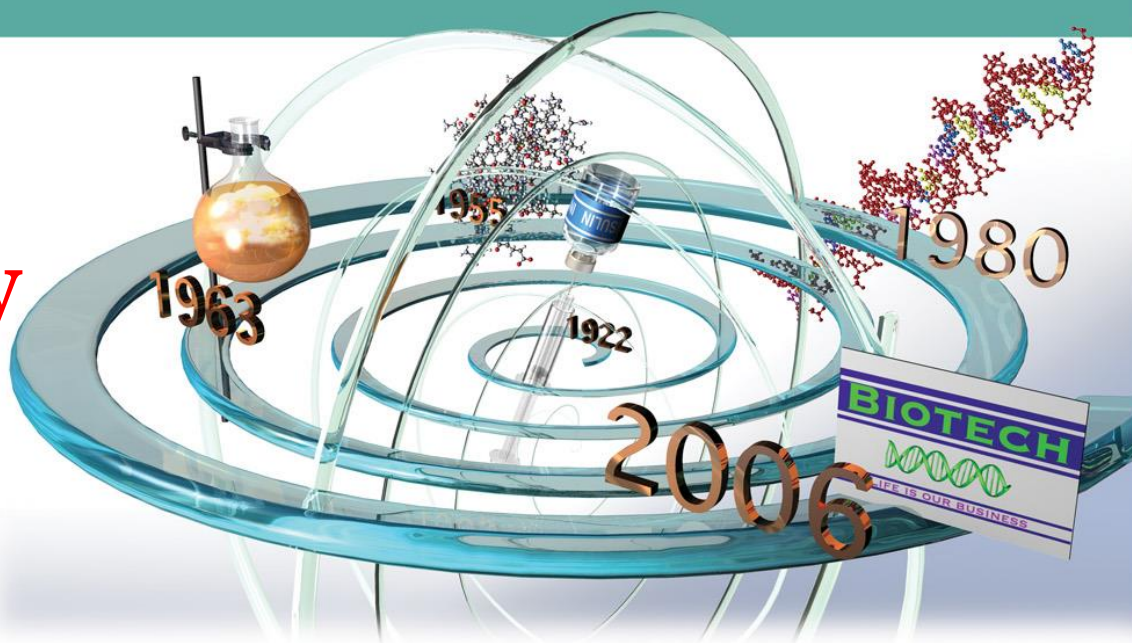


Chemistry: A Molecular Approach, 1st Ed.

Nivaldo Tro

Chapter 21 Biochemistry



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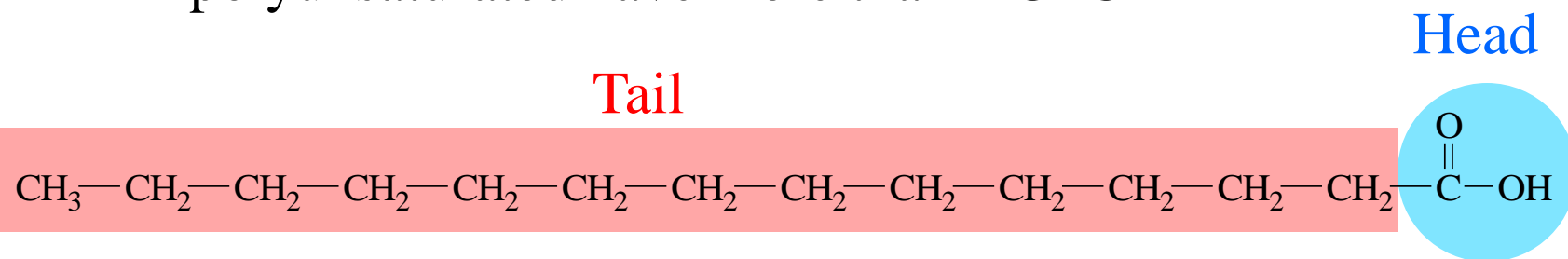
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Lipids

- chemicals of the cell that are insoluble in water, but soluble in nonpolar solvents
- fatty acids, fats, oils, phospholipids, glycolipids, some vitamins, steroids, and waxes
- structural components of cell membrane
 - ✓ because they don't dissolve in water
- long-term energy storage
- insulation

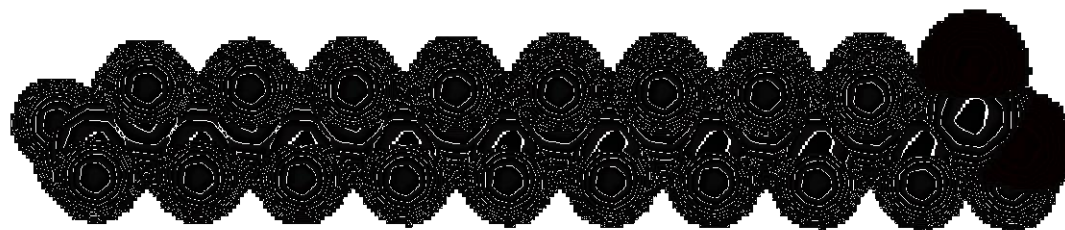
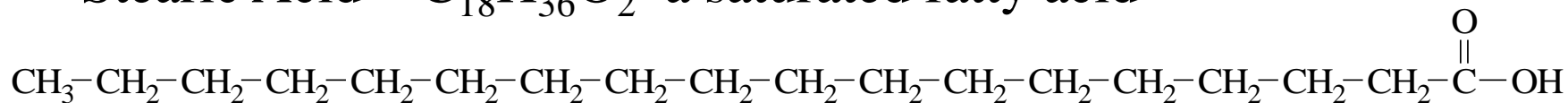
Fatty Acids

- carboxylic acid (head) with a very long hydrocarbon side-chain (tail)
- saturated fatty acids contain no C=C double bonds in the hydrocarbon side-chain
- unsaturated fatty acids have C=C double bonds
 - ✓ monounsaturated have 1 C=C
 - ✓ polyunsaturated have more than 1 C=C

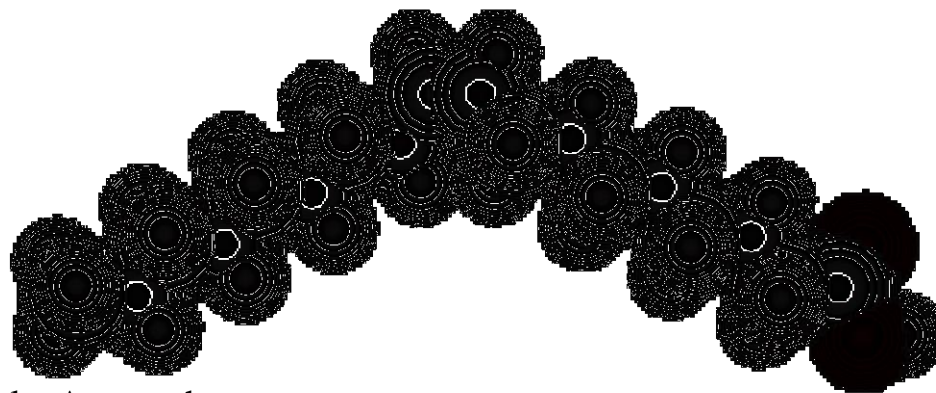
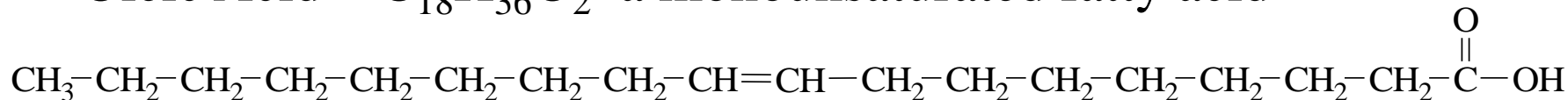


Fatty Acids

Stearic Acid – $C_{18}H_{36}O_2$ a saturated fatty acid



Oleic Acid – $C_{18}H_{34}O_2$ a monounsaturated fatty acid



Fatty Acids

TABLE 21.1 Fatty Acids

Saturated Fatty Acids					
Name	Number of Carbons		mp (°C)	Structure	Sources
Butyric acid	4		-7.9	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Milk fat
Caproic acid	10		31	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	Milk fat, whale oil
Myristic acid	14		59	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Butterfat, coconut oil
Palmitic acid	16		64	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Beef fat, butterfat
Stearic acid	18		70	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Beef fat, butterfat
Unsaturated Fatty Acids					
Name	Number of Carbons	Number of Double Bonds	mp (°C)	Structure	Sources
Oleic acid	18	1	4	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Olive oil, peanut oil
Linoleic acid	18	2	-5	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$	Linseed oil, corn oil
Linolenic acid	18	3	-11	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$	Linseed oil, corn oil

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Structure and Melting Point

- Larger fatty acid = Higher melting point
- Double bonds decrease the melting point
 - ✓ More DB = lower MP
- Saturated = no DB
- Monounsaturated = 1 DB
- Polyunsaturated = many DB

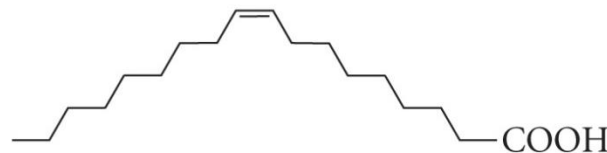
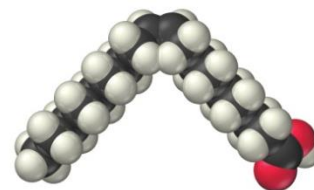
Name	MP °C	Class
Myristic Acid	58	Sat., 14 C
Palmitic Acid	63	Sat, 16 C
Stearic Acid	71	Sat, 18 C
Oleic Acid	16	1 DB, 18 C
Linoleic Acid	-5	2 DB, 18 C
Linolenic Acid	-11	3 DB, 18 C

Effect on Melting Point

- since fatty acids are largely nonpolar, the main attractive forces are dispersion forces
- larger size = more electrons = larger dipole = stronger attractions = higher melting point
- more straight = more surface contact = stronger attractions = higher melting point



Stearic acid, mp 70 °C



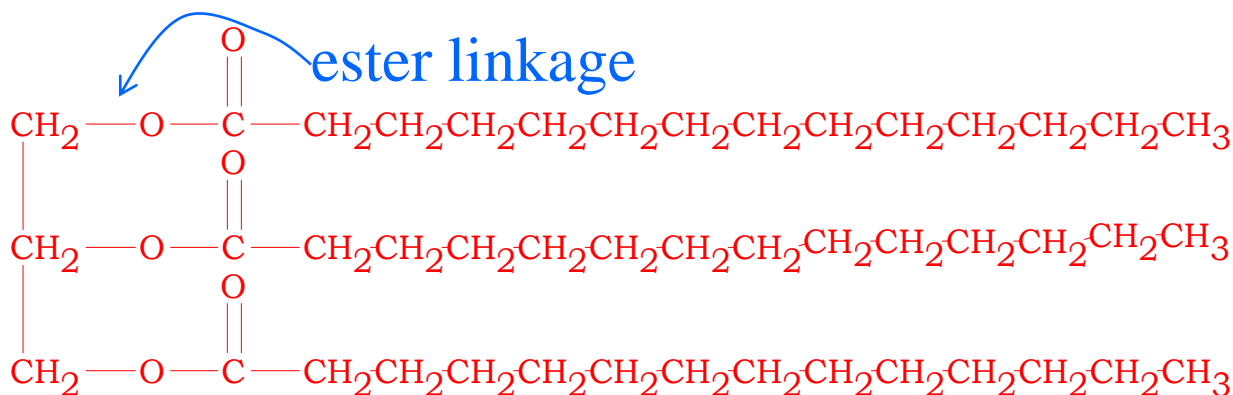
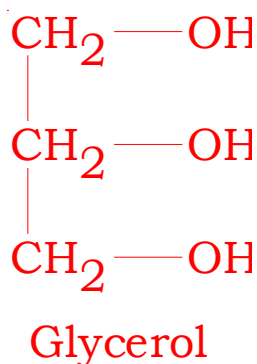
Oleic acid, mp 4 °C

cis Fats and *trans* Fats

- naturally unsaturated fatty acids contain *cis* double bonds
- processed fats come from polyunsaturated fats that have been partially hydrogenated – resulting in *trans* double bonds
- *trans* fats seem to increase the risk of coronary disease

Fats and Oils: Triglycerides

- fats are solid at room temperature, oils are liquids
- triglycerides are triesters of glycerol with fatty acids
 - ✓ the bonds that join glycerol to the fatty acids are called **ester linkages**



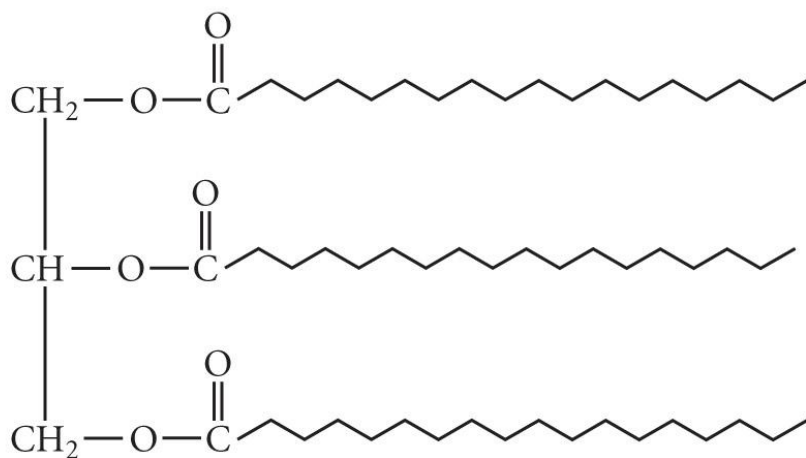
Triglycerides

- triglycerides differ in the length of the fatty acid side-chains and degree of unsaturation
 - ✓ side chains range from 12 to 20 C
 - ✓ most natural triglycerides have different fatty acid chains in the triglyceride, simple triglycerides have 3 identical chains
- saturated fat = all saturated fatty acid chains
 - ✓ warm-blooded animal fat
 - ✓ solids
- unsaturated fats = some unsaturated fatty acid chains
 - ✓ cold-blooded animal fat or vegetable oils
 - ✓ liquids

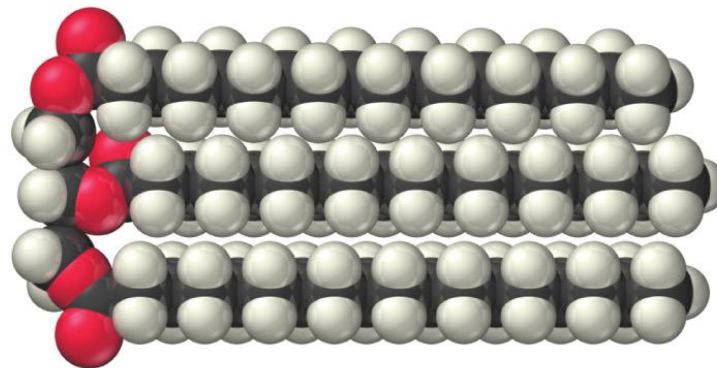
Tristearin

a simple triglyceride found in lard

Tristearin: A Saturated Fat



Tristearin, mp 72 °C

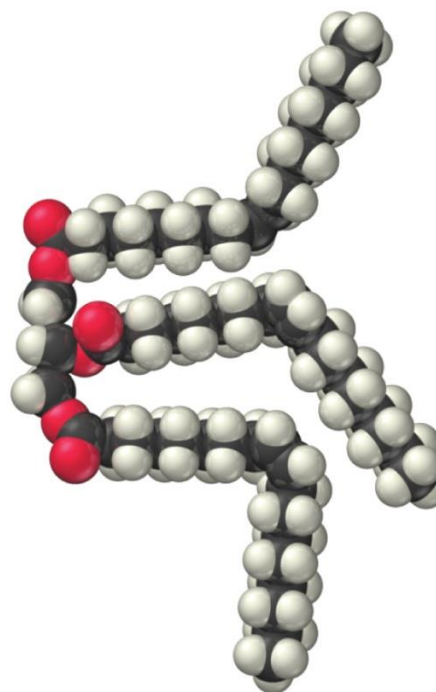
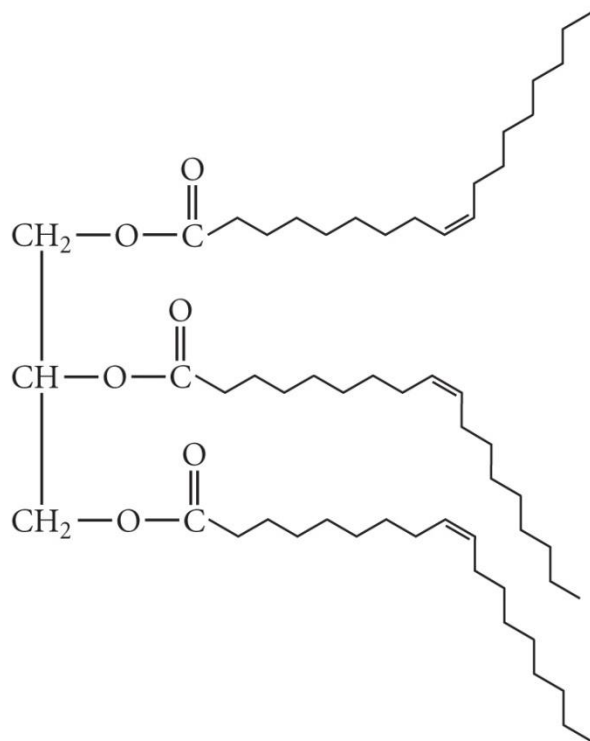


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Triolein

a simple triglyceride found in olive oil

Triolein: A Monounsaturated Fat

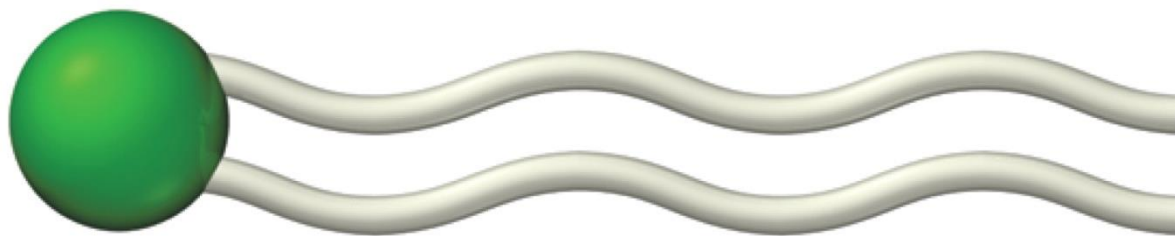


Triolein, mp $-4\text{ }^{\circ}\text{C}$

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Phospholipids

- Esters of glycerol
- Glycerol attached to 2 fatty acids and 1 phosphate group
- Phospholipids have a **hydrophilic head** due to phosphate group, and a **hydrophobic tail** from the fatty acid hydrocarbon chain
- part of **lipid bilayer** found in animal cell membranes

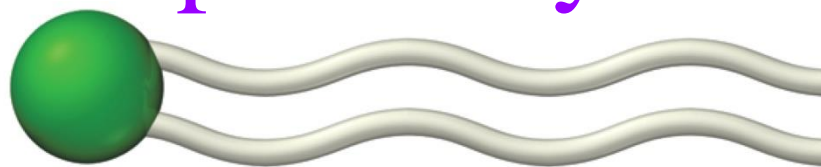


Polar head

Nonpolar tails

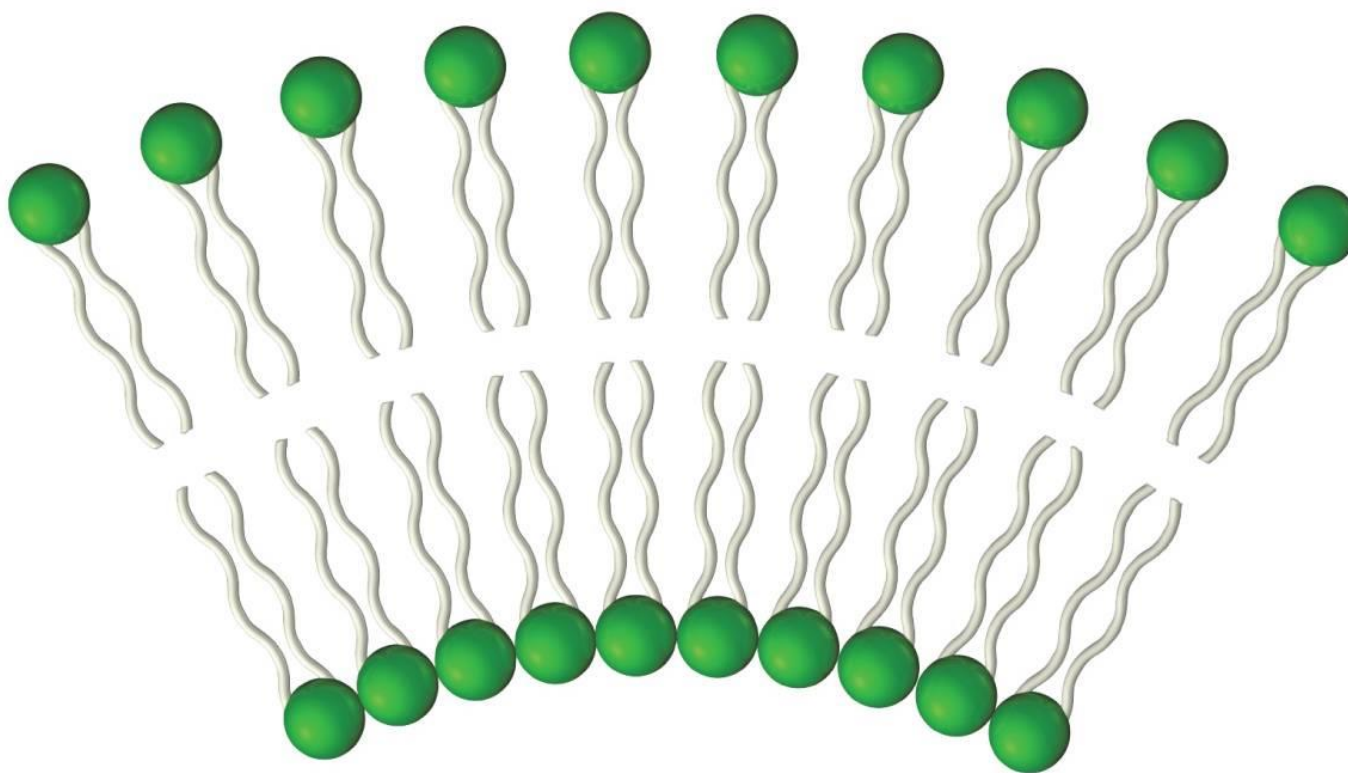
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Lipid Bilayer



Polar head

Nonpolar tails

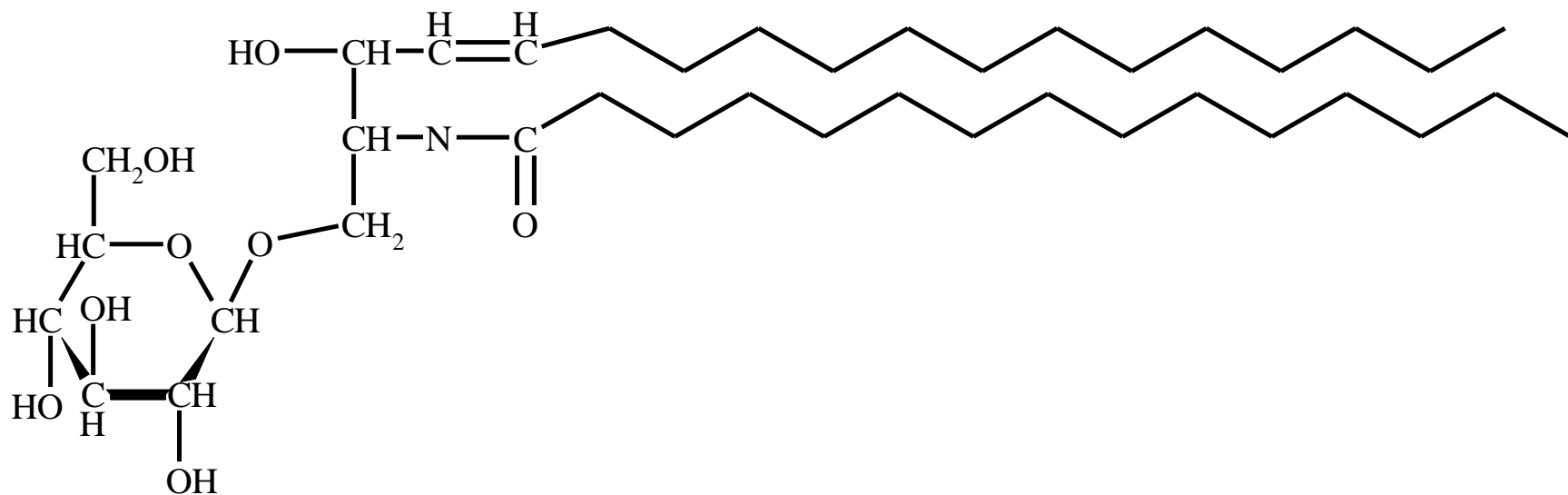


Glycolipids

- similar structure and properties to the phospholipids
- the nonpolar part composed of a fatty acid chain and a hydrocarbon chain
- the polar part is a sugar molecule
 - ✓ e.g., glucose

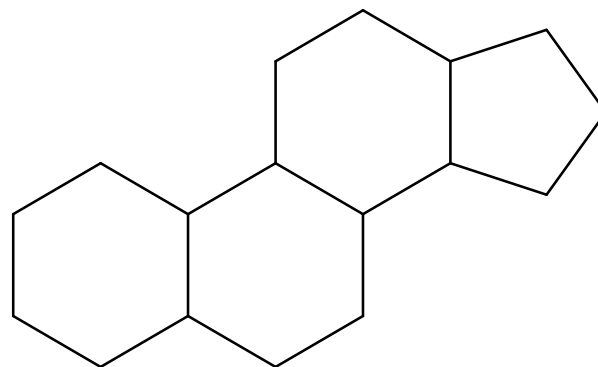
Glucosylcerebroside

(found in plasma membranes of nonneural cells)

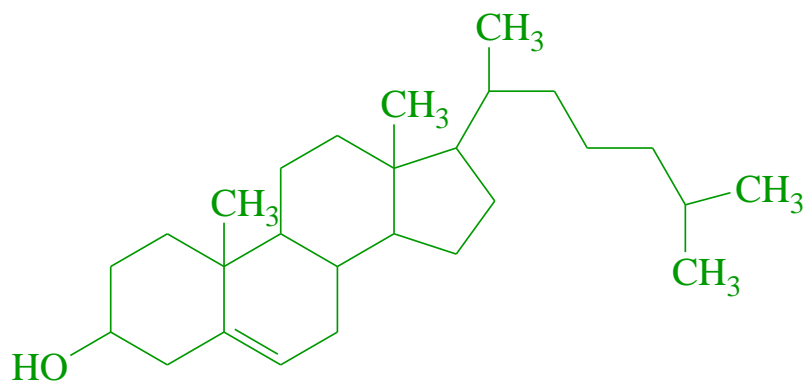


Steroids

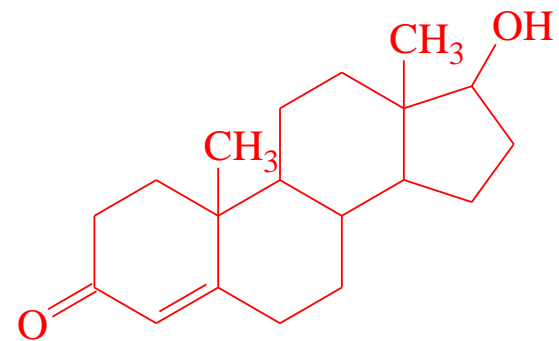
- characterized by 4 linked carbon rings
- mostly hydrocarbon-like
 - ✓ dissolve in animal fat
- mostly have hormonal effects
- serum cholesterol levels linked to heart disease and stroke
 - ✓ levels depend on diet, exercise, emotional stress, genetics, etc.
- cholesterol synthesized in the liver from saturated fats



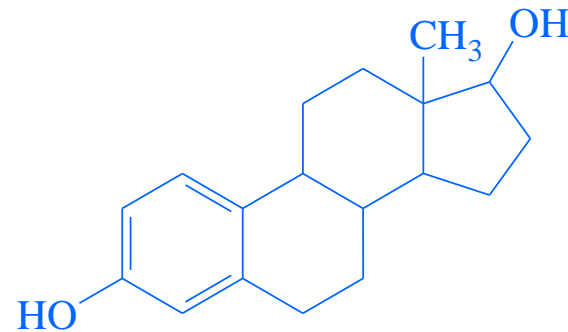
Steroids



cholesterol



testosterone



estrogen
 β -estradiol

Carbohydrates

- carbon, hydrogen, and oxygen
- ratio of H:O = 2:1
 - ✓ same as in water
- contain carbonyl groups and alcohol groups
- the many polar groups make simple carbohydrates soluble in water
 - ✓ blood transport
- also known as sugars, starches, cellulose, dextrans, and gums

Classification of Carbohydrates

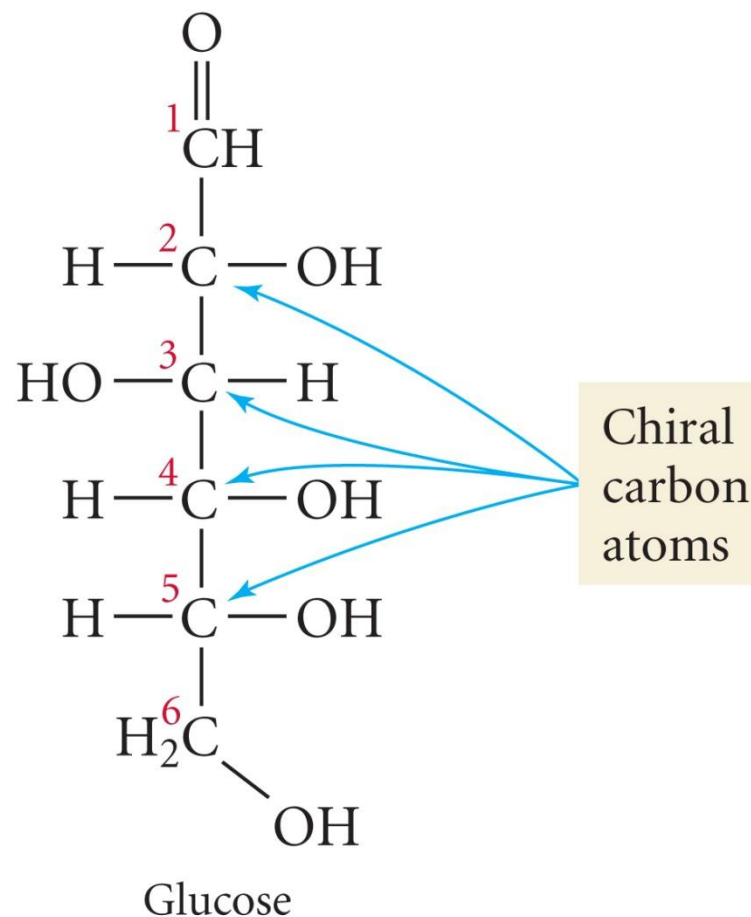
- hydroxycarbonyls - have many OH and one C=O
 - ✓ aldose when C=O is aldehyde, ketose when C=O is ketone
- names of mono and disaccharides all end in **ose**
- **monosaccharides** - cannot be broken down into simpler carbohydrates
 - ✓ triose, tetrose, pentose, hexose
- **disaccharides** - two monosaccharides linked
 - ✓ lose H from one and OH from other
- **polysaccharides** - 3 or more monosaccharides linked into complex chains
 - ✓ starch and cellulose polysaccharides of glucose

Saccharides

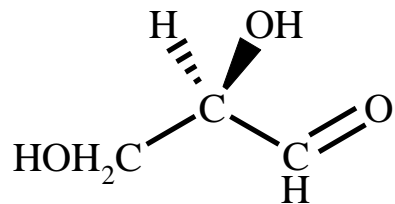
Carbohydrate	Formula	Source
Glucose (mono)	$C_6H_{12}O_6$	blood, plants, fruit, honey
Fructose (mono)	$C_6H_{12}O_6$	plants, fruit, honey
Galactose (mono)	$C_6H_{12}O_6$	
Sucrose (disac)	$C_{12}H_{22}O_{11}$	sugar cane & beets, maple syrup, fruits & veggies
Maltose (disac)	$C_{12}H_{22}O_{11}$	partial hydrolysis of starch
Lactose (disac)	$C_{12}H_{22}O_{11}$	milk (5%)
Starch (poly)		potatoes, corn, grains
Cellulose (poly)		cell wall of plants

Optical Activity

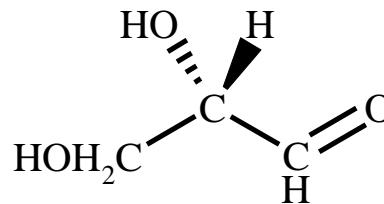
- there are always several chiral carbons in a carbohydrate – resulting in many possible optical isomers



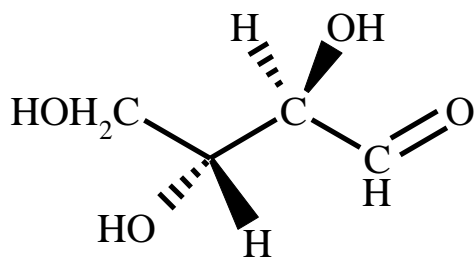
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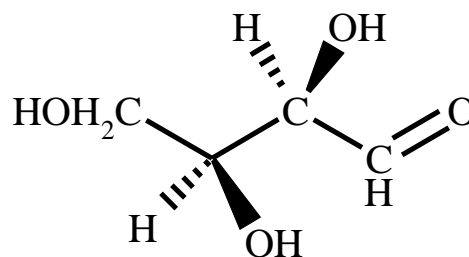
D-(*d*)-Glyceraldehyde



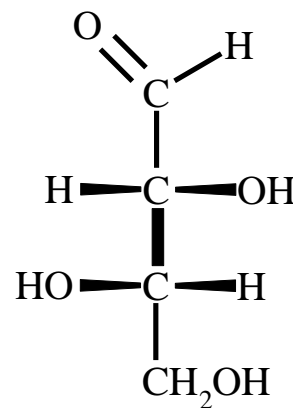
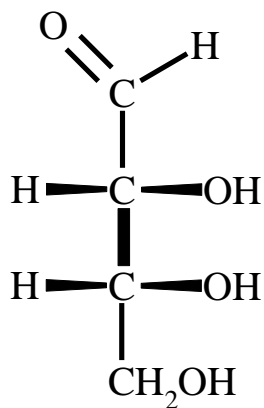
L-(*l*)-Glyceraldehyde



D-(*l*)-Erythrose

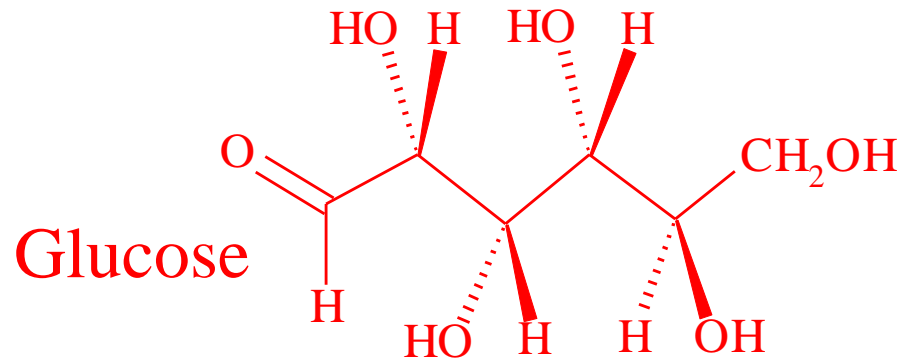
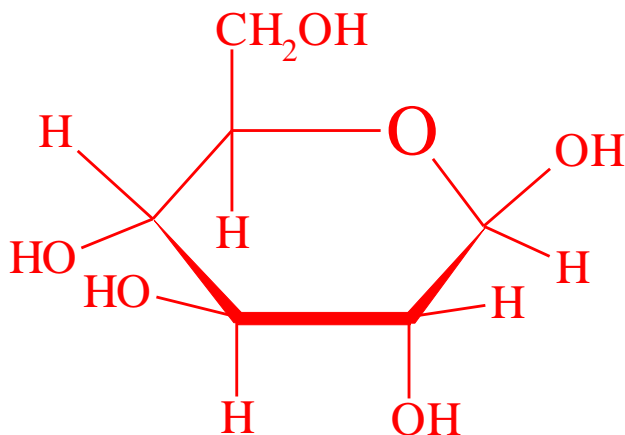
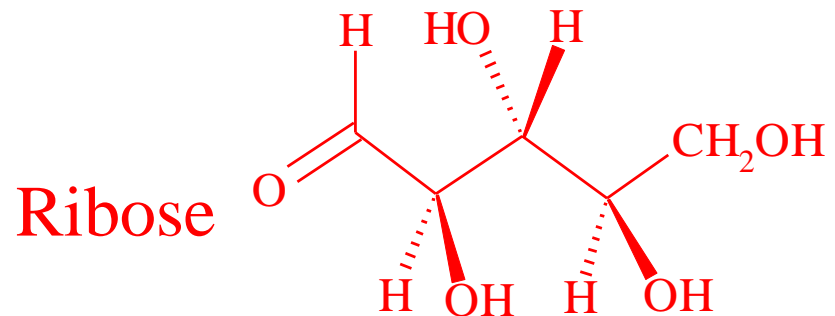
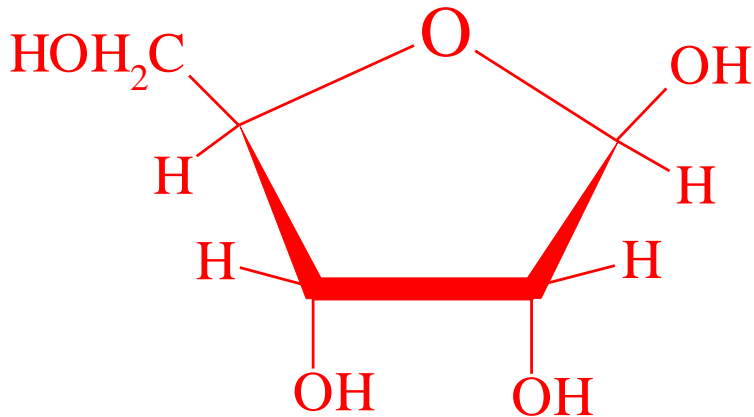


D-(*l*)-Threose



Ring Structure

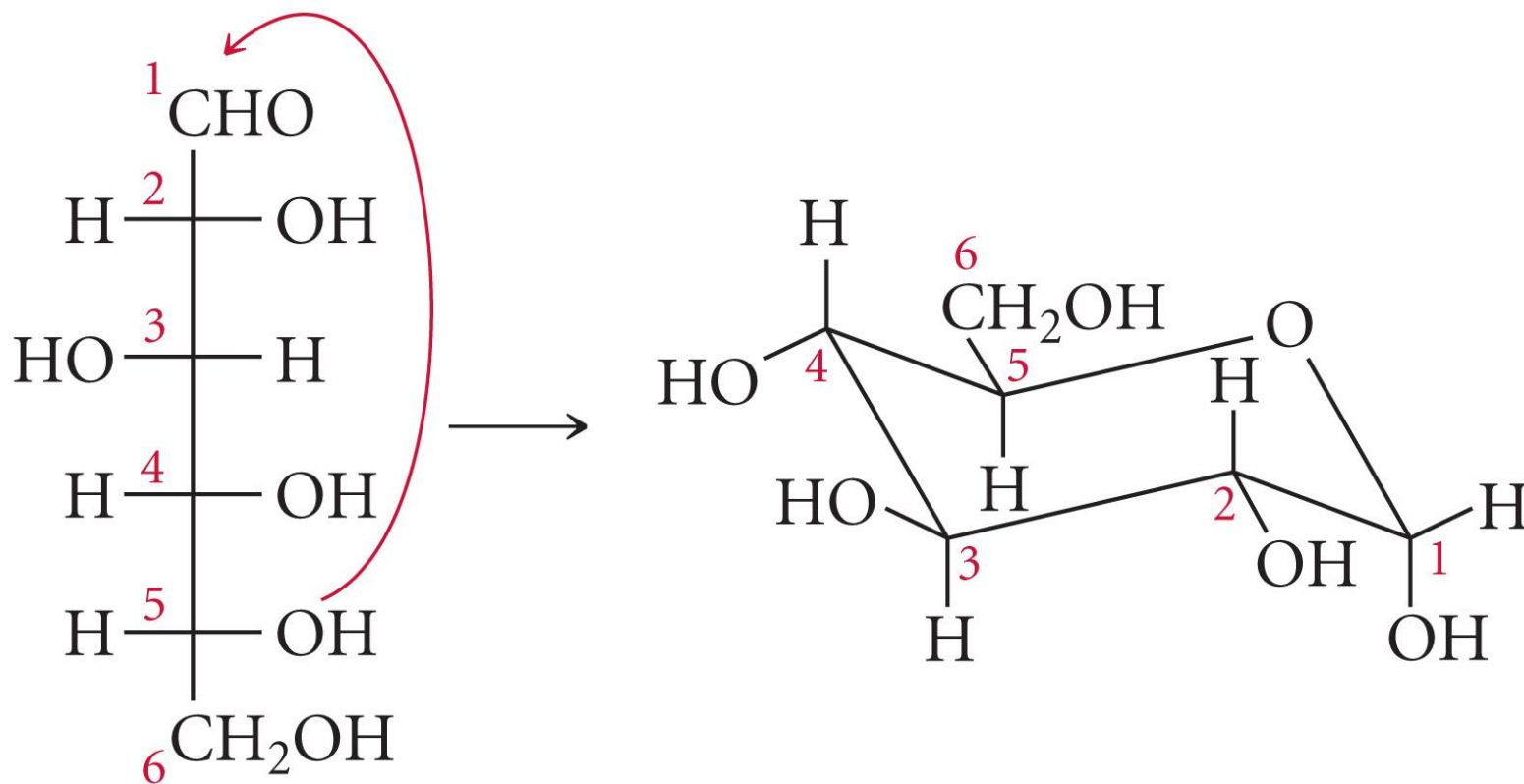
- in aqueous solution, monosaccharides exist mainly in the ring form
 - ✓ though there is a small amount of chain form in equilibrium



Cyclic Monosaccharides

- oxygen attached to second last carbon bonds to carbonyl carbon
 - ✓ acetal formation
- convert carbonyl to OH
 - ✓ transfer H from original O to carbonyl O
- new OH group may be same side as CH₂OH (β) or opposite side (α)
- Haworth Projection

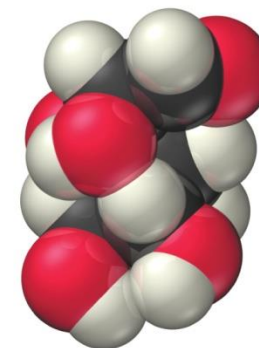
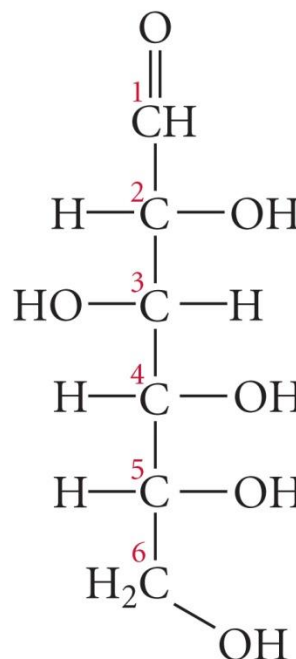
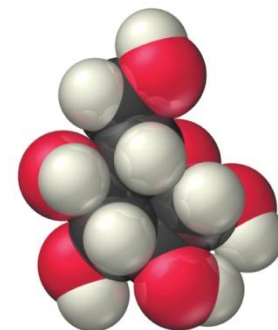
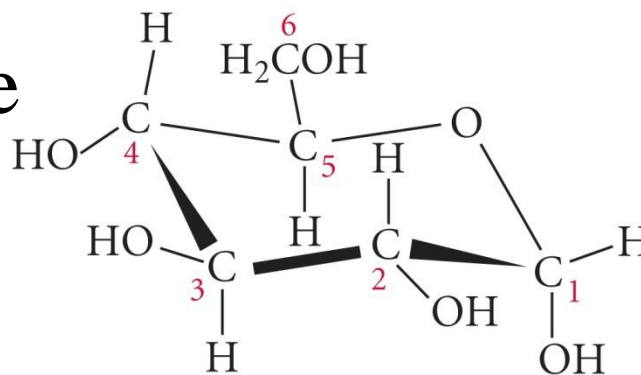
Formation of Ring Structure



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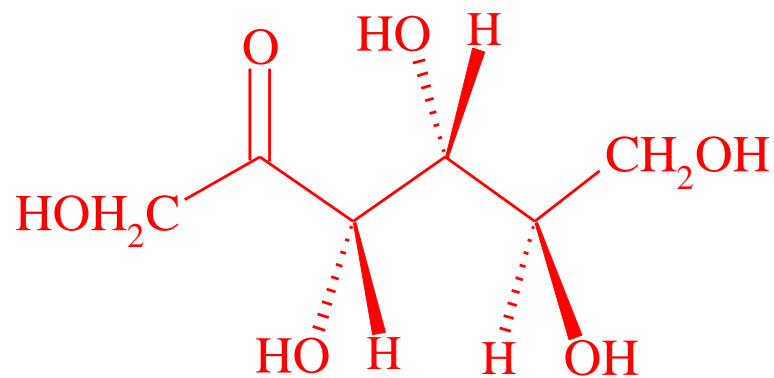
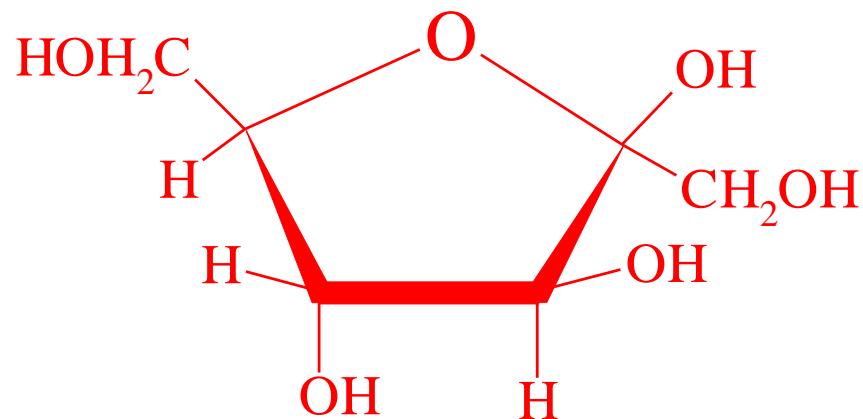
Glucose

- aka blood sugar, grape sugar, and **dextrose**
- aldohexose = sugar containing aldehyde group and 6 carbons
- source of energy for cells
 - ✓ 5 to 6 grams in blood stream
 - ✓ supply energy for about 15 minutes



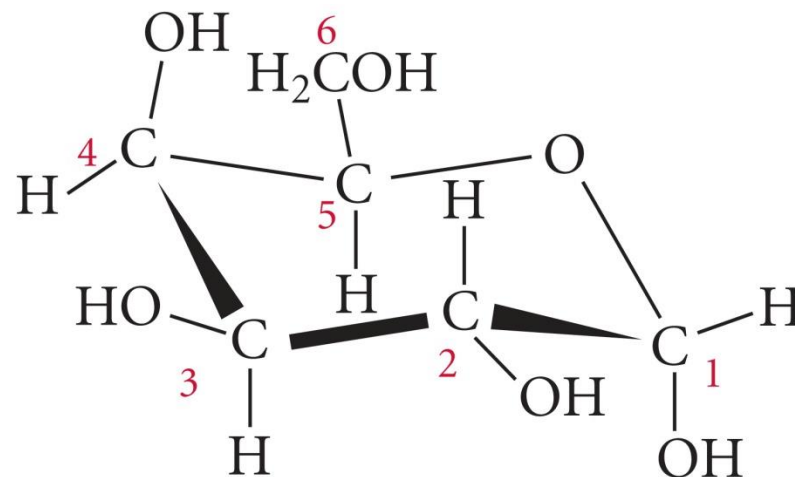
Fructose

- aka **levulose**, fruit sugar
- ketohexose = sugar containing ketone group and 6 carbons
- sweetest known natural sugar

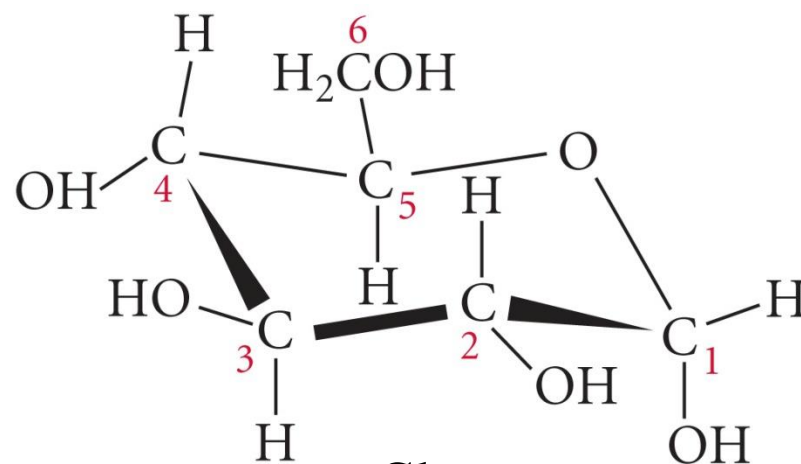


Galactose

- occurs in brain and nervous system
- only difference between glucose and galactose is spatial orientation of groups on C4



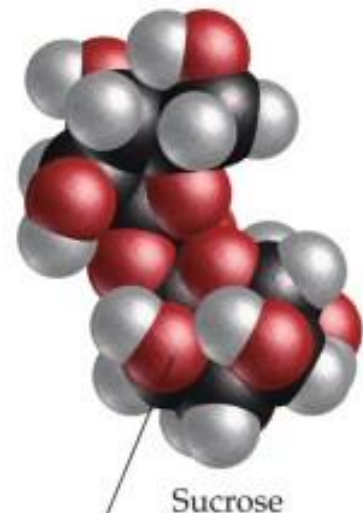
Galactose



Glucose

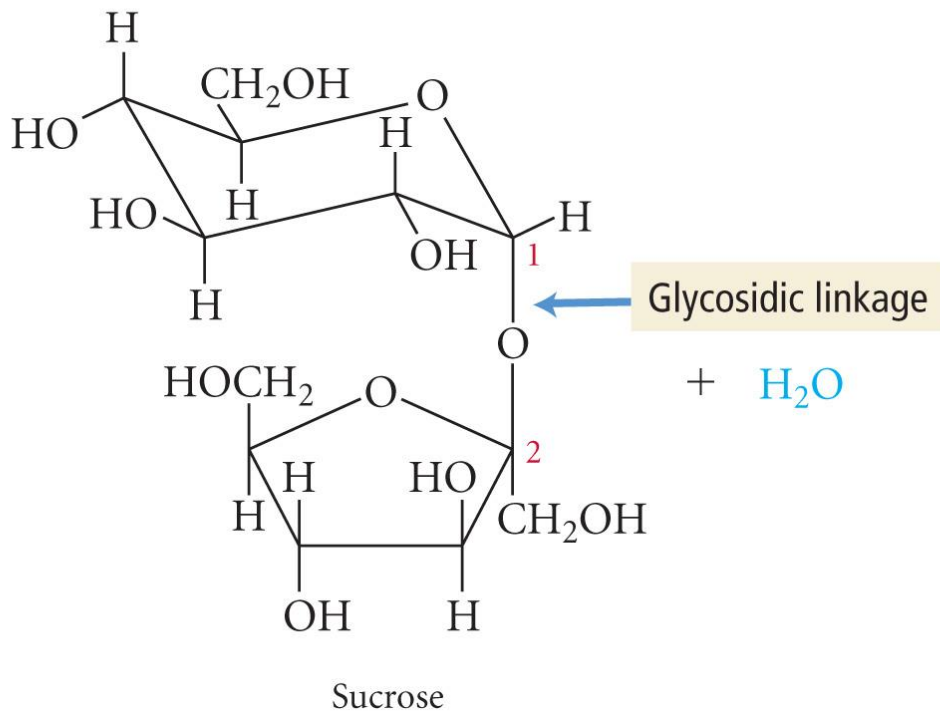
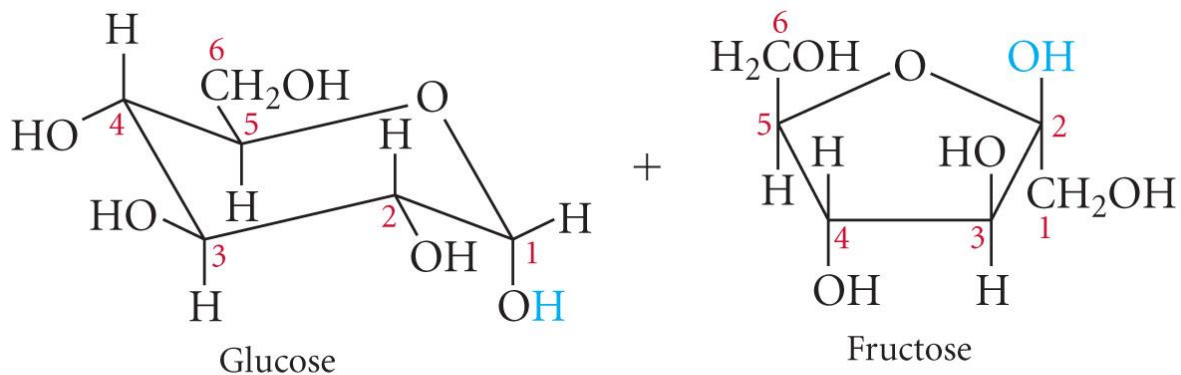
Sucrose

- also known as table sugar, cane sugar, beet sugar
- glucose + fructose = sucrose
- α - 1:2-linkage involves aldehyde group from glucose and ketone group from fructose
 - **glycosidic link**
- nonreducing



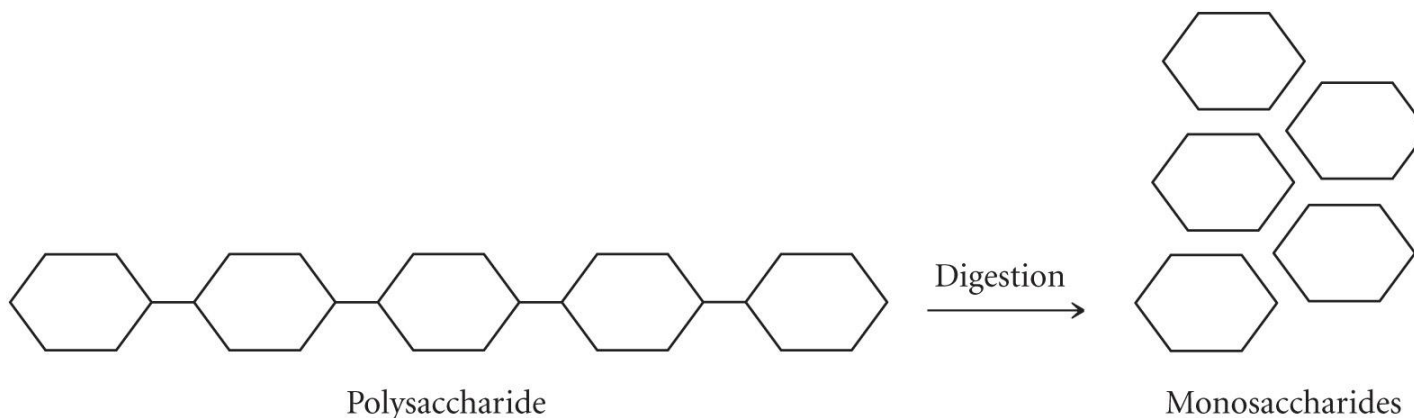
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Sucrose



Digestion and Hydrolysis

- digestion breaks polysaccharides and disaccharides into monosaccharides
- **hydrolysis** is the addition of water to break glycosidic link
 - ✓ under acidic or basic conditions
- monosaccharides can pass through intestinal wall into the blood stream



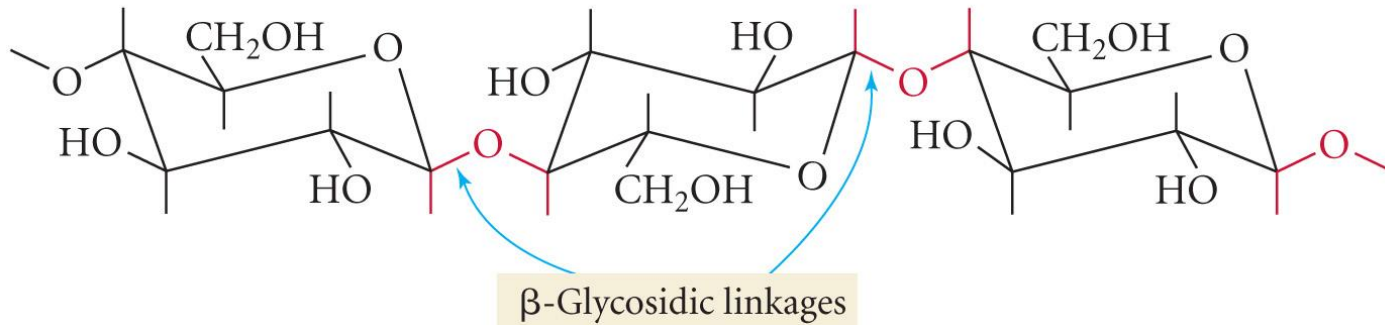
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Polysaccharides

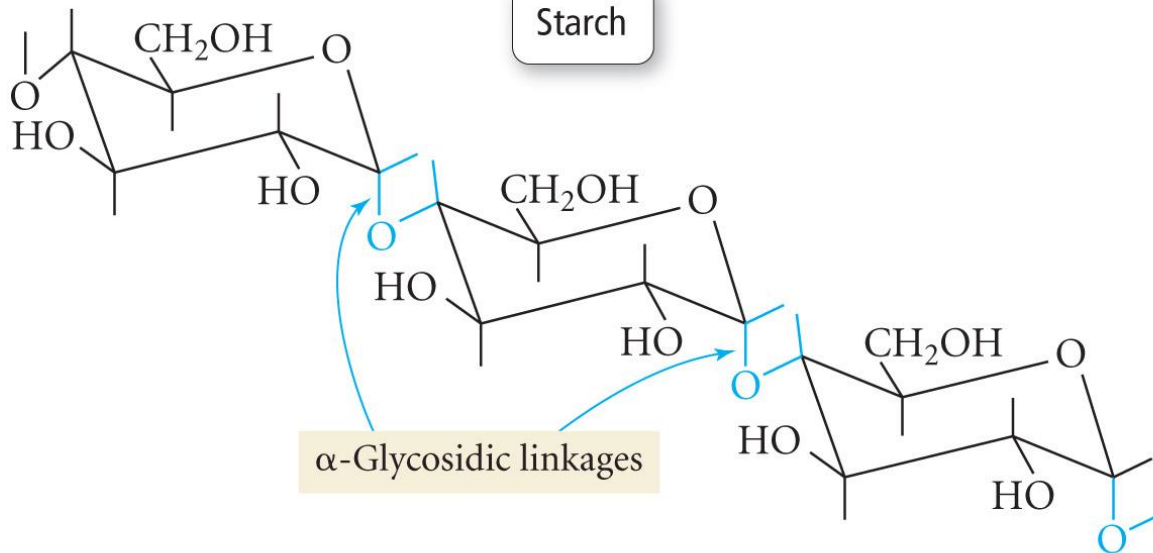
- aka **complex carbohydrates**
- polymer of monosaccharide units bonded together in a chain
- the glycosidic link between units may be either α or β
 - ✓ in α , the rings are all oriented the same direction
 - ✓ in β , the rings alternate orientation

α and β Glycosidic Links

Cellulose



Starch



Starch, Cellulose, and Glycogen

- made of glucose rings linked together
 - ✓ give only glucose on hydrolysis
- starch
 - ✓ main energy storage medium
 - ✓ digestible, soft, and chewy
 - ✓ 1,4 - α link
 - ✓ amylose and amylopectin
 - amylopectin chains branch
- cellulose
 - ✓ not digestible
 - ✓ fibrous, plant structural material
 - ✓ 1,4 - β link
 - ✓ allows neighboring chains to H-bond
 - resulting in rigid structure
- glycogen
 - ✓ structure similar to amylopectin, except highly branched
 - ✓ used for excess glucose storage in animal muscles

Proteins

- involved in practically all facets of cell function
- polymers of amino acids

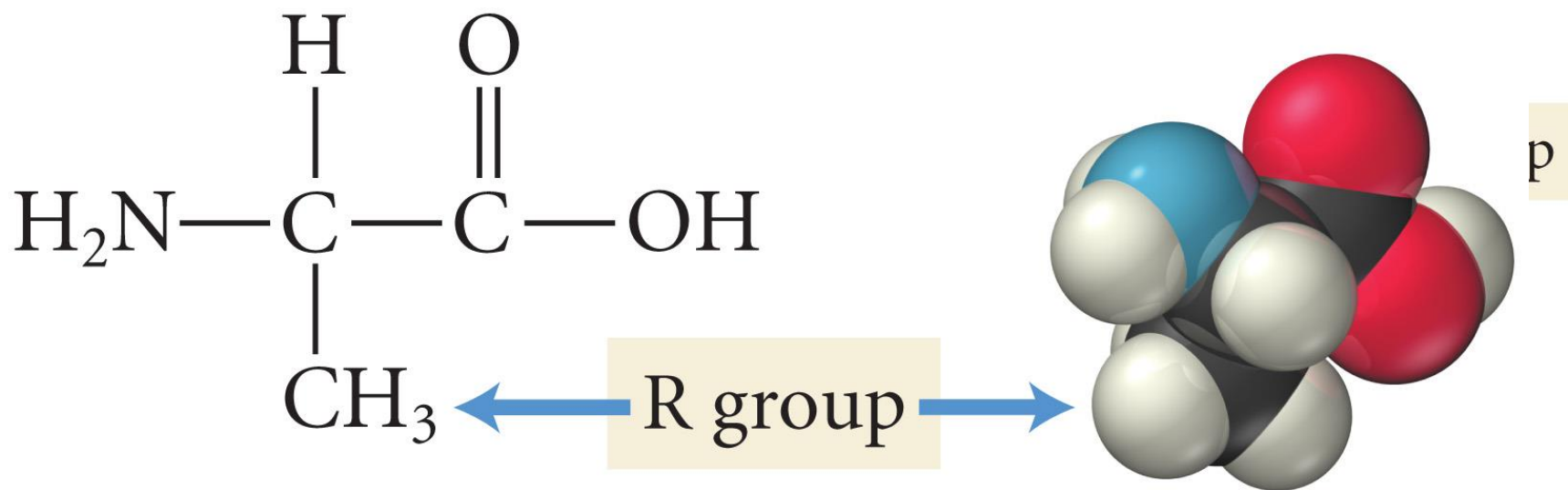
TABLE 21.2 Protein Functions

Class of Protein	Primary Function	Example
Structural proteins	Compose structures within living organisms	Collagen (skin, tendon, cartilage), keratin (hair, fingernails)
Enzymes	Catalyze and control biochemical reactions	DNA polymerase (involved in replication of DNA)
Hormones	Regulate metabolic processes	Insulin (regulates glucose metabolism)
Transport proteins	Transport substances from one place to another	Hemoglobin (transports oxygen)
Storage proteins	Provide source of essential nutrients	Casein (protein in mammalian milk)
Contractile and motile proteins	Mediate motion and muscle contraction	Actin and myosin (provide muscle contraction)
Protective proteins	Protect and defend cells	Antibodies (neutralize infectious agents)

Amino Acids

- NH_2 group on carbon adjacent to COOH
 - ✓ α -amino acids
- about 20 amino acids found in proteins
 - ✓ 10 synthesized by humans, 10 “essential”
- each amino acid has 3 letter abbreviation
 - ✓ glycine = Gly
- high melting points
 - ✓ generally decompose at temp $> 200^\circ\text{C}$
- good solubility in water
- less acidic than most carboxylic acids and less basic than most amines

Basic Structure of Amino Acids



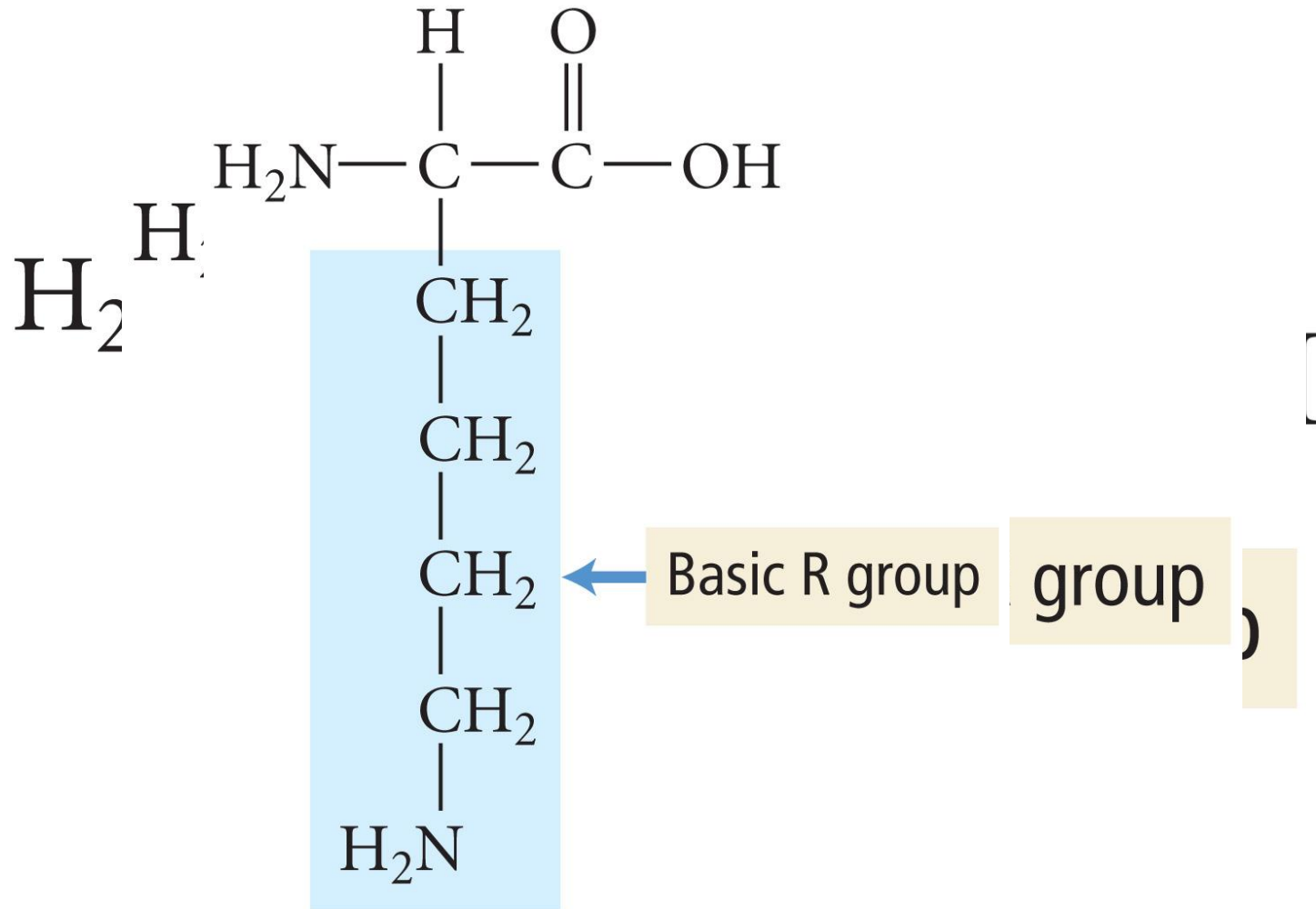
Alanine

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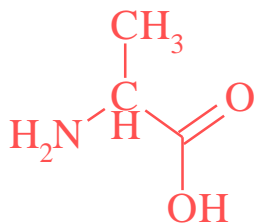
Amino Acids

- building blocks of proteins
- main difference between amino acids is the side chain
 - ✓ **R group**
- some R groups are polar, others are nonpolar
- some polar R groups are acidic, others are basic
- some R groups contain O, others N, and others S
- some R groups are rings, other are chains

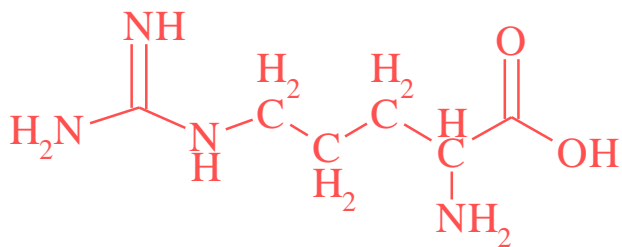
Some Amino Acids



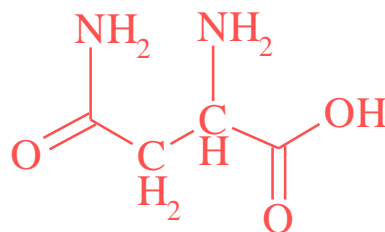
Lysine



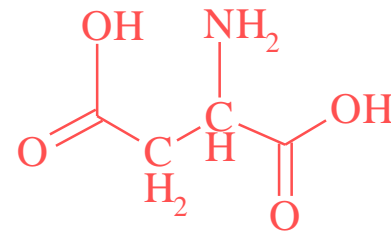
Alanine
Ala



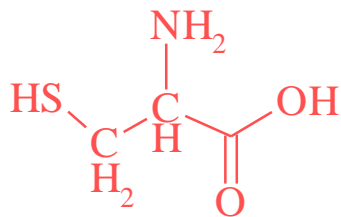
Arginine
Arg



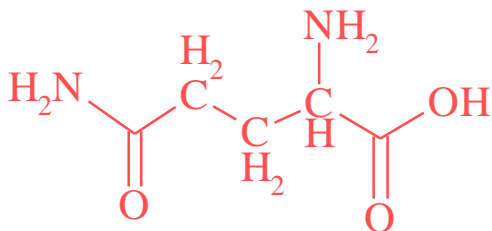
Asparagine
Asn



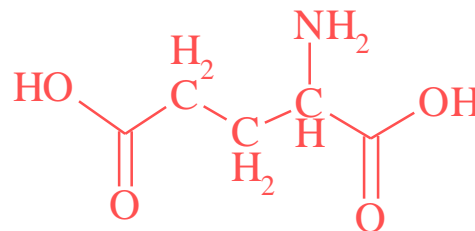
Aspartic Acid
Asp



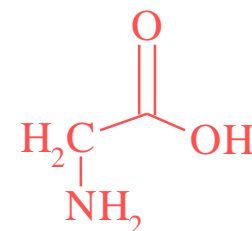
Cysteine
Cys



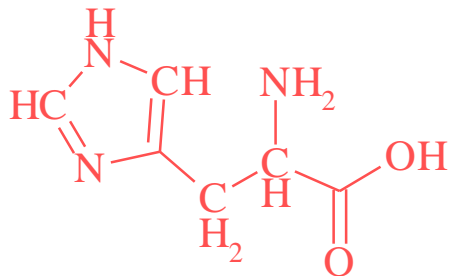
Glutamine
Gln



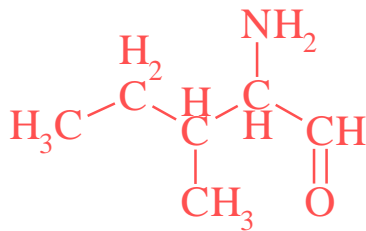
Glutamic Acid
Glu



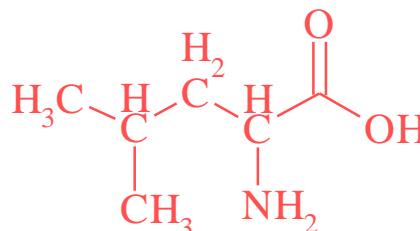
Glycine
Gly



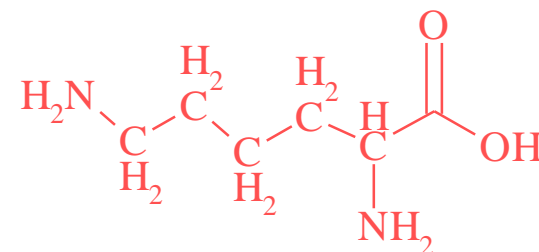
Histidine
His



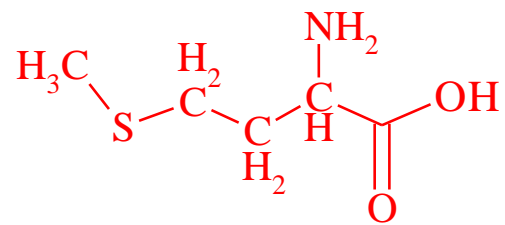
Isoleucine
Ile



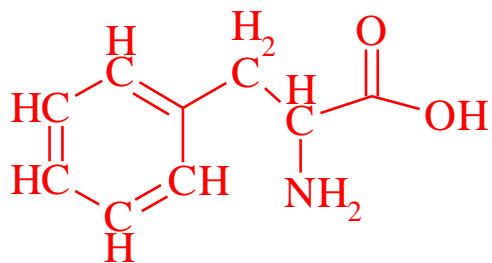
Leucine
Leu



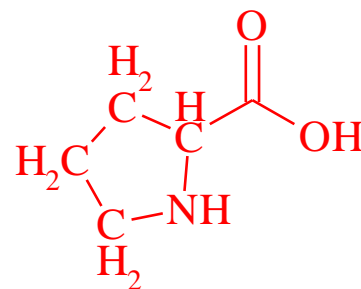
Lysine
Lys



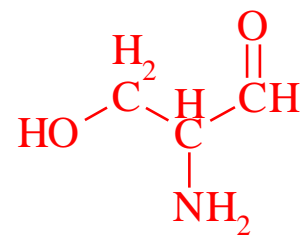
Methionine
Met



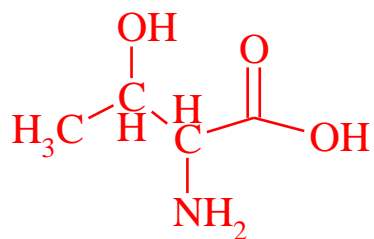
Phenylalanine
Phe



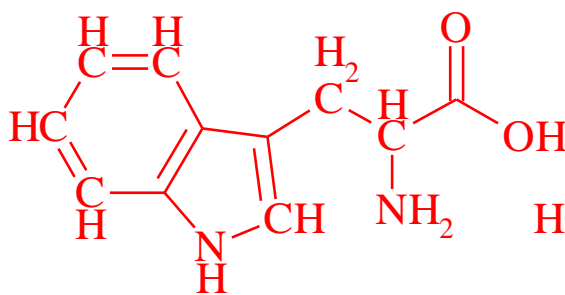
Proline
Pro



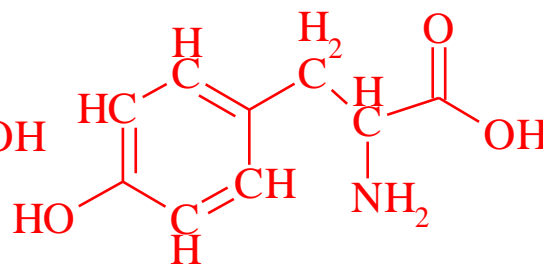
Serine
Ser



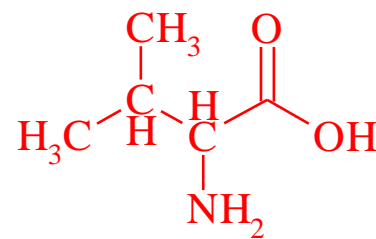
Threonine
Thr



Tryptophan
Trp



Tyrosine
Tyr



Valine
Val

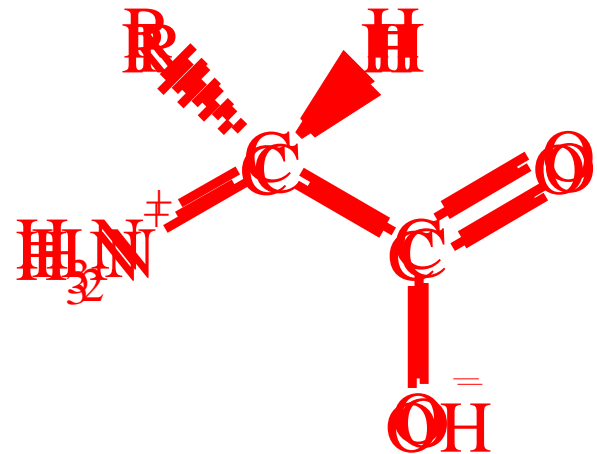
Optical Activity

- the α carbon is chiral on the amino acids
 - ✓ except for glycine
- most naturally occurring amino acids have the same orientation of the groups as occurs in L-(*l*)-glyceraldehyde
- therefore they are called the L-amino acids
 - ✓ not *l* for levorotatory

Ionic Amino Acids

- the form of the amino acid depends on the pH

at a high pH, both the α -carboxyl and the β -amino groups are deprotonated, resulting in a net negative charge. At a low pH, both the α -carboxyl and the β -amino groups are protonated, resulting in a net positive charge. At the isoelectric point, the amino acid exists in its zwitterion form.



Protein Structure

- the structure of a protein is key to its function
- most proteins are classified as either fibrous or globular
- fibrous proteins have linear, simple structure
 - ✓ insoluble in water
 - ✓ used in structural features of the cell
- globular proteins have complex, 3-dimensional structure
 - ✓ generally have polar R groups of the amino acids pointing out – so they are somewhat soluble, but also maintain an area that is nonpolar in the interior

Fibrous and Globular Proteins

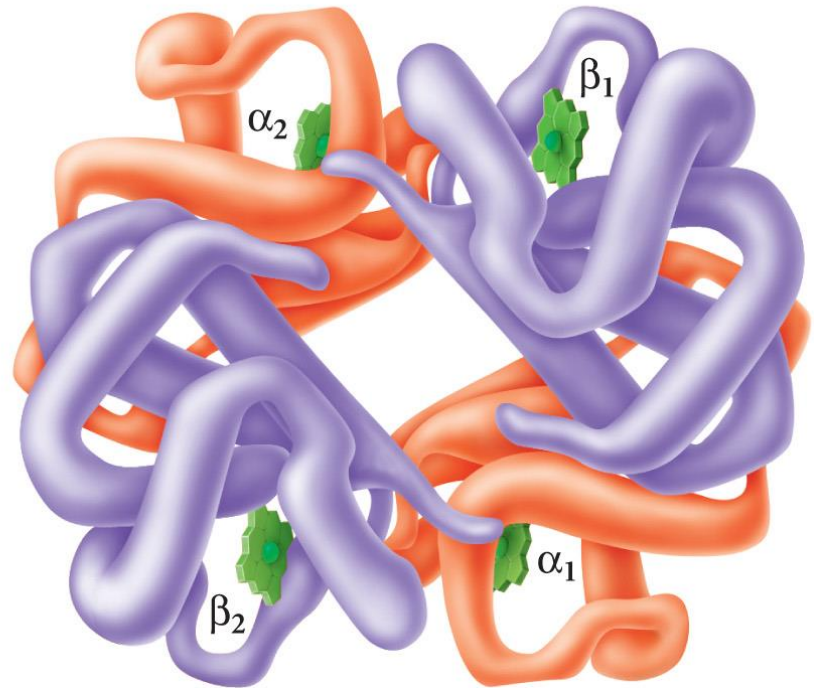
Fibrous protein

- Glycine
 - ◇ X
 - Y
- } Other amino acids, often proline or hydroxyproline



Collagen

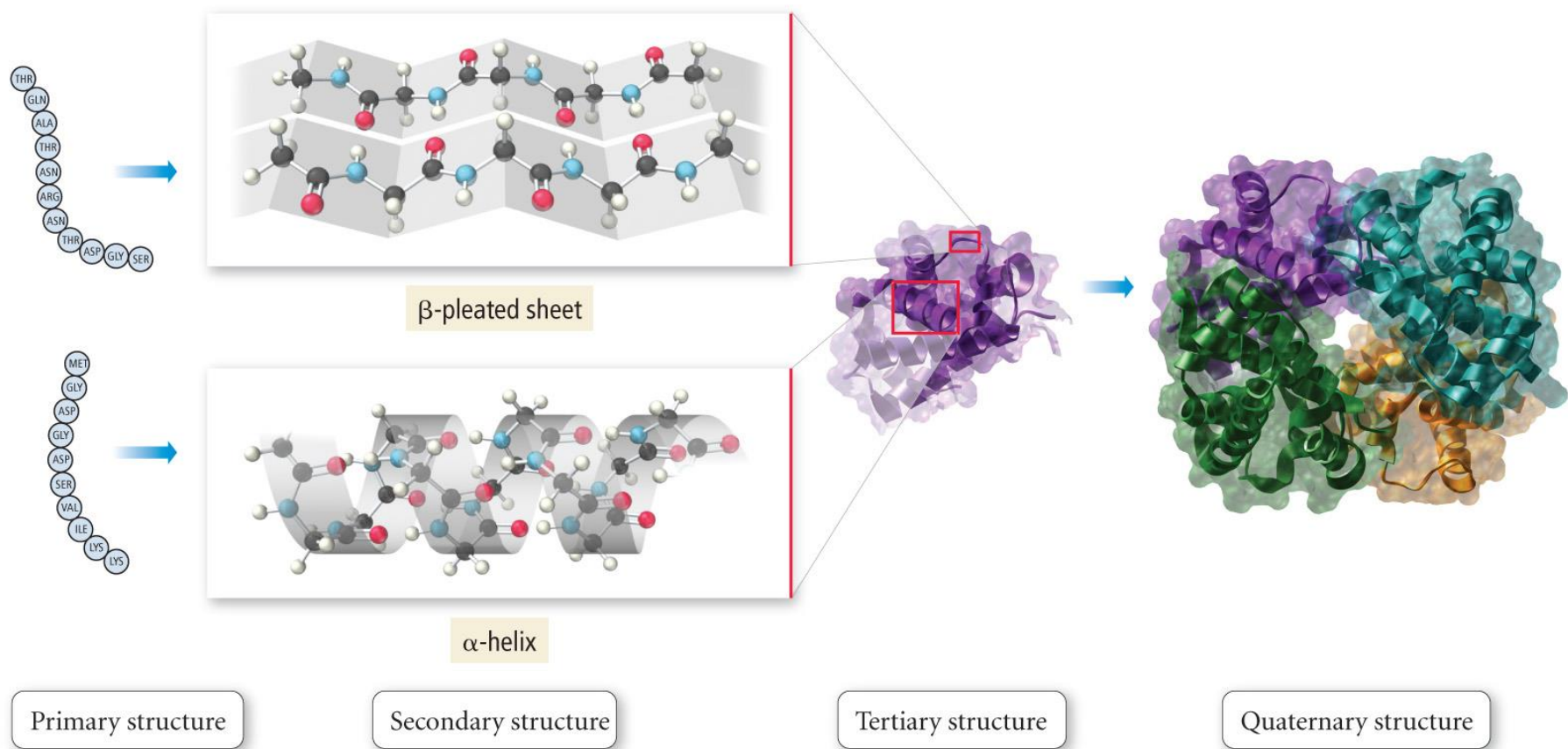
Globular protein



Hemoglobin

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Levels of Protein Structure

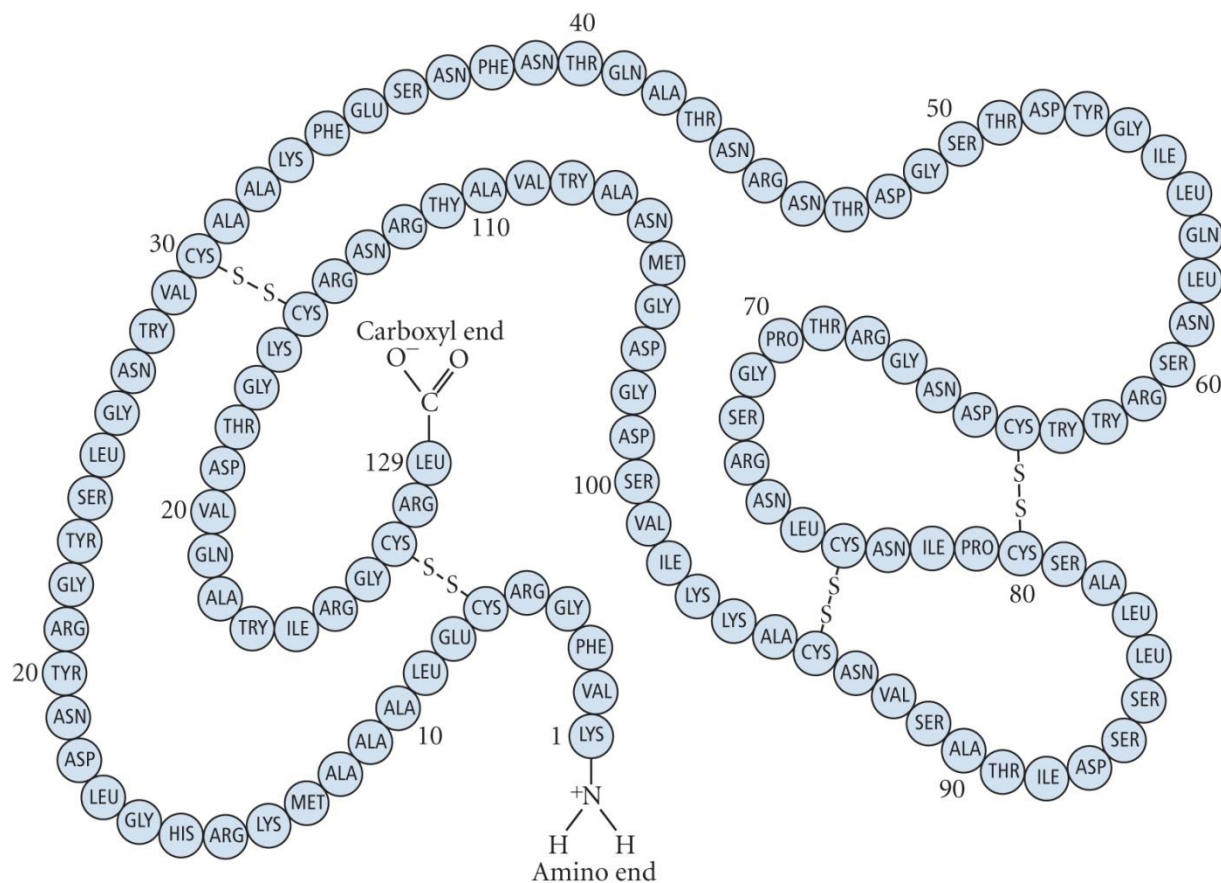


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Primary Protein Structure

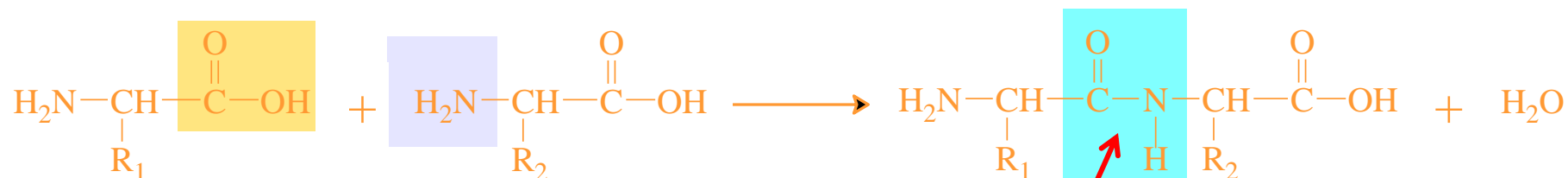
- the primary structure is determined by the order of amino acids in the polypeptide
- link COOH group of first to NH₂ of second
 - ✓ loss of water, condensation
 - ✓ form an **amide** structure
 - ✓ peptide bond
- linked amino acids are called **peptides**
 - ✓ dipeptide = 2 amino acids, tripeptide = 3, etc.
 - ✓ oligopeptides are short peptide chains
 - ✓ polypeptides = many linked amino acids in a long chain

Egg-White Lysozyme Primary Structure

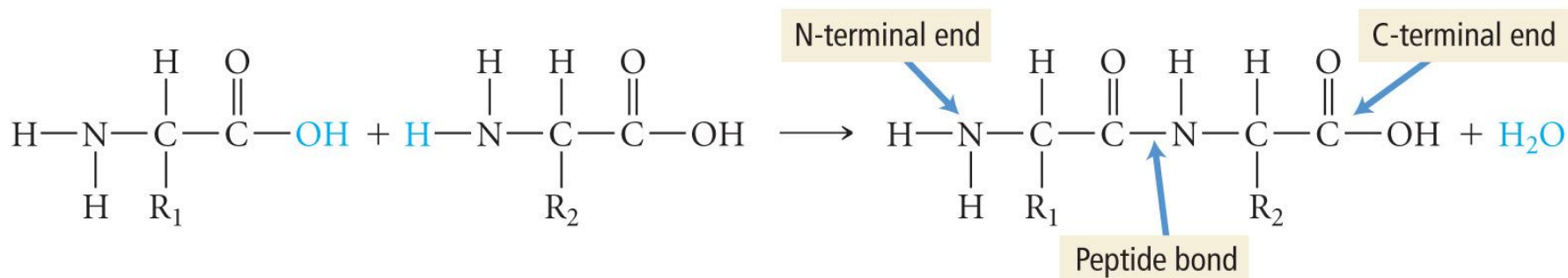


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Peptide Bond Formation: a Condensation Reaction



peptide bond

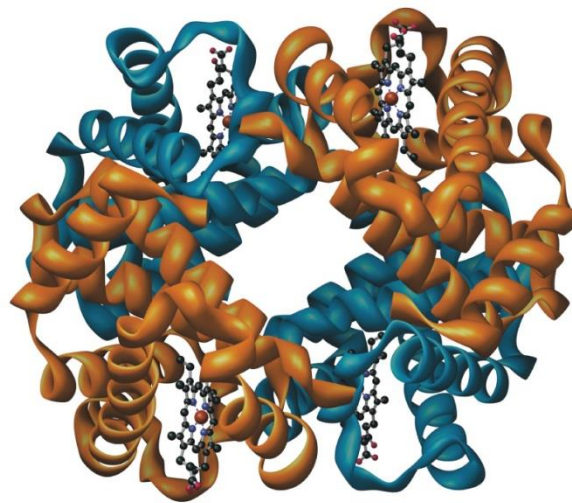


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Primary Structure

Sickle-Cell Anemia

- changing one amino acid in the protein can vastly alter the biochemical behavior
- sickle-cell anemia
 - ✓ replace one Val amino acid with Glu on two of the four chains
 - ✓ red blood cells take on sickle shape that can damage organs



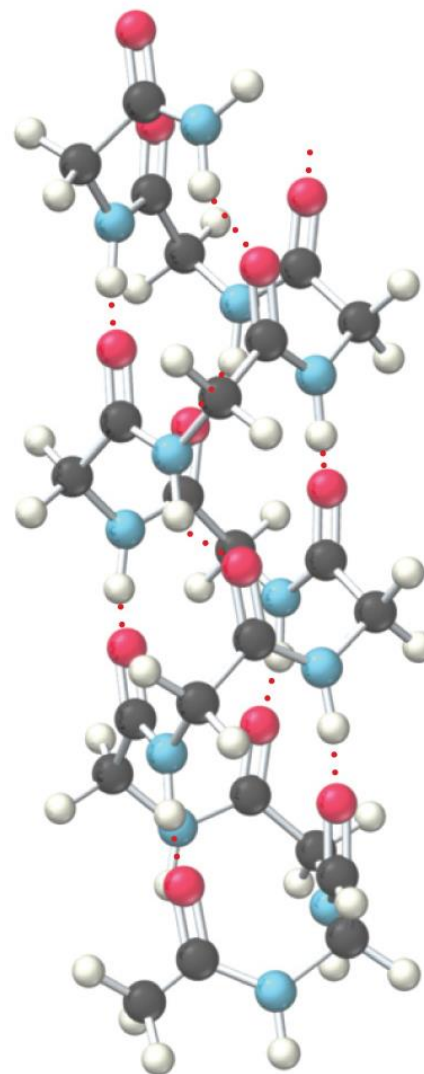
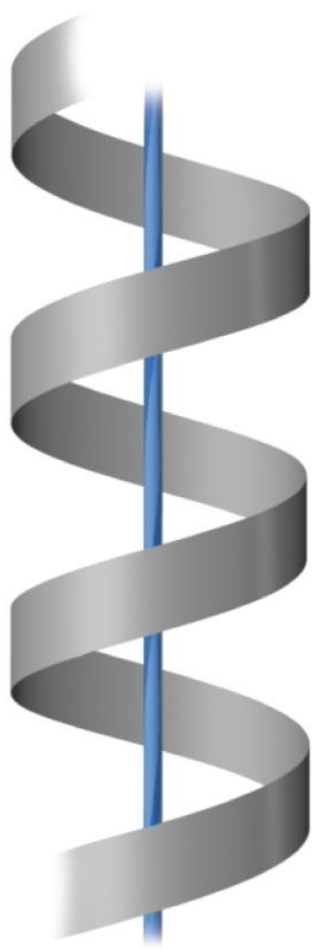
Secondary Structure

- short range repeating patterns found in protein chains
- maintained by interactions between amino acids that are near each other in the chain
- formed and held by H-bonds between NH and C=O
- α -helix
 - ✓ most common
- β -pleated sheet
- many proteins have sections that are α -helix, other sections are β -sheets and others are **random coils**

α -Helix

- amino acid chain wrapped in a tight coil with the R groups pointing outward from the coil
- the **pitch** is the distance between the coils
- the pitch and helix diameter ensure bond angles are not strained and H-bonds are as strong as possible

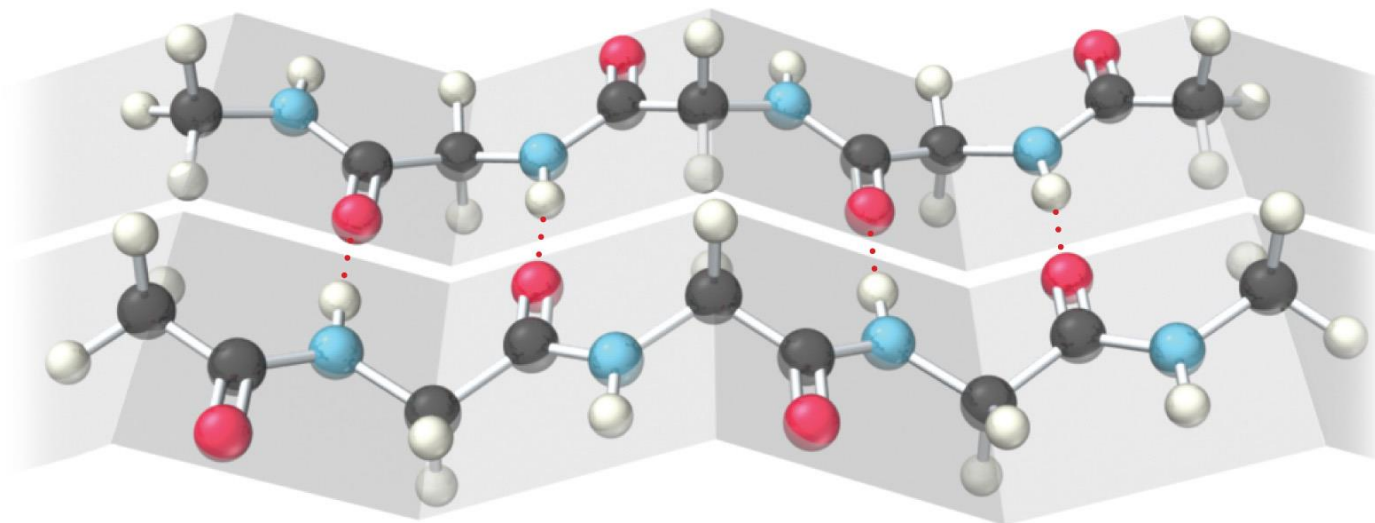
α -Helix



β -Pleated Sheet

- extended chain forms a zig-zag pattern
- chains linked together by H-bonds
- silk

β -Pleated sheet protein structure

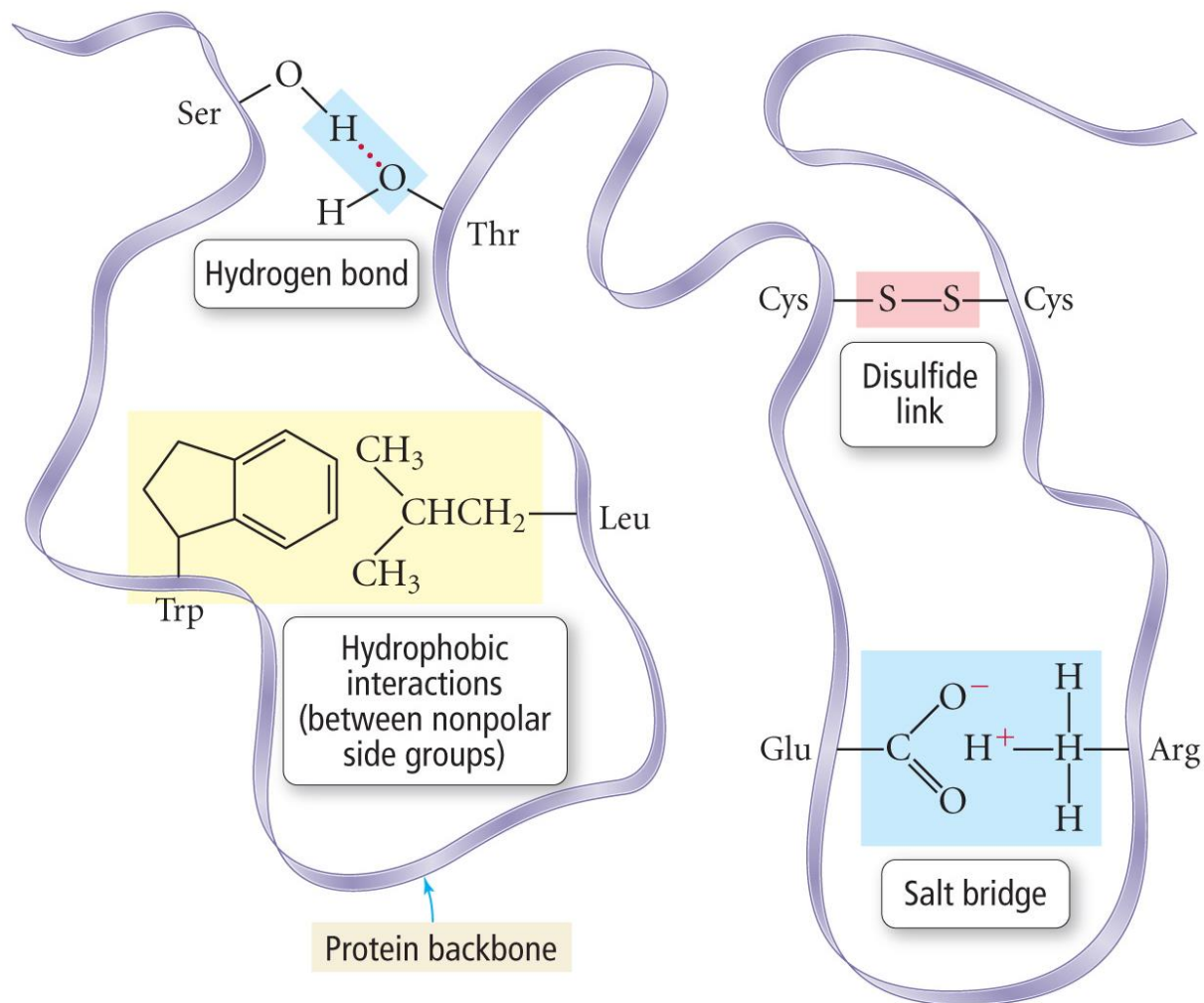


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Tertiary Structure

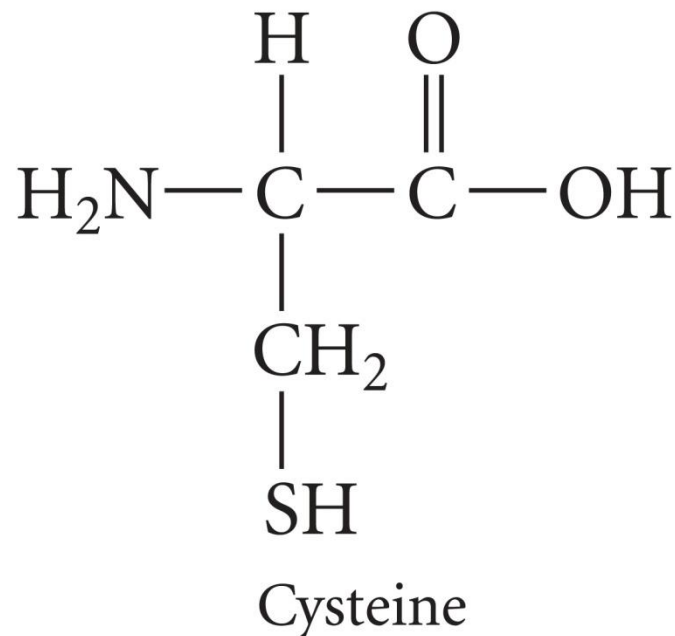
- large-scale bends and folds due to interactions between R groups separated by large distances on the chains
- types of interactions include:
 - ✓ H-bonds
 - ✓ disulfide linkages
 - between cysteine amino acids
 - ✓ hydrophobic interactions
 - between large, nonpolar R groups
 - ✓ salt bridges
 - between acidic and basic R groups

Interactions that Create Tertiary Structure



Cysteine

- the amino acid cysteine performs a unique function in protein structure
- cysteine units on remote parts of the peptide chain can react together, forming a **disulfide bond**
- the disulfide bond ties parts of the chain together, contributing to the tertiary structure



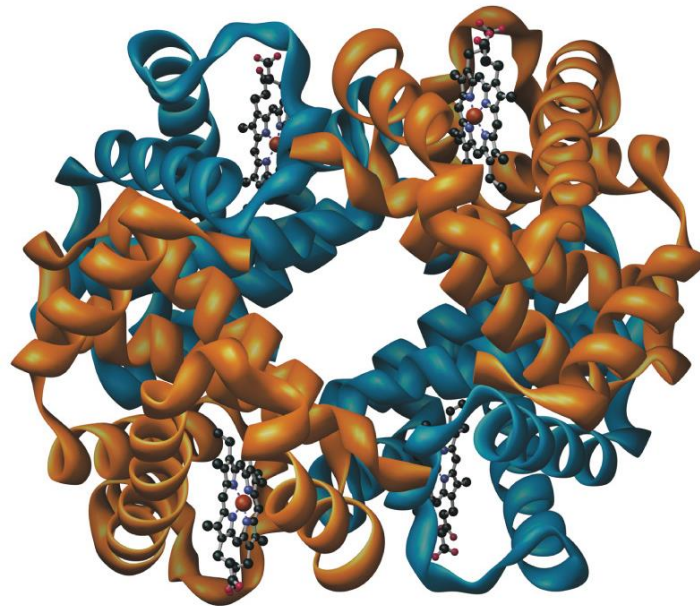
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Tertiary Structure and Protein Type

- fibrous proteins generally lack tertiary structure
 - ✓ extend as long, straight chains with some secondary structure
- globular proteins fold in on themselves, forming complex shapes due to the tertiary interactions

Quaternary Structure

- many proteins are composed of multiple amino acid chains
- the way the chains are linked together is called **quaternary structure**
- interactions between chains the same as in tertiary structure

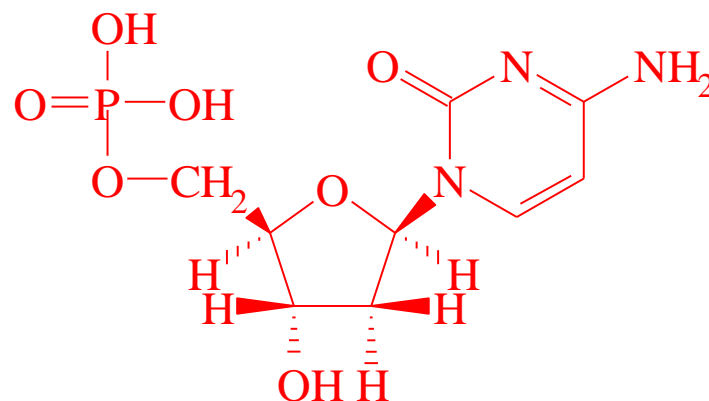
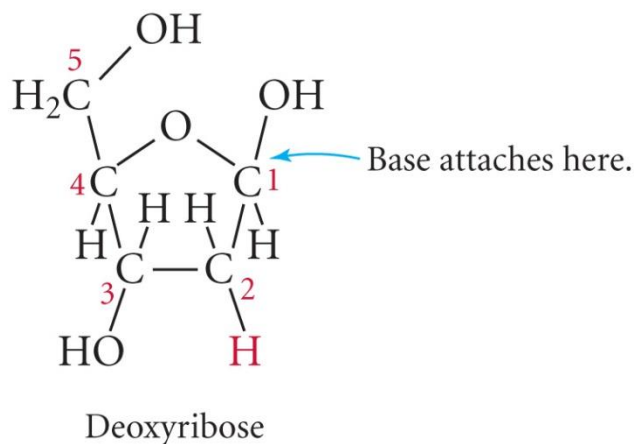


Nucleic Acids

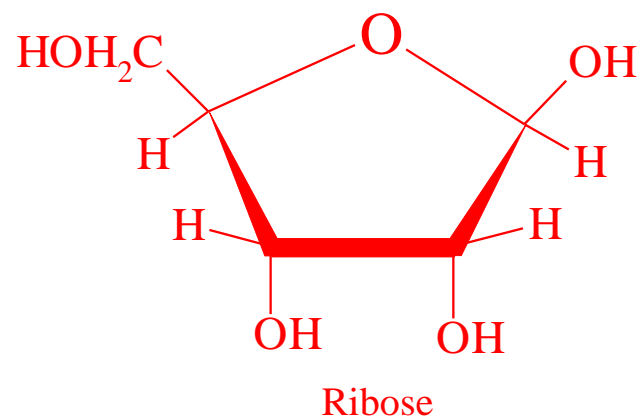
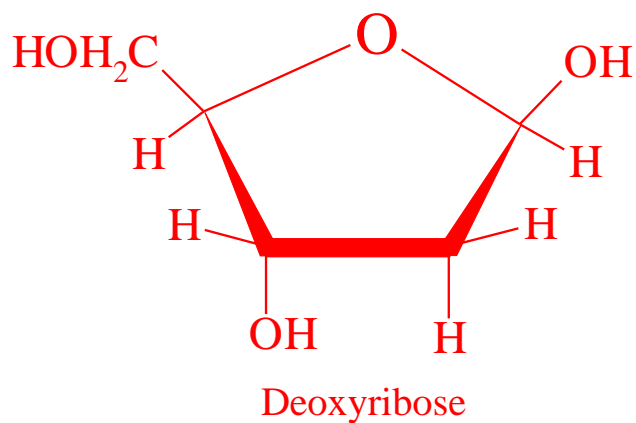
- carry genetic information
- DNA molar mass = 6 to 16 million amu
- RNA molar mass = 20K to 40K amu
- made of nucleotides
 - ✓ phosphoric acid unit
 - ✓ 5 carbon sugar
 - ✓ cyclic amine (base)
- nucleotide joined by **phosphate linkages**

Nucleotide Structure

- each nucleotide has 3 parts – a cyclic pentose, a phosphate group, and an organic aromatic base
- the pentoses are ribose or deoxyribose
- the pentoses are the central backbone of the nucleotide
- the pentose is attached to the organic base at C1 and to the phosphate group at C5

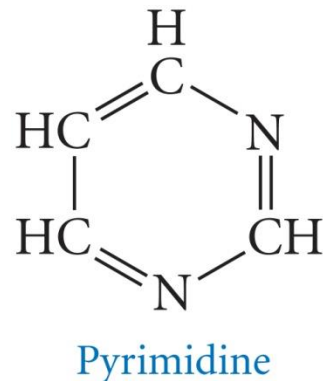
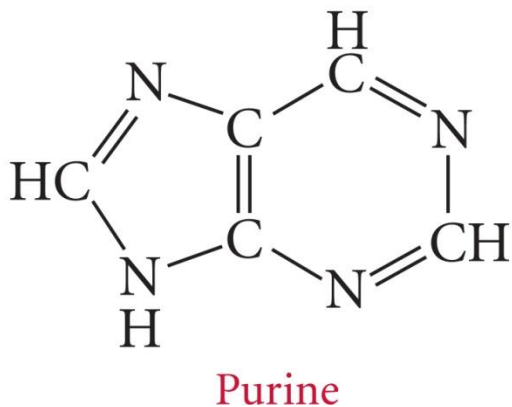


Sugars

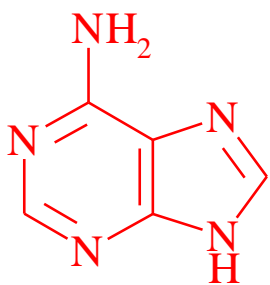


Bases

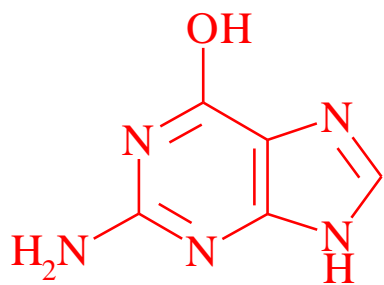
- the bases are organic amines that are aromatic
 - ✓ like benzene, except containing N in the ring
 - ✓ means the rings are flat rather than puckered like the sugar rings
- two general structures: two of the bases are similar in structure to the organic base **purine**; the other two bases are similar in structure to the organic base **pyrimidine**



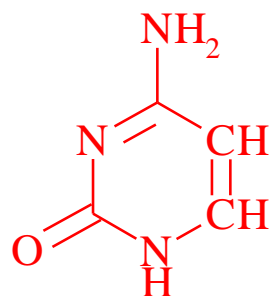
Organic Bases



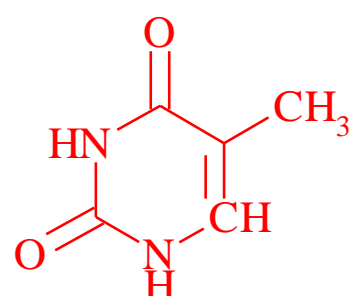
Adenine



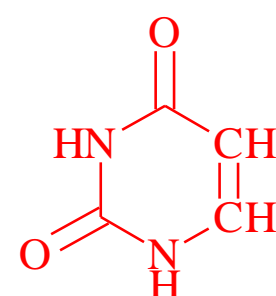
Guanine



Cytosine



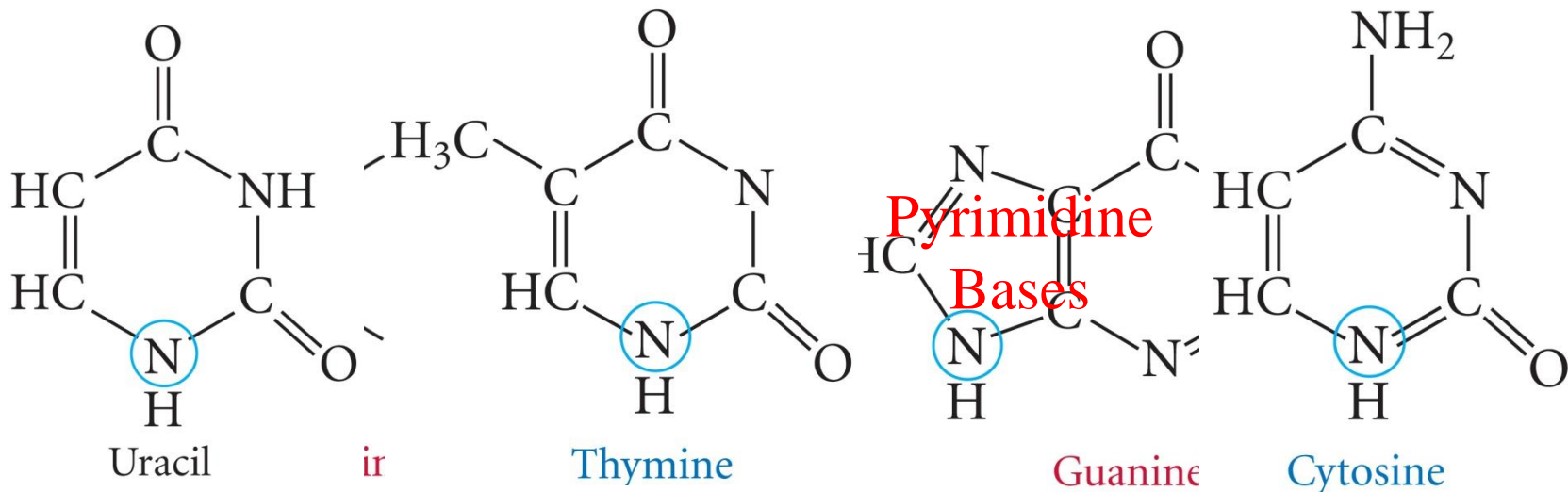
Thymine



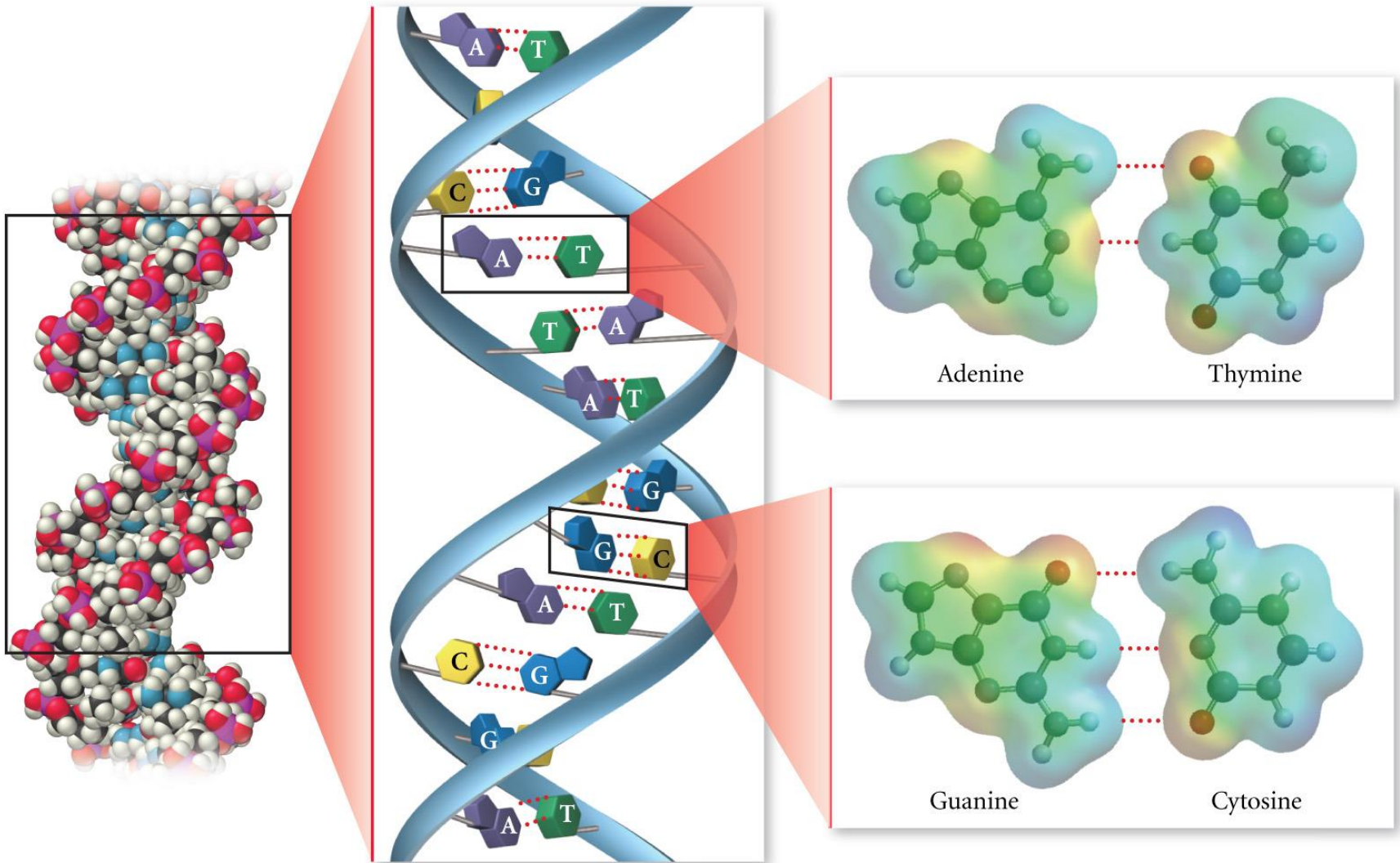
Uracil

Bases

- the structures of the base are **complementary**, meaning that a purine and pyrimidine will precisely align to H-bond with each other
 - ✓ adenine matches thymine or uracil
 - ✓ guanine matches cytosine
- attach to sugar at C1 of the sugar through circled N

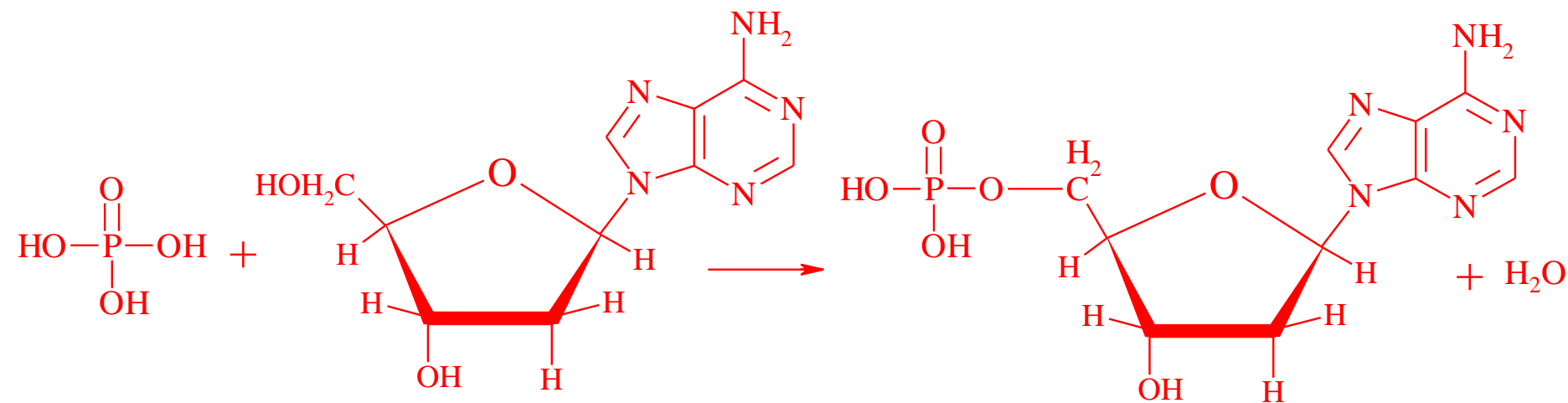
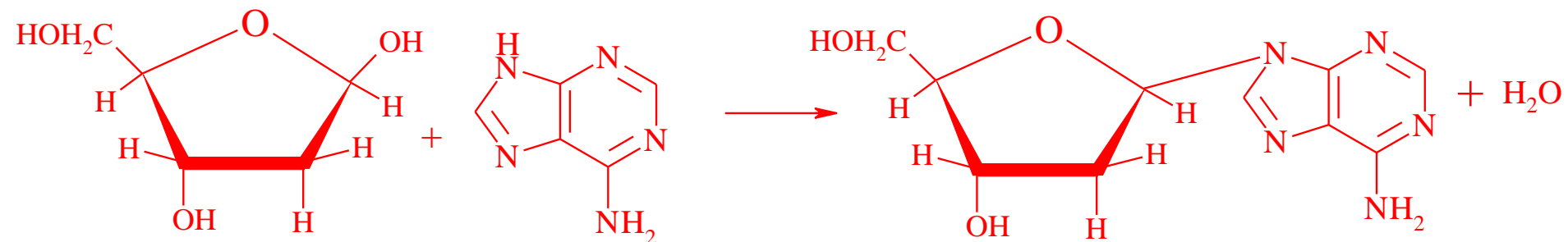


Base-pairing in DNA



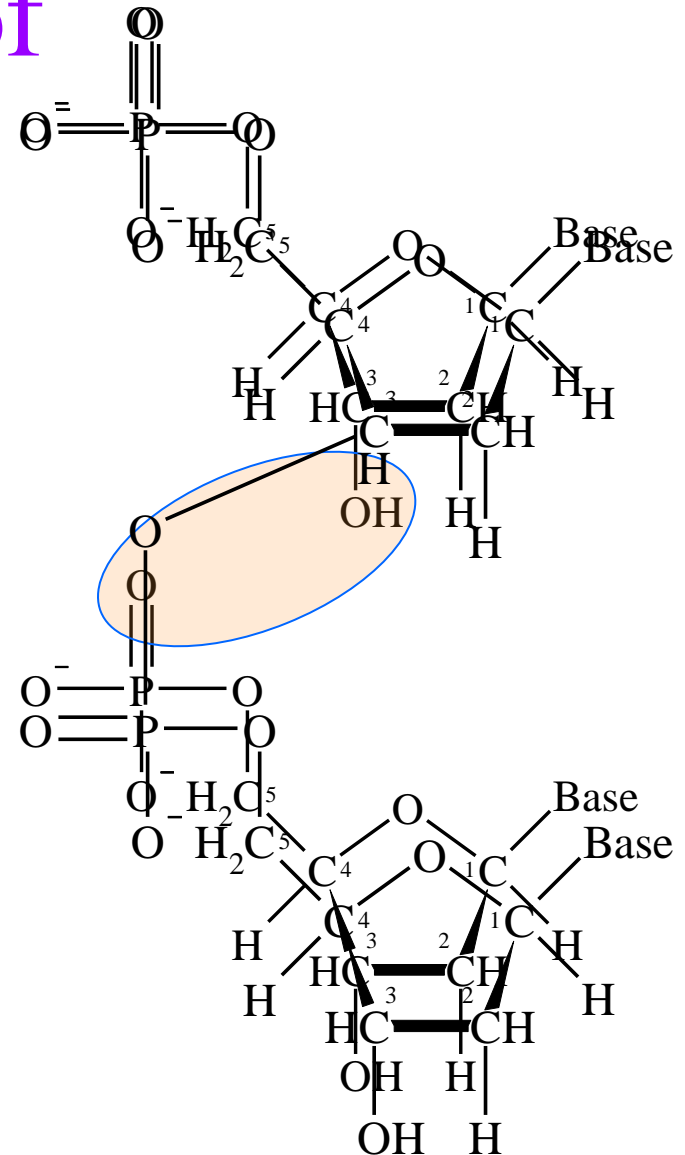
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Nucleotide Formation

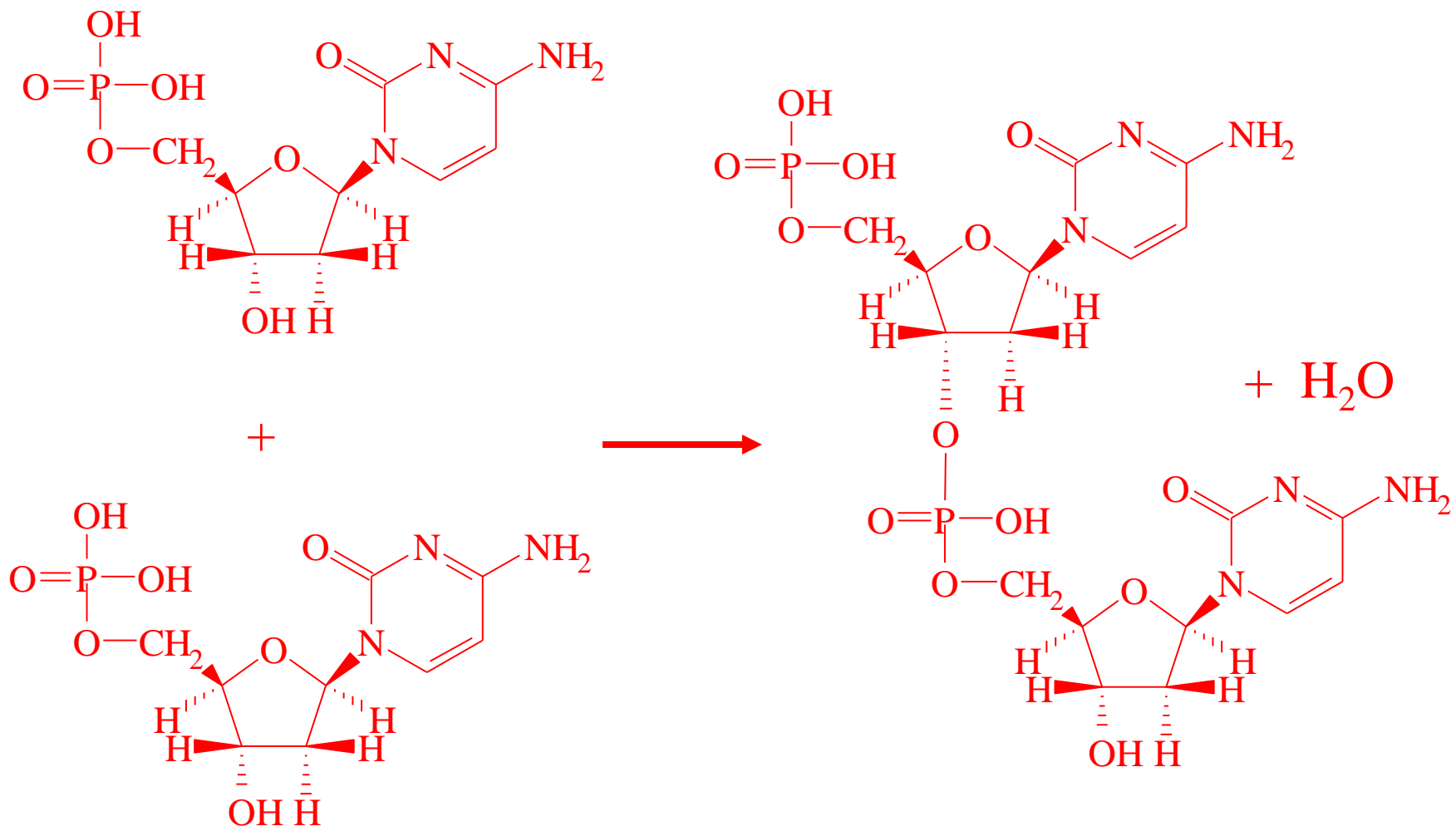


Primary Structure of Nucleic Acids

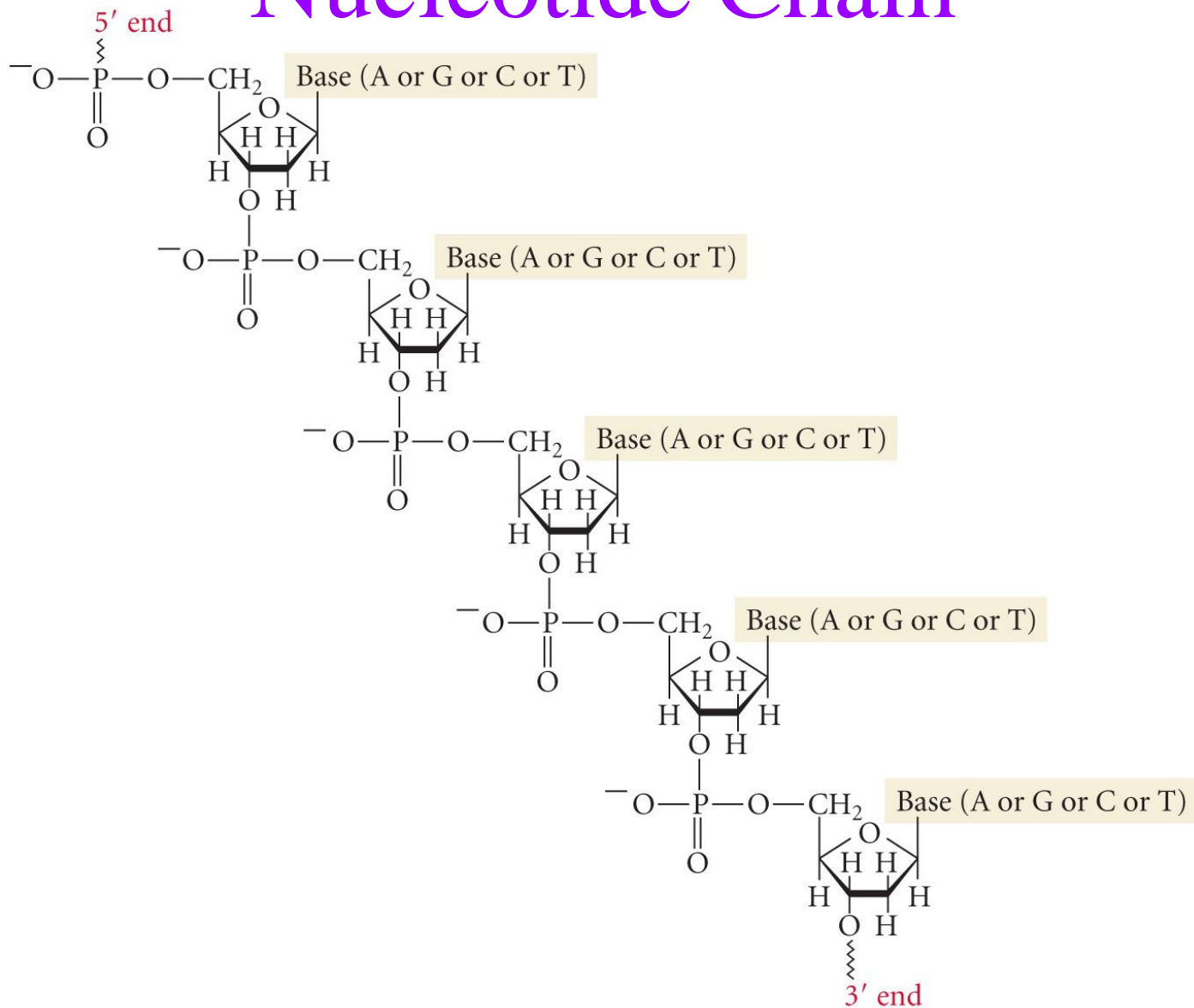
- nucleotides are linked together by attaching the phosphate group of one to the sugar of another at the O of C3
- the attachment is called an **phosphate ester bond**
- the phosphate group attaches to C3 of the sugar on the next nucleotide



Linking Nucleotides



Nucleotide Chain



The Genetic Code

- the order of nucleotides on a nucleic acid chain specifies the order of amino acids in the primary protein structure
- a sequence of 3 nucleotide bases determines which amino acid is next in the chain – this sequence is called a **codon**
- the sequence of nucleotide bases that code for a particular amino acid is practically universal

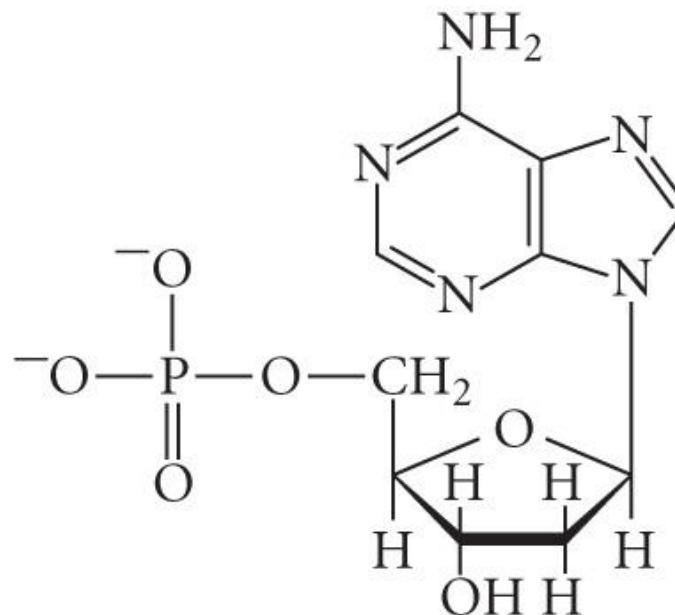
Genetic Structure

Chromosomes—within cells, chromosomes house DNA.

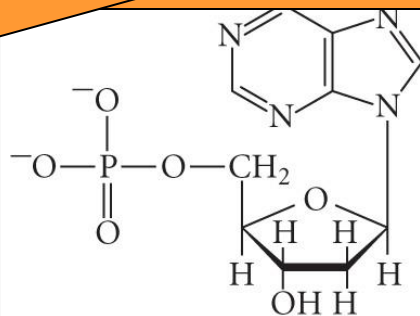
Gene—portion of DNA that codes for a single protein.

Code—three nucleotides code for one amino acid.

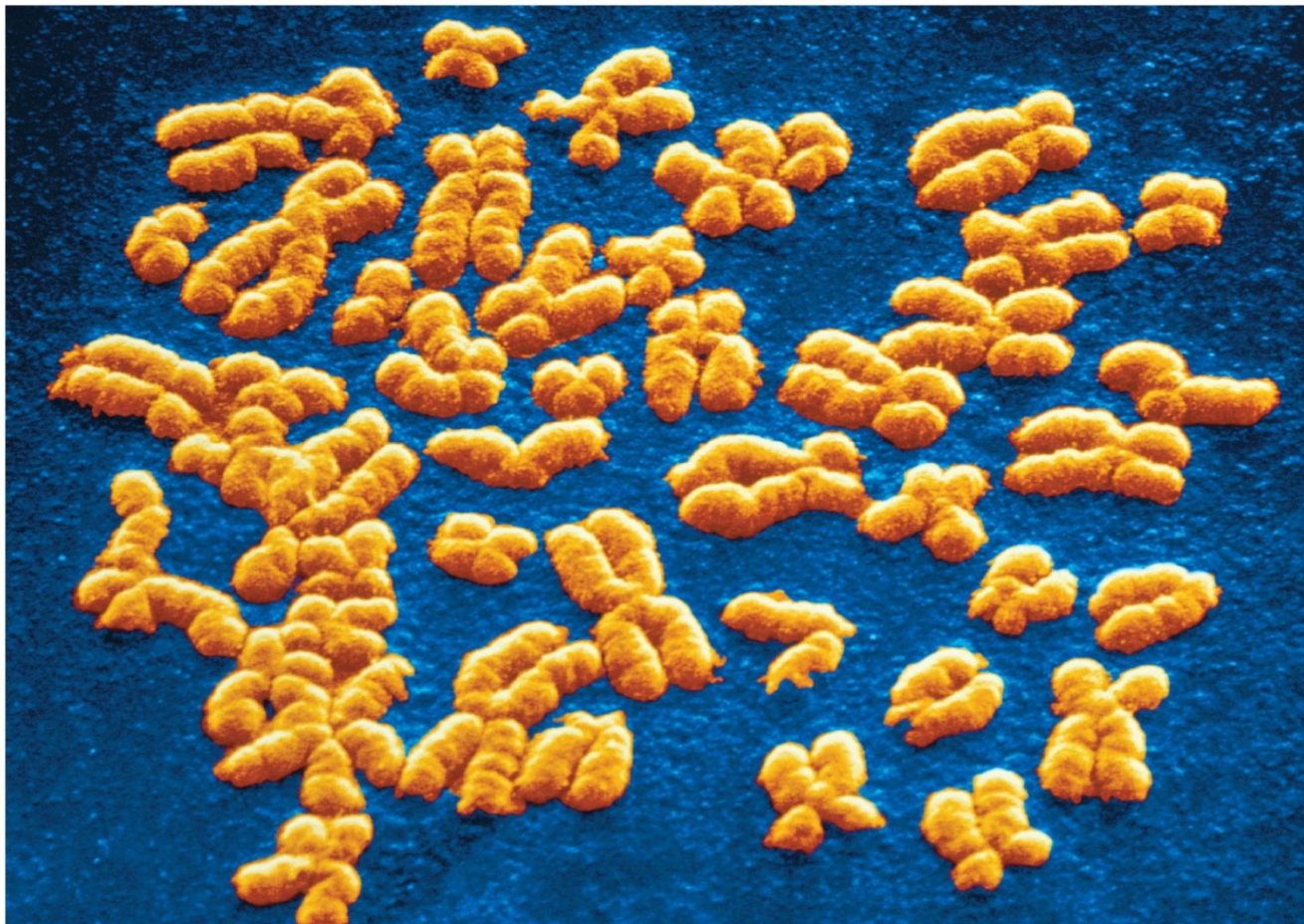
Nucleotide—individual links in the nucleic acid chain. Nucleotides are composed of a sugar group, a phosphate group, and a base.



Nucleotide—individual links in the nucleic acid chain. Nucleotides are composed of a sugar group, a phosphate group, and a base.



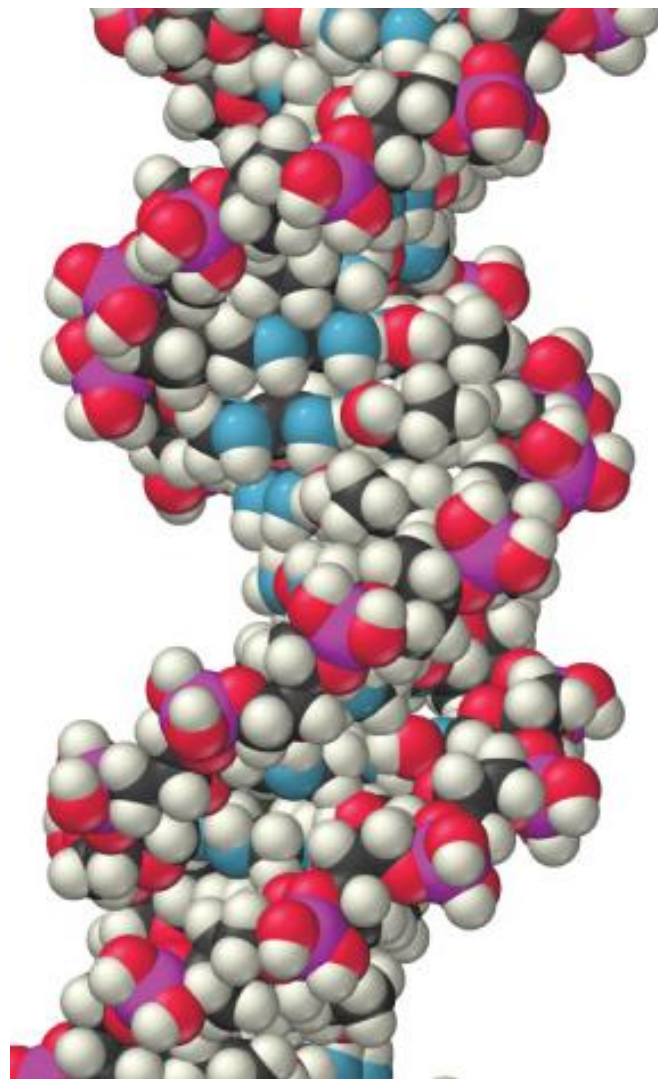
Chromosomes



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DNA

- deoxyribonucleic acid
- sugar is deoxyribose
- one of the following amine bases
 - ✓ adenine (A)
 - ✓ guanine (G)
 - ✓ cytosine (C)
 - ✓ thymine (T)
- 2 DNA strands wound together in double helix
- each of the 10 trillion cells in the body has entire DNA structure



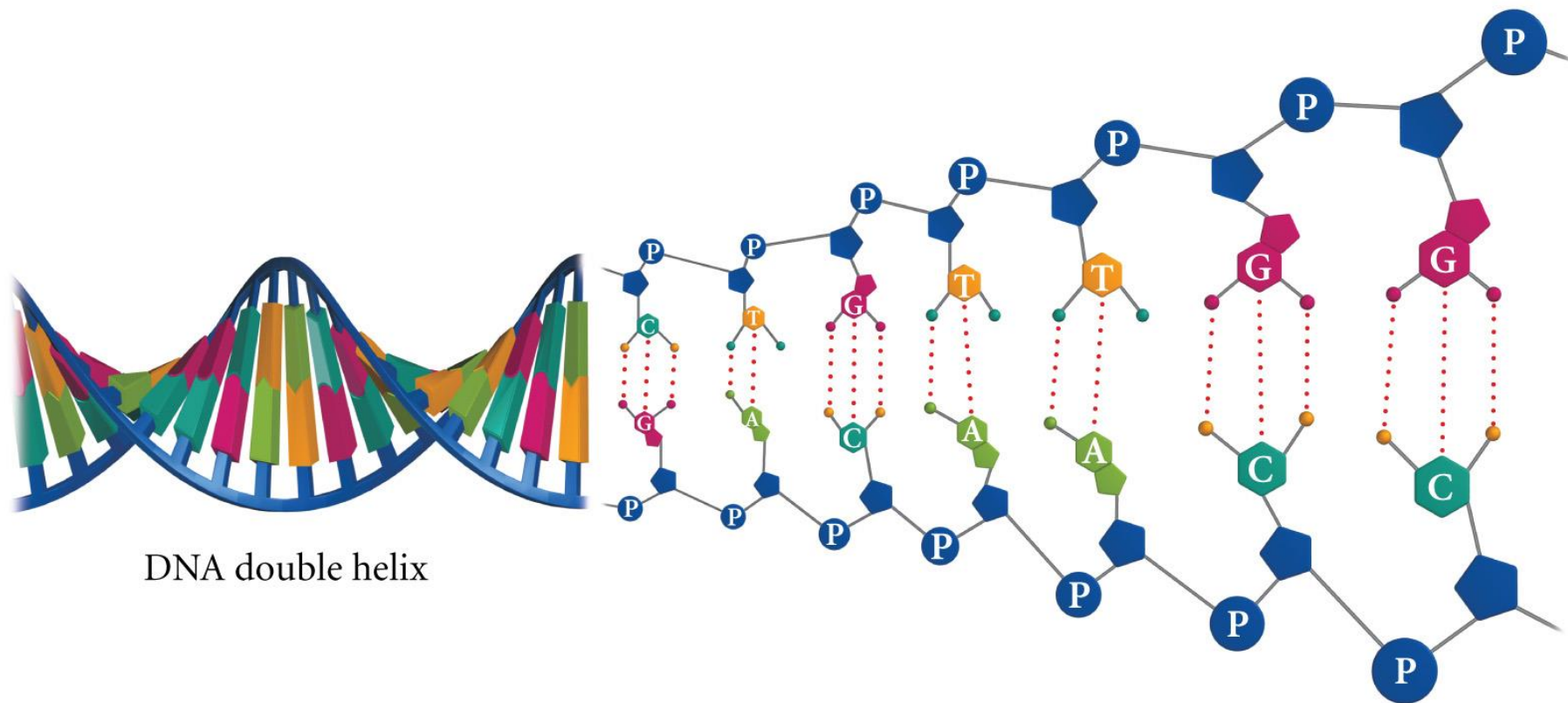
RNA

- ribonucleic acid
- sugar is ribose
- one of the following amine bases
 - ✓ adenine (A)
 - ✓ guanine (G)
 - ✓ cytosine (C)
 - ✓ uracil (U)
- single strands wound in helix

DNA Structure

- DNA made of two strands linked together by H-bonds between bases
- strands are antiparallel
 - ✓ one runs $3' \rightarrow 5'$, other runs $5' \rightarrow 3'$
- bases are complementary and directed to the interior of the helix
 - ✓ A pairs with T, C with G

DNA Double Helix

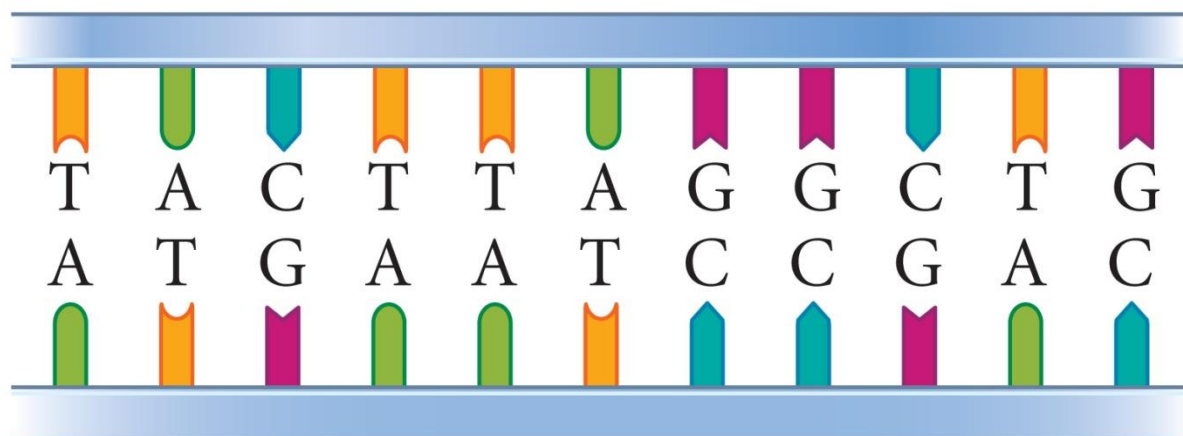
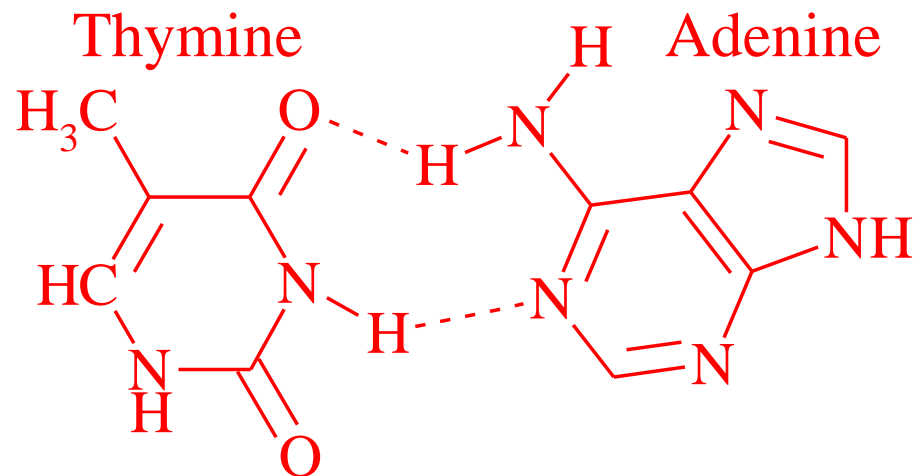


DNA double helix

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Base Pairing

- base pairing generates the helical structure
- in DNA, the complementary bases hold strands together by H-bonding
 - ✓ allow replication of strand



DNA Replication

- when the DNA is to be replicated, the region to be replicated uncoils
- this H-bond between the base pairs is broken, separating the two strands
- with the aid of enzymes, new strands of DNA are constructed by linking the complementary nucleotides to the original strand together

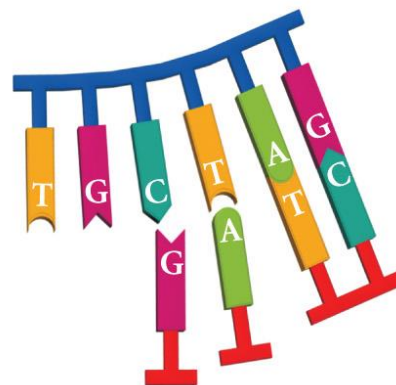
DNA Replication



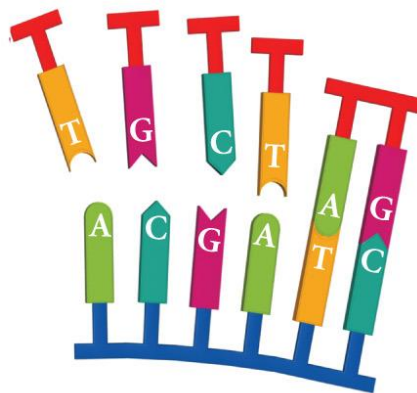
DNA to be replicated



Strands separate



A complement to each daughter strand is formed.



Two complete copies of original DNA.

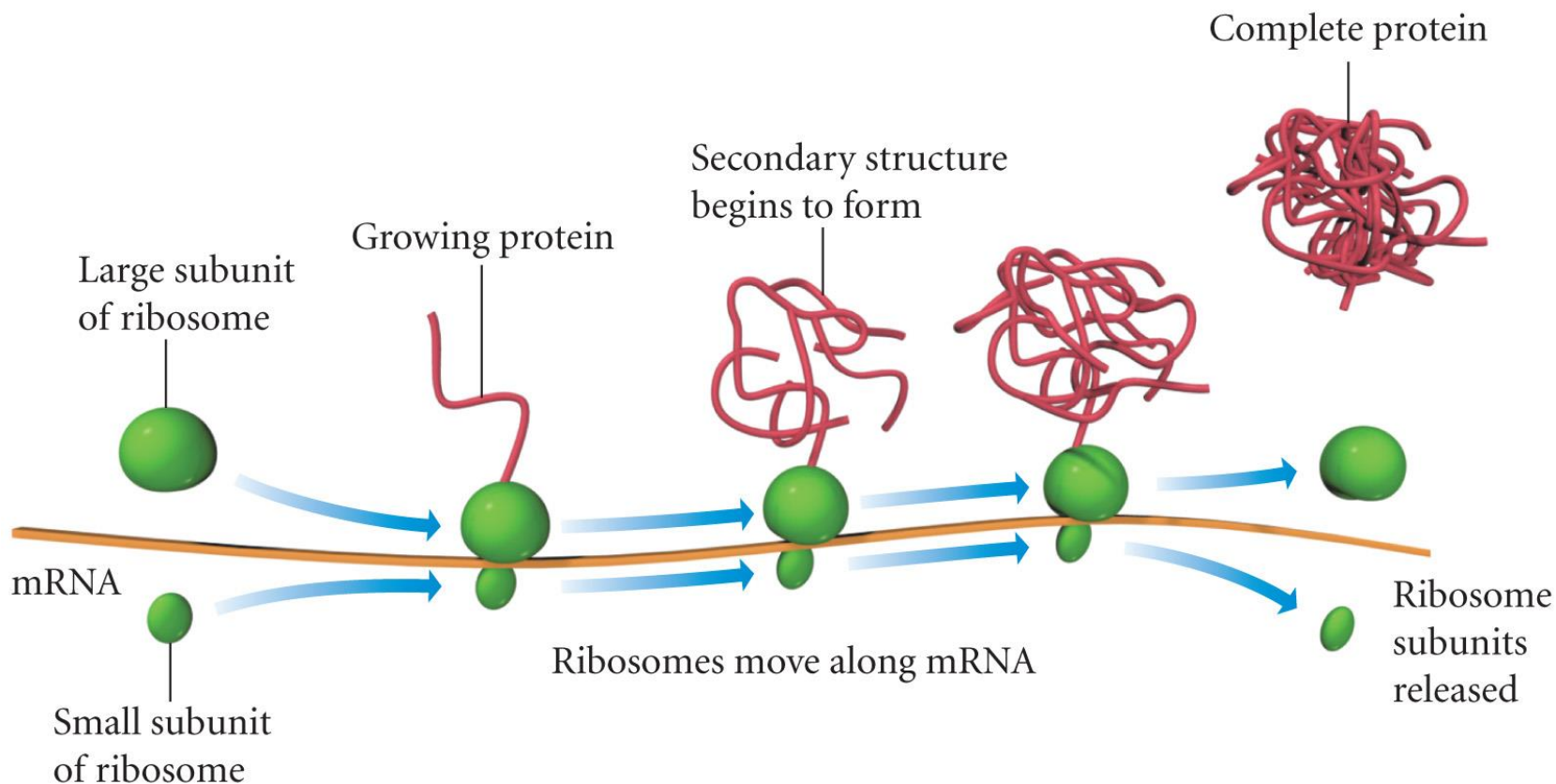


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Protein Synthesis

- transcription → translation
- in nucleus, DNA strand at gene separates and a complementary copy of the gene is made in RNA
 - ✓ messenger RNA = mRNA
- the mRNA travels into the cytoplasm where it links with a **ribosome**
- at the ribosome, each codon on the RNA codes for a single amino acid, which are joined together to form the polypeptide chain

Protein Synthesis



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