



# 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.

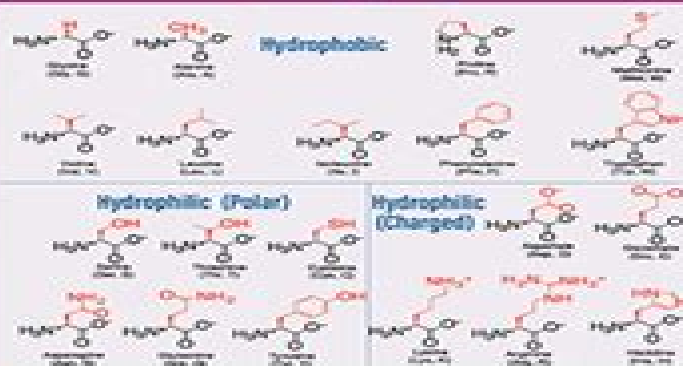
- Drug molecules that are highly ionized are more water soluble, so they need less metabolism to be eliminated.
- There are specific transport proteins of certain organic acids within the renal tubules that actively secrete acidic molecules:

- 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
Sulfonic acid	Acidic	0-2
Phosphonic acid and phosphonates	Acidic	1.5-2.5 (first phosphate) 6.5-7.5 (second phosphate) 2-3 (third phosphate) 7-9 (fourth phosphate)
Alkaline structure	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)
Guanidine	Basic	12-13 (after protonation)
Organic containing amine	Basic	3-5 (after protonation)

## Amino Acids



## pH & pK<sub>a</sub>

- pH**
  - $\text{pH} = -\log[\text{H}^+]$
  - Refers to the solution, not a functional group
  - Indicates how many "free"  $\text{H}^+$ 's there are in the solution
- EN: pH of 0.1M  $\text{H}^+$
- pH =  $-\log(0.1) = -(-1) = 1$
- EN: pH of 0.0001 M  $\text{H}^+$
- pH =  $-\log(0.0001) = -(-4) = 4$
- Acid Strength (pK<sub>a</sub>)**
  - 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<sub>a</sub> value = stronger acid (wants to lose the  $\text{H}^+$ )
  - Rule 2: Higher pK<sub>a</sub> value = stronger conjugate base/weak acid (wants to gain the  $\text{H}^+$ )

- $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
- Low pK<sub>a</sub>: Reaction is to the right
- High pK<sub>a</sub>: 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<sub>a</sub> 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 -)

# Medicinal Chemistry Study Guide

**Julia Schneider**



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