



# 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

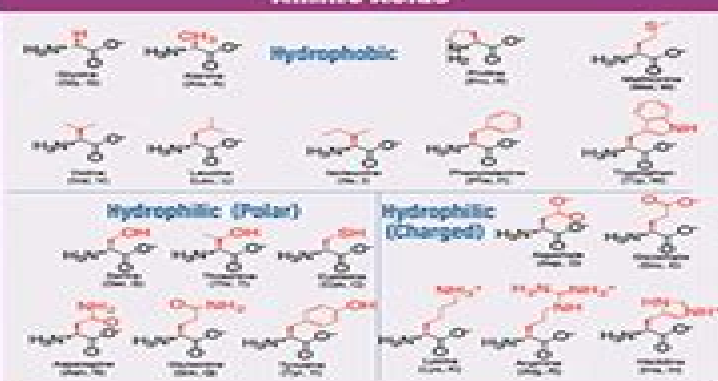
- The addition of a sterically bulky functional group can:
  - Increase selectivity for its biological target
  - Enhance binding interactions with its biological target
  - Cause favorable alterations in the rate of metabolism
- The acidic/basic nature of a drug molecule influences its chemical, pharmaceutical, 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) 7-8 (fourth phosphate)
Alkaline structure	Basic	9-11 (after protonation)
Aniline	Basic	2-5 (after protonation)
Tetrazine	Basic	3-4 (after protonation)
Hydrazine	Basic	7.5-8.5 (after protonation)
Amidine	Basic	10-11 (after protonation)
Guanidine	Basic	12-13 (after protonation)
Organic containing amine	Basic	8-9 (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  $\text{H}^+$
- $\text{pH} = -\log(0.1) = -(-1) = 1$
- EN: pH of 0.0001 M  $\text{H}^+$
- $\text{pH} = -\log(0.0001) = -(-4) = 4$

### 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  $\text{pK}_a$  value = stronger acid (wants to lose the  $\text{H}^+$ )
  - Rule 2: Higher  $\text{pK}_a$  value = stronger conjugate base/weak acid (wants to gain the  $\text{H}^+$ )



- Low  $\text{pK}_a$ : Reaction is to the right
- High  $\text{pK}_a$ : 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  $\text{pK}_a$  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 -)

# Medicinal Chemistry Study Guide

**Marco Cascella**



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drug binding interactions stereochemistry and drug metabolism Numerous examples and expanded discussions for complex concepts Therapeutic examples that link the importance of medicinal chemistry to pharmacy and healthcare practice An overview of structure activity relationships SARs and concepts that govern drug design Review questions and practice problems at the end of each chapter that allow readers to test their understanding with the answers provided in an appendix Whether you are just starting your education toward a career in a healthcare field or need to brush up on your organic chemistry concepts this book is here to help you navigate medicinal chemistry About the Authors Marc W Harrold BS Pharm PhD is Professor of Medicinal Chemistry at the Mylan School of Pharmacy Duquesne University Pittsburgh PA Professor Harrold is the 2011 winner of the Omicron Delta Kappa Teacher of the Year award at Duquesne University He is also the two time winner of the TOPS Teacher of the Pharmacy School award at the Mylan School of Pharmacy Robin M Zavod PhD is Associate Professor for Pharmaceutical Sciences at the Chicago College of Pharmacy Midwestern University Downers Grove IL where she was awarded the 2012 Outstanding Faculty of the Year award Professor Zavod also serves on the adjunct faculty for Elmhurst College and the Illinois Institute of Technology She currently serves as Editor in Chief of the journal *Currents in Pharmacy Teaching and Learning* Basic Concepts in Medicinal Chemistry, 2001 These tutorials focus on the basic chemical concepts which govern drug action and are meant to serve as a review for the sequence of Biomedical Science Therapeutics courses PHBMS 422 PHBMS 427 These concepts are first introduced in the stand alone Medicinal Chemistry course PHBMS 421 taught in the Fall semester of the PIV year and should not be foreign to those who have completed this course It is the expectation of the author that each student understands and masters these concepts since he she is expected to apply these concepts and understand how they relate to the drugs and drug classes discussed in the BMS T modules

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## **Table of Contents Medicinal Chemistry Study Guide**

1. Understanding the eBook Medicinal Chemistry Study Guide
  - The Rise of Digital Reading Medicinal Chemistry Study Guide
  - Advantages of eBooks Over Traditional Books
2. Identifying Medicinal Chemistry Study Guide
  - Exploring Different Genres
  - Considering Fiction vs. Non-Fiction
  - Determining Your Reading Goals
3. Choosing the Right eBook Platform
  - Popular eBook Platforms
  - Features to Look for in an Medicinal Chemistry Study Guide
  - User-Friendly Interface
4. Exploring eBook Recommendations from Medicinal Chemistry Study Guide
  - Personalized Recommendations
  - Medicinal Chemistry Study Guide User Reviews and Ratings
  - Medicinal Chemistry Study Guide and Bestseller Lists
5. Accessing Medicinal Chemistry Study Guide Free and Paid eBooks
  - Medicinal Chemistry Study Guide Public Domain eBooks

- Medicinal Chemistry Study Guide eBook Subscription Services
- Medicinal Chemistry Study Guide Budget-Friendly Options
- 6. Navigating Medicinal Chemistry Study Guide eBook Formats
  - ePub, PDF, MOBI, and More
  - Medicinal Chemistry Study Guide Compatibility with Devices
  - Medicinal Chemistry Study Guide Enhanced eBook Features
- 7. Enhancing Your Reading Experience
  - Adjustable Fonts and Text Sizes of Medicinal Chemistry Study Guide
  - Highlighting and Note-Taking Medicinal Chemistry Study Guide
  - Interactive Elements Medicinal Chemistry Study Guide
- 8. Staying Engaged with Medicinal Chemistry Study Guide
  - Joining Online Reading Communities
  - Participating in Virtual Book Clubs
  - Following Authors and Publishers Medicinal Chemistry Study Guide
- 9. Balancing eBooks and Physical Books Medicinal Chemistry Study Guide
  - Benefits of a Digital Library
  - Creating a Diverse Reading Collection Medicinal Chemistry Study Guide
- 10. Overcoming Reading Challenges
  - Dealing with Digital Eye Strain
  - Minimizing Distractions
  - Managing Screen Time
- 11. Cultivating a Reading Routine Medicinal Chemistry Study Guide
  - Setting Reading Goals Medicinal Chemistry Study Guide
  - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Medicinal Chemistry Study Guide
  - Fact-Checking eBook Content of Medicinal Chemistry Study Guide
  - Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
  - Utilizing eBooks for Skill Development
  - Exploring Educational eBooks

#### 14. Embracing eBook Trends

- Integration of Multimedia Elements
- Interactive and Gamified eBooks

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