



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

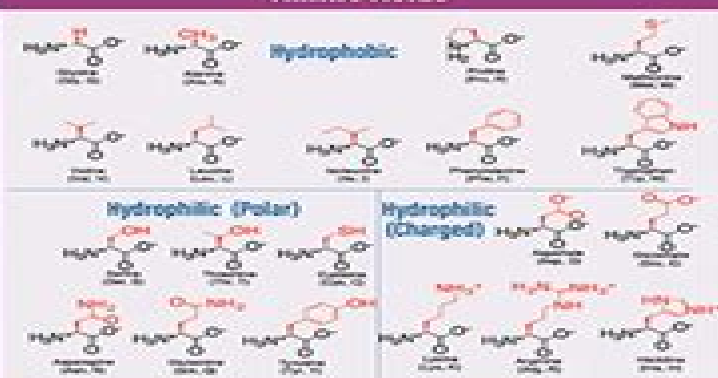
- The addition of a sterically bulky functional group can:
 - Increase selectivity for its biological target
 - Enhance binding interactions with its biological target
 - Cause favorable alterations in the rate of metabolism
- The acidic/basic nature of a drug molecule influences its chemical, pharmaceutical, 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 |
| Sulfonamides | Acidic | 5-10 |
| N-sulfonamides | Acidic | 5-6 |
| Tetracycline | Acidic | 4.5-6 |
| Phenol | Acidic | 7-10 |
| Sulfonic | Acidic | 0-2 |
| Phosphonic and phosphonates | Acidic | 1.5-2.5 (first phosphate) 6.5-7.5 (second phosphate) 2-3 (third phosphate) 7-9 (fourth phosphate) |
| Alkaline | Basic | 9-11 (after protonation) |
| Amine | Basic | 2-5 (after protonation) |
| Tertiary | 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 | 3-5 (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 -)

Medicinal Chemistry Study Guide

John Attfield



Medicinal Chemistry Study Guide:

Medicinal Chemistry of Drugs Affecting Cardiovascular and Endocrine Systems M. O. Faruk Khan, 2024-02-19

The primary objective of this 4 volume book series is to educate PharmD students on the subject of medicinal chemistry. The book set serves as a reference guide to pharmacists on aspects of the chemical basis of drug action. Medicinal Chemistry of Drugs Affecting Cardiovascular and Endocrine Systems is the third volume of the series. This volume features 8 chapters focusing on a comprehensive account of drugs affecting both the cardiovascular system and the endocrine functions. The volume informs readers about the medicinal chemistry of relevant drugs which includes the mechanism of drug action, detailed structure-activity relationships, and metabolism. Topics covered include drugs that affect the renin-angiotensin system, calcium channel blockers, diuretics, hematological agents, anticoagulants, thrombolytic and antiplatelet agents, antidiabetics, antihistamines, proton pump inhibitors, and therapeutic hormones. Each chapter also offers case studies and self-assessments to facilitate discussion and learning. The book equips students with a scientific foundation to competently evaluate, recommend, and counsel patients and health care professionals regarding the safe, appropriate, and cost-effective use of medications. Students and teachers will also be able to integrate the knowledge presented in the book and apply medicinal chemistry concepts to understand the pharmacodynamics and pharmacokinetics of therapeutic agents in the body. The information offered by the book chapters will give readers a strong neuropharmacology knowledge base required for a practicing pharmacist. Readership: PharmD, pharmacology students and teachers.

A Laboratory Guide in Pharmaceutical Chemistry with Two Hundred Experiments F. P. Vandenberg, 1888

Organic Chemistry Fundamentals Study Guide

Speedy Publishing, 2014-11-26. In order to fully understand any subject, the fundamentals must be understood and kept in the back of the mind. Organic Chemistry is one of the most difficult subjects a college student can take, especially if they are not a Chemistry major. A lot goes into the fundamentals of the subject. That is why an Organic Chemistry Fundamentals book can be so helpful to a student. When studying the material, if the student discovers they do not understand something, they can reference the book and continue with studying in no time at all. Having a reference book is the key to success in an Organic Chemistry class.

Lecture Notes for Chemical Students Edward Frankland, 1876

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Library of Medicine Current Catalog National Library of Medicine (U.S.), 1993

Basic Concepts in Medicinal Chemistry

Marc Harrold, Robin Zavod, 2013-01-18. Medicinal chemistry is a complex topic. Written in an easy-to-follow and conversational style, *Basic Concepts in Medicinal Chemistry* focuses on the fundamental concepts that govern the discipline of medicinal

chemistry as well as how and why these concepts are essential to therapeutic decisions The book emphasizes functional group analysis and the basics of drug structure evaluation In a systematic fashion learn how to identify and evaluate the functional groups that comprise the structure of a drug molecule and their influences on solubility absorption acid base character binding interactions and stereochemical orientation Relevant Phase I and Phase II metabolic transformations are also discussed for each functional group Key features include Discussions on the roles and characteristics of organic functional groups including the identification of acidic and basic functional groups How to solve problems involving pH pKa and ionization salts and solubility 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
 Marc W. Harrold, Robin M. Zavod, 2023 Designed to help students incrementally build their knowledge of fundamental concepts of medicinal chemistry and their applications to therapeutic decisions it is progressively organized Specific sections of the text have been updated to make potentially confusing concepts easier to understand Numerous examples and review questions further reinforce learning and analytical skills This updated and expanded edition of the popular textbook Basic Concepts in Medicinal Chemistry has been enhanced with new subject material numerous self assessment tools and special features to advance and strengthen the learning process New in the Third Edition Enhanced explanations discussions and examples in many key chapters Additional summary tables to help readers better select the proper drug binding interaction Expanded discussion on Pharmacogenomics including multiple specific examples Updated examples throughout the text to include a wider range of drugs and drug classes Increased focus on application of concepts to therapeutic decisions and pharmacy practice

Medical Technology Examination Review and Study Guide Anna P. Ciulla, Georganne K. Buescher, Joan H. Youse, 1988

A Text-book of medical chemistry Elias Hudson Bartley, 1895

Chemistry: General, Medical, and

Pharmaceutical, Etc. (Second Edition of “An Introduction to Pharmaceutical Chemistry” .) John Attfield,1875

Pharmaceutical Chemistry - I Dr. A. V. Kasture, Dr. S. G. Wadodkar, 2015-07 Quality Control in Pharmacy Errors in Analysis Impurities in Pharmaceutical Substances and Limit Tests Water Solubility of Pharmaceuticals Acids Bases and Buffers Antioxidants Gastrointestinal Agents Topical Agents Dental Products Inhalants Expectorants Emetics and Respiratory Stimulants Major Intra and Extracellular Electrolytes Official Compounds of Iron Official Compounds of Iodine Official Compounds of Calcium Radiopharmaceuticals and Contrast Media Antidotes in Poisoning Identification Tests for Ions and Radicals Appendix Index Bibliography *Chemistry: General, Medical, and Pharmaceutical, Including the Chemistry of the U.S. Pharmacopœia* John Attfield, 1879 *Catalog of Copyright Entries. Third Series* Library of Congress. Copyright Office, 1971 A Text-book of the principles and practice of medicine Henry Munson Lyman, 1892 Chemistry: general, medical, and pharmaceutical John Attfield, 1875 Text-book of Medical Chemistry for Medical and Pharmaceutical Students and Practitioners Elias Hudson Bartley, 1894 *Introduction To Medicinal Chemistry*, 2024-04-02 Introduction to Medicinal Chemistry serves as a comprehensive guide to exploring the dynamic and evolving field of medicinal chemistry. Written with precision and expertise, this book provides a practical journey into the principles and applications underpinning the development of pharmaceutical agents. With a focus on the intersection of chemistry and medicine, the text delves deeply into the molecular mechanisms controlling drug action, emphasizing the importance of understanding structure-activity relationships. This book highlights the complexities of drug design, synthesis, and optimization through the fundamental concepts of medicinal chemistry. It meets the needs of both novice learners and experienced practitioners in the field, offering a balanced mix of theoretical foundations and practical applications. Readers will find explanations on the chemical basis of various diseases, identification of drug targets, and design of molecules with therapeutic potential. Notably, the author uses a clear writing style which highlights complex concepts and facilitates an intuitive understanding of the subject matter. The inclusion of case studies and real-world examples further enhances the practical relevance of the book, fostering a deeper appreciation for the role of medicinal chemistry in modern health care. Introduction to Medicinal Chemistry stands as an indispensable resource for students, researchers, and professionals seeking a holistic understanding of the principles of drug discovery and development. Its broad coverage and accessible approach make it an invaluable tool for those wishing to unravel the secrets of medicinal chemistry and contribute to the advancement of pharmaceutical science. **A Manual of medical jurisprudence** Alfred Swaine Taylor, 1892 Applied Medical Chemistry Lawrence Wolff, 1885

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