



MEDICINAL CHEMISTRY



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

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
 - Suitability for specific therapeutic situations
 - Tendency to cause adverse effects or drug interactions
- Three 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.
 - Adding functional groups can enhance activity, increase absorption, decrease adverse effects, and provide other therapeutic benefits.
- Three major chemical properties that need to be analyzed for every functional group:
 - Electronic effects:** 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.
 - Steric effects:** Each functional group has a finite size and steric dimension; 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

- F, 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

- Overall 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.

- Terms to know:
 - Hydrophobicity (a.k.a. lipophilicity):** How water-dissolving (i.e., oil-dissolving) a drug molecule is.
 - Hydrophilicity (a.k.a. lipophobicity):** How water-dissolving (i.e., oil-dissolving) a drug molecule is.
- The contribution to solubility by a functional group may be increased or decreased depending upon adjacent groups.
- Water soluble functional groups:
 - Enhance water solubility; often referred to as hydrophilic groups.
 - The two major properties that contribute to water solubility:
 - Whether the group is or can be ionized
 - Either positive (+) or negative (-)
 - EN: Quaternary amine—no matter what pH the molecule finds itself in, it will always have a + charge.
 - The group's ability to hydrogen bond with water

Size & Steric Dimension

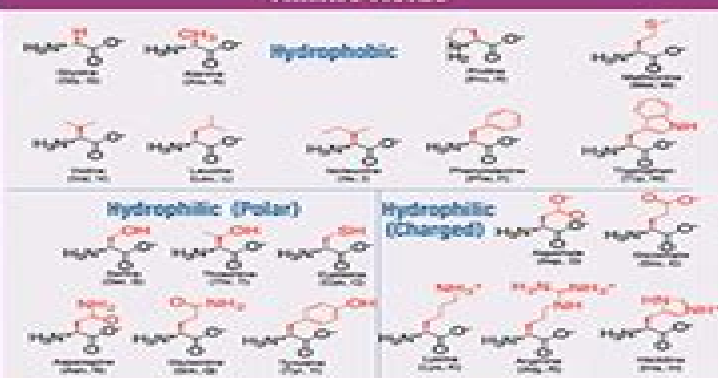
- The addition of a sterically bulky functional group can:
 - Increase selectivity for its biological target
 - Enhance binding interactions with its biological target
 - Cause favorable alterations in the rate of metabolism
- The acidic/basic nature of a drug molecule influences its chemical, pharmaceutical, and therapeutic properties.
- If a functional group can be ionized at a certain pH, its water solubility will increase.
 - While this helps the gastrointestinal (GI) tract dissolve the molecule, the unionized form (without a charge) is better for passage through the lipid membrane.
- Ionization: Equilibrium process that allows for functional groups to form electrostatic interactions with target receptors, transport proteins, enzymes, and other endogenous biological targets.
 - Electrostatic (a.k.a. ionic) interactions are the strongest noncovalent bonds.
- Drug molecules can interact with plasma proteins (usually via electrostatics).
 - This sequesters them from metabolic/elimination pathways and extends the duration of action.
- The human serum albumin is a major transporter of drug molecules but is nonspecific. It generally binds acid drug molecules to a greater extent than basic drug molecules.
 - Albumin also binds hydrophobic compounds more tightly than hydrophilic ones.
- What if you are taking two different drugs and both contain an acidic functional group?
 - Plasma protein displacement interactions can occur.
 - This could greatly affect the half-life of the drug, particularly when the drug is 90% plasma protein bound.

- Drug molecules that are highly ionized are more water soluble, so they need less metabolism to be eliminated.
- There are specific transport proteins of certain organic acids within the renal tubules that actively secrete acidic molecules:
 - From the plasma to the urine
 - This decreases the half-life of the drug molecules.
 - From the urine to the plasma
 - This increases the half-life of the drug molecules.

Acidic & Basic Functional Groups

Functional Group	Acid or Base?	pH, Range
Carboxylic acid	Acidic	2.5-5
2-hydroxyethyl	Acidic	4.5-6.5
Sulfonamide	Acidic	5-10
N-sulfonamide	Acidic	5-6
Tetracycline	Acidic	4.5-6
Phenol	Acidic	7-10
Sulfone	Acidic	0-2
Phosphonic acid	Acidic	1.5-2.5 (first phosphate) 6.5-7.5 (second phosphate) 2-3 (third phosphate) 7-8 (fourth phosphate)
Alkaline	Basic	9-11 (after protonation)
Amine	Basic	2-5 (after protonation)
Tertiary amine	Basic	3-4 (after protonation)
Hydroxyl	Basic	7.5-8.5 (after protonation)
Amide	Basic	10-11 (after protonation)
Carbamate	Basic	12-13 (after protonation)
Organic containing amine	Basic	1-5 (after protonation)

Amino Acids



pH & pK_a

pH

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

Acid Strength (pK_a)

- Property of functional groups
- Affected by steric 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^+)



- Low pK_a : Reaction is to the right
- High pK_a : Reaction is to the left
- $\text{pK}_a = -\log(K_a)$
- $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
- Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{Unprotonated form}]}{[\text{Protonated form}]} \right)$$
- 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

EN: Flurbiprofen's functional group has a pK_a of 4.5, so it must be carboxylic acid. Will it be primary protonated or unprotonated if it is in the urine at pH 5.0?

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{Unprotonated form}]}{[\text{Protonated form}]} \right)$$

$$5.0 = 4.5 + \log \left(\frac{[\text{Unprotonated form}]}{[\text{Protonated form}]} \right)$$

$$1.4 = \log \left(\frac{[\text{Unprotonated form}]}{[\text{Protonated form}]} \right)$$

$$23.1 = \left(\frac{[\text{Unprotonated form}]}{[\text{Protonated form}]} \right)$$

Answer: More unprotonated

- The protonation state affects:
 - The charge of a functional group (+ or -)

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Wolfgang Guggemos



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