1. (a) Define (Any five) 3182011101 Bioorganic Chemistry

(i) Geometric isomer

- Geometric isomers are stereoisomers that differ in the spatial arrangement of atoms or groups around a double bond or a ring structure, where rotation around the bond is restricted.
- They are often referred to as cis-trans isomers.

(ii) Conditionally essential amino acids

- Conditionally essential amino acids are amino acids that are normally non-essential but become essential under specific physiological or pathological conditions.
- Examples include arginine, cysteine, glutamine, glycine, proline, and tyrosine, which may become essential during periods of rapid growth, illness, or trauma when the body's synthesis cannot meet the demand.



(iii) Peptide group

- The peptide group is the amide functional group that links amino acids together in a peptide or protein chain.
- It consists of a carbonyl group ($C = O$) directly bonded to a nitrogen atom ($N - H$), formed by the condensation reaction between the carboxyl group of one amino acid and the amino group of another.

(iv) Phospholipids

- Phospholipids are a class of lipids that are a major component of all cell membranes.
- They consist of a glycerol backbone to which two fatty acids and a phosphate group are attached. The phosphate group is often further modified with an alcohol, such as choline, ethanolamine, or serine.

- They are amphipathic molecules, meaning they have both hydrophobic (fatty acid tails) and hydrophilic (phosphate head) regions, which allows them to form lipid bilayers.

(v) Racemic modification

- A racemic modification, also known as a racemate, is an equimolar mixture of two enantiomers (a pair of stereoisomers that are non-superimposable mirror images of each other).
- A racemic mixture is optically inactive because the optical rotation of one enantiomer is cancelled out by the equal and opposite optical rotation of the other enantiomer.

(vi) Conformation

- Conformation refers to the different spatial arrangements of atoms in a molecule that can be interconverted by rotation around single bonds without breaking any bonds.
- Different conformations of a molecule are called conformers or rotamers and can have different energies and stabilities.



(b) Differentiate (Any three)

(i) Glycogen and cellulose

- Glycogen:
    - Glycogen is a branched polysaccharide that serves as the primary form of glucose storage in animals and fungi.
    - It is composed of glucose units linked by $\alpha(1 \rightarrow 4)$ glycosidic bonds with $\alpha(1 \rightarrow 6)$ branches.
    - It is readily hydrolyzed by enzymes to release glucose for energy.
- Cellulose:

- Cellulose is an unbranched polysaccharide that is the main component of plant cell walls.
- It is composed of glucose units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds.
- Due to the $\beta$ linkages, cellulose forms linear fibrils and is generally not digestible by most animals, including humans, but is a major component of dietary fiber.

(ii) Cis and trans fatty acid

- Cis fatty acid:
  - In a cis fatty acid, the hydrogen atoms on the two carbons of the double bond are on the same side of the double bond.
  - This arrangement causes a "kink" or bend in the hydrocarbon chain, preventing efficient packing and leading to lower melting points.
  - Most naturally occurring unsaturated fatty acids are cis.
- Trans fatty acid:
  - In a trans fatty acid, the hydrogen atoms on the two carbons of the double bond are on opposite sides of the double bond.
  - This arrangement allows the hydrocarbon chain to remain relatively straight, enabling more efficient packing and leading to higher melting points.
  - Trans fats can be formed during the partial hydrogenation of vegetable oils.

(iii) Sawhorse and Newman projections

- Sawhorse projection:

- A sawhorse projection represents a molecule as if viewed from an oblique angle, showing the carbon-carbon bond diagonally across the page.
- Both the front and back carbon atoms and all substituents are shown.
- It provides a clear three-dimensional perspective and is useful for visualizing the relative positions of substituents.

- Newman projection:
  - A Newman projection represents a molecule as if viewed directly down a carbon-carbon bond.
  - The front carbon is represented by a dot, and the back carbon is represented by a circle.
  - Substituents on the front carbon are drawn from the dot, and substituents on the back carbon are drawn from the circle.
  - It is particularly useful for analyzing the dihedral angles and conformational relationships between substituents around a specific bond.



(iv) Monosaccharides and Disaccharides

- Monosaccharides:
  - Monosaccharides are the simplest forms of carbohydrates and are often called simple sugars.
  - They cannot be hydrolyzed into smaller carbohydrate units.
  - Examples include glucose, fructose, and galactose.
  - They typically have a general formula of $(CH_2O)_n$, where $n$ is usually between 3 and 7.
- Disaccharides:

- Disaccharides are carbohydrates formed by the glycosidic linkage of two monosaccharide units.
- They can be hydrolyzed into their constituent monosaccharides.
- Examples include sucrose (glucose + fructose), lactose (glucose + galactose), and maltose (glucose + glucose).

(c) Give the structure of the following :

(i) $\alpha(1 \rightarrow 6)$ linkage in carbohydrates

- This linkage involves the anomeric carbon (C1) of one monosaccharide unit and the C6 of another monosaccharide unit, with the $\alpha$ configuration at the C1 of the first monosaccharide.
- Example with two glucose units:
  - Imagine two glucose rings. The C1 of the first glucose, in its alpha configuration (OH pointing down in the Haworth projection), forms a glycosidic bond with the C6 (the carbon of the $-CH_2OH$ group) of the second glucose.



(ii) PUFA

- PUFA stands for Polyunsaturated Fatty Acid. These are fatty acids that contain more than one carbon-carbon double bond in their hydrocarbon chain.
- Example: Linoleic acid (an omega-6 fatty acid)
  - $CH_3(CH_2)_4CH = CHCH_2CH = CH(CH_2)_7COOH$
- Example: Alpha-linolenic acid (an omega-3 fatty acid)
  - $CH_3CH_2CH = CHCH_2CH = CHCH_2CH = CH(CH_2)_7COOH$

(iii) Zwitter ion

- A zwitterion is a molecule that contains both positively and negatively charged functional groups, resulting in a net charge of zero. Amino acids exist as zwitterions at their isoelectric point.
- Example: Alanine at its isoelectric point
  - $^{+}NH_3 - CH(CH_3) - COO^{-}$

(iv) Inosine

- Inosine is a nucleoside that consists of the purine base hypoxanthine attached to a ribose sugar.
- Structure:
  - A ribose sugar (five-membered ring with −OH groups)
  - Attached to the N9 position of a hypoxanthine base. Hypoxanthine is a purine with an oxygen atom at the C6 position (instead of an amino group like in adenine).



(v) Tryptophan

- Tryptophan is an essential amino acid with an indole side chain.
- Structure:
  - Standard amino acid backbone ($^{+}NH_3 - CH(R) - COO^{-}$)
  - R group is an indole ring system:
    - $CH_2$ linked to the $\alpha$-carbon
    - Indole ring is a bicyclic aromatic heterocycle containing a benzene ring fused to a pyrrole ring (five-membered ring with an −NH- group).

2. (a) What are anomers? Giving the structure of anomeric forms of glucose, explain what happens when they interconvert in aqueous solution.

- Anomers are stereoisomers of cyclic saccharides that differ in configuration only at the anomeric carbon. The anomeric carbon is the new chiral center formed when a monosaccharide cyclizes.
- In the case of glucose, the anomeric carbon is C1. When D-glucose cyclizes, it can form two anomers: $\alpha$-D-glucose and $\beta$-D-glucose.
- Structures of anomeric forms of glucose (Haworth projections):
    - $\alpha$-D-Glucose: In the Haworth projection, the $-OH$ group on the anomeric carbon (C1) is drawn *down* (on the opposite side of the ring from the $-CH_2OH$ group at C5).
    - $\beta$-D-Glucose: In the Haworth projection, the $-OH$ group on the anomeric carbon (C1) is drawn *up* (on the same side of the ring as the $-CH_2OH$ group at C5).
- What happens when they interconvert in aqueous solution (Mutarotation):
    - When either pure $\alpha$-D-glucose or pure $\beta$-D-glucose is dissolved in water, their optical rotation slowly changes until a constant value is reached. This phenomenon is called mutarotation.
    - This change occurs because, in aqueous solution, the cyclic anomers are in equilibrium with each other via the open-chain aldehyde form.
    - The cyclic forms constantly open and close. During the brief period when the molecule is in its open-chain aldehyde form, rotation around the C1-C2 bond can occur.
    - When the molecule re-cyclizes, the $-OH$ group at C1 can orient either below or above the plane of the ring, leading to the formation of both $\alpha$ and $\beta$ anomers.
    - At equilibrium, an aqueous solution of D-glucose contains approximately 36% $\alpha$-D-glucose, 64% $\beta$-D-glucose, and a very

small percentage (less than 0.1%) of the open-chain aldehyde form.

- This interconversion allows for the rapid establishment of equilibrium between the anomeric forms, leading to the observed mutarotation.

(b) Draw a labelled diagram of titration curve for Aspartic acid. Answer the following questions after looking at the curve

- (Diagram of Titration Curve for Aspartic Acid - Conceptual Description)
    - The x-axis represents the equivalents of $OH^-$ added (or pH value).
    - The y-axis represents the pH.
    - The curve will show three distinct buffering regions (relatively flat segments) and three equivalence points (steep rises).
    - The initial pH will be very low (acidic, due to $-$COOH groups).
    - First buffering region: Around pK1 (for $\alpha$-carboxyl group, ~2.09).
    - First equivalence point: After the first $-$COOH group is deprotonated.
    - Second buffering region: Around pK2 (for $\alpha$-amino group, ~9.82).
    - Second equivalence point: After the $\alpha$-amino group is deprotonated.
    - Third buffering region: Around pKR (for the side chain carboxyl group of aspartic acid, ~3.86). This pKR will be between pK1 and pK2.
    - The curve will start low, rise through the first buffering region, rise steeply, rise through the side chain buffering region, rise

steeply, rise through the alpha-amino buffering region, and finally rise steeply to a high pH.

- The isoelectric point (pI) will be found between pK1 and pKR for aspartic acid, where the net charge is zero.

(i) Range in which it has buffering capacity

- Aspartic acid has buffering capacity in the following pH ranges, corresponding to its pKa values:
  - Around pK1 ($-$COOH of $\alpha$-carboxyl group): Approximately pH 1.09 to 3.09.
  - Around pKR (side chain $-$COOH group): Approximately pH 2.86 to 4.86.
  - Around pK2 ($-NH_3^+$ of $\alpha$-amino group): Approximately pH 8.82 to 10.82.



(ii) Point at which it is a zwitterionic

- Aspartic acid is a zwitterion at its isoelectric point (pI).
- For aspartic acid, with three ionizable groups (pK1 = 2.09, pKR = 3.86, pK2 = 9.82), the pI is calculated as the average of the two pKa values that bracket the zwitterionic form (where the molecule has a net zero charge). In this case, it's the pKa of the $\alpha$-carboxyl group and the side chain carboxyl group.
- $pI = (pK_1 + pK_R)/2 = (2.09 + 3.86)/2 = 5.95/2 = 2.975$
- So, aspartic acid is predominantly in its zwitterionic form at a pH of approximately 2.975.

(iii) Equation showing successive ionization of groups due to change in pH of medium

- Let's denote Aspartic acid as $H_3A^+$ (fully protonated form, net charge +1)

- $H_3A^+ \rightleftharpoons H_2A + H^+$ (Deprotonation of $\alpha$-carboxyl group; pK1 ≈ 2.09; $H_2A$ is the zwitterionic form with side chain -COOH still protonated)
- $H_2A \rightleftharpoons HA^- + H^+$ (Deprotonation of side chain carboxyl group; pKR ≈ 3.86; $HA^-$ has a net charge of -1)
- $HA^- \rightleftharpoons A^{2-} + H^+$ (Deprotonation of $\alpha$-amino group; pK2 ≈ 9.82; $A^{2-}$ has a net charge of -2)

3. Give mechanism and biological importance of the following : (Any three)

(i) Aldol condensation

- Mechanism:
    - Aldol condensation is a reaction where an enolate ion reacts with a carbonyl compound (aldehyde or ketone) to form a $\beta$-hydroxy aldehyde or $\beta$-hydroxy ketone (an aldol).
    - Step 1 (Enolate formation): A base deprotonates an $\alpha$-hydrogen of one carbonyl compound to form a resonance-stabilized enolate ion.
    - Step 2 (Nucleophilic addition): The enolate ion acts as a nucleophile and attacks the electrophilic carbonyl carbon of another aldehyde or ketone molecule.
    - Step 3 (Protonation): The alkoxide intermediate is protonated to form the $\beta$-hydroxy carbonyl compound (aldol).
    - Step 4 (Dehydration - Condensation step): If heated or under more vigorous basic/acidic conditions, the $\beta$-hydroxy carbonyl compound can undergo dehydration to form an $\alpha,\beta$-unsaturated carbonyl compound. This is the "condensation" part, as a molecule of water is eliminated.
- Biological importance:

- Aldol condensation reactions are crucial in many metabolic pathways.
- For example, in glycolysis, the enzyme aldolase catalyzes the reversible aldol condensation of dihydroxyacetone phosphate (DHAP) and glyceraldehyde-3-phosphate (G3P) to form fructose-1,6-bisphosphate. This reaction is essential for breaking down glucose to produce energy.

(ii) Cannizzaro reaction

- Mechanism:
  - The Cannizzaro reaction is a disproportionation reaction (redox reaction) undergone by aldehydes that lack $\alpha$-hydrogens when treated with a strong base. One aldehyde molecule is oxidized to a carboxylic acid (or carboxylate salt), and another is reduced to an alcohol.
  - Step 1 (Nucleophilic attack): The hydroxide ion attacks the carbonyl carbon of one aldehyde molecule.
  - Step 2 (Hydride transfer): A hydride ion is transferred from the resulting tetrahedral intermediate to a second aldehyde molecule. Simultaneously, the first intermediate collapses to form a carboxylate.
  - Step 3 (Proton exchange): The alkoxide ion formed from the second aldehyde rapidly abstracts a proton from the carboxylic acid (or water in the case of strong base), leading to the alcohol and carboxylate salt.
- Biological importance:
  - While direct Cannizzaro reactions in biological systems are less common in the exact chemical sense as in organic synthesis, the principle of hydride transfer, a key step in the Cannizzaro reaction, is fundamental to many biological redox processes.

- Enzymes such as alcohol dehydrogenases and aldehyde dehydrogenases catalyze similar hydride transfers using cofactors like NADH or NADPH to interconvert aldehydes, alcohols, and carboxylic acids, which are vital for metabolism and detoxification.

(iii) Michael addition

- Mechanism:
  - The Michael addition (or Michael reaction) is a nucleophilic addition of a carbanion or another nucleophile to an $\alpha,\beta$-unsaturated carbonyl compound (or other electron-deficient alkene).
  - Step 1 (Enolate formation): A strong base deprotonates a carbon acid (e.g., a $\beta$-dicarbonyl compound, a malonate ester, or another compound with an activated $\alpha$-hydrogen) to form a resonance-stabilized nucleophilic enolate.
  - Step 2 (Nucleophilic attack): The enolate (Michael donor) attacks the $\beta$-carbon of the $\alpha,\beta$-unsaturated carbonyl compound (Michael acceptor). This is a conjugate addition.
  - Step 3 (Protonation): The resulting enolate intermediate is protonated, typically by a proton source (e.g., water or acid) to yield the final product.
- Biological importance:
  - Michael addition reactions are important in various biosynthetic pathways.
  - For example, in the biosynthesis of nucleotides, the addition of ammonia to fumarate to form aspartate can be considered analogous to a Michael addition.
  - It is also relevant in the mechanism of action of certain enzymes and in the formation of complex natural products.

Many enzymatic reactions involve the addition of a nucleophile to an activated double bond.

(iv) Baeyer Villiger oxidation

- Mechanism:
    - The Baeyer-Villiger oxidation is a reaction where a ketone or aldehyde is oxidized by a peroxy acid (like m-CPBA or peracetic acid) to an ester or a carboxylic acid, respectively. An oxygen atom is inserted between the carbonyl carbon and one of the adjacent carbon atoms.
    - Step 1: The peroxy acid adds to the carbonyl carbon of the ketone/aldehyde.
    - Step 2: An intramolecular migration of one of the groups (alkyl or aryl) from the carbonyl carbon to the oxygen of the peroxy acid occurs. The migratory aptitude follows the order: tertiary alkyl > secondary alkyl > aryl > primary alkyl > methyl.
    - Step 3: The leaving group (carboxylate anion from the peroxy acid) departs, and the product (ester or carboxylic acid) is formed.
- Biological importance:
    - Baeyer-Villiger monooxygenases (BVMOs) are a class of enzymes that catalyze similar reactions in biological systems.
    - These enzymes use molecular oxygen and NADPH to insert an oxygen atom into a carbon-carbon bond of ketones, forming esters or lactones.
    - BVMOs are involved in the metabolism of xenobiotics (foreign compounds), the degradation of natural products, and the biosynthesis of various compounds, including steroids and antibiotics. They are also of interest in biotechnology for the synthesis of fine chemicals.

4. (a) Giving the structure of sucrose explain why a solution of sucrose gives negative Benedict's test, however upon boiling with concentrated HCl the solution becomes positive for Benedict's Test.

- Structure of Sucrose:
    - Sucrose is a disaccharide composed of one unit of $\alpha$-D-glucose and one unit of $\beta$-D-fructose.
    - The glucose and fructose units are linked by a glycosidic bond between the anomeric carbon of glucose (C1 of glucose in $\alpha$ configuration) and the anomeric carbon of fructose (C2 of fructose in $\beta$ configuration). This specific linkage is called an $\alpha(1 \rightarrow 2)\beta$ glycosidic bond.
- Why a solution of sucrose gives negative Benedict's test:
    - Benedict's test is a chemical test used to detect the presence of reducing sugars. Reducing sugars are carbohydrates that have a free aldehyde or ketone group (or can readily form one in solution, like through mutarotation) that can be oxidized.
    - In sucrose, the glycosidic bond is formed between the anomeric carbon of glucose (C1) and the anomeric carbon of fructose (C2).
    - This means that both anomeric carbons are involved in the glycosidic linkage and are therefore "locked" in their cyclic forms.
    - Neither the glucose unit nor the fructose unit in sucrose has a free anomeric hydroxyl group that can open up to form a free aldehyde or ketone group.
    - Consequently, sucrose cannot act as a reducing agent, and thus it gives a negative Benedict's test (the blue copper(II) sulfate solution remains blue, no red-orange precipitate of copper(I) oxide forms).

- However upon boiling with concentrated HCl the solution becomes positive for Benedict's Test:
    - When sucrose is boiled with concentrated HCl, the acidic conditions cause the hydrolysis of the glycosidic bond.
    - Hydrolysis breaks the $\alpha(1 \rightarrow 2)\beta$ glycosidic linkage, releasing the constituent monosaccharides: $\alpha$-D-glucose and $\beta$-D-fructose.
    - Both glucose and fructose are monosaccharides and are reducing sugars. Glucose has an aldehyde group (in its open-chain form), and fructose has a ketone group (which can isomerize to an aldehyde in basic solution, via enediol intermediate, under the conditions of the Benedict's test).
    - Once liberated, these free monosaccharides can open their cyclic forms to expose their aldehyde or ketone groups.
    - These exposed reducing groups can then reduce the copper(II) ions in the Benedict's reagent to copper(I) oxide, leading to a positive Benedict's test (formation of a red-orange precipitate).
    - This process is often called "inversion" because the hydrolysis of sucrose, which is dextrorotatory, produces a mixture of glucose (dextrorotatory) and fructose (levorotatory), and since fructose is more strongly levorotatory, the overall solution becomes levorotatory.



(b) Write all the possible isomers for 2,3 dichloropentanoic acid. Classify them as threo or erythro isomer. Specify the stereochemical relationship between these isomers.

- 2,3-Dichloropentanoic acid has two chiral centers at C2 and C3.
- A molecule with n chiral centers can have a maximum of $2^n$ stereoisomers. Here, $2^2 = 4$ possible stereoisomers.
- The structure is $CH_3 - CH_2 - CHCl - CHCl - COOH$.

- Possible stereoisomers (using Fischer projections for clarity):

(1) (2R, 3R)-2,3-Dichloropentanoic acid * Place the -COOH group at the top and the $CH_3CH_2$ group at the bottom. * At C2 (top chiral center), Cl on the right, H on the left. * At C3 (bottom chiral center), Cl on the right, H on the left. * Classification: Erythro isomer (identical groups on the same side in Fischer projection).

(2) (2S, 3S)-2,3-Dichloropentanoic acid * Enantiomer of (1). * At C2, Cl on the left, H on the right. * At C3, Cl on the left, H on the right. * Classification: Erythro isomer.

(3) (2R, 3S)-2,3-Dichloropentanoic acid * Diastereomer of (1) and (2). * At C2, Cl on the right, H on the left. * At C3, Cl on the left, H on the right. * Classification: Threo isomer (identical groups on opposite sides in Fischer projection).

(4) (2S, 3R)-2,3-Dichloropentanoic acid * Enantiomer of (3). * At C2, Cl on the left, H on the right. * At C3, Cl on the right, H on the left. * Classification: Threo isomer.



- Stereochemical relationship between these isomers:
    - (1) and (2) are enantiomers (non-superimposable mirror images).
    - (3) and (4) are enantiomers (non-superimposable mirror images).
    - (1) and (3) are diastereomers (stereoisomers that are not mirror images).
    - (1) and (4) are diastereomers.
    - (2) and (3) are diastereomers.
    - (2) and (4) are diastereomers.

(c) RNA undergoes hydrolysis under basic condition but DNA does not. Justify giving the mechanism involved.

- Justification:
    - The primary reason for the difference in alkaline hydrolysis stability between RNA and DNA lies in the presence of a 2'-hydroxyl group (−OH) on the ribose sugar in RNA, which is absent in DNA (deoxyribose has a hydrogen at the 2' position).
- Mechanism involved in RNA hydrolysis under basic conditions:
    - Step 1 (Intramolecular nucleophilic attack): Under basic conditions, the 2'-hydroxyl group of the ribose sugar in RNA is deprotonated by a base to form a highly reactive 2'-alkoxide ion.
    - Step 2 (Formation of cyclic intermediate): This 2'-alkoxide ion acts as a strong intramolecular nucleophile. It attacks the adjacent phosphodiester bond, specifically the phosphorus atom. This nucleophilic attack leads to the formation of a five-membered cyclic 2',3'-phosphate intermediate. During this attack, the phosphodiester bond is cleaved, and the 5'-oxygen of the downstream nucleotide is displaced as a leaving group.
    - Step 3 (Hydrolysis of cyclic intermediate): The cyclic 2',3'-phosphate intermediate is then hydrolyzed by water (or another hydroxide ion) in a subsequent step, leading to a mixture of 2'-monophosphate and 3'-monophosphate products. This ultimately breaks the RNA backbone.
- Why DNA does not undergo hydrolysis under basic conditions:
    - DNA lacks the 2'-hydroxyl group on its deoxyribose sugar.
    - Without this crucial 2'-hydroxyl group, the intramolecular nucleophilic attack on the phosphodiester bond cannot occur.
    - The formation of the strained cyclic 2',3'-phosphate intermediate is prevented, which is the key step in alkaline hydrolysis.

- Therefore, the phosphodiester bonds in DNA are stable to basic conditions, and the DNA backbone remains intact.

5. (a) Give the structure for various conformation of cyclohexane. Give their stability order and justify your answer.

- Structures for various conformations of cyclohexane (Conceptual Description):
  - Cyclohexane exists in various conformations due to rotation around its C-C single bonds. The most important conformations are:
    - Chair conformation: This is the most stable and prevalent conformation. It resembles a lounge chair with six carbons arranged in a puckered ring. It has two distinct types of positions for substituents: axial (pointing straight up or down, parallel to the principal axis) and equatorial (pointing outwards, roughly perpendicular to the principal axis).
    - Half-chair conformation: A high-energy intermediate between the chair and twist-boat. It has significant angle strain and torsional strain.
    - Twist-boat (or skew-boat) conformation: This conformation is more stable than the boat but less stable than the chair. It can be thought of as a twisted version of the boat, which relieves some of the flagpole interactions and torsional strain.
    - Boat conformation: This is a high-energy conformation. It has a shape resembling a boat, with two "flagpole" hydrogens pointing upwards at opposite ends of the "boat" and eclipsing interactions along the sides. It suffers from significant torsional strain and steric repulsion (flagpole interaction).

- (Visual representation would involve 3D drawings of these shapes, showing the puckering and bond angles).

- Stability order:
  - Chair > Twist-boat > Boat > Half-chair
- Justification for stability order:
  - **Chair Conformation (Most Stable):**
    - It is free of angle strain: All C-C-C bond angles are approximately $109.5°$, which is the ideal tetrahedral angle.
    - It is free of torsional strain: All adjacent C-H bonds (and C-C bonds) are staggered, minimizing torsional strain (eclipsing interactions).
    - Steric interactions are minimized: Large groups can adopt equatorial positions, avoiding 1,3-diaxial interactions.
  - **Twist-Boat Conformation (Less stable than chair, more stable than boat):**
    - It is approximately 5.5 kcal/mol higher in energy than the chair.
    - It reduces some of the torsional strain present in the boat form by twisting the molecule.
    - It also alleviates some of the flagpole steric interactions found in the boat.
  - **Boat Conformation (Much Less Stable):**
    - It is approximately 7.1 kcal/mol higher in energy than the chair.
    - It has significant torsional strain: There are several eclipsed interactions along the "sides" of the boat.

- It has significant steric strain: The two "flagpole" hydrogens (or substituents) at C1 and C4 are very close in space, leading to significant van der Waals repulsion (flagpole interactions).

- **Half-Chair Conformation (Least Stable):**
  - It is approximately 10.8 kcal/mol higher in energy than the chair.
  - It represents the transition state between the chair and boat forms (or chair and twist-boat).
  - It possesses considerable angle strain (four carbons are planar) and significant torsional strain due to extensive eclipsing interactions.

(b) What are triacylglycerols? Why are they preferred for storing energy?



- What are triacylglycerols?
  - Triacylglycerols (also known as triglycerides or neutral fats) are the most common type of lipid found in the body and in nature.
  - They are esters derived from glycerol and three fatty acids.
  - Glycerol is a three-carbon alcohol with a hydroxyl group on each carbon. Fatty acids are long hydrocarbon chains with a carboxyl group at one end.
  - In a triacylglycerol, each of the three hydroxyl groups of glycerol is esterified with a fatty acid molecule. The fatty acids can be the same or different (saturated or unsaturated, long or short chain).
- Why are they preferred for storing energy?
  - **High Energy Density:**

- Triacylglycerols are highly reduced molecules, meaning they have a high proportion of carbon-hydrogen bonds and a low proportion of oxygen.
- The complete oxidation of triacylglycerols yields significantly more energy per gram (approximately 9 kcal/g) compared to carbohydrates or proteins (approximately 4 kcal/g). This makes them a very efficient form of energy storage by weight.

- **Anhydrous Storage (Water-Free):**
  - Triacylglycerols are nonpolar and hydrophobic, meaning they are stored in an anhydrous (water-free) form within cells (e.g., in adipose tissue).
  - In contrast, carbohydrates (like glycogen) are highly hydrated, carrying about 2 grams of water per gram of carbohydrate. Storing energy as glycogen would require a much greater mass and volume to achieve the same energy content due to the associated water. This anhydrous storage makes fat a much more compact energy reserve.
- **Insulation and Protection:**
  - Beyond energy storage, the hydrophobic nature of triacylglycerols allows them to serve as excellent thermal insulation (e.g., in subcutaneous fat) and provide cushioning for vital organs against physical shock. While these are not directly related to energy *storage efficiency*, they are added benefits of their physical properties.
- **Metabolic Inertness (Relatively):**
  - In their storage form, triacylglycerols are relatively unreactive and stable, making them suitable for long-term

storage without undergoing undesirable chemical reactions. They are mobilized when energy is needed.

(c) Enlist five bioactive compounds and their precursor amino acids.

- Here are five bioactive compounds and their precursor amino acids:

2. **Bioactive Compound:** Histamine
    - **Precursor Amino Acid:** Histidine
    - (Role: Mediator of allergic reactions, gastric acid secretion, neurotransmitter.)
3. **Bioactive Compound:** Serotonin (5-hydroxytryptamine)
    - **Precursor Amino Acid:** Tryptophan
    - (Role: Neurotransmitter, mood regulation, sleep, appetite.)
4. **Bioactive Compound:** Dopamine (and other catecholamines like Norepinephrine, Epinephrine)
    - **Precursor Amino Acid:** Tyrosine (which is derived from Phenylalanine)
    - (Role: Neurotransmitter, reward system, motor control. Norepinephrine and Epinephrine are hormones and neurotransmitters involved in fight-or-flight response.)
5. **Bioactive Compound:** Nitric Oxide (NO)
    - **Precursor Amino Acid:** Arginine
    - (Role: Vasodilator, neurotransmitter, immune response.)
6. **Bioactive Compound:** Creatine (and Phosphocreatine)
    - **Precursor Amino Acids:** Glycine, Arginine, and Methionine
    - (Role: Energy storage in muscle, rapid ATP regeneration.)

7. (a) Assigning priority order and assign E/Z configuration to each of the following :

(i) $H_3C$-Et-C=CHCH$Cl_2$-Cl

- This structure seems to be written in a linear fashion, making it difficult to visualize the double bond geometry. Assuming it refers to a substituted alkene, let's break it down based on typical representations.
- Assuming the double bond is between the C where $H_3C$ and Et are attached and the C where CHCH$Cl_2$-Cl is attached.
- Let's interpret it as: $(CH_3)(CH_3CH_2)C = CH(CHCl_2)Cl$ - This also doesn't make sense as CHCH$Cl_2$-Cl suggests two groups on the same carbon.
- Let's re-interpret the structure, as it must be an alkene with two substituents on each carbon of the double bond.
- Let's assume the question intends:
    - $C_1 = C_2$
    - On $C_1$: $H_3C$ and $CH_3CH_2$ (Ethyl)
    - On $C_2$: $CHCl_2$ and $Cl$ (Chlorine)
- This interpretation is still problematic because a carbon cannot have 5 bonds.
- Let's assume the question is implying a double bond with substituents on each side. A more standard representation of a compound that might lead to E/Z would be something like:
    - (i) R1-C=C-R2-R3 (where R1, R2, R3, R4 are the groups on the carbons of the double bond)
- Given the unusual notation, it's hard to definitively interpret. However, I must answer the question as given. Let's assume the intention is for

a disubstituted alkene where the C=C is between a carbon attached to methyl and ethyl, and a carbon attached to $-CHCHCl_2$ and $-Cl$. This still leads to valency issues.

- Given the constraint "Structure represented by drawing", and the input is textual, I must interpret based on the most likely chemical structure for E/Z isomerism. E/Z configuration applies to double bonds where each carbon of the double bond is attached to two different groups.
- The notation "$H_3C$-Et-C=CHCH$Cl_2$-Cl" is highly ambiguous for a double bond structure.
- If it's intended to be:
    - Carbon 1 of double bond has $CH_3$ and $CH_3CH_2$ (Ethyl).
    - Carbon 2 of double bond has $H$ and $CHCl_2Cl$ (This is $CHCl_3$ with an extra C, not possible).
- Let's consider the most charitable interpretation that allows for E/Z. It seems there's a typo in the provided linear representation.
- Perhaps it means: ($H_3C$)(Et)C = C($CHCl_2$)(Cl) or ($H_3C$)C(Et)=C($CHCl_2$)(Cl) if the "Et" is also attached to the first carbon of the double bond.
- Let's assume the molecule is something like 3-chloro-2-ethyl-3-(dichloromethyl)pent-2-ene or similar, but the given structure is just linear elements.
- **Given the exact string "$H_3C$-Et-C=CHCH$Cl_2$-Cl"**
    - It looks like two parts connected by C=CH.
    - Left side of C=CH: $H_3C - Et - C$. This means Carbon 1 of the double bond is attached to $CH_3$ and $Et$. And this Carbon 1 is also attached to $C_2$ (the next carbon in the chain) where the

double bond is. This makes no sense, a carbon can't have 5 bonds.

- **Re-interpreting as substituents on a double bond for E/Z:**
    - Let's assume the double bond is $C = C$.
    - On one carbon, the groups are $H_3C$ and $Et$.
        - Priority for $H_3C$ vs $Et$: $Et$ (C connected to $CH_3$, $H$, $H$) > $CH_3$ (C connected to $H$, $H$, $H$). So $Et$ has higher priority.
    - On the other carbon, the groups are $CHCl_2$ and $Cl$.
        - Priority for $CHCl_2$ vs $Cl$:
            - $Cl$ (Atomic number 17) has higher priority than C. So $Cl$ has higher priority.
- Without a clear drawing, assigning E/Z is impossible due to the ambiguity of where the groups are attached to the double bond. The linear notation "$H_3$C-Et-C=CHCH$Cl_2$-Cl" does not represent a clear structure for E/Z assignment. E/Z requires explicit positioning of four distinct groups around the C=C bond.
- **Assuming a simplified interpretation for the purpose of answering:** Let's assume the intention was two groups on one carbon and two on the other. For example:
    - $(CH_3)(CH_3CH_2)C = C(H)(CHCl_2)$ or similar.
    - If it's $(CH_3)(Et)C = C(CHCl_2)(Cl)$ (this interpretation also has issues with valency as $CHCl_2$ has 3 bonds).
- **Let's assume the input is for a C=C bond, and the listed items are the four substituents. This is the only way to proceed with the E/Z assignment given the lack of explicit structure.**
- Suppose the double bond has groups:
    - Carbon 1: $H_3C$ and $Et$

- Carbon 2: $CHCl_2$ and $Cl$

- **Priority order on Carbon 1:**
  - $Et$ ($CH_2CH_3$) has higher priority than $CH_3$.
    - (C bonded to C, H, H vs C bonded to H, H, H)
- **Priority order on Carbon 2:**
  - $Cl$ has higher priority than $CHCl_2$.
    - ($Cl$ atomic number 17 vs $C$ atomic number 6. Even if we expanded $CHCl_2$ as C bonded to Cl, Cl, H, the first point of difference is $Cl$ itself which is higher than C).
- **E/Z assignment:** Requires knowing the relative positions. Since no drawing is provided, I cannot assign E or Z. I can only provide the priority.
  - **If higher priority groups are on opposite sides: E configuration.**
  - **If higher priority groups are on the same side: Z configuration.**



(ii) $IH_2C$-CHO-C=C-$NH_2$

- Again, the linear representation is ambiguous for E/Z. Let's assume it refers to a disubstituted alkene.
- Assume the double bond is between two carbons, each with two substituents.
- Let's assume the double bond is between C1 and C2, and the groups are:
  - On Carbon 1: $CH_2I$ and $CHO$
  - On Carbon 2: $H$ and $NH_2$

- **Priority order on Carbon 1 (left carbon of C=C):**
    - Compare $CH_2I$ and $CHO$ (aldehyde)
    - $CH_2I$: C is bonded to I, H, H.
    - $CHO$: C is double bonded to O, and single bonded to H. (Treated as C bonded to O, O, H)
    - Comparing the first atoms attached to the double bond carbon: C vs C.
    - Go to next atoms: For $CH_2I$, it's I (atomic number 53). For $CHO$, it's O (atomic number 8) and O (atomic number 8) and H.
    - Iodine (I) has much higher atomic number than Oxygen (O).
    - So, $CH_2I$ has higher priority than $CHO$.
- **Priority order on Carbon 2 (right carbon of C=C):**
    - Compare $H$ and $NH_2$.
    - $NH_2$: N (atomic number 7)
    - $H$: H (atomic number 1)
    - So, $NH_2$ has higher priority than $H$.
- **E/Z assignment:** Requires knowing the relative positions. Since no drawing is provided, I cannot assign E or Z.
    - **If higher priority groups ($CH_2I$ and $NH_2$) are on opposite sides: E configuration.**
    - **If higher priority groups ($CH_2I$ and $NH_2$) are on the same side: Z configuration.**

6. (b) Assigning priority order and assign R/S configuration to each of the following :

R/S configuration is for chiral centers. Each chiral center needs four different groups.

(i) CN-Cl-Ph-H

- This looks like a list of four groups around a single chiral carbon.
- Let the central chiral carbon be C*.
- The four groups are: $CN$, $Cl$, $Ph$ (phenyl), $H$.
- **Priority order (Cahn-Ingold-Prelog rules):**
  - i. $Cl$ (Atomic number 17) - Highest priority.
  - ii. $Ph$ (Phenyl group, $-C_6H_5$) - C attached to 3 C's (treated as C, C, C for ring), vs CN (C triple bonded to N, treated as N, N, N). C is atomic number 6, N is 7.
    - Expanding $Ph$: C of benzene ring is bonded to C (double bond), C (double bond), C (single bond). So, effectively C bonded to C, C, C.
  - iii. $CN$ (Cyano group, $-C \equiv N$) - C is triple bonded to N. Treated as C bonded to N, N, N.
    - Comparing $Ph$ (C, C, C) vs $CN$ (N, N, N): N (atomic number 7) is higher than C (atomic number 6). So, $CN$ has higher priority than $Ph$.
  - **Correction:** For Phenyl ($C_6H_5$), the carbon directly attached to the chiral center is bonded to two carbons within the ring and one hydrogen. For the purposes of CIP rules, we look at the first atoms directly attached. Phenyl carbon is bonded to C, C, H (and phantom atoms for double bond). Cyano carbon is

bonded to N, N, N (due to triple bond). So N is higher than C. Therefore, CN > Phenyl.

- So, correct order:
  - 1. $Cl$
  - 2. $CN$
  - 3. $Ph$ ($C_6H_5$)
  - 4. $H$ (Atomic number 1) - Lowest priority.

- **R/S assignment:**
  - To assign R/S, we need the 3D orientation. Assuming the lowest priority group ($H$) is pointing away from the viewer (dashed line), then trace from 1 to 2 to 3.
    - If clockwise: R configuration.
    - If counter-clockwise: S configuration.
  - Without a drawing, the R/S configuration cannot be definitively assigned.

(ii) COOH-Cl-H-$NH_2$

- This looks like a list of four groups around a single chiral carbon.
- Let the central chiral carbon be C*.
- The four groups are: $COOH$, $Cl$, $H$, $NH_2$.
- **Priority order (Cahn-Ingold-Prelog rules):**

- ii. $Cl$ (Atomic number 17) - Highest priority.
- iii. $NH_2$ (Amino group, $-NH_2$) - N (Atomic number 7)
- iv. $COOH$ (Carboxyl group, $-COOH$) - C double bonded to O, single bonded to O, single bonded to H. Treated as C bonded to O, O, O.
- v. $H$ (Atomic number 1) - Lowest priority.

- **R/S assignment:**
  - To assign R/S, we need the 3D orientation. Assuming the lowest priority group ($H$) is pointing away from the viewer (dashed line), then trace from 1 to 2 to 3.
    - If clockwise: R configuration.
    - If counter-clockwise: S configuration.
  - Without a drawing, the R/S configuration cannot be definitively assigned.

(iii) $CH{=}CH_2\text{-}O_2N\text{-}NH_2\text{-}CONH_2$

- This also looks like a list of four groups around a single chiral carbon.
- Let the central chiral carbon be C*.
- The four groups are: $CH = CH_2$ (Vinyl group), $NO_2$ (Nitro group), $NH_2$ (Amino group), $CONH_2$ (Amide group).
- **Priority order (Cahn-Ingold-Prelog rules):**

iii. $NO_2$ (Nitro group, $-NO_2$) - N bonded to O, O (and double bond to O, so N bonded to O, O, O in CIP terms). O (atomic number 8) is higher than C (atomic number 6) or N (atomic number 7, in $NH_2$ or $CONH_2$).

- iv. $CONH_2$ (Amide group, $-CONH_2$) - C double bonded to O, single bonded to N, single bonded to H. Treated as C bonded to O, N, O (since O is double bonded, it counts twice).
- v. $NH_2$ (Amino group, $-NH_2$) - N (atomic number 7).
- vi. $CH=CH_2$ (Vinyl group, $-CH=CH_2$) - C bonded to C, H, H (C double bonded to C, so effectively C bonded to C, C, H).



- **Re-evaluating based on CIP rules carefully:**
  - $NO_2$**:** N directly attached to chiral center. N is bonded to 2 O atoms (one double bond counts as 2 single bonds). So N is bonded to (O, O, O). Atomic number of O is 8.
  - $CONH_2$**:** C directly attached to chiral center. C is bonded to O (double bond, so O, O), N, H. So C is bonded to (O, O, N). Atomic number of O is 8, N is 7.
  - $NH_2$**:** N directly attached to chiral center. N is bonded to H, H.
  - $CH=CH_2$**:** C directly attached to chiral center. C is bonded to C (double bond, so C, C), H. So C is bonded to (C, C, H).
- **Comparing the first atoms (and phantom atoms from multiple bonds):**

  - $NO_2$: N (O, O, O) - O is highest atomic number so far.
  - $CONH_2$: C (O, O, N) - O is highest atomic number.
  - $NH_2$: N (H, H)
  - $CH = CH_2$: C (C, C, H)
- This means $NO_2$ is not necessarily highest. We compare the first atom and then what it's attached to in order of decreasing atomic number.
- Let's list the direct atoms: N ($NO_2$), C ($CONH_2$), N ($NH_2$), C ($CH = CH_2$).
- Between N and C: N (atomic number 7) > C (atomic number 6).
- So $NO_2$ and $NH_2$ are higher than $CONH_2$ and $CH = CH_2$.
- **Now compare $NO_2$ and $NH_2$:**
  - $NO_2$: N is attached to (O, O, O).
  - $NH_2$: N is attached to (H, H, phantom atom).
  - O (atomic number 8) > H (atomic number 1). So $NO_2$ has higher priority than $NH_2$.
  - Therefore, 1. $NO_2$. 2. $NH_2$.
- **Now compare $CONH_2$ and $CH = CH_2$:**
  - $CONH_2$: C is attached to (O, O, N).
  - $CH = CH_2$: C is attached to (C, C, H).
  - O (atomic number 8) > C (atomic number 6). So $CONH_2$ has higher priority than $CH = CH_2$.
  - Therefore, 3. $CONH_2$. 4. $CH = CH_2$.
- **Final Priority Order:**

- iv. $NO_2$
- v. $NH_2$
- vi. $CONH_2$
- vii. $CH = CH_2$

- **R/S assignment:**
  - To assign R/S, we need the 3D orientation. Assuming the lowest priority group ($CH = CH_2$) is pointing away from the viewer (dashed line), then trace from 1 to 2 to 3.
    - If clockwise: R configuration.
    - If counter-clockwise: S configuration.
  - Without a drawing, the R/S configuration cannot be definitively assigned.