



MEDICINAL CHEMISTRY

Medicinal chemistry deals with the design, optimization and development of chemical compounds for use as drugs.

TOPIC

TERM

Functional Groups

- Functional groups play a significant role in:
 - Water/lipid solubility
 - Route of administration
 - Ability to interact with the specific biological target
 - Mechanism (mode or method) of action
 - Route of metabolism and elimination
 - Duration of action
 - Susceptibility for specific therapeutic situations
 - Tendency to cause adverse effects or drug interactions
- These concepts that should always be considered when examining a drug molecule:
 - Every atom within the structure belongs to some functional group.
 - Within a drug molecule, some functional groups may be more "important" than others. The opposite may be true for a different drug molecule.
 - Altering functional groups can enhance activity, increase absorption, decrease adverse effects, and provide other therapeutic benefits.
 - These major chemical properties that need to be analyzed for every functional group:
 - Electrostatic effect:** The components that comprise the overall electronic effect of a functional group are induction and resonance.
 - Measured by a functional group's ability to donate its electrons to adjacent atoms or functional groups
 - Solubility effects:** Overall solubility is a composite sum of all the functional groups found as part of a drug molecule.
 - Size effect:** Each functional group has a finite size and some dimensions; this contributes to the overall conformation and thus the 3-D shape of a given drug.
 - The three major chemical properties combined need to be considered when evaluating the overall pharmacodynamic and pharmacokinetic properties of any given drug molecule.

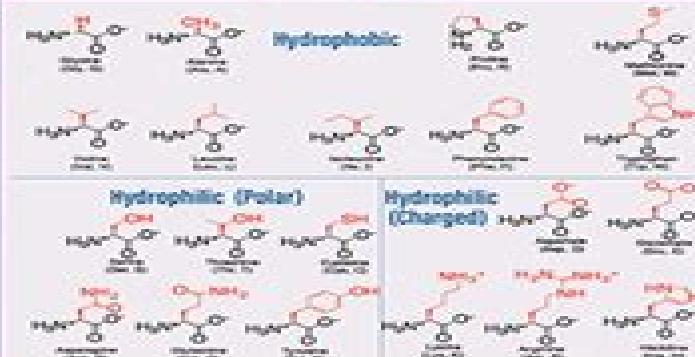
ELECTRONEGATIVITY: KEY POINTS

- C, O, Cl, and N are the most electronegative elements.
- O will always attract electrons to it, unless it is attached to a F.
- All the halogens (F, Cl, Br, and I) as well as O and N will attract electrons away from C.
- C will slightly attract electrons away from H (inductive effect).
- The difference in electronegativity causes a dipole.

Solubility

- Universal water and/or lipid solubility of a drug molecule affects its route(s) of administration, distribution within the body, metabolism, duration of action, and route(s) of elimination.

Amino Acids



pH & pK_a

pH

- pH = $-\log[H^+]$
- Refers to the solution, not a functional group
- Indicates how many " H^+ " there are in the solution
- ICN: pH of 0.1M HCN
- pH = $-\log(0.1) = -(-1) = 1$
- ICN: pH of 0.0001M HCN
- pH = $-\log(0.0001) = -(-4) = 4$

Acid Strength (pK_a)

- Property of functional groups
- Affected by size and electronic effects
- Can be used to compare the relative acidity of functional groups
 - Rule 1: Lower pK_a value → stronger acid (wants to lose the H⁺)
 - Rule 2: Higher pK_a value → stronger conjugate base/weak acid (wants to gain the H⁺)

pK_a

- Low pK_a: Reaction is to the right
- High pK_a: Reaction is to the left

$$pK_a = -\log(K_a)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Henderson-Hasselbach equation:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

- Used to calculate the:
 - pH change in buffered solutions
 - pH change in the molar ratio of salt to acid concentrations needed to prepare a buffer solution at a certain pH
 - Percent ionization of a functional group at a certain solution pH

ICN: Fluorine's functional group has a pK_a of 4.5, so it must be carboxylic acid. Will it be protonated or deprotonated if it is in the urine at pH 5.5?



$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$5.5 = 4.5 + \log \frac{[A^-]}{[HA]}$$

$$1.0 = \log \frac{[A^-]}{[HA]}$$

$$10^1.0 = \frac{[A^-]}{[HA]}$$

$$10 = \frac{[A^-]}{[HA]}$$

$$10 = \frac{[A^-]}{[A^-] + [HA]}$$

$$10 = \frac{1}{1 + \frac{[HA]}{[A^-]}}$$

$$10 = \frac{1}{1 + \frac{10^4.5}{10^5.5}}$$

$$10 = \frac{1}{1 + 10^{-1}}$$

Answers: More unprotonated

The protonation state affects:

- The charge of a functional group (+ or -)

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Xiang Xie

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