic orbitals

Geometry

Occurrence

Electronegativity

Acidity (increasing with s character)

BDE (increasing with s character)

Hybridization of cyclopropane and H being negative

Symmetry Classification of Bonds: sigma and pi

H₂

N₂

Resonance

Carboxylic acids vs alcohols

Basicity of aniline

Rotational barrier of amides

Basicity of (NH₂)₂C=NH and stabilizing one side of an equilibrium

Molecular Orbital picture of Bond Formation

H₂

Allylic Pi System (full Huckel treatment)

Basis functions

Schrödinger Equation

Normalization of MO and AO

Construction of Hamiltonian Equations via premultiplication

Determinant and Huckel approximations yielding energies

Obtaining of MO coefficients

Allylic Pi System from Perturbation Treatment of ethylene and methyl

Symmetry in MO construction

Methane using cube and C₂ axes

Ethylene using three reflection planes

Molecular Orbital Interpretation of Addition Reactions

Comparison of Ethylene and Formaldehyde

Ethylene subject to Electrophilic Addition

Formaldehyde subject to Nucleophilic Addition

Polarization of pi and pi* orbitals

Pi (Pi*) orbital of Formaldehyde more stable than pi (pi*) of ethylene

Nucleophile lone pair donates into lower lying, favorably polarized pi* of formaldehyde

Higher lying pi orbital of mixes with empty electrophile orbital

Substituent Effects

Bond Dissociation Energies

(Methane 104; Ethane 98; propane 95; isobutene 92) and radical stability

Toluene 85

Carboxylic Acid Strength

Inductive and Field Effect

Solvation Effects: Solvent vs Gas Phase on larger alkanolic acids

Aromaticity

Evidence related to Benzene

Heat of Hydrogenation of Benzene to cyclohexane (-49.8) – 3 x Heat of Hydrogenation of cyclohexene (-85.8) = Resonance Energy (36)

Induced Ring Current resulting in downfield shift of ~ 2ppm relative to olefinic

Huckel systems

4 n+2 pi electrons aromatic; 4n antiaromatic

Orbital energy pattern

Benzene

Tropylium carbocation

Orbital diagrams and nodal surfaces

Examples

Benzene

Cyclopropane carbocation

Tropylium carbocation

Cyclopentadienyl anion

Cyclooctatetraene

Heterocycles

pyridine

pyrrole

Mobius

Orbital picture

4 n pi electrons

orbital disposition

Mobius benzene

Mobius Tropylium

Oxidation States

Each atom bonded to a carbon makes a contribution to the oxidation state

Single covalent bonds

Another carbon contributes zero

More electronegative atoms contribute +1

More electropositive elements, including H, contribute -1

Double bonds counted twice, Triple thrice

Positive charge contributes +1

Pair of electrons contributes -1

Oxidation implies reduction

Examples

Chlorine oxidation of methane

Dissociation of t-butyl iodide (no change)

Reductive hydrogenation of alkene

Glycol formation using dilute KMnO_4 ; carbon oxidized and Mn reduced to MnO_2

Oxidation of 1,3,5-triethylbenzene to triacid and three acetic acid with dichromate

Role of oxidizing or reducing agent.

Elimination of Br_2 from a 1,2 dibromide using zinc ozonolysis