



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.

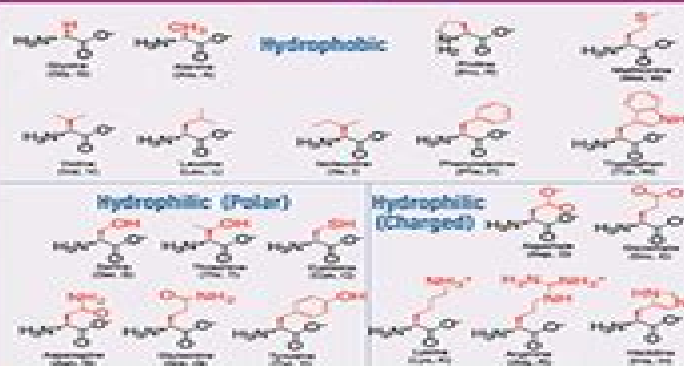
- Drug molecules that are highly ionized are more water soluble, so they need less metabolism to be eliminated.
- There are specific transport proteins of certain organic acids within the renal tubules that actively secrete acidic molecules:

- 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)
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_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^+
- pH = $-\log(0.1) = -(-1) = 1$
- EN: pH of 0.0001 M H^+
- 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^+)

- $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
- 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

Hussin A.Rothana



Medicinal Chemistry Study Guide:

Fundamentals of Medicinal Chemistry and Drug Metabolism M. O. Faruk Khan, Ashok Philip, 2018-06-01 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 chemical basis of drug action This first volume of the series is comprised of 8 chapters focusing on basic background information about medicinal chemistry It takes a succinct and conceptual approach to introducing important fundamental concepts required for a clear understanding of various facets of pharmacotherapeutic agents drug metabolism and important biosynthetic pathways that are relevant to drug action Notable topics covered in this first volume include the scope and importance of medicinal chemistry in pharmacy education a comprehensive discussion of the organic functional groups present in drugs and information about four major types of biomolecules proteins carbohydrates lipids nucleic acids and key heterocyclic ring systems The concepts of acid base chemistry and salt formation and their applications to the drug action and design follow thereafter These include concepts of solubility and lipid water partition coefficient LWPC isosterism stereochemical properties mechanisms of drug action drug receptor interactions critical for pharmacological responses of drugs and much more Students and teachers will 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 *Oxford IB Study Guides: Chemistry for the IB Diploma* Geoff Neuss, 2014-10-02 This comprehensive Study Guide reinforces all the key concepts for the 2014 syllabus ensuring students develop a clear understanding of all the crucial topics at SL and HL Breaking concepts down into manageable sections and with diagrams and illustrations to cement understanding exam preparation material is integrated to build student confidence and assessment potential Directly linked to the new Oxford Chemistry Course Book to extend and sharpen comprehension this book supports maximum achievement in the course and assessment Fully comprehensive and matched to the new 2014 syllabus Concise and focused approach simplifies complex ideas building truly confident understanding Clear and explanatory style uses plenty of visuals to make each concept accessible easing comprehension Build a strong foundation of assessment skills strengthening potential with integrated exam questions Develop assessment confidence drawing on thorough assessment support and advice Clear and straightforward lan 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

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BIOS Instant Notes in Chemistry for Biologists Julie Fisher, John Arnold, 2003-09-25 Instant Notes in Chemistry for Biologists is a concise book for undergraduates who have a limited background in chemistry This book covers the main concepts in chemistry provides simple explanations of chemical terminology and illustrates underlying principles and phenomena in the life sciences with clear biological examples Building on the success of the first edition the second edition has been fully revised and updated and comprises new sections on water as a biological solvent inorganic molecules and biological macromolecules

Foye's Principles of Medicinal Chemistry Marc W. Harrold, Kimberly Beck, Victoria F. Roche, S. William Zito, Thomas L. Lemke, David A. Williams, 2025-08-26 Maintaining its status as the gold standard in medicinal chemistry education Foye's Principles of Medicinal Chemistry 9th Edition presents a renewed focus on the fundamental concepts that form the backbone of this critical discipline This latest edition helmed by new senior editors Marc Harrold and Kim Beck continues the text's legacy of excellence while streamlining content for today's pharmacy students and practitioners Expert contributions from experienced educators research scientists and clinicians clarify the chemical basis of drug action emphasizing the structure activity relationships physicochemical pharmacokinetic properties and metabolic profiles of the most commonly used drugs

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