

Primary Metabolism

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

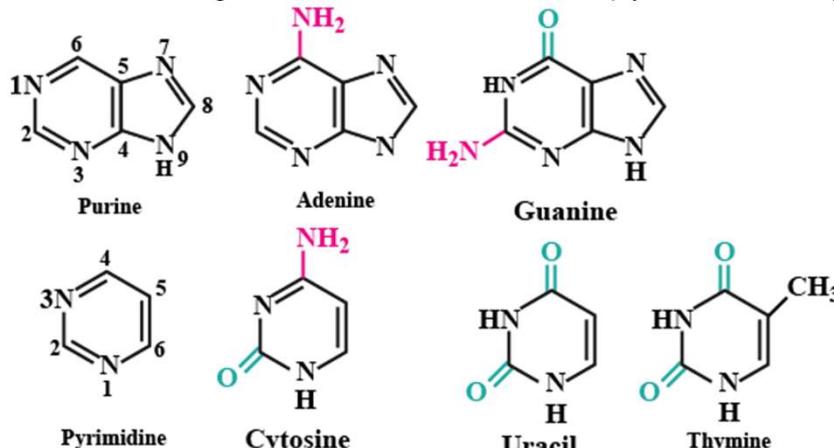
Dept. of Science & Mathematics

IITG, Guwahati

Monomers of Nucleic acids are nucleotides, made of three parts:

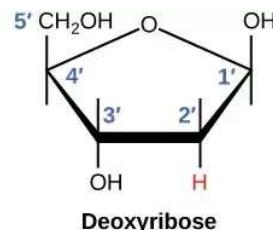
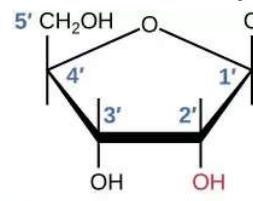
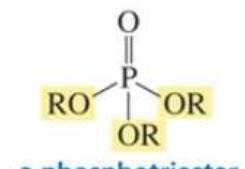
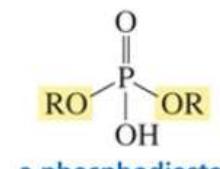
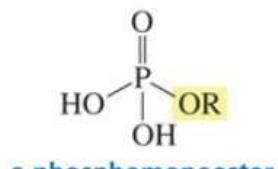
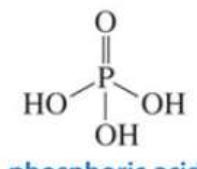
1. A heterocyclic base: substituted purines (adenine and guanine), and substituted pyrimidines (cytosine and thymine).

In RNA, it is uracil instead of thymine.

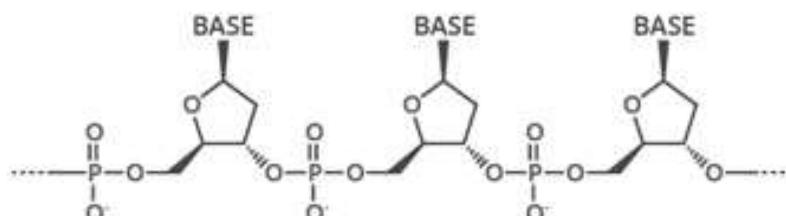


2. A sugar: In RNA the five-membered-ring sugar is D-ribose and in DNA it is 2-deoxy-D-ribose (D-ribose without an OH group in the 2-position).

3. A phosphate ester:



THE SUGAR PHOSPHATE 'BACKBONE'



Course Code: SC202

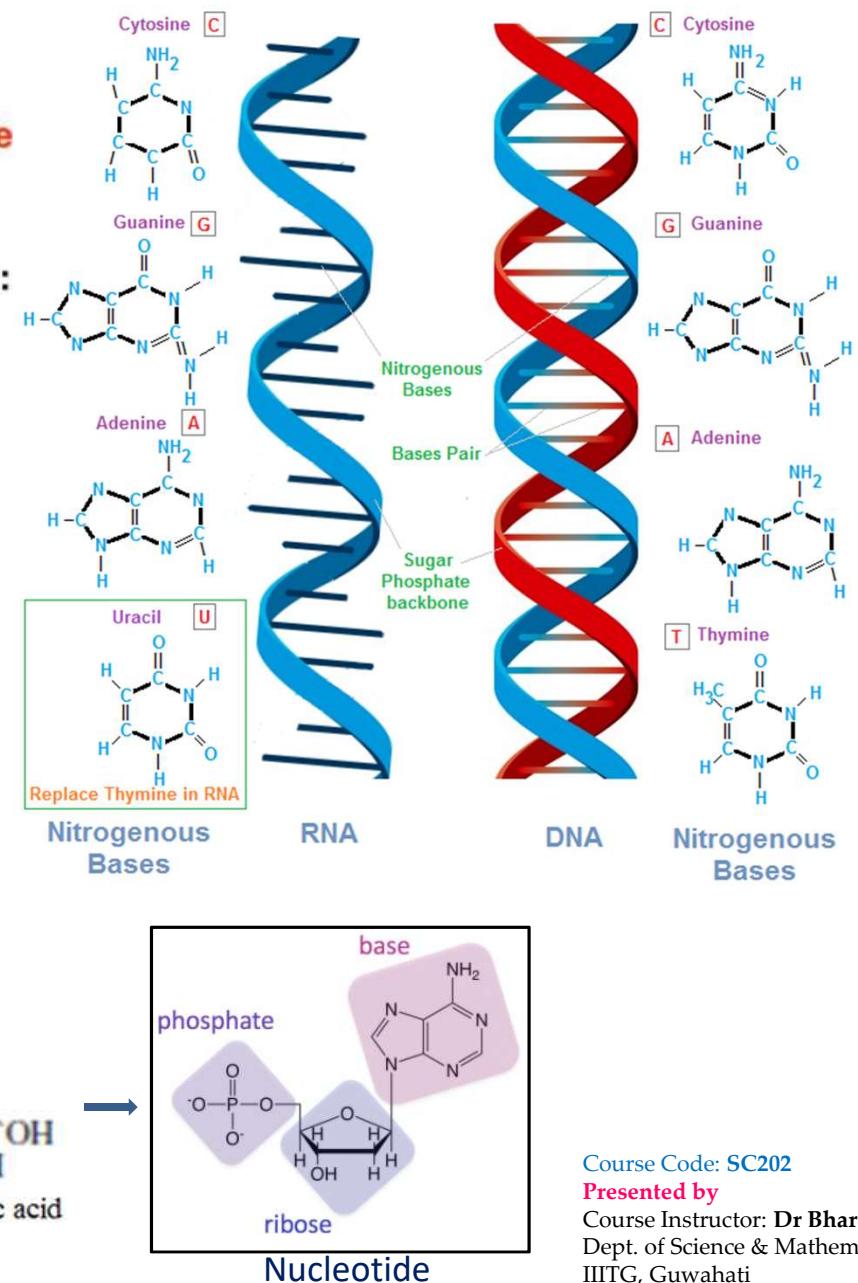
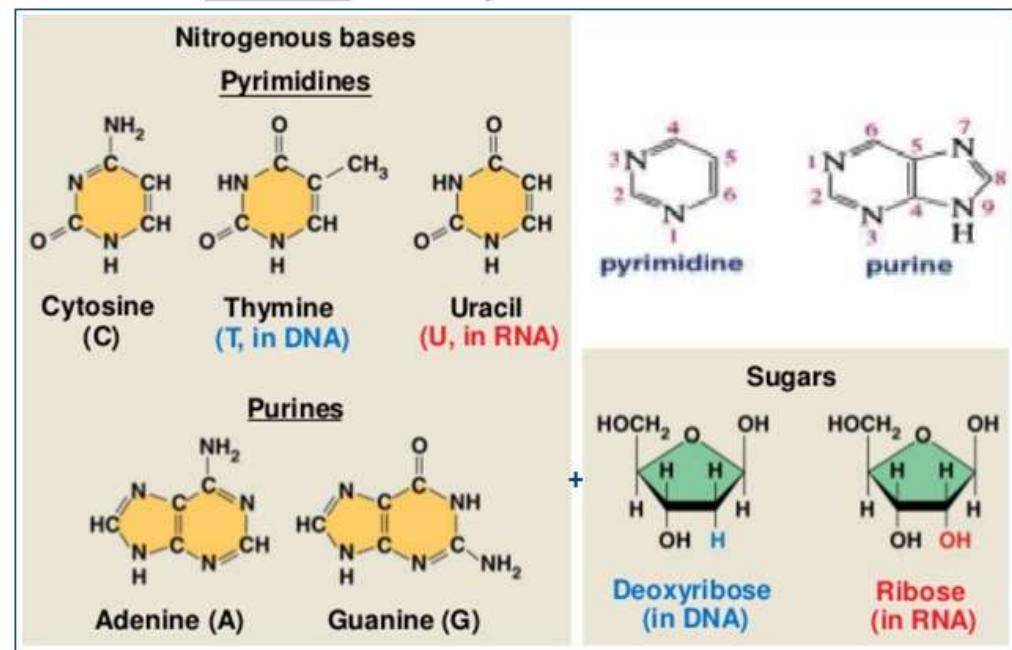
Presented by

Course Instructor: Dr Bhar Sah

Dept. of Science & Mathematics

IITG, Guwahati

- Nucleic acids are polymers of monomers called nucleotides.
- Each nucleotide consists of three parts: a **nitrogen base**, a **pentose sugar**, and a **phosphate group**.
- The nitrogen bases (rings of carbon and nitrogen) come in two types: **Purines** and **Pyrimidines**.
- The pentose sugar joined to the nitrogen base is **ribose** in nucleotides of RNA and **deoxyribose** in DNA.
- The only difference between the sugars is the lack of an oxygen atom on carbon 2 in deoxyribose.



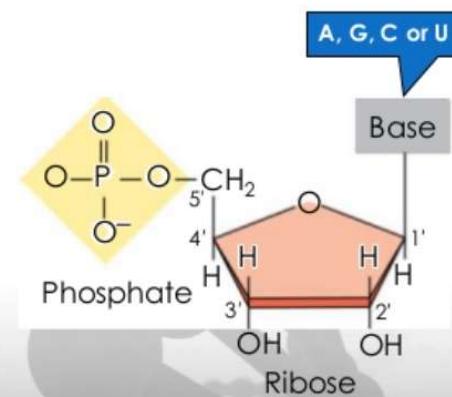
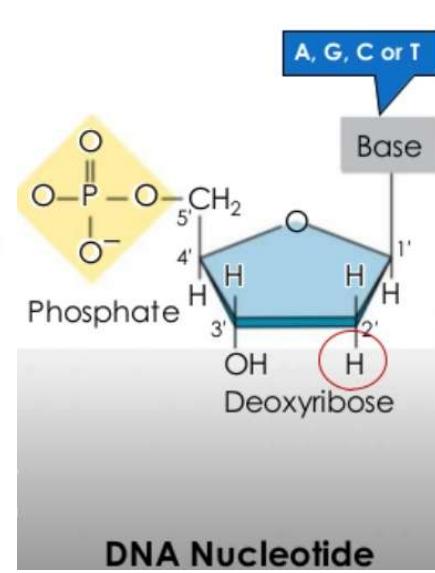
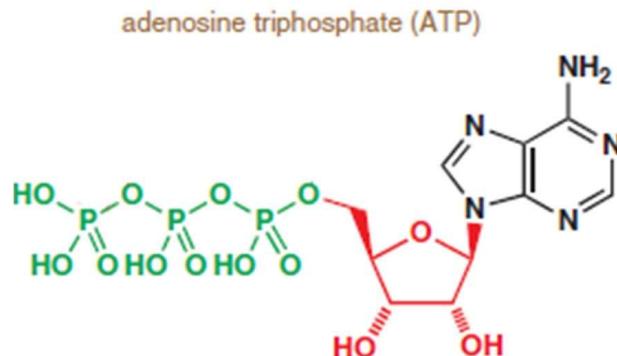
Course Code: SC202
Presented by

Course Instructor: Dr Bhar Sahai
Dept. of Science & Mathematics
IIITG, Guwahati

Nucleic acids exist in 3-D helices comprising chains of five-membered-ring sugars linked by phosphate groups in which the anomeric C of each sugar is bonded to a nitrogen of a heterocyclic amine (base) in a β -glycosidic linkage. (substituents at C-1 and C-4 are on the same side of the furanose ring).

There are two types of nucleic acids— deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA encodes an organism's entire hereditary information and controls the growth and division of cells, which is in turn transcribed into RNA.

Phosphoric acid links the sugars in both RNA and DNA. The acid has three dissociable OH groups with pK_a values of 1.9, 6.7, and 12.4 respectively. Each of the OH groups can react with an alcohol to form a phosphomonoester, a phosphodiester, or a phosphotriester. In nucleic acids the phosphate group is a phosphodiester. The most important nucleotide is adenosine triphosphate or ATP [Energy source, product of respiration].



Course Code: SC202

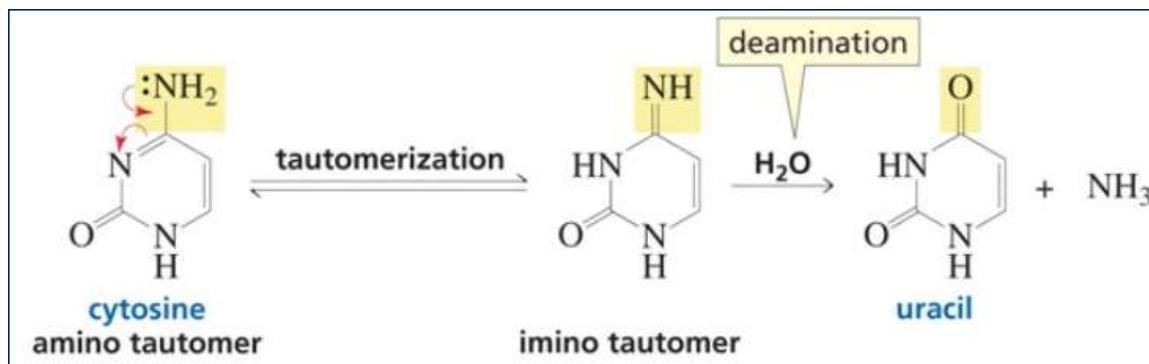
Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

There are four bases in DNA – two substituted purines (adenine and guanine), and two substituted pyrimidines (cytosine and thymine). The fourth base in RNA is uracil instead of thymine. Synthesis of thymine is energetically more expensive than uracil. The presence of thymine in DNA instead of uracil prevents potentially lethal mutations. In DNA, cytosine is readily deaminated, forming uracil.



Imagine that during replication, a C–G base pair separates. If at that moment the C deaminates to U, it would tend to base-pair to A instead of to G. If U were a natural base in DNA, the DNA polymerases would just line up an adenine across from the uracil, and there would be no way to know that the uracil was a mistake. This would lead to a much higher level of mutation during replication. Because uracil is an unnatural base in DNA, DNA polymerases can recognize it as a mistake and can replace it. Thus, the incorporation of thymine into DNA, though energetically more costly, helps ensure that the DNA is replicated faithfully.

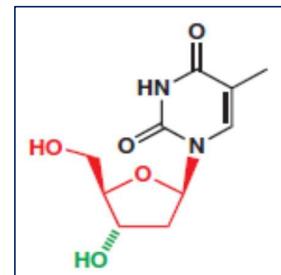
Course Code: SC202

Presented by

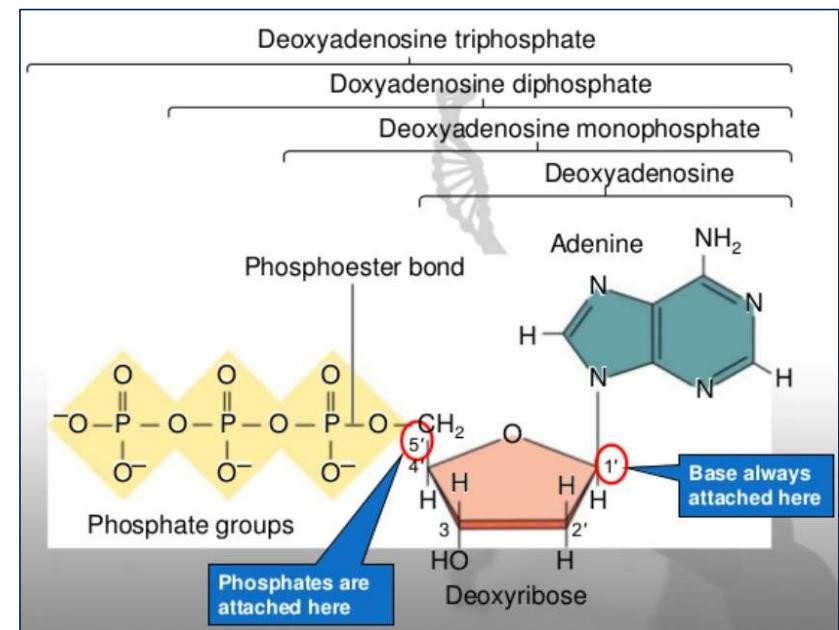
Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IITG, Guwahati

A nucleoside differs from a nucleotide in lacking the phosphate—a nucleoside is just a base and a sugar. The purines and pyrimidines are bonded to the anomeric carbon of the furanose ring—purines at N-9 and pyrimidines at N-1—in a -glycosidic linkage. A compound containing a base bonded to D-ribose or to 2- deoxy-D-ribose is called a nucleoside. The ring positions of the sugar are indicated by primed numbers to distinguish them from the ring positions of the base e.g. 2'-deoxy-D-ribose.

Therefore, **nucleoside=base + sugar**.



BASE	NUCLEOSIDE	NUCLEOTIDE
ADENINE (A)	ADENOSINE	ADENOSINE MONOPHOSPHATE (AMP)
GUANINE (G)	GUANOSINE	GUANOSINE MONOPHOSPHATE (GMP)
XANTHINE (X)	XANTHOSINE	XANTHOSINE MONOPHOSPHATE (XMP)
HYPOXANTHINE (I)	INOSINE	INOSINE MONOPHOSPHATE (IMP)
CYTOSINE (C)	CYTIDINE	CYTIDINE MONOPHOSPHATE (CMP)
URACIL (U)	URIDINE	URIDINE MONOPHOSPHATE (UMP)
THYMINE (T)	THYMIDINE	THYMIDINE MONOPHOSPHATE



Course Code: SC202

Presented by

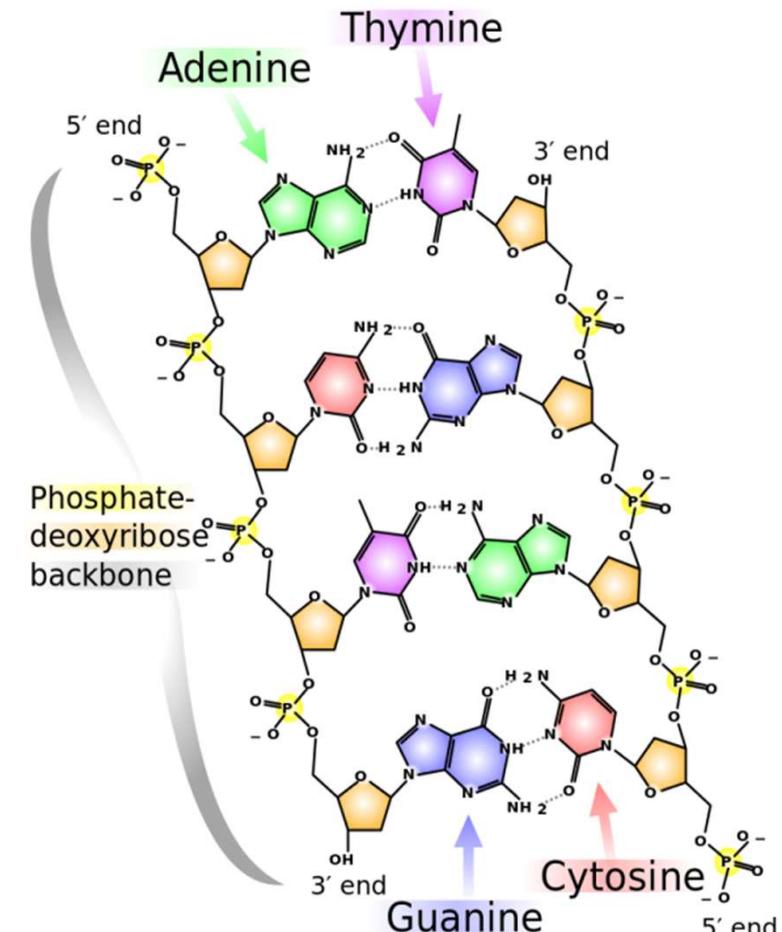
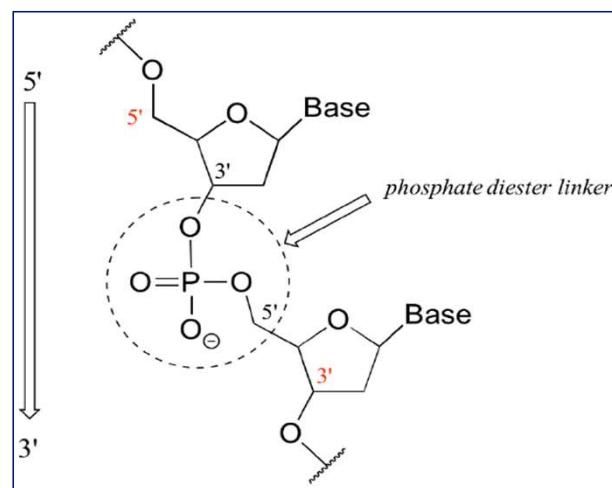
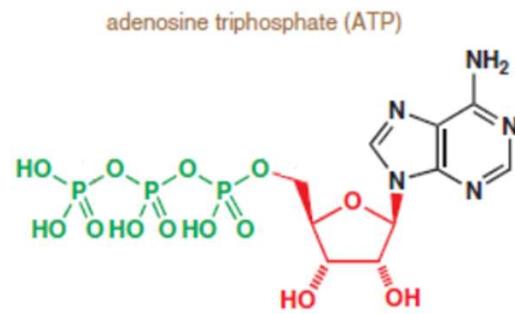
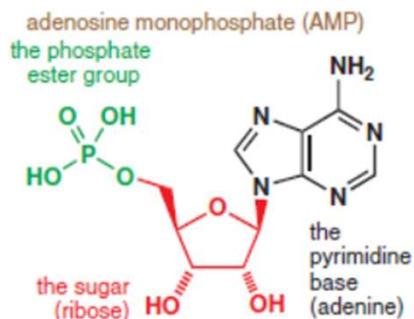
Course Instructor: Dr Bhar Sah

Dept. of Science & Mathematics

IITG, Guwahati

A nucleotide is a nucleoside with either the 5' or the 3'-OH group bonded in an ester linkage to phosphoric acid. The nucleotides of RNA—where the sugar is D-ribose—are more precisely called ribonucleotides, whereas the nucleotides of DNA—where the sugar is 2-deoxy-D-ribose—are called deoxyribonucleotides.

Therefore, Nucleotide = base + sugar + phosphate.



Course Code: SC202

Presented by

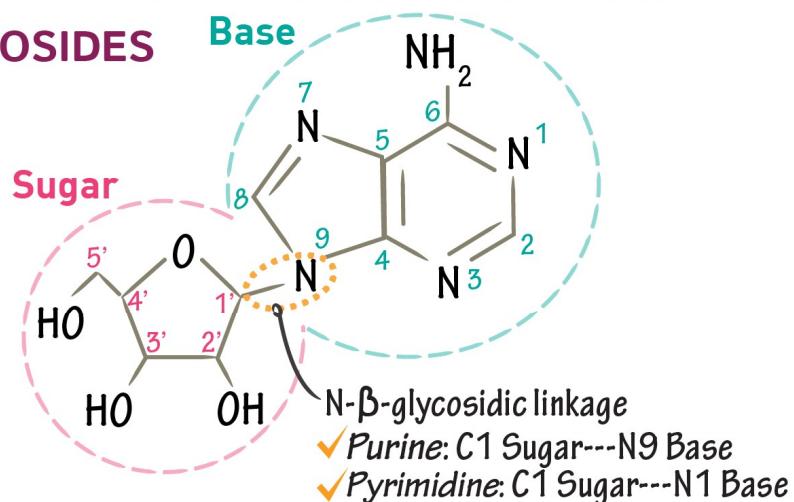
Course Instructor: Dr Bhar Sah

Dept. of Science & Mathematics

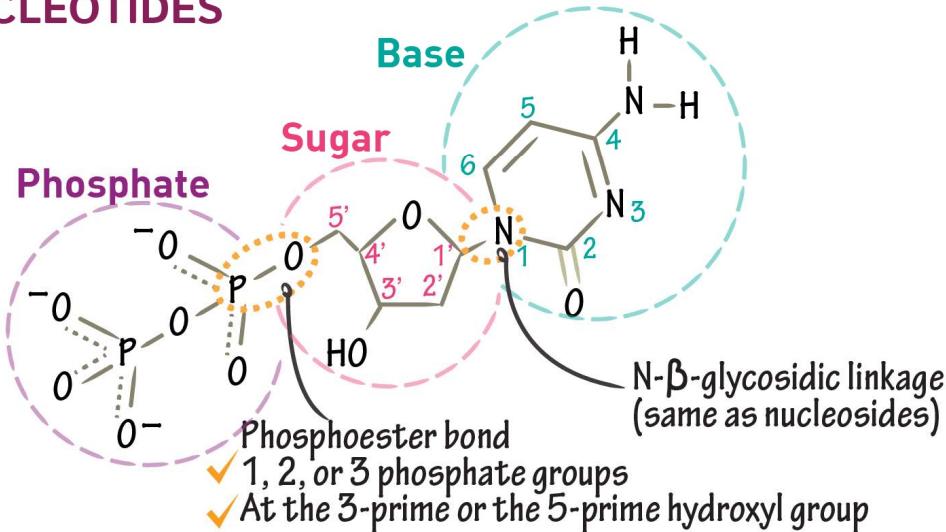
IITG, Guwahati

Nucleosides vs. Nucleotides

NUCLEOSIDES



NUCLEOTIDES



Course Code: SC202

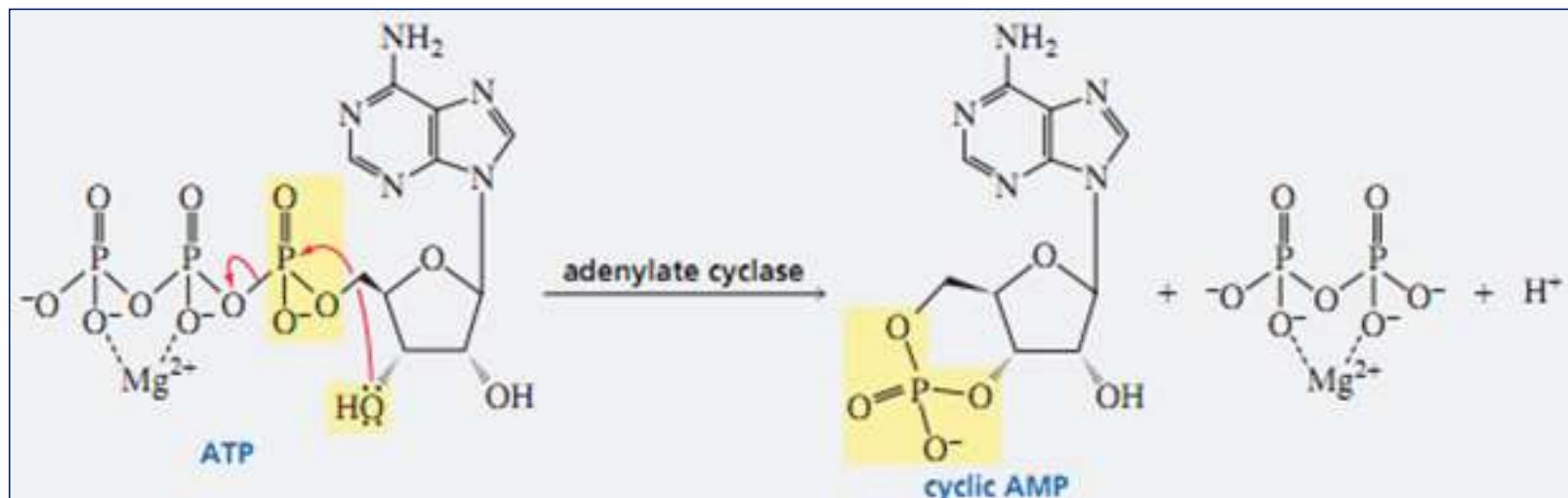
Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Cyclic AMP



cAMP or Cyclic AMP, present in all life forms, plays an important role as a second messenger as it serves as a link between more than 20 different hormones and enzymes regulating cellular functions

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Nucleic acids are the fundamental units of information transfer in biological systems. They are biopolymers comprised of nucleotide monomers, and store information for cellular growth and reproduction.

There are two types of Nucleic acids:

Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA).

DNA is of 3 types: A-DNA, B-DNA, Z-DNA.

RNA is of 3 types: messenger RNA (mRNA), ribosomal RNA (rRNA), and tRNA

Functions:

DNA:

Genetic information (DNA) \Rightarrow mRNA \Rightarrow proteins

- *for information storage, It is Double stranded (double helix), contains β -2-deoxy-D-ribose as its sugar unit.*
- *Energy Transfer in the form of*
 - *ATP (adenosine triphosphate)*
 - *NAD (Nicotinamide adenine dinucleotide)*

RNA: role in protein synthesis, Single stranded, contains D-ribose as its sugar unit.

It delivers instructions from DNA to ribosome

Course Code: SC202

Presented by

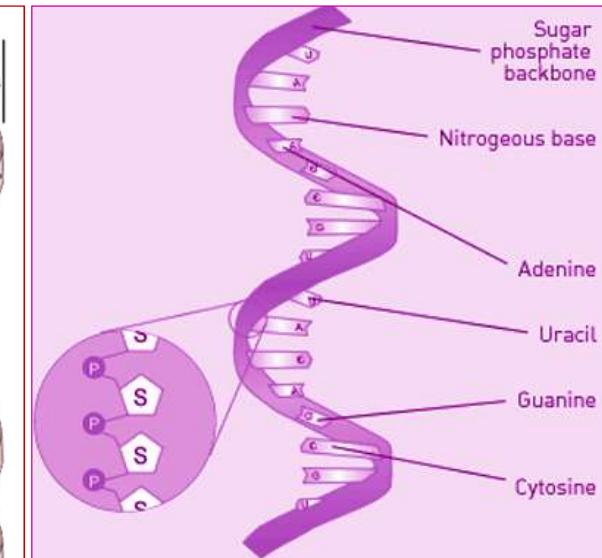
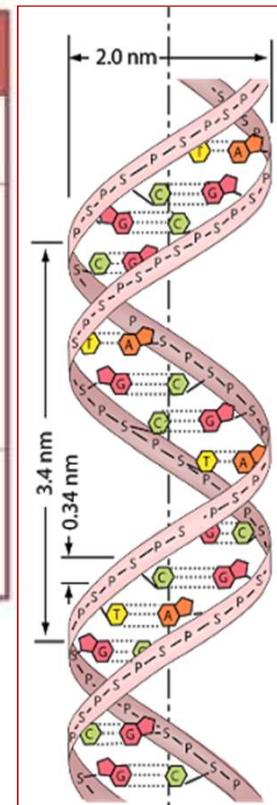
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

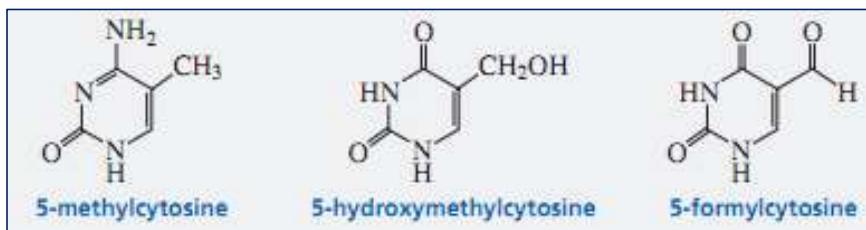
Differences between DNA and RNA

	DNA	RNA
Pentose sugar	Deoxyribose	Ribose
Base Composition	Adenine (A) Guanine (G) Cytosine (C) Thymine (T)	Adenine (A) Guanine (G) Cytosine (C) Uracil (U)
Number of strands	Double stranded (forms a double helix)	Single stranded



RNA

Rare bases found in DNA



DNA

Course Code: SC202

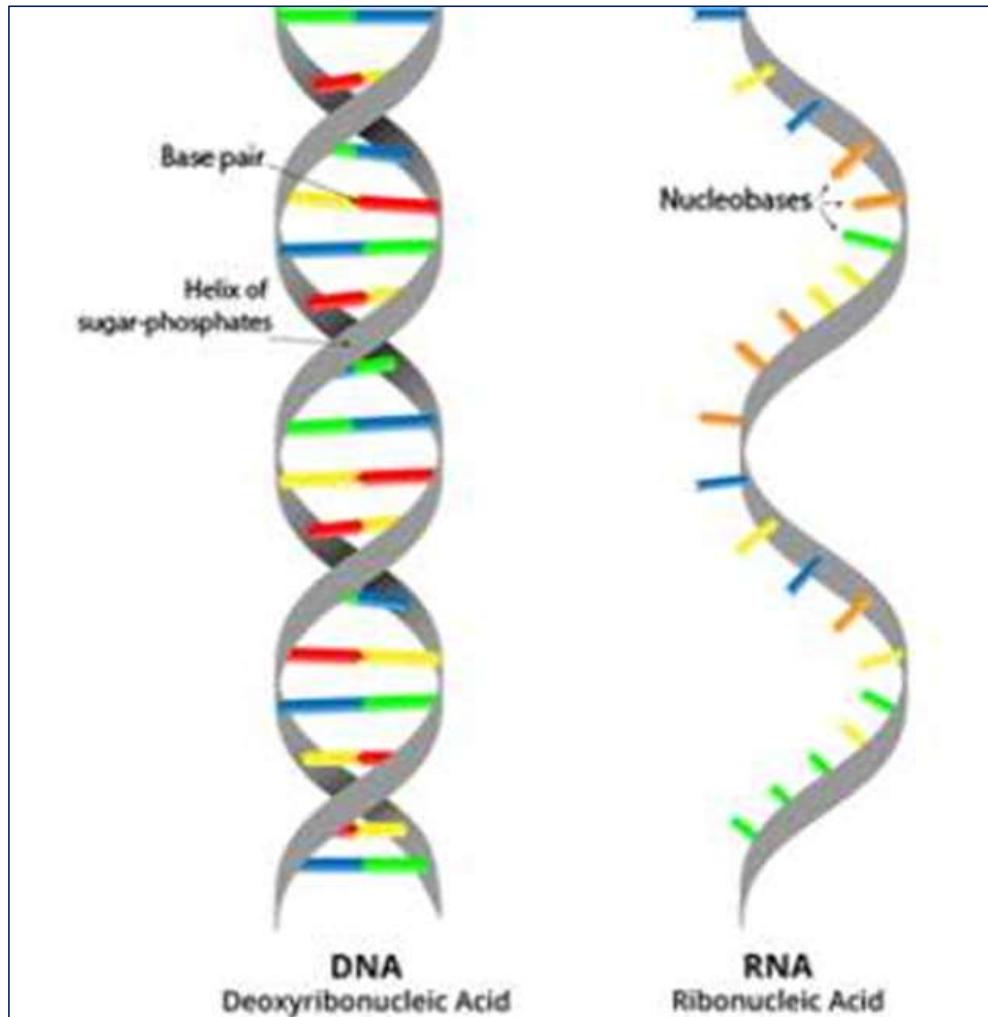
Presented by

Course Instructor: Dr Bhar Sah

Dept. of Science & Mathematics

IITG, Guwahati

Structural Differences



Course Code: SC202

Presented by

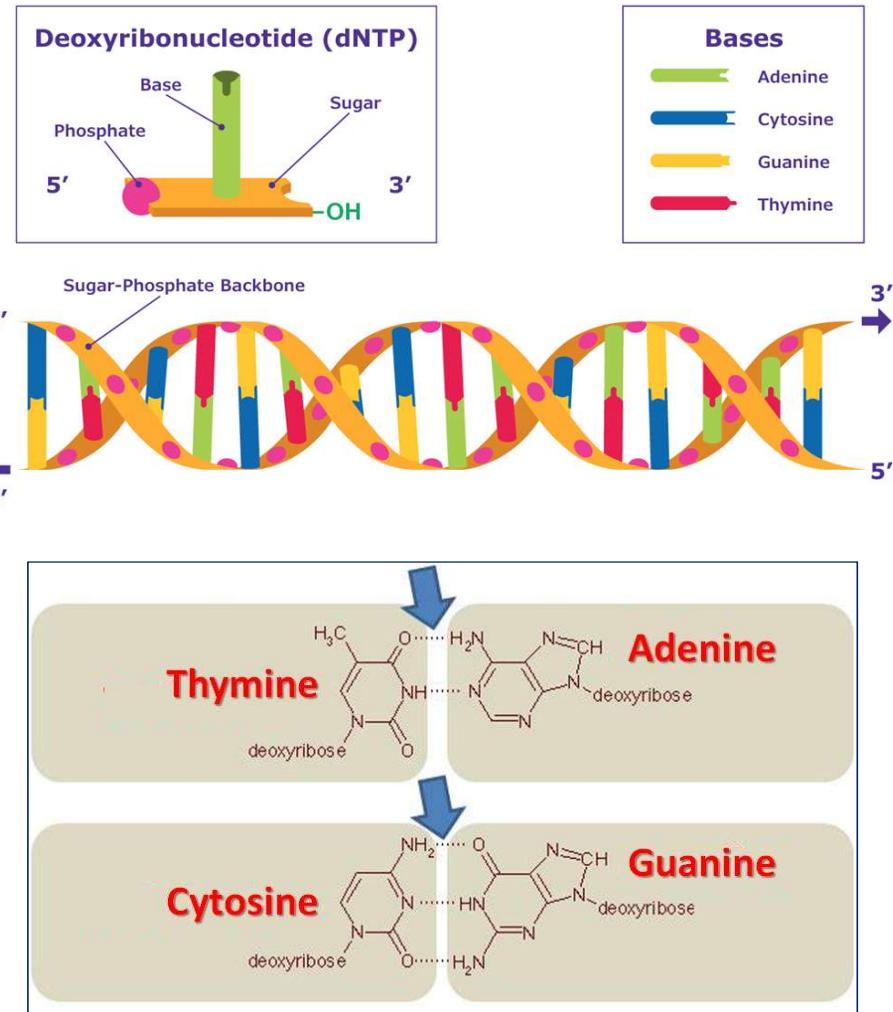
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Salient features of Double-helix structure of DNA:

- It is made up of two polynucleotide chains with a sugar-phosphate backbone, and bases projecting inwards.
- The two chains have anti-parallel polarity: if one chain has polarity 5'→3', the other has 3'→5'
- the planar nitrogenous bases from the two strands are pointing toward each other, in the middle of the helix.
- Pairs of nitrogenous bases are set in the same plane, and interact with each other via hydrogen bonding. These pairs are often referred to as base pairs, abbreviated 'bp.' [A-T: 2 H bonds; G-C: 3 H bonds]
- Chargaff's Rule: Ratios between Adenine & Thymine; Guanine & Cytosine are constant and equal one.
- Heating to about 95°C causes the strands to separate [denaturation]



Course Code: SC202

Presented by

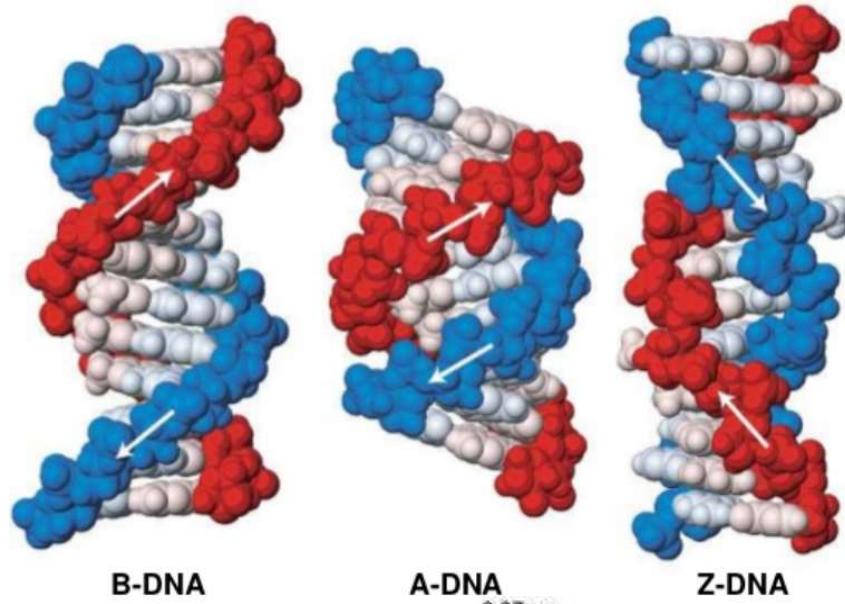
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Important features of A-, B- and Z-DNA

	A-DNA	B-DNA	Z-DNA
Diameter	2.3 nm	2.0 nm	1.8 nm
Rise per turn (pitch)	2.7 nm	3.4 nm	4.4 nm
Rise per base pair	0.25 nm	0.34 nm	0.37 nm
Number of base pairs per turn	11	10	12
Glycosidic bond	<i>syn</i>	<i>anti</i>	<i>syn</i> (purines) <i>anti</i> (pyrimidines)
Major groove	Narrow	Wide	Flat
Minor groove	Wide	Narrow	Very narrow
Direction of helix	Right-handed	Right-handed	Left-handed

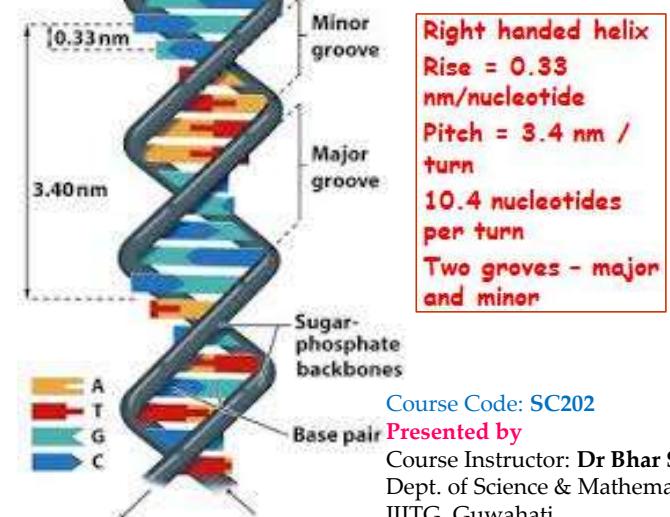


B-DNA \Leftrightarrow Watson and Crick model. *Most common*

A-DNA \Leftrightarrow right-handed double helix wider and shorter than B-form. 11 pb per turn and 26 Å diameter. It is present when the relative humidity is reduced up to 75%.

On dehydration

Z-DNA \Leftrightarrow left-handed double helix. 12 pb per turn and 18 Å diameter. Dinucleotide(XpYp). *In high salt concentrations*



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Sah
Dept. of Science & Mathematics
IITG, Guwahati

Right handed helix
Rise = 0.33 nm/nucleotide
Pitch = 3.4 nm / turn
10.4 nucleotides per turn
Two grooves - major and minor

Distance between the 2 sugar-phosphate backbones is always the same, giving DNA molecule a regular shape.

Plane of bases are oriented perpendicular to backbone

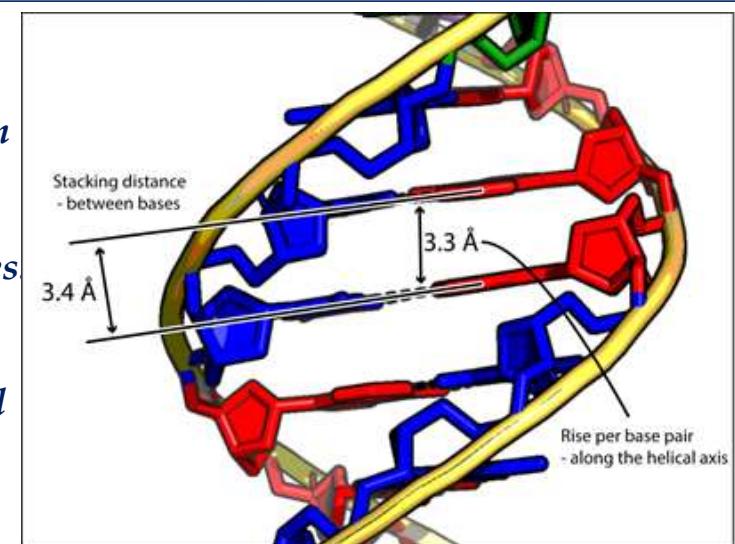
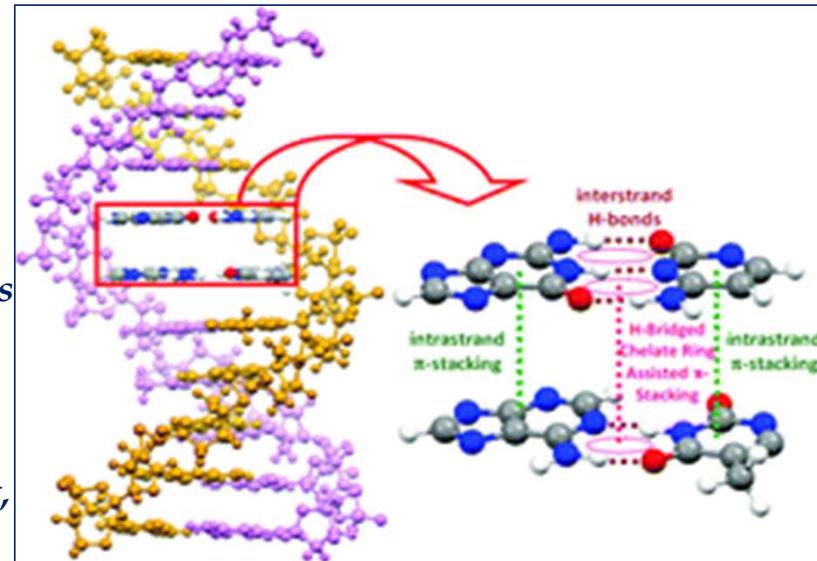
Hydrophilic sugar phosphate backbone winds around outside of helix

Noncovalent interactions between upper and lower surfaces of base-pairs (stacking) forms a closely packed hydrophobic interior.

Hydrophobic environment makes H-bonding between bases stronger (no competition with water) & cause the sugar-phosphate backbone to twist, stabilizing the 3-D structure of the nucleic acids

Thus, factors stabilizing DNA double Helix:

- ✓ *Hydrophobic interactions – burying hydrophobic purine, pyrimidine rings in interior*
- ✓ *π - Stacking interactions – van der Waals interactions between stacked bases*
- ✓ *Hydrogen Bonding – H-bonding between bases*
- ✓ *Charge-Charge Interactions – Electrostatic repulsions of negatively charged phosphate groups are minimized by interaction with cations (e.g. Mg^{2+})*
- ✓ *Base orientation inwards in the helix reduces surface area of non-polar residues exposed to water molecules, thereby increasing entropy of the latter*



Course Code: SC202

Presented by

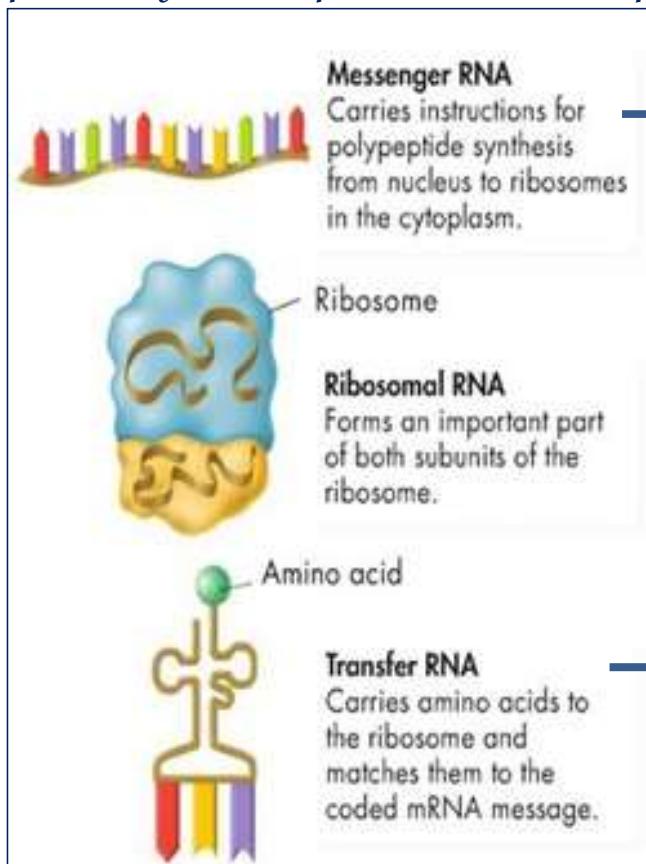
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

There are three important types of RNA in living systems:

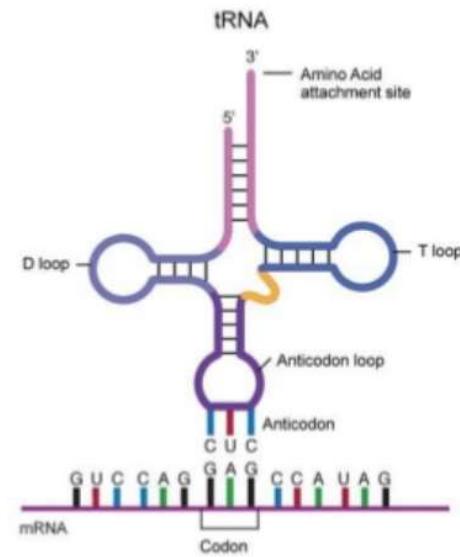
- *Messenger RNA carries genetic information from DNA to ribosomes for the synthesis of proteins (template: sequence of bases determining sequence of amino acids in proteins).*
- *Transfer RNA brings amino acids to the mRNA (carrier: delivering the proper amino acid at the right time)*
- *Ribosomal RNA is the RNA component of the ribosome where proteins are synthesized in the cell (site of protein synthesis: particles on which protein biosynthesis takes place from N- to C-terminal end).*



Contain protein coding information

- ATG start codon to UAA, UAG, UGA Stop Codon
- A cistron is the unit of RNA that encodes one polypeptide chain

- There are 20 different tRNAs, one for each amino acid.
- A particular amino acid is attached to the tRNA by an ester linkage involving the carboxyl group of the amino acid and the 3' oxygen of the tRNA.



Types of RNA

mRNA

"messenger"

made using DNA

carries genetic info
from the nucleus to
the ribosome

every 3 bases
(codon) specifies
an amino acid

tRNA

"transfer"

transfers an amino
acid to the growing
protein

cloverleaf shape

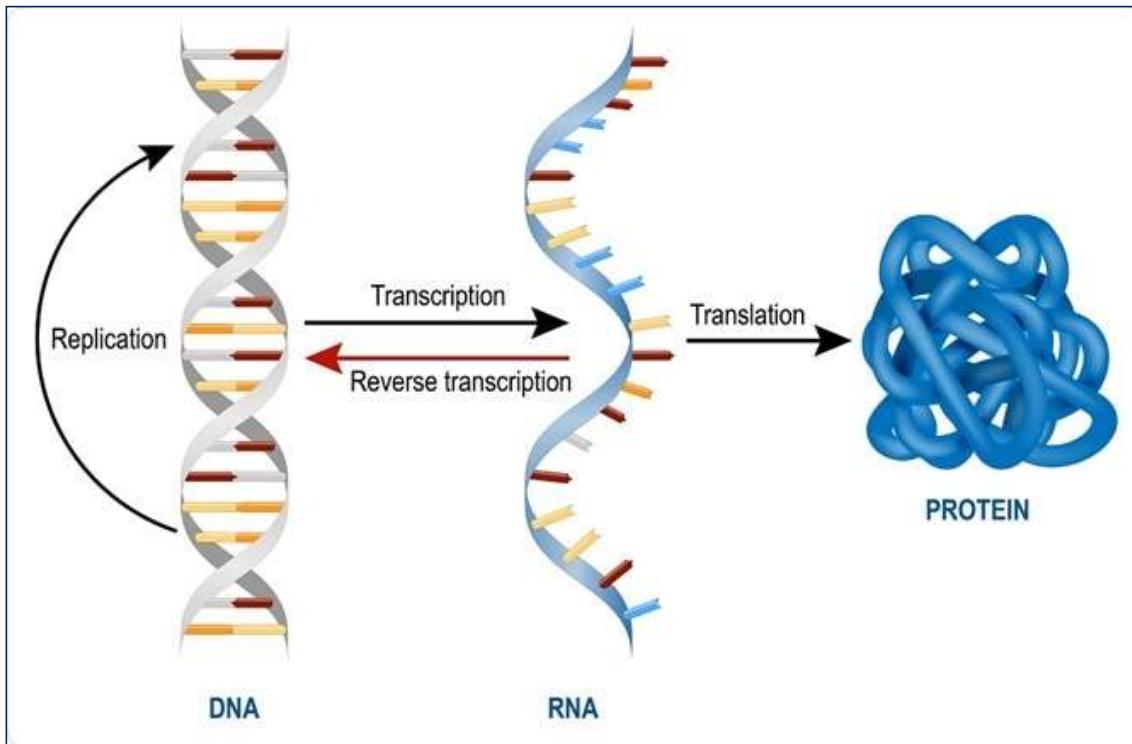
3 complimentary
bases (anticodon)
binds to the mRNA
codon

rRNA

"ribosomal"

makes up the
bulk of ribosomes

Relation between DNA and RNA



The sequence of bases in DNA provides a blueprint for the synthesis of RNA; the synthesis of RNA from a DNA blueprint is called **transcription**

The sequence of bases in RNA determines the sequence of amino acids in a protein; the synthesis of a protein from an RNA blueprint is called **translation**



An enzyme, RNA polymerase, transcribes DNA into mRNA (messenger ribonucleic acid). It splits apart the two strands that form the double helix, then reads a strand and copies the sequence of nucleotides. The only difference between the RNA and the original DNA is that in the place of thymine (T), another base with a similar structure is used: uracil (U).

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati



In multicellular organisms, the mRNA carries genetic code out of the cell nucleus, to the cytoplasm. Here, protein synthesis takes place. 'Translation' is the process of turning the mRNA's 'code' into proteins. Molecules called ribosomes carry out this process, building up proteins from the amino acids coded for.

Thus biosynthesis of proteins is called translation. A codon is a sequence of three DNA or RNA nucleotides that corresponds with a specific amino acid or stop signal during protein synthesis. DNA and RNA molecules are written in a language of four nucleotides; meanwhile, the language of proteins includes 20 amino acids. Codons provide the key that allows these two languages to be translated into each other. Each codon corresponds to a single amino acid (or stop signal), and the full set of codons is called the genetic code. The genetic code includes 64 possible permutations, or combinations, of three-letter nucleotide sequences that can be made from the four nucleotides. Of the 64 codons, 61 represent amino acids, and three are stop signals. For example, the codon CAG represents the amino acid glutamine, and TAA is a stop codon. The genetic code is described as degenerate, or redundant, because a single amino acid may be coded for by more than one codon. When codons are read from the nucleotide sequence, they are read in succession and do not overlap with one another.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

RNA codon table

1st position	2nd position				3rd position
	U	C	A	G	
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	stop	stop	A
	Leu	Ser	stop	Trp	G
	Leu	Pro	His	Arg	U
C	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
	Met	Thr	Asn	Ser	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G
Amino Acids					

Ala: Alanine
 Arg: Arginine
 Asn: Asparagine
 Asp: Aspartic acid
 Cys: Cysteine

Gln: Glutamine
 Glu: Glutamic acid
 Gly: Glycine
 His: Histidine
 Ile: Isoleucine

Leu: Leucine
 Lys: Lysine
 Met: Methionine
 Phe: Phenylalanine
 Pro: Proline

Ser: Serine
 Thr: Threonine
 Trp: Tryptophane
 Tyr: Tyrosine
 Val: Valine

- A **codon** is a **triplet** of bases along the mRNA that codes for a particular amino acid
- Each of the 20 amino acids needed to build a protein has at least 2 codons
- There are also codons that signal the “start” and “end” of a polypeptide chain
- The amino acid sequence of a protein can be determined by reading the triplets in the DNA sequence that are complementary to the codons of the mRNA, or directly from the mRNA sequence

Course Code: SC202

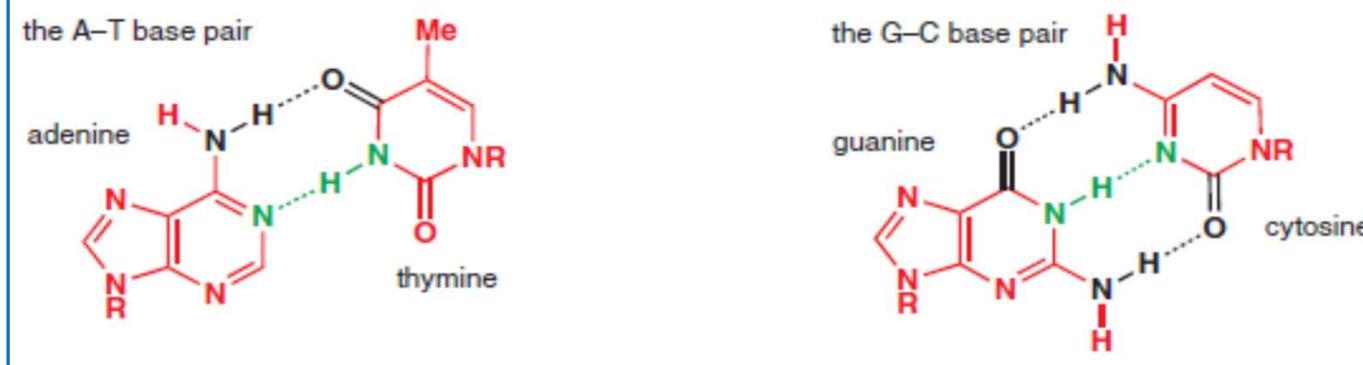
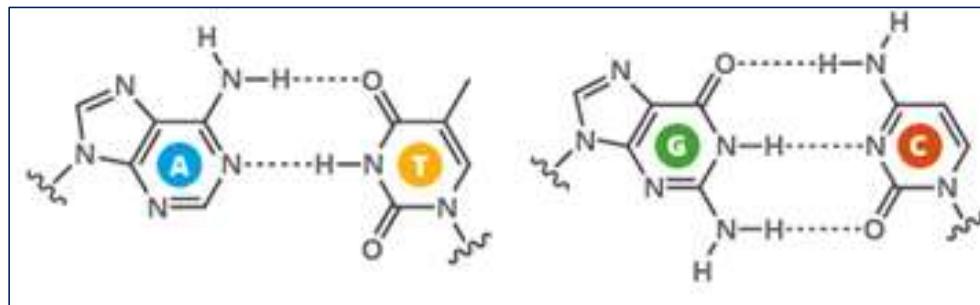
Presented by

Course Instructor: Dr Bhar Saha
 Dept. of Science & Mathematics
 IIITG, Guwahati

Stop codons tell the cell to “stop protein synthesis here”

Each polymeric strand of DNA coils up into a helix and is bonded to another strand by hydrogen bonds between the bases. Each base pairs up specifically with another base — adenine with thymine (A-T) and guanine with cytosine (G-C). Each purine (A or G) is bonded to a specific pyrimidine (T or C) by two-three hydrogen bonds. [Chargaff's Rule]

The hydrogen bonds are of two kinds: one links **an amine to a carbonyl group** and one links **an amine to an imine**. A purine has to pair with a pyrimidine because only a combination of larger purine and smaller pyrimidine can bridge the gap between the nucleic acid coils. In this way, each nucleotide recognizes another and reliably pairs with its partner.



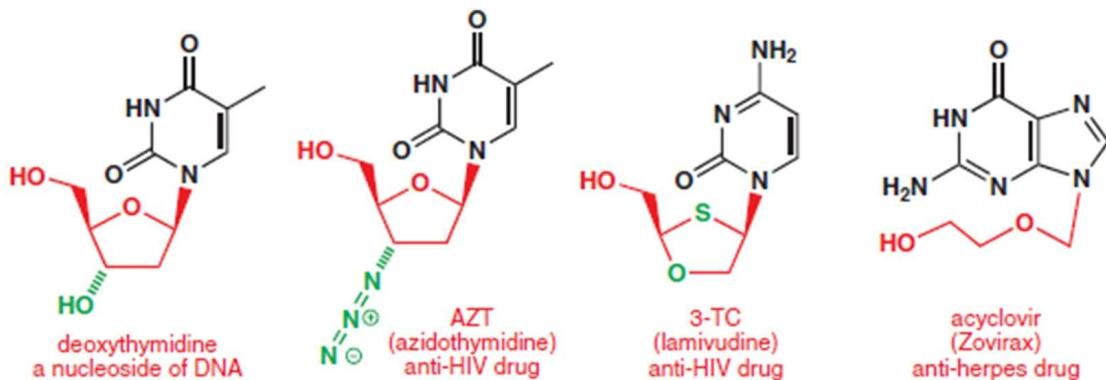
Course Code: SC202
Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

DNA is more stable than RNA because its sugars lack the 2' hydroxyl groups. In ribonucleic acids, since the 2'- and 3'-OH groups are on the same side of the ring, alkaline hydrolysis is extremely rapid by intramolecular nucleophilic catalysis.

Modified nucleosides are used as antiviral compounds to treat diseases like HIV & AIDS.

The anti-HIV drug AZT (zidovudine) is a slightly modified DNA nucleoside (3'-azidothymidine). It has an azide at C-3' instead of the hydroxyl group in the natural nucleoside.



Course Code: SC202

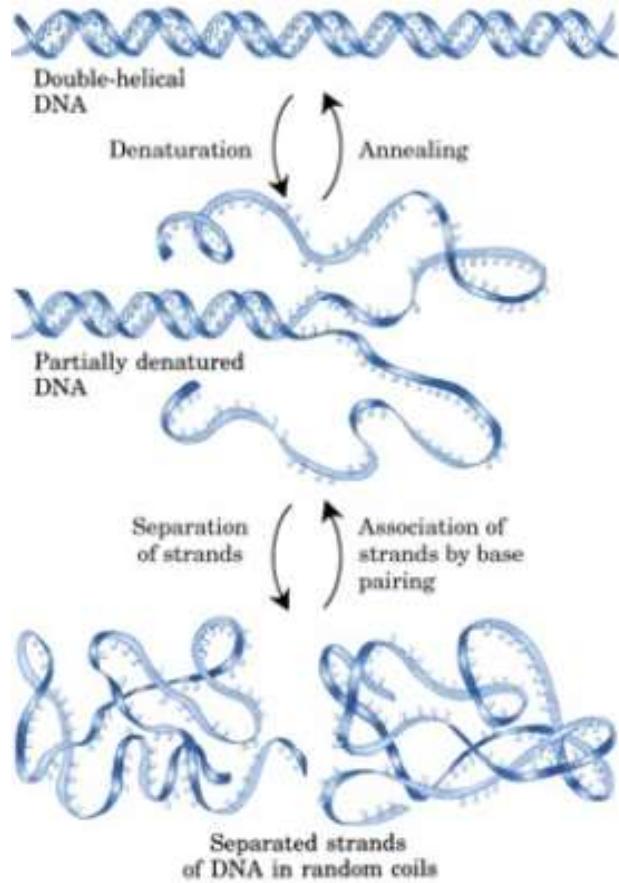
Presented by

Course Instructor: Dr Bhar Saha

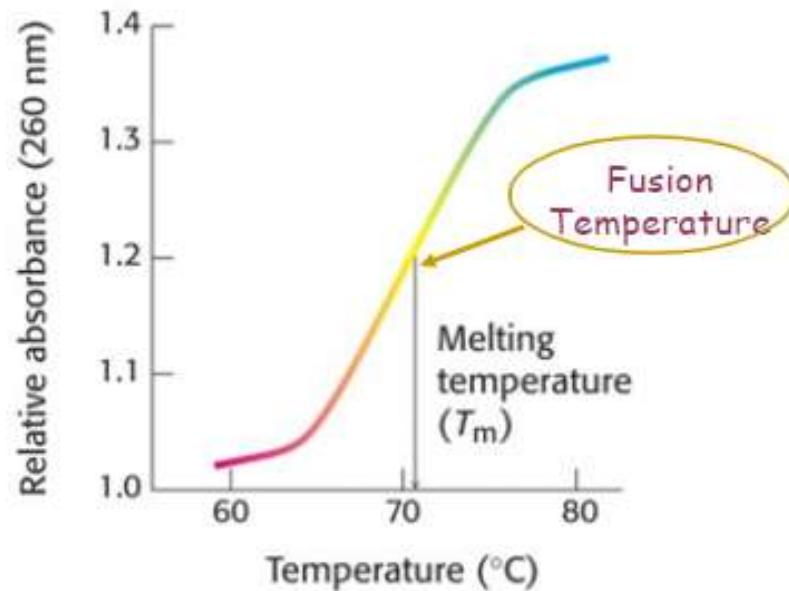
Dept. of Science & Mathematics

IITG, Guwahati

PHYSICO-CHEMICAL PROPERTIES OF THE NUCLEIC ACIDS



- T_m depends on the bases composition.
- T_m (high % G+C) > T_m (high % A+T).



- Separation of the strands → increase of the A_{260} $\Leftrightarrow \Leftrightarrow$ HYPERCHROMIC EFFECT

Course Code: SC202

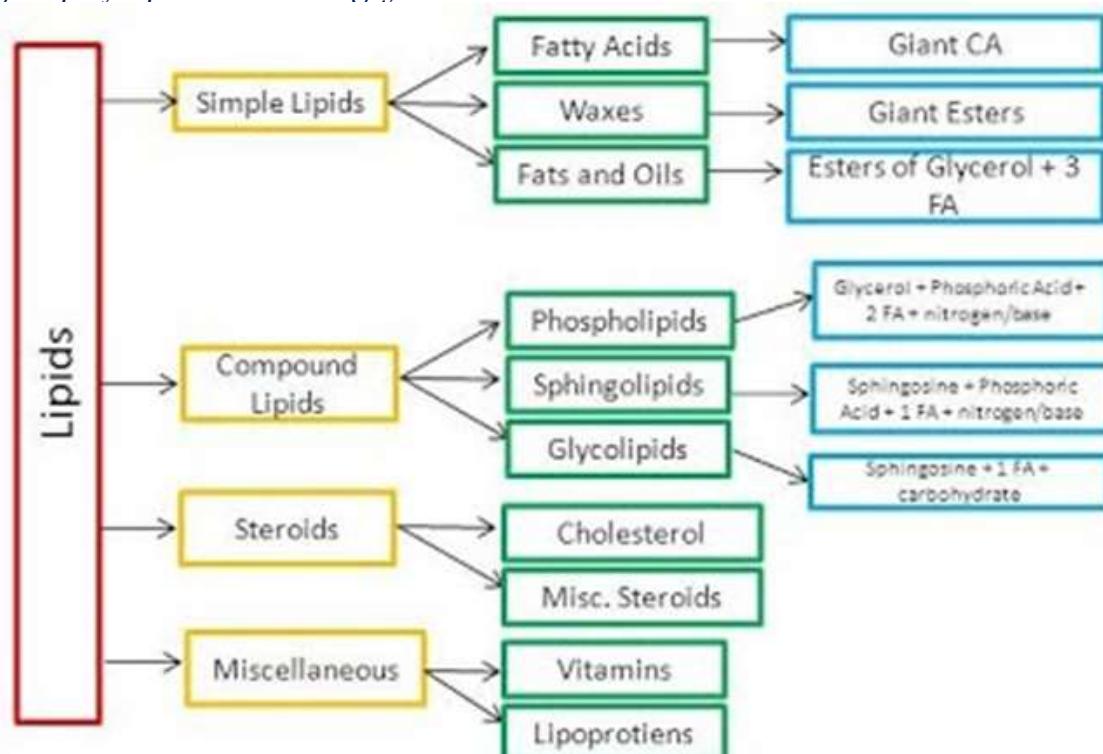
Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Lipids are the principal components of cell membranes which function as selective barriers to the movement of molecules. Lipids comprise a group of naturally occurring molecules that include fats, waxes, sterols, fat-soluble vitamins (such as vitamins A, D, E, and K), glycerides and phospholipids, and other non-glycerol based molecules having similar function. The main biological functions of lipids include storing energy, signalling, and acting as structural components of cell membranes. Fats are a subgroup of lipids called triglycerides.



Lipids may be regarded as organic substances relatively insoluble in water, soluble in organic solvents, potentially related to fatty acids and utilized by the living cells.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Lipid Functions

Bile acids	Steroids that aid in fat digestion and nutrient absorption
Cholesterol	Component of cell membranes; precursor of other steroids
Eicosanoids	Chemical messengers between cells
Fat-soluble vitamins (A, D, E, and K)	Involved in a variety of functions including blood clotting, wound healing, vision, and calcium absorption
Fatty acids	Precursor of triglycerides; source of energy
Phospholipids	Major component of cell membranes; aid in fat digestion
Steroid hormones	Chemical messengers between cells
Triglycerides	Energy storage; thermal insulation; filling space; binding organs together; cushioning organs

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Simple Lipids

The simple lipids include fats, oils, and waxes. These simple lipids are derivatives of lipid-like substances called fatty acids.

Fatty acids are long-chain carboxylic acids (*generally greater than about 12 carbons*) that have no solubility in water.

The hydrophilic -COOH group is referred to as a polar head and the hydrophobic hydrocarbon portion is referred to as a nonpolar tail.

Course Code: SC202

Presented by

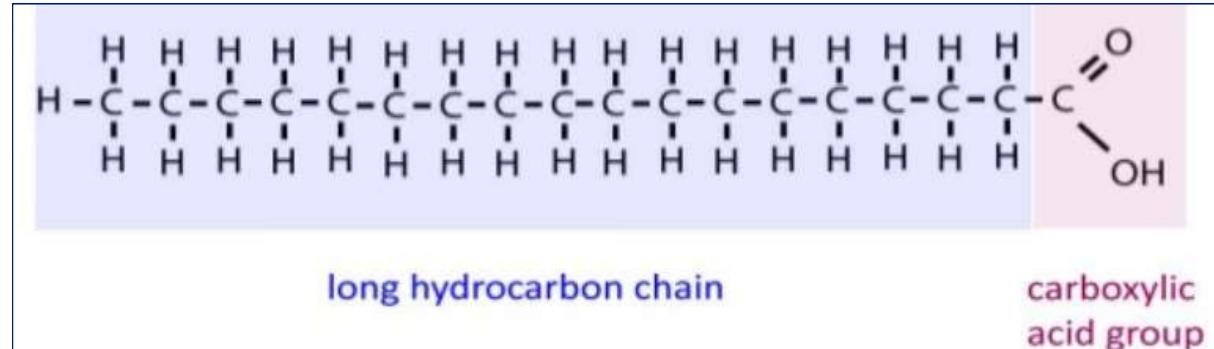
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Fatty acids

- Fatty acids are carboxylic acids with hydrocarbon side chain.
- They are the simplest form of lipids.



Waxes

- They are esters of higher fatty acids with higher mono hydroxy aliphatic alcohols (e.g. Cetyl alcohol)
- Have very long straight chain of 60-100 carbon atoms
- They can take up water without getting dissolved in it.
- Used as bases for the preparation of cosmetics, ointments, polishes, lubricants and candles.
- In nature, they are found on the surface of plants and insects.

Fats [Triglycerides]

- Esters of fatty acids with glycerol.
- Solid at room temperature.
- Some are liquid at room temperature, and are known as oils.
- Physical state depends upon the nature of fatty acids.
- Fats are rich in saturated fatty acids.
- Oils are rich in unsaturated fatty acids.

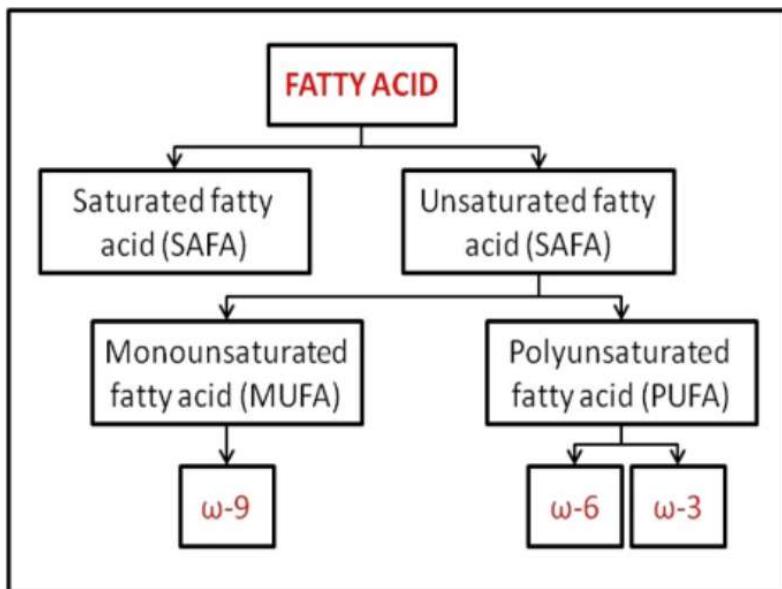
Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati



Fatty acids are the simplest form of lipids. These are monocarboxylic, straight, unbranched hydrocarbon chains containing even number of carbon atoms (between 4-36)

Fatty acids are also known as acyl group when it is a part of ester.

Fatty acids are amphipathic in nature. The fatty acids may be free or esterified with glycerol to form triglycerides.

Saturated fatty acids have no double bonds in the chain or contain single chain.

Their general formula is $\text{CH}_3\text{-}(\text{CH}_2)_n\text{-COOH}$, where n specifies the number of methylene groups between the methyl and carboxyl carbons.

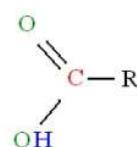
They have higher melting points

They are solid at room temperature.

Examples- lauric, myristic, palmitic acid etc.

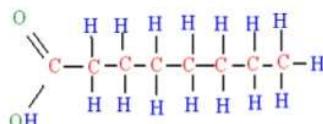
FATTY ACIDS

General formula: RCOOH or



R is H or, usually, a long hydro carbon tail,
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ etc

This forms the "tail" in lipids



$$\text{R} = \text{C}_7\text{H}_{15}$$

Tails are Hydrophobic because they are non-polar

COOH is polar (COO^- and H^+)

Unsaturated fatty acid (SAFA)

These fatty acid contain one or more double bonds along the length of the hydrocarbon chain.

They are liquid at room temperature.

Have low melting point.

The commonly used system for designating the position of double bond in unsaturated fatty acid is the delta(Δ) numbering system.

Example- linoleic acid, oleic acid, palmitoleic acid.

In the naturally occurring unsaturated fatty acid the double bond are in cis configuration and trans fatty acid are produced by fermentation in the rumen of dairy animals and are obtained from dairy products and meat.

Course Code: SC202
Presented by

Course Instructor: Dr Bhar Sah
Dept. of Science & Mathematics
IITG, Guwahati

Saturated Fatty Acids

No. of C atoms	Common name	Scientific name	Formula
2	Acetic acid	Ethanoic acid	CH_3COOH
4	Butyric acid	Butanoic acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
6	Caproic acid	Hexanoic acid	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$
8	Caprylic acid	Octanoic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
10	Capric acid	Decanoic acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
12	Lauric acid	Dodecanoic acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
14	Myristic acid	Tetradecanoic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$

Unsaturated Fatty Acids

Name of Fatty Acids	Structures
Palmitoleic Acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Oleic Acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic Acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
γ -linolenic Acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$
Erucic Acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$
Arachidonic Acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$
Parinaric Acid	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Compound Lipids

They are fatty acids esterified with alcohol; but in addition they contain other groups.

Depending on these extra groups, they are sub-classified as:

Phospholipids containing phosphoric acid.

Nonphosphorylated lipids.

Contain some non-lipid substances in addition to fatty acids and alcohol.

Non-lipids include proteins, carbohydrates, phosphate, sulphate, nitrogen etc.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

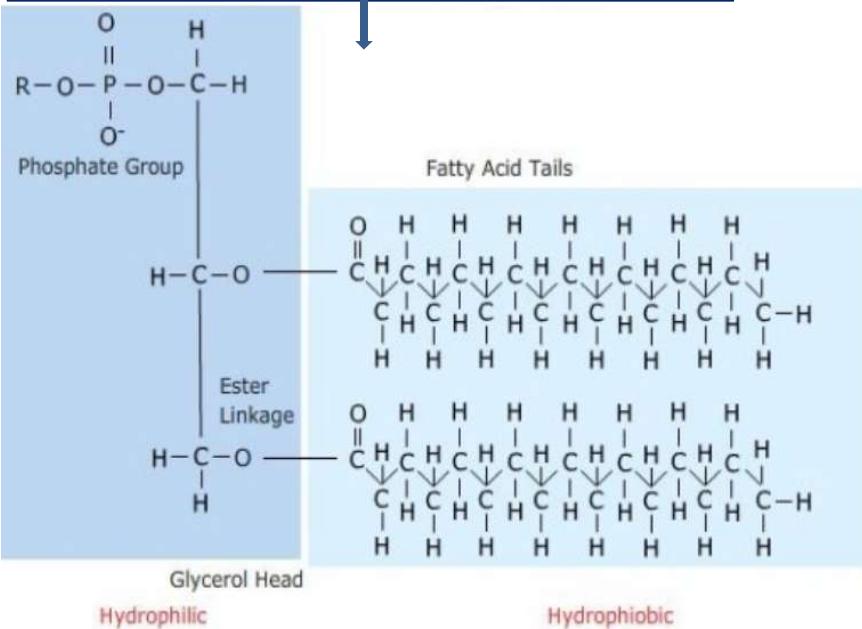
A phospholipid is an amphipathic molecule constructed from four components: fatty acids, phosphate, alcohol and glycerol or sphingosine.

Also called as phosphatides, contains a phosphorous atom.

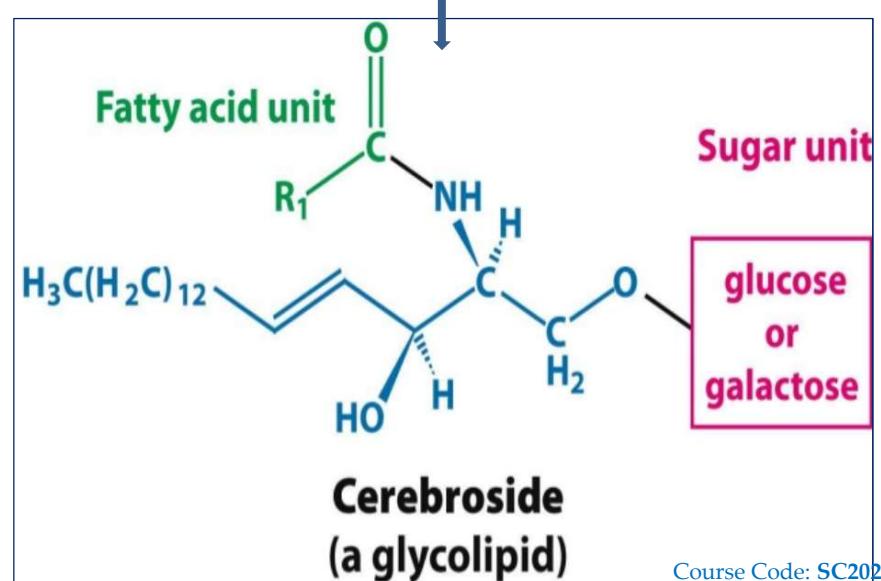
The phospholipids are very important structural components of all cell membranes including those of the cell organelles.

Lecithin may also play an important role in transport of ion across the membranes.

Phospholipids are of different kinds but all of them contain a glyceryl residue to which are attached in ester linkage two long chain fatty acid and a phosphorylated component.



Glycolipids are molecules that contain both carbohydrate and lipid components. Like the phospholipid sphingomyelin, glycolipids are derivatives of ceramides in which a long-chain fatty acid is attached to the amino alcohol sphingosine. They are, therefore, more precisely called glycosphingolipids. Like the phospholipids, glycosphingolipids are essential components of all membranes in the body, but they are found in greatest amounts in nerve tissue. They are located in the outer leaflet of the plasma membrane, where they interact with the extracellular environment. As such, they play a role in the regulation of cellular interactions (for example, adhesion and recognition), growth, and development.



Course Code: SC202

Presented by

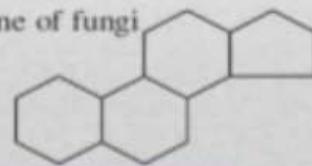
Course Instructor: Dr Bhar Sah
Dept. of Science & Mathematics
IIITG, Guwahati

Derived lipids are the substances derived from simple and compound lipids by hydrolysis.

These includes fatty acids, alcohols, monoglycerides and diglycerides, steroids, carotenoids.

Derived Lipids

- Sterol
 - also known as steroid alcohols
 - occur naturally in plants, animals, and fungi, with the most familiar type of animal sterol being cholesterol
 - TYPES:
 - Phytosterols – plant sterol (campesterol, sitosterol, and stigmasterol)
 - blocks cholesterol absorption sites in the human intestine, thus helping to reduce cholesterol in humans
 - Zoosterol – animal sterol (cholesterol)
 - Ergosterol – sterol present in the cell membrane of fungi



It is a subgroup of steroids with a hydroxyl group at the 3- position of the A- ring. And the hydroxyl group is polar, and rest of the aliphatic chain is non-polar.

They are amphipathic lipid synthesized from acetyl-coenzyme A via the HMG-CoA reductase pathway.

The overall molecule is quite flat

Cholesterol forms part of the cellular membrane in animals and serve as secondary messenger in developmental signaling.
Cortisol act as signaling compound in cellular communication and general metabolism.

It is common component of human skin oils.
Sterols functions as a precursor to fat soluble vitamins and steroid hormones.
cholesterol is vital to cell membrane.

Course Code: SC202

Presented by

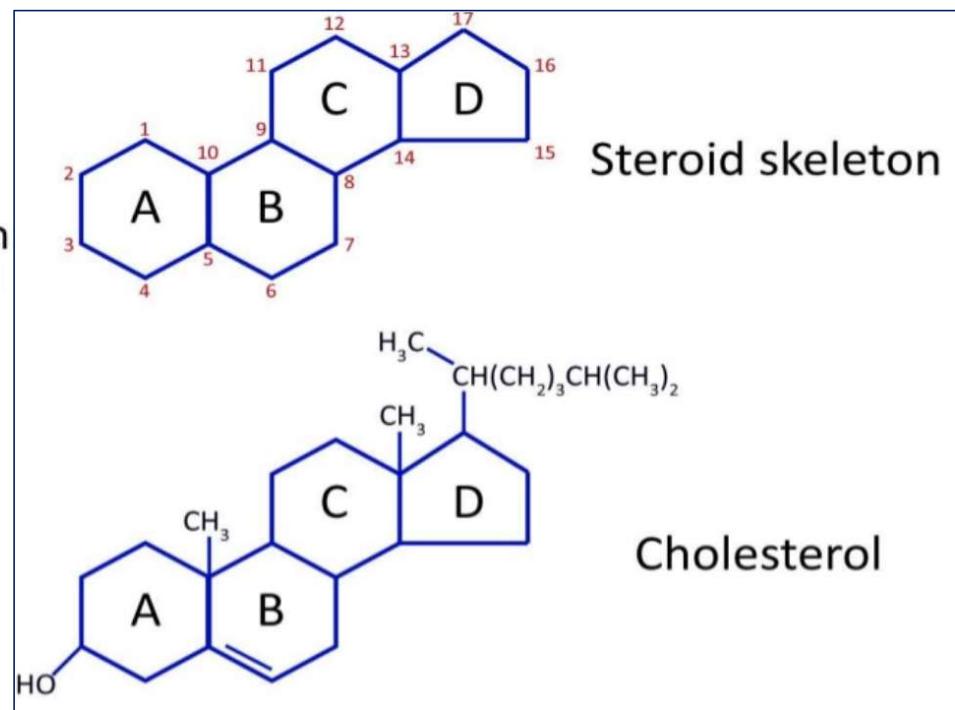
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Steroids

- **Steroids** are lipids containing a steroid nucleus (core structure).
- The **steroid nucleus** is a fused ring system consisting of three cyclohexane rings and one cyclopentane ring.
- The rings are designated A, B, C and D.
- Attachment of different groups to the core steroid structure leads to a wide variety of steroid compounds, including cholesterol, bile salts and steroid hormones.



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Chemical reactions of lipids

- Lipids can undergo:
- **Hydrolysis:** The ester bonds of lipids can be hydrolysed by specific enzymes.
- **Saponification:** Hydrolysis of triglycerides by alkalis is known as saponification. It results in the formation of alkali salts of fatty acids (soaps).
- **Hydrogenation:** Double bonds of unsaturated fatty acids can be hydrogenated in the presence of catalysts e.g. nickel
- **Iodination:** Iodine can also reduce the double bonds of unsaturated fatty acids.
- **Oxidation:** Unsaturated fatty acids can react with atmospheric oxygen to form:
 - ❖ Fatty acid peroxides
 - ❖ Fatty acids epoxides
 - ❖ Fatty acid aldehydes

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

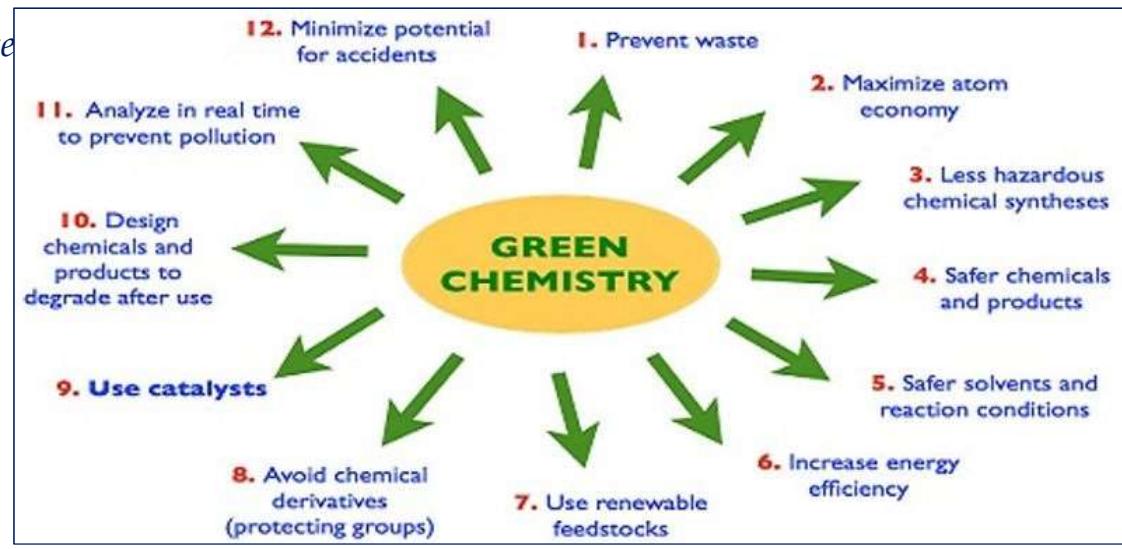
Green Chemical Processes

Green chemistry or sustainable chemistry, is an interdisciplinary overlap of chemistry and chemical engineering for processes and products involving minimization of the use and generation of hazardous substances. It is defined as

The invention, design and application of chemical products and processes to reduce or eliminate the use and the production of harmful substances

This comprises

- Design of processes to maximize the amount of raw material that ends up in the product
- Use of renewable energy sources and material feedstocks
- Use of safe, environmentally benign substances, including solvents, wherever possible
- Design of energy efficient processes
- Avoiding the production of waste



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Principles of Green Chemistry

- 1. Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
- 2. Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3. Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4. Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
- 5. Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
- 6. Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
- 7. Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
- 8. Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .
- 9. Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 10. Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
- 11. Real-time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
- 12. Inherently Safer Chemistry for Accident Prevention.** Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Strategies of solvent replacement

- Avoid or minimise solvents in first place
- Use less toxic solvents
- Use renewable solvents (not derived from petrochemicals)
- Avoid VOC's – solvents with low vapour pressure / high boiling points may be preferable as long as this does not lead to other complications.

Problems with VOC's

Direct

- Varying toxicity depending on nature of VOC, exposure method and duration.
E.g. DMF (teratogenic), CHCl_3 (suspected carcinogen)
- Flammability (fire hazards)
- Peroxide formation (usually ethers)

Indirect

- Ozone depletion
- Chlorofluorocarbons (CFC's) now phased out E.g. CF_3Cl , lifetime in atmosphere 640 years, GWP 14,000 CCl_4 – now much more limited use (35yrs, GWP 1400)
- Global warming potential (GWP)
- Does not have to be ozone depleting to have GWP
E.g. HFC134a (CH_2FCF_3) used in refrigerants and air conditioning units

Current approaches to solvent replacement in synthetic chemistry

- No solvent
- Water
- Carbon dioxide
- Ionic liquids
- Fluorous phase reactions

Water as a reaction medium

- One of the most obvious alternatives to VOCs.
- Cheap, readily available, and plentiful.
- Useful for certain types of reaction but limited because of:
 - Low solubility of organic substrates
 - Compatibility with reagents
- Clean up of aqueous waste difficult
- Useful in biphasic processes in conjunction with other solvents

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Solvent Selection

Preferred	Useable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	Methyl t-butyl ether	Dichloromethane
Ethyl acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-MethylTHF	Dimethyl formamide
Methyl ethyl ketone	Tetrahydrofuran	N-Methylpyrrolidinone
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethyl sulfoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Dimethoxyethane
		Benzene
		Carbon tetrachloride

Undesirable Solvent	Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or <i>tert</i> -butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or <i>tert</i> -butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or N-methylpyrrolidinone	Acetonitrile
Pyridine	Et ₃ N (if pyridine is used as a base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Three key developments in green chemistry in the field of organic synthesis are:

1. *Use of supercritical CO₂ as green solvent*
2. *Aqueous H₂O₂ for oxidations*
3. *the use of hydrogen in asymmetric synthesis.*

Applied green chemistry also includes supercritical H₂O oxidation, reactions in water and neat/ dry medium reactions. Another branch contributing to green chemistry is biotechnology/ bioengineering. In addition, the class of cascade, multicomponent & domino reactions also have positive effect on reduction of pollutants.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Supercritical Carbon Dioxide

- Similar advantages to water
 - Natural, cheap, plentiful
 - Available in >99.9% pure form
 - By-product of brewing, ammonia synthesis, combustion
- Already being adopted in a variety of commercial processes
- Non-toxic and properties well understood
 - asphyxiant at high concentrations
- Easily removed and recycled, and can be disposed of with no net increase in global CO₂
 - Simple product isolation by evaporation, to 100% dryness.
- No solvent effluent
- Potential for product processing (extraction, particle formation, chromatography)

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

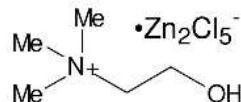
IITG, Guwahati

Ionic liquids (IL's)

- Typically consist of organic cation (often ammonium or phosphonium salt) and inorganic anion



1. Ethylmethylimidazolium tetrafluoroborate, [emim][BF₄]
ionic liquid



2. Choline chloride/Zinc chloride
ionic liquid

- Usually only consider IL's which are liquid at room temperature
- Great variety of structures possible
- Very low vapour pressure – attractive alternative to VOCs.

- Good solvents for a wide range of organic, inorganic and polymeric compounds
- Anion and cation can be fine tuned to give a wide range of solvent properties (e.g. hydrophilic, hydrophobic) which can be exploited
- Wide range of reactions already demonstrated in this medium
- Can be used in conjunction with other alternative solvents (particularly CO₂)
- Claimed to be recyclable (essential for widespread use) although there may be regulatory problems with this.
- Effectively, properties similar to many other high boiling, polar solvents.

Course Code: SC202

Presented by

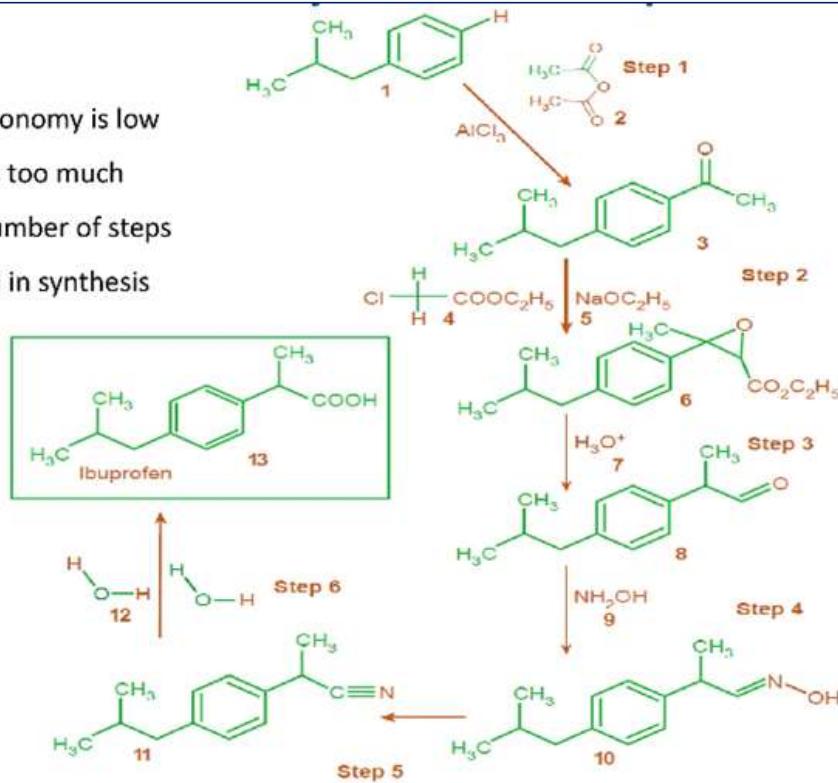
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

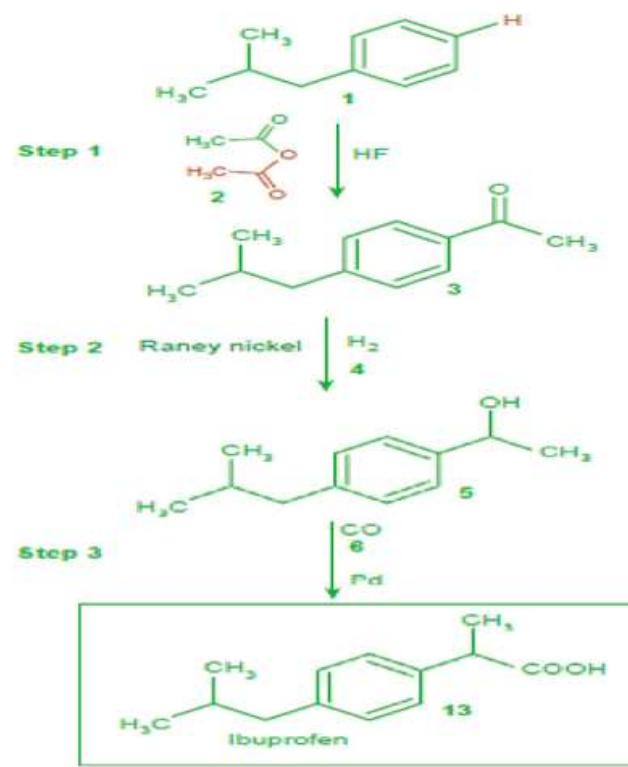
IITG, Guwahati

Traditional vs Green synthesis of Ibuprofen

- Atom Economy is low
- Waste is too much
- Large number of steps
- involved in synthesis



- Lesser Water
- Atom Economic
- Lesser number of steps



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati