

FIRST YEAR ORGANIC CHEMISTRY - TUTORIAL 1

STRUCTURE, BONDING AND REACTIVITY IN ORGANIC CHEMISTRY

READING: **Maitland-Jones – Ch 1**
Sykes – Ch 1 and 3
Moloney – Ch 1 and 2
Clayden, Greeves, Warren, Wothers – Ch 1, 2, 4 and 8

A. *STRUCTURE AND BONDING*:

Any given molecule can only exist if there is a stable bonding arrangement to hold it together. This bonding will in turn determine the structure of the molecule. Since bonding arises fundamentally from a sharing of electrons, a consideration therefore of the electronic structure of a compound is crucial in order to understand its structure. We do this making use of the following concepts:

1. Lewis Structures: The concept of the stable octet of electrons. Rules for writing Lewis structures.
2. Valence Electrons: We do not need to consider all of the electrons in any atom or molecule to be able to understand its chemistry; rather, examination of its valence electrons is generally sufficient.
3. Atomic (AO) Theory: the energies of electrons of an atom to be quantised, and we describe this using the Atomic Orbitals: s,p,d. We can construct the AO diagram for any given atom using the Pauli Exclusion Principle, Hund's rule, and the Aufbau Principle.
4. Molecular Orbital (MO) Theory – we can extend simple AO theory to molecules: Molecular Orbitals can be considered to be a Linear Combination of Atomic Orbitals (LCAO). However, some modifications are necessary, and these include:
 - (i) Hybridisation (sp , sp^2 , sp^3), and
 - (ii) Valence Shell Electron Pair Repulsion (VSEPR).
5. Bonding. By drawing the appropriate orbital overlap, we can account for σ - and π -bonds (single, double and triple bonds). MO theory also requires the existence of antibonding orbitals (σ^* , π^*).
6. Structure. A consideration of bonding allows the determination of molecular structure (geometry): the more *s* character of any hybrid orbital, the shorter and stronger bonds it will form, the larger its bond angles and the more electronegative it is. Stereoelectronics describes the spatial arrangement of electron density, both bonding and non-bonding, in a molecule.
7. Long range effects.
 - (i) Conjugation and Delocalisation. Hyperconjugation.
 - (ii) Electronic effects - two types:
 - (a) *inductive*: the importance of electronegativity. Order indicated by the position of an element in the Periodic Table: $F > O > N > C$ and $F > Cl > Br > I$.
 - (b) *mesomeric* (also called *resonance*): arises by the delocalisation of electron pairs (requirement for co-planarity of orbitals). Some of the rules of resonance are described on the attached sheet.
7. Steric effects - the concept of bulk in organic chemistry. Steric crowding.
8. Typical bond lengths and bond enthalpies - for all types of C-H, C-C, C-O bonds.

B. REACTIVITY: ACIDS AND BASES

A consideration of *structure* and *bonding* allows us to understand the *reactivity* of compounds. This is exemplified in this tutorial using acids and bases:

1. Lowry-Bronsted - Proton acceptors/donors. The concept of conjugate acids and bases.

- Acids: What makes organic compounds acidic? Acidity as an equilibrium phenomenon, therefore governed by thermodynamics. The effect of compound structure on acidity: for any given acid H-A, the strength of the H-A bond, the electronegativity of A and the stability of A⁻ are of considerable importance. The equilibrium position is influenced by solvent and temperature.

- Acidity of various compound classes (substituted and unsubstituted aliphatic carboxylic acids, phenols, aromatic carboxylic acids, and hydrocarbons): you need to have a general knowledge of pK_a values for common functional groups. Some typical pK_a values worth remembering:

HI	-10	H ₂ O	15.7
HBr	-9	MeOH	16
HCl	-7	EtOH	16
H ₂ SO ₄	-4.8	CH ₃ C(O)CH ₃	20
Cl ₃ CC(O)OH	0.9	HC≡CH	26
NCCH ₂ C(O)OH	2.5	Ph ₃ CH	32
FCH ₂ C(O)OH	2.6	NH ₃	36
<i>p</i> -NO ₂ C ₆ H ₄ C(O)OH	3.4	Benzene	43
HF	3.5	H ₂ C=CH ₂	45
PhC(O)OH	4.2	CH ₄	60
CH ₃ C(O)OH	4.7	Me ₃ CH	71

- Bases: What makes organic compounds basic? The effect of compound structure on basicity. Aliphatic, aromatic and heterocyclic bases.

2. Lewis acids and bases - Electron pair acceptors/donors.

3. Electrophiles and nucleophiles: the concept of Lewis acids and bases can be generalised to electrophiles and nucleophiles in organic chemistry. Definition of each, and typical reactions of these species.

TUTORIAL QUESTIONS

1. Draw an MO picture for each of the following. Sketch σ and π , and σ^* and π^* , frameworks on separate diagrams, where appropriate.

- (a) CH₃F (b) FCH=CHF (c) CH₃OCH₃ (d) CH₃COCH₃ (e) CH₃O₂CCH₃