



#### Organic and Biological Molecules

# Chapter 22 *Table of Contents*



- (22.1) Alkanes: Saturated hydrocarbons
- (22.2) Alkenes and alkynes
- (22.3) Aromatic hydrocarbons
- (22.4) Hydrocarbon derivatives
- (22.5) Polymers
- (22.6) Natural polymers



Organic Chemistry

- Study of carbon-containing compounds and their properties
  - Organic compounds contain chains or rings of carbon atoms
  - Helps understand living systems
- Biomolecules: Compounds that are responsible for the maintenance and reproduction of life



Hydrocarbons

- Compounds composed of carbon and hydrogen
  - Saturated hydrocarbons (Alkanes): Compounds that contain carbon–carbon single bonds
  - Unsaturated hydrocarbons: Compounds that contain carbon–carbon multiple bonds



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Saturated Hydrocarbons - Methane (CH<sub>4</sub>)

- Simplest member of saturated hydrocarbons
- Has a tetrahedral structure
  - Carbon atom uses sp<sup>3</sup> hybrid orbitals to bond to four hydrogen atoms



Saturated Hydrocarbons - Ethane (C<sub>2</sub>H<sub>6</sub>)

- Contains two carbon atoms
- Has a tetrahedral structure
- sp<sup>3</sup> hybridized





Saturated Hydrocarbons - Propane ( $C_3H_8$ ) and Butane ( $C_4H_{10}$ )

- Each carbon atom is bonded to four atoms
- sp<sup>3</sup> hybridized





Unbranched Hydrocarbons

- Alkanes in which the carbon atoms form long strings or chains
  - Chains are zig-zag due to the tetrahedral C–C–C bond angle of 109.5°
- Known as normal or straight-chain hydrocarbons
- Example
  - Butane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) has a bond angle of 109.5°

**Normal Alkanes** 

Structure of a normal alkane, where n is an integer:



Condensed general formula

 $CH_3 - (CH_2)_n - CH_3$ 



# **Table 22.1** - Selected Properties of the First Ten NormalAlkanes

Name	Formula	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Number of Structural Isomers
Methane	CH₄	16	-182	-162	1
Ethane	$C_2H_6$	30	-183	-89	1
Propane	$C_3H_8$	44	-187	-42	1
Butane	$C_{4}H_{10}$	58	-138	0	2
Pentane	$C_{5}H_{12}$	72	-130	36	3
Hexane	$C_{6}H_{14}$	86	-95	68	5
Heptane	$C_7H_{16}$	100	-91	98	9
Octane	C <sub>8</sub> H <sub>18</sub>	114	-57	126	18
Nonane	C <sub>9</sub> H <sub>20</sub>	128	-54	151	35
Decane	$C_{10}H_{22}$	142	-30	174	75



Isomerism in Alkanes

- Structural isomerism: Two molecules have the same atoms but different bonds
  - Example Butane can exist as a straight chain structure (*n*-butane) or as a branched-chain structure (isobutane)
    - Different structures lead to different properties



#### Figure 22.4 - Structural Isomerism of Butane





Example 22.1 - Structural Isomerism

Draw the isomers of pentane

Example 22.1 - Solution

- Pentane (C<sub>5</sub>H<sub>12</sub>) has the following isomeric structures:
  - n-Pentane



Example 22.1 - Solution (Continued)

Isopentane



Neopentane





**Rules for Naming Alkanes** 

- 1. For alkanes beyond butane, add -ane to the Greek root for the number of carbon atoms
  - For a branched hydrocarbon, the longest continuous chain of carbon atoms determines the root name
- 2. When alkane groups appear as substituents, drop the -ane and add -yl



Rules for Naming Alkanes (Continued 1)

- Positions of substituent groups are specified by numbering the longest chain of carbon atoms sequentially
  - Start at the end closest to the branching
  - Hyphen is written between the number and the substituent name



Rules for Naming Alkanes (Continued 2)

- 4. Location and name of each substituent are followed by the root alkane name
  - Substituents are listed in alphabetical order
  - Prefixes di-, tri-, and so on are used to indicate multiple, identical substituents



Exercise

- Draw all the structural isomers for C<sub>8</sub>H<sub>18</sub> that have the root name (longest carbon chain) heptane
  - Name the structural isomers



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Interactive Example 22.3 - Structures from Names

- Determine the structure for each of the following compounds:
  - a. 4-ethyl-3,5-dimethylnonane
  - b. 4-tert-butylheptane



Interactive Example 22.3 - Solution (a)

- The root name nonane signifies a nine-carbon chain
  - Thus, we have





Interactive Example 22.3 - Solution (b)

 Heptane signifies a seven-carbon chain, and the tert-butyl group is

$$H_3C - C - CH_3$$

CH<sub>3</sub>

Thus, we have  $1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$  $H_3C - C - CH_3$ 



Reactions of Alkanes

- Fairly unreactive
  - They are saturated compounds
  - The C—C and C—H bonds are strong
- Do not react with acids, bases, or strong oxidizing agents at 25°C
  - Makes them valuable lubricating materials and the backbone for structural materials



**Combustion Reactions of Alkanes** 

- Alkanes react vigorously and exothermically with oxygen at high temperatures
  - Basis for use as fuels

 $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$ 



Substitution Reactions of Alkanes

- Occur primarily where halogen atoms replace hydrogen atoms
- Example Chlorination of methane

$$CH_{4} + Cl_{2} \xrightarrow{hv} CH_{3}Cl + HCl$$

$$CH_{3}Cl + Cl_{2} \xrightarrow{hv} CH_{2}Cl_{2} + HCl$$

$$CH_{2}Cl_{2} + Cl_{2} \xrightarrow{hv} CHCl_{3} + HCl$$

$$CHCl_{3} + Cl_{2} \xrightarrow{hv} CCl_{4} + HCl$$



**Dehydrogenation Reactions of Alkanes** 

- Hydrogen atoms are removed
- Product is an unsaturated hydrocarbon
- Example Dehydrogenation of ethane

$$CH_{3}CH_{3} \xrightarrow{Cr_{2}O_{3}} CH_{2} = CH_{2} + H_{2}$$
  
Ethylene



**Cyclic Alkanes** 

- Carbon atoms can form rings containing only C—C single bonds
  - General formula C<sub>n</sub>H<sub>2n</sub>
- Represented by the following figures for sake of simplicity:



# Cyclopropane (C<sub>3</sub>H<sub>6</sub>)

- Carbon atoms form an equilateral triangle with 60° bond angles
  - The *sp*<sup>3</sup> hybrid orbitals do not overlap
    - Results in weak or strained C—C bonds
- Highly reactive molecule





Cyclopentane ( $C_5H_{10}$ ) and Cyclohexane ( $C_6H_{12}$ )

- Rings have bond angles that are close to the tetrahedral angles
  - Permits sp<sup>3</sup> hybrid orbitals on adjacent carbon atoms to overlap head-on and form normal C—C bonds
- Cyclohexane
  - Ring must become nonplanar to attain tetrahedral angles
  - Exists in the chair and the boat forms



#### Figure 22.6 - The Chair and Boat Forms of Cyclohexane





Nomenclature for Cycloalkanes

- Follows the same rules as those used in naming other alkanes
  - Exception Root name is preceded by the prefix cyclo-
- Ring is numbered to yield the smallest substituent numbers possible

Interactive Example 22.4 - Naming Cyclic Alkanes

Name each of the following cyclic alkanes:



b. CH<sub>2</sub>CH<sub>3</sub> CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>



Interactive Example 22.4 - Solution (a)

The six-carbon cyclohexane ring is numbered as follows: CH<sub>3</sub>-CH-CH<sub>3</sub>



- There is an isopropyl group at carbon 1 and a methyl group at carbon 3
- The name is 1-isopropyl-3-methylcyclohexane, since the alkyl groups are named in alphabetical order



Interactive Example 22.4 - Solution (b)

This is a cyclobutane ring, which is numbered as follows:



The name is 1-ethyl-2-propylcyclobutane

Section 22.2 *Alkenes and Alkynes* 



Alkenes

- Hydrocarbons that contain at least one carbon– carbon double bond
- General formula C<sub>n</sub>H<sub>2n</sub>
- Simplest alkene Ethylene (C<sub>2</sub>H<sub>4</sub>)
  - Each carbon atom is sp<sup>2</sup> hybridized
    - C—C σ bond is formed by sharing an electron pair between sp<sup>2</sup> orbitals
    - π bond is formed by sharing a pair of electrons between p orbitals

Section 22.2 Alkenes and Alkynes



#### Figure 22.7 - The Bonding in Ethylene




**Rules for Naming Alkenes** 

- 1. Root hydrocarbon name ends in -ene
- In alkenes containing more than 3 carbon atoms, the location of the double bond is indicated by the lowest-numbered carbon atom in the bond



Isomerism of Alkenes

- Restricted rotation around double bonded carbon atoms implies that alkenes exhibit *cis-trans* isomerism
- Example Stereoisomers of 2-butene



Cis-2-butene





Alkynes

- Unsaturated hydrocarbons that contain at least one triple carbon–carbon bond
- Simplest alkyne Acetylene or ethyne (C<sub>2</sub>H<sub>2</sub>)
- Nomenclature
  - -yne is used as a suffix to replace the -ane of the parent alkane



#### Figure 22.10 - The Bonding in Acetylene





**Alkynes as Ringed Structures** 





Interactive Example 22.5 - Naming Alkenes and Alkynes

Name the following molecule:





Interactive Example 22.5 - Solution

The longest chain, which contains six carbon atoms, is numbered as follows:



Thus, the hydrocarbon is a 2-hexene



#### Interactive Example 22.5 - Solution (Continued)

- Since the hydrogen atoms are located on opposite sides of the double bond, this molecule corresponds to the *trans* isomer
- The hydrocarbon is *trans*-4-methyl-2-hexene



Exercise

Name each of the following alkenes:





Addition Reactions

- Involve breaking  $\pi$  bonds and forming new  $\sigma$  bonds
- Example
  - Hydrogenation reaction: Involves the addition of hydrogen atoms

$$CH_2 = CHCH_3 + H_2 \xrightarrow{Catalyst} CH_3CH_2CH_3$$

1-Propene

Propane

Nickel, palladium, or platinum acts as a catalyst for this reaction



Halogenation and Polymerization

- Halogenation: Involves the addition of halogen atoms
- Polymerization: Reaction that involves joining small molecules to form a large molecule



Aromatic Hydrocarbons - An Introduction

- A special class of cyclic unsaturated hydrocarbons
- Benzene (C<sub>6</sub>H<sub>6</sub>)
  - Simplest aromatic hydrocarbon
  - Has a planar ring structure



The structure of benzene with bond angles of 120°



# **Figure 22.11** - Resonance Structures and the Usual Representation of Benzene



Two of the resonance structures of benzene

The usual representation of benzene



Benzene

- Delocalization of the *π* electrons makes the benzene ring behave differently from a typical unsaturated hydrocarbon
  - Benzene undergoes substitution reactions in which hydrogen atoms are replaced by other atoms





Benzene (Continued)

- Reacts more like a saturated hydrocarbon
  - Indicates the great stability of the delocalized π electron system
- Phenyl group: Benzene that is used as a substituent



Nomenclature of Benzene Derivatives

- When there is more than one substituent, numbers are used to indicate their positions
- Alternate nomenclature system suggests the usage of the following prefixes:
  - Ortho- (o-) for two adjacent substituents
  - Meta- (m-) for two substituents with one carbon in between
  - Para- (p-) for two substituents that are opposite to each other



#### Figure 22.12 - Some Selected Substituted Benzenes





#### Table 22.3 - More Complex Aromatic Systems

Structural Formula	Name	Use of Effect
	Naphthalene	Formerly used in mothballs
	Anthracene	Dyes
	Phenanthrene	Dyes, explosives, and synthesis of drugs
	3,4-Benzpyrene	Active carcinogen found in smoke and smog



Hydrocarbon Derivatives - An Introduction

- Molecules that are fundamentally hydrocarbons but have functional groups
  - Functional group: An atom or group of atoms that contains elements in addition to carbon and hydrogen
    - Each group exhibits its own characteristic chemistry



#### Table 22.4 - The Common Functional Groups

Class	Functional Group	General Formula*	Example
Halohydrocarbons	—X (F, Cl, Br, I)	R—X	CH₃I Iodomethane (methyl iodide)
Alcohols	—ОН	R—OH	CH₃OH Methanol (methyl alcohol)
Ethers	—0—	R—O—R′	CH₃OCH₃ Dimethyl ether
Aldehydes	О    —С—Н	$\stackrel{O}{\overset{\parallel}{\overset{\parallel}{\overset{\scriptstyle}}{\overset{\scriptstyle}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}{}{\overset{\scriptstyle}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}}{\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{\overset{\scriptstyle}}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}{}}}}{}\overset{\scriptstyle}}}{}\overset{\scriptstyle}}{}}$ }{}\overset{\scriptstyle}}{}\overset{\scriptstyle}}}}{}}}{}}}{}\tilde	CH <sub>2</sub> O Methanal (formaldehyde)

\*R and R' represent hydrocarbon fragments.



#### Table 22.4 - The Common Functional Groups (Continued)

Class	Functional Group	General Formula*	Example
Ketones		$\stackrel{O}{\stackrel{\parallel}{\stackrel{\parallel}{\scriptstyle \parallel}}}_{R-C-R'}$	CH <sub>3</sub> COCH <sub>3</sub> Propanone (dimethyl ketone or acetone)
Carboxylic acids	$\mathbf{O}$ $\mathbf{H}$ $\mathbf{C}$ $\mathbf{O}$ $\mathbf{O}$	$\stackrel{\mathrm{O}}{\overset{\mathrm{\parallel}}{\overset{\mathrm{\parallel}}{\overset{\mathrm{C}}}}}_{\mathrm{R-C-OH}}$	CH₃COOH Ethanoic acid (acetic acid)
Esters	$\overset{\mathrm{O}}{\overset{\parallel}{\overset{\parallel}{\overset{}}}}}}}}$	$\stackrel{O}{\stackrel{\parallel}{\scriptstyle \parallel}}_{R-C-O-R'}$	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub> Ethyl acetate
Amines	-NH <sub>2</sub>	R—NH <sub>2</sub>	CH <sub>3</sub> NH <sub>2</sub> Aminomethane (methylamine)

\*R and R' represent hydrocarbon fragments.



Alcohols

- Contain the hydroxyl group (—OH)
- Systematic nomenclature
  - Replace the final -e of the parent hydrocarbon with the -ol
  - Position of the —OH group is specified by a number
    - Chosen number is the smallest of the substituent numbers
- Have higher boiling points than what is expected from their molar masses



Alcohols - Boiling Point and Intermolecular Forces

- Higher boiling point is attributed to the types of intermolecular attractions in the liquids
  - Example Methanol and ethane have a molar mass of 30
    - Boiling point of methanol is 65° C, and it exhibits hydrogen bonding
    - Boiling point of ethane is -89° C, and it exhibits weak London dispersion interactions



**Classification of Alcohols** 

- Based on the number of hydrocarbon fragments that are bonded to the carbon where the —OH group is attached
  - R, R', and R" represent hydrocarbon fragments





### Table 22.5 - Some Common Alcohols

Formula	Systematic Name	Common Name
CH <sub>3</sub> OH	Methanol	Methyl alcohol
CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	Ethyl alcohol
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-Propanol	<i>n</i> -Propyl alcohol
CH <sub>3</sub> CHCH <sub>3</sub>	2-Propanol	Isopropyl alcohol



## Methanol

- Known as wood alcohol
  - Prepared by heating wood in the absence of air
- Industrial preparation
  - Hydrogenation of carbon monoxide

$$\text{CO} + 2\text{H}_2 \xrightarrow{400^{\circ}\text{C}} \text{CH}_3\text{OH}$$



Methanol (Continued)

- Uses
  - Starting material for the synthesis of acetic acid and for adhesives, fibers, and plastics
  - Motor fuel
- Highly toxic when ingested by humans
  - Leads to blindness and death



### Ethanol

- Found in beer, wine, and whiskey
- Produced by the fermentation of glucose in grapes, corn, and barley

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2CH_3CH_2OH + 2CO_2$$
  
Glucose Ethanol

- When the alcohol content reaches 13%, the yeast can no longer survive, and the reaction stops
- Beverages with higher alcohol content are made by distilling the fermentation mixture



Ethanol (Continued)

- Uses
  - Can be burned in the internal combustion engine of an automobile
  - Used as a solvent and for the preparation of acetic acid
- Industrially produced by the reaction of water with ethylene

$$CH_2 = CH_2 + H_2O \xrightarrow{Acid} CH_3CH_2OH$$



Polyhydroxyl Alcohols

- Contain more than one hydroxyl group
- Example 1,2-ethanediol (ethylene glycol)

- Major constituent of automobile antifreeze solutions
- Toxic in nature



Phenol

 Simplest aromatic compound with an attached —OH group



Looks like an alcohol but has different properties



Interactive Example 22.6 - Naming and Classifying Alcohols

 For the following alcohol, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary

$$CH_3 \\ CH_3CCH_2CH_2CH_2CH_2Br \\ | \\ OH$$



Interactive Example 22.6 - Solution

The chain is numbered as follows:



- The name is 6-bromo-2-methyl-2-hexanol
  - This is a tertiary alcohol
    - The carbon where the —OH is attached also has three other R groups attached



## Aldehydes and Ketones

- Contain the carbonyl group, which has the following structure:
  - Ketones: Carbonyl group is bonded to 2 carbon atoms
    - Example Acetone
  - Aldehydes: Carbonyl group is bonded to at least 1 hydrogen atom
    - Example Formaldehyde and acetaldehyde



Systematic Nomenclature of Aldehydes and Ketones

- Aldehydes
  - Name is obtained from the parent alkane by removing the final -e and adding -al
- Ketones
  - Replace the final -e with -one
  - Position of the carbonyl group is indicated by a number where necessary



Aldehydes and Ketones - Uses

- Ketones are useful solvents
- Aldehydes have strong odors
  - Examples
    - Vanillin is responsible for the sweet odor in vanilla beans
    - Cinammaldehyde produces the distinct odor of cinnamon
    - Butyraldehyde contributes to the unpleasant smell in rancid butter


Aldehydes and Ketones - Method of Preparation

- Prepared by the oxidation of alcohols
  - Aldehydes are prepared by oxidizing primary alcohols

$$CH_3CH_2OH \xrightarrow{Oxidation} CH_3C$$

Ketones are prepared by oxidizing secondary alcohols

$$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{Oxidation}} \text{CH}_3\text{CCH}_3\\ | & ||\\ \text{OH} & \text{O} \end{array}$$

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### Figure 22.13 - Some Common Ketones and Aldehydes





**Carboxylic Acids** 

- Contain the carboxyl group
  - Carboxyl group: Gives an acid the general formula RCOOH



- Appear as weak acids in aqueous solutions
- Named from the parent alkane by dropping the final -e and adding -oic



**Carboxylic Acids - Synthesis** 

- Conducted by oxidation of primary alcohols with a strong oxidizing agent
- Example
  - Oxidation of ethanol in the presence of potassium permanganate to produce acetic acid

$$CH_3CH_2OH \xrightarrow{KMnO_4(aq)} CH_3COOH$$



Esters

- Carboxylic acid reacts with an alcohol to form an ester and a water molecule
- Example Reaction of acetic acid with ethanol produces ethyl acetate and water





Esters (Continued)

- Have a sweet and fruity odor
  - Example Smell of oranges is caused by *n*-octyl acetate
- Systematic nomenclature
  - Change the -oic ending in the parent acid to -oate
  - The parent alcohol chain is named first with a -yl ending



Aspirin - An Ester

 Acetylsalicylic acid is the product of the reaction between salicylic acid and acetic acid



Used as an analgesic



### Amines

- Derivatives of ammonia
  - One or more N—H bonds are replaced by N—C bonds

### Classification

- Primary amines One N—C bond exists
- Secondary amines Two N—C bonds exist
- Tertiary amines All three N—H bonds have been replaced by N—C bonds



**Figure 22.15** - The General Formulas for Primary, Secondary, and Tertiary Amines



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Amines (Continued)

- Systematic nomenclature
  - Common names are used for simple amines
  - Complex molecules in the —NH<sub>2</sub> functional group are given the prefix amino-
- Have an unpleasant, fishlike odor
- Aromatic amines are used for making dyes



### Table 22.6 - Some Common Amines

Formula	Common Name	Туре
CH <sub>3</sub> NH <sub>2</sub>	Methylamine	Primary
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	Ethylamine	Primary
(CH <sub>3</sub> ) <sub>2</sub> NH	Dimethylamine	Secondary
$(CH_3)_3N$	Trimethylamine	Tertiary
NH <sub>2</sub>	Aniline	Primary
Н	Diphenylamine	Secondary



### **Polymers - An Introduction**

- Large, chainlike molecules that are built from small molecules called monomers
- Form the basis for:
  - Synthetic fibers
  - Plastics
  - Rubbers



**Development of Polymers** 

- Christian Schoenbein
  - Found a new material that had surprising properties and was extremely flammable
- The first synthetic polymers were by-products of various organic reactions
  - Regarded as unwanted contaminants
- Leo H. Baekeland's work resulted in the creation of Bakelite, a synthetic plastic
  - Used in telephones, insulators, and billiard balls



Development of Polymers (Continued 1)

- Thermoset polymer: Substance that cannot be softened again after being molded into a certain shape under high temperature and pressure
  - Example Bakelite
- Thermoplastic polymer: Substance that can be remelted or remolded
  - Example Cellulose nitrate



Development of Polymers (Continued 2)

- Nylon Prepared by Wallace H. Carothers
  - Julian Hill realized that nylon could be used as fibers
- Crosslinking: Existence of covalent bonds between adjacent chains
  - Contributes to the strength of polymers
- Charles Goodyear developed vulcanization
  - Vulcanization: Adding sulfur to rubber and heating the mixture to produce stronger, elastic rubber



Polyethylene

- Simplest polymer
- Constructed from ethylene monomers

$$n CH_2 = CH_2 \xrightarrow{Catalyst} \begin{pmatrix} H & H \\ | & | \\ C & C \\ | & | \\ H & H \end{pmatrix}_n$$

*n* represents a large number
Tough, flexible plastic



### Polyethylene (Continued)

- Uses
  - Piping, bottles, electrical insulation, packaging films, and garbage bags
- Properties can be modified by using substituted ethylene monomers
  - Example Teflon is obtained when the monomer is tetrafluoroethylene



# **Table 22.7** - Some Common Synthetic Polymers andTheir Monomers and Applications

Monomer		Polymer		
Name	Formula	Name	Formula	Uses
Ethylene	$H_2C = CH_2$	Polyethylene	$-(CH_2-CH_2)_n$	Plastic piping, bottles, electrical insulation, toys
Propylene	$\substack{\overset{H}{\substack{l\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	Polypropylene	$\begin{array}{c} -(CH-CH_2-CH-CH_2)_n \\   \\ CH_3 \\ CH_3 \\ \end{array}$	Film for packaging, carpets, lab wares, toys
Vinyl chloride	$\substack{\overset{H}{\underset{\substack{l\\ l\\ Cl}}{H_2C=\overset{l}{C}}}$	Polyvinyl chloride (PVC)	$-(CH_2 - CH)_{\overline{n}}$	Piping, siding, floor tile, clothing, toys
Acrylonitrile	$\substack{H_{2}C=C \\ \mid \\ CN \\ CN \\ H_{2}C = 0 \\ H_$	Polyacrylonitrile (PAN)	$-(CH_2-CH)_{\overline{h}}$	Carpets, fabrics



# Table 22.7 - Some Common Synthetic Polymers andTheir Monomers and Applications (Continued)





## Types of Polymerization

- Addition polymerization
  - Monomers add together to form the polymer
  - No other product is formed
  - Initiated by a free radical
    - Free radical: Species with an unpaired electron
    - Repeatedly attacks and breaks the π bonds to form a new free radical and to create a long-chain polymer



Types of Polymerization (Continued)

# Condensation polymerization

- A small molecule is formed for each extension of the polymer chain
- Used for the production of nylon
  - Nylon is a copolymer that contains two types of monomers that combine to form a chain
- Homopolymer: Result of polymerizing a single type of monomer
- Dimer: Two monomers joined



Structures of Nylon and Polyester

Nylon



### Polyester

Example - Dacron





**Polymers Based on Ethylene** 

 Ethylene undergoes addition polymerization after the double bond has been broken by an initiator



 Process continues by adding new ethylene molecules to eventually give polyethylene



## Forms of Polyethylene

- Low-density polyethylene (LDPE)
  - Contains branched chains
  - Manufactured under conditions of high temperature (500°C) and high pressure (≈20,000 psi)
    - Lower reaction pressures and temperatures have become possible through the use of catalysts
  - Used to manufacture transparent film that is used in packaging consumer goods



Forms of Polyethylene (Continued)

- High-density polyethylene (HDPE)
  - Comprises straight-chain molecules
  - Used for blow-molded products such as bottles
  - Linear low-density polyethylene
    - Product of the reaction between chromium(III) oxide and aluminosilicate catalyst
    - Similar to HDPE



Reason for the Usefulness of Polyethylene

- Polyethylene has a high molecular weight (molecular mass)
  - Strengths of the interactions between points on the nonpolar chains are small
    - Length of the chains accumulate the attractions to a significant value, which help the chains stick together
    - Provides strength and toughness
  - As the molecular weight increases, polyethylene becomes more difficult to process



- Polymer Properties That Are Not Influenced by Molecular Weight
- Resistance to chemical attack
- Color and refractive index
- Hardness
- Density
- Electrical conductivity



Methods to Alter the Strength of Polymeric Material

- Change in chain length
- Change in substituents
  - Properties of a polymer depend on the identity of the substituent
    - Example If one uses the following monomer type, the resulting polymer will have properties based on the identity of X



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Types of Chain Arrangements

- Isotactic chain: CH<sub>3</sub> groups arranged on the same side of the chain
- Syndiotactic chain: CH<sub>3</sub> groups arranged in an alternate fashion on the chain
- Atactic chain: CH<sub>3</sub> groups randomly distributed on the chain



Proteins

- Have molar masses that range from about 6000 to over 1,000,000 g/mol
- Constitute 15% of the human body
- Fibrous proteins
  - Provide structural integrity and strength for tissues
  - Main components of muscle, hair, and cartilage



Proteins (Continued)

- Globular proteins: Worker molecules of the human body
  - Roughly spherical in shape
  - Transport and store oxygen and nutrients
  - Act as catalysts
  - Fight invasion by foreign objects
  - Participate in the body's regulatory systems
  - Transport electrons in metabolism



 $\alpha$ -Amino Acids

- Building blocks of all proteins
- R can represent H, CH<sub>3</sub>, or a more complex substituent
- $-NH_2$  is always attached to the  $\alpha$ -carbon
- 20 amino acids commonly found in proteins



 $\alpha$ -Amino Acids (Continued)

- Amino acids are grouped into polar and nonpolar classes that are determined by the R groups or side chains
  - Polar side chains Contain a large number of nitrogen and oxygen atoms
    - Hydrophilic (water-loving)
  - Nonpolar side chains Composed of carbon and hydrogen atoms
    - Hydrophobic (water-fearing)



Bonding in Amino Acids

- Protein polymers are built by condensation reactions between amino acids
- Example Dipeptide





#### Levels of Structure in Proteins





### **Primary Structure**

- Sequence of amino acids in the protein chain
  - Indicated using three-letter codes for amino acids
    - Terminal carboxyl group is on the right, and the terminal amino group is on the left

The amino acid sequences in (a) oxytocin and (b) vasopressin The differing amino acids are boxed




Interactive Example 22.7 - Tripeptide Sequences

 Write the sequences of all possible tripeptides composed of the amino acids tyrosine, histidine, and cysteine



## Interactive Example 22.7 - Solution

- There are six possible sequences
  - tyr-his-cys
  - tyr-cys-his
  - his-tyr-cys
  - his-cys-tyr
  - cys-tyr-his
  - cys-his-tyr



Interactive Example 22.8 - Polypeptide Sequences

What number of possible sequences exists for a polypeptide composed of 20 different amino acids?



Interactive Example 22.8 - Solution

The answer is 20!, or

## $20 \times 19 \times 18 \times 17 \times 16 \times \ldots \times 5 \times 4 \times 3 \times 2 \times 1$

$$= 2.43 \times 10^{18}$$



Secondary Structure

 Determined by hydrogen bonding between lone pairs on an oxygen atom in the carbonyl group of one amino acid and a hydrogen atom attached to a nitrogen of another amino acid



 $\alpha$ -Helical Arrangement

- α-helix: Result of intrachain hydrogen bonding
  - Occurs within a given protein chain
  - Provides the protein chain with its elasticity





Pleated Sheet Arrangement of Proteins

- Arrangement that results from interchain hydrogen bonding
  - Interchain Bonding that occurs between different protein chains
- Found in:
  - Silk
  - Natural fibers
  - Muscle fibers



#### Figure 22.22 - Pleated Sheet Arrangement





**Random-Coil Arrangement of Proteins** 

- Structure that results from the breakage of the αhelix to provide a secondary configuration
  - Occurs in certain areas where the chain bends to give the protein a compact globular structure



**Tertiary Structure** 

- Long and narrow or globular
- Maintained by several types of interactions
  - Hydrogen-bonding
  - Dipole-dipole interactions
  - Ionic bonds
  - Covalent bonds
  - London dispersion forces



# **Figure 22.24** - Summary of the Various Types of Interactions in the Tertiary Structure of a Protein





Tertiary Structure (Continued)

Cysteine is an amino acid with the following structure:
 H O
 HS-CH2-C-OH

- Plays a role in stabilizing the tertiary structure of proteins
  - SH groups on two cysteines can react in the presence of an oxidizing agent to form a S—S bond called a disulfide linkage



**Protein Damage** 

- Denaturation: Process of breaking down the three-dimensional structure of a protein
  - Initiated by any source of energy and is considered to be dangerous to living organisms
  - Caused by metals like lead and mercury by disrupting disulfide bonds between protein chains
- Can result from chemicals such as benzene, trichloroethane, and 1,2-dibromoethane



# **Figure 22.26** - Schematic Representation of the Thermal Denaturation of a Protein





**Critical Thinking** 

- What if you contracted a disease that prevents all hydrogen bonding in proteins?
  - Could you live with such a condition?



Carbohydrates

- Serve as a food source for most organisms and as structural material for plants
- Empirical formula CH<sub>2</sub>O
- Monosaccharides (simple sugars): Polyhydroxy ketone and aldehyde monomers
  - Pentoses: Contain five carbon atoms
  - Hexoses: Contain six carbon atoms



**Optical Isomerism in Simple Sugars** 

 A carbon atom with four different groups bonded to it in a tetrahedral arrangement will always have a nonsuperimposable mirror image





### Table 22.8 - Some Important Monosaccharides





### Table 22.8 - Some Important Monosaccharides (Continued)





Interactive Example 22.9 - Chiral Carbons in Carbohydrates

 Determine the number of chiral carbon atoms in the following pentose:



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Interactive Example 22.9 - Solution

- We must look for carbon atoms that have four different substituents
  - The top carbon has only three substituents and thus cannot be chiral
  - The three carbon atoms (shown in blue) have four different groups attached to them



#### Interactive Example 22.9 - Solution (Continued 1)



 Since the fifth carbon atom has only three types of substituents (it has two hydrogen atoms), it is not chiral



Interactive Example 22.9 - Solution (Continued 2)

 Thus, the three chiral carbon atoms in this pentose are those shown in blue:



Note that D-ribose and D-arabinose are two of the eight isomers of this pentose



Cyclic Structure of Monosaccharides

- Monosaccharides cyclize or form a ring structure in aqueous solutions
  - Example Cyclization of D-fructose





Disaccharides

- Formed from two monosaccharides joined by a glycoside linkage
  - Glycoside linkage: C—O—C bond formed between the rings of two cyclic monosaccharides by the elimination of water
- Example Sucrose (common table sugar)
  - When consumed in food, the reaction is reversed due to an enzyme in the saliva



#### Figure 22.31 - Formation of Sucrose, a Disaccharide





Polysaccharides

- Large polymers that are composed of many monosaccharide units
- Formed when each ring forms two glycoside linkages
- Important polysaccharides
  - Starch
  - Cellulose
  - Glycogen



## Starch

- Polymer of α-D-glucose
- Consists of two parts
  - Amylose Straight-chain polymer of α-glucose
  - Amylopectin Highly branched polymer of α-glucose
- Branching occurs when a third glycoside linkage attaches a branch to the main polymer chain



#### Figure 22.32 - The Polymer Amylose





## Cellulose

- Major structural component of:
  - Woody plants
  - Natural fibers such as cotton
- Polymer of  $\beta$ -D-glucose monomers





Glycogen

- Structure is similar to that of amylopectin but with more branching
  - Branching facilitates rapid breakdown of glycogen into glucose when energy is required
- Main carbohydrate reservoir in animals



Nucleic Acids

- DNA (deoxyribonucleic acid): Stores and transmits genetic information
  - Molecular weight is as high as several billion g/mol
  - Responsible for protein synthesis in combination with RNA (ribonucleic acid)
    - Molecular weight 20,000–40,000 g/mol



# **Figure 22.33** - Structure of the Pentoses, Deoxyribose and Ribose





## Nucleotides

- Monomers of the nucleic acids
- Composed of:
  - A five-carbon sugar, deoxyribose in DNA and ribose in RNA
  - A nitrogen-containing organic base
  - A phosphoric acid molecule (H<sub>3</sub>PO<sub>4</sub>)



Figure 22.34 - Organic Bases Found in DNA and RNA



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# Section 22.6 Natural Polymers

- DNA
- Key to DNA's functioning is its double-helical structure with complementary bases on the two strands
  - Contains two sugar—phosphate backbones whose bases form hydrogen bonds to each other
    - Facilitated by thymine-adenine and cytosine-guanine pairs






# **Figure 22.37** - Complementarity of the Thymine-Adenine and Cytosine-Guanine Pairs





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Unwinding of DNA Strands

- Occurs during cell division
- New complementary strands are constructed on the unraveled ones
  - Each unraveled strand serves as a template for attaching the complementary bases
- Replication of DNA allows for the transmission of genetic information





**Protein Synthesis** 

- Gene: Segment of the DNA that contains the genetic code for a certain protein
  - Codes transmit the primary structure of the protein to the construction machinery of the cell
    - Consist of a set of three bases called a codon



**Protein Synthesis - Process** 

- DNA creates a special RNA molecule called mRNA (messenger RNA), which is built in the cell nucleus on the gene
  - Double helix is unzipped
    - Complementarity of the bases is used in a process similar to that used in DNA replication
  - mRNA migrates into the cytoplasm
    - Protein synthesis occurs with the assistance of ribosomes



Protein Synthesis - Process (Continued)

# **tRNA (transfer RNA)**: Small RNA fragments

- Search for specific amino acids to attach them to the growing protein chain as dictated by the codons
- Has a lower molecular weight
- Consists of a chain of 75 to 80 nucleotides
- Anticodon: Complementary triplet of bases used to decode genetic messages from the mRNA
  - Nature of the anticodon governs which amino acid will be brought to the protein under construction

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#### Figure 22.39 - Process of Building a Protein



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