Udai Pratap (Autonomous) College, Varanasi

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E-Content

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1. Formation of Peptide Bonds

Peptide bond is formed by removal of the elements of water from the α-carboxyl group (–COOH) of one amino acid and from the α-amino ($–NH_2$) group of another amino acid molecule. Thus two amino acid molecules are covalently joined together through a substituted amide linkage, called '***peptide bond***', to yield a dipeptide. In other words, a peptide bond is a chemical bond that is formed by joining the carboxyl group of one amino acid to the amino group of another with a release of water molecule.

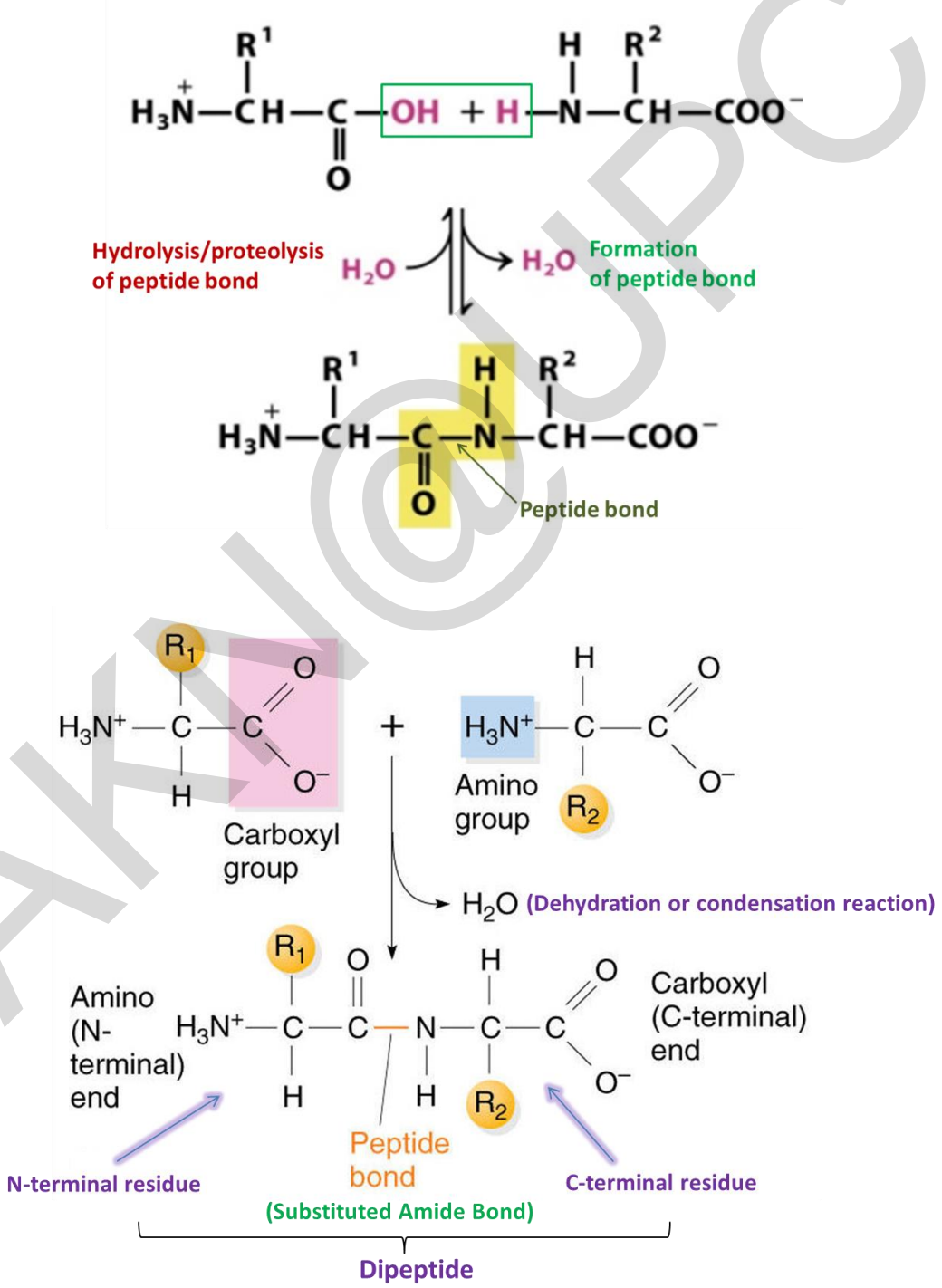


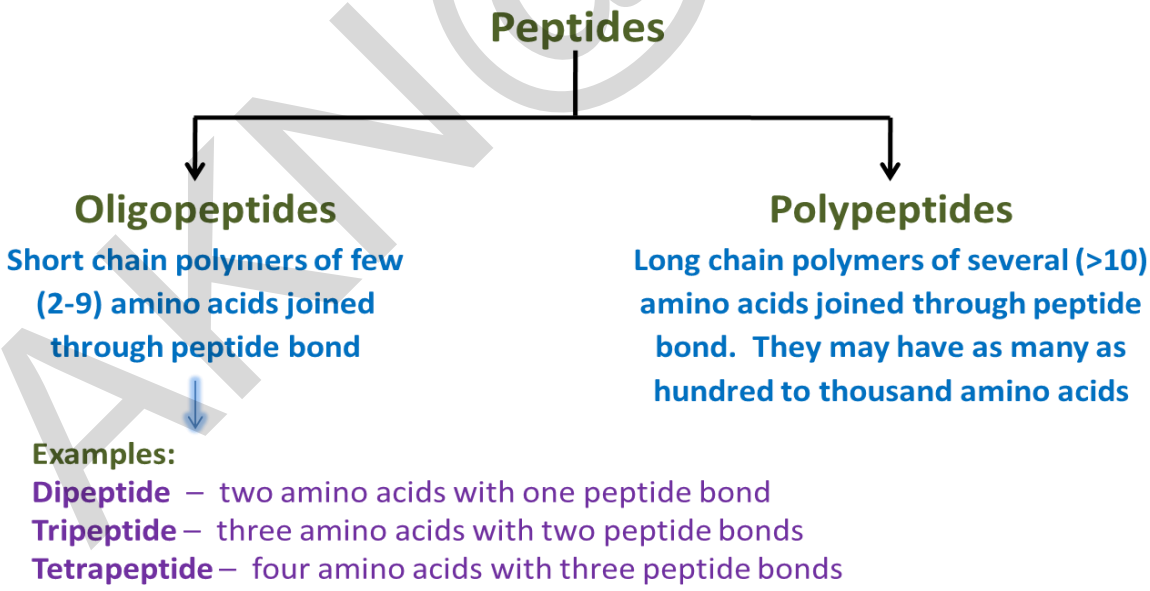
Figure 1. Formation of peptide bond

Due to removal of water molecule, peptide bond formation is a type of dehydration reaction, and due to condensation of two or more amino acid molecules to form one molecule of peptide, the reaction is said to be condensation reaction. In cells, peptide bond is formed by the action of peptidyl transferase enzyme on the ribosomal assembly governed by genetic codes on mRNA.

An amino acid unit in a peptide is often referred to as '***residue***' (the part left over after losing a hydroxyl moiety from α-carboxyl group and a hydrogen atom from its α-amino group). In a peptide chain, the amino acid residue at one end with free $–NH_2$ group is designated as N-terminal or amino–terminal residue, and the residue at the other end with free –COOH group is called carboxyl-terminal or C-terminal residue. Thus, peptide or polypeptide chains have two free ends or terminals (or termini) – one N-terminus and one C-terminus. The amino acid residue bearing free amino group (at N-terminus) is designated as first residue, and the last residue is the C-terminus amino acid residue with free carboxyl group.

2. Types of Peptides

Peptides are short or long chain polymers of L-α-amino acids joined together by peptide bonds



Above mentioned classification is arbitrary on the basis of the number of amino acid residues present in peptide chain. In general, the term '***peptide***' is exclusively used to denote short chain peptides, and the larger peptides are called polypeptides or protein.

Nomenclature of peptides

Any peptide can be named by replacing 'ine' suffix with 'yl' in all amino acid residues except for the last C-terminus residue. For naming a dipeptide N-Gly-Ala-C, 'ine' of N-terminus residue glycine is to be replaced with 'yl' forming 'glycyl' and then writing C-terminus residue without any change as 'alanine'. Thus name of the dipeptide will be written in single word as 'glycylalanine.' Examples of other peptides are given in figure 2.

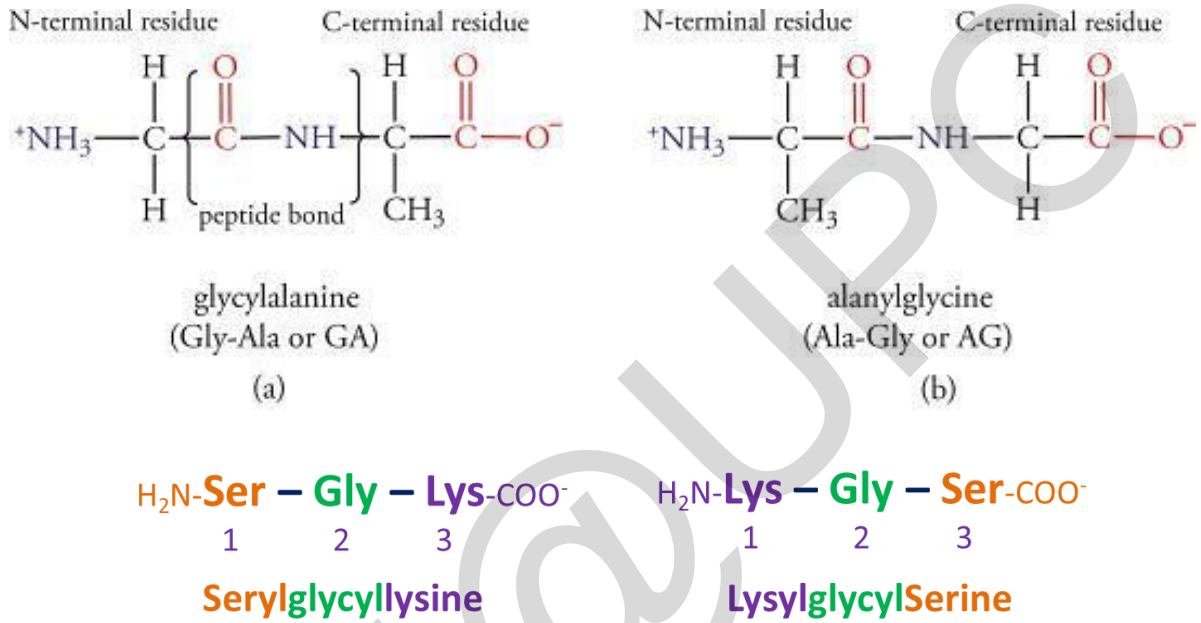
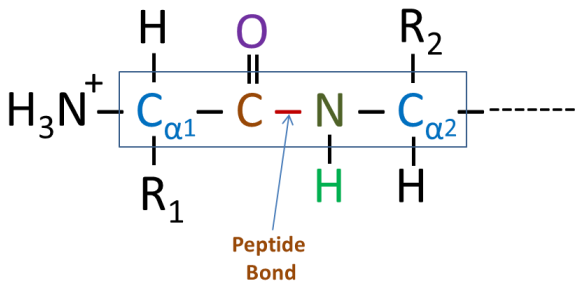


Figure 2. Nomenclature of different di- and tri-peptides.

Nature and Properties of peptide bonds

Peptide bonds are the covalent bonds that link two or more amino acid molecules to form peptide or polypeptide chain. Due to this peptide bond, alpha-carbons of two adjacent or successive amino acid residues are separated by three covalent bonds (as Cα – C – N – Cα) in the following manner:

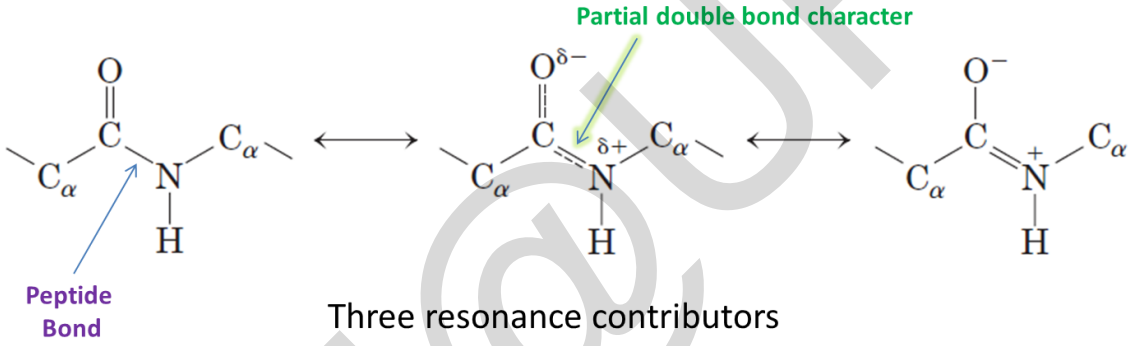


Due to higher electronegativity of carbonyl oxygen, there exists a resonance or partial sharing of two pairs of electrons between the carbonyl oxygen and the amide nitrogen.

Therefore, the oxygen has a partial negative charge and the nitrogen a partial positive charge, setting up a small electric dipole. The six atoms of the peptide group lie in a single plane, with the oxygen atom of the carbonyl group and the hydrogen atom of the amide nitrogen *trans* to each other.

Thus co-planer atoms associated with single peptide groups are:

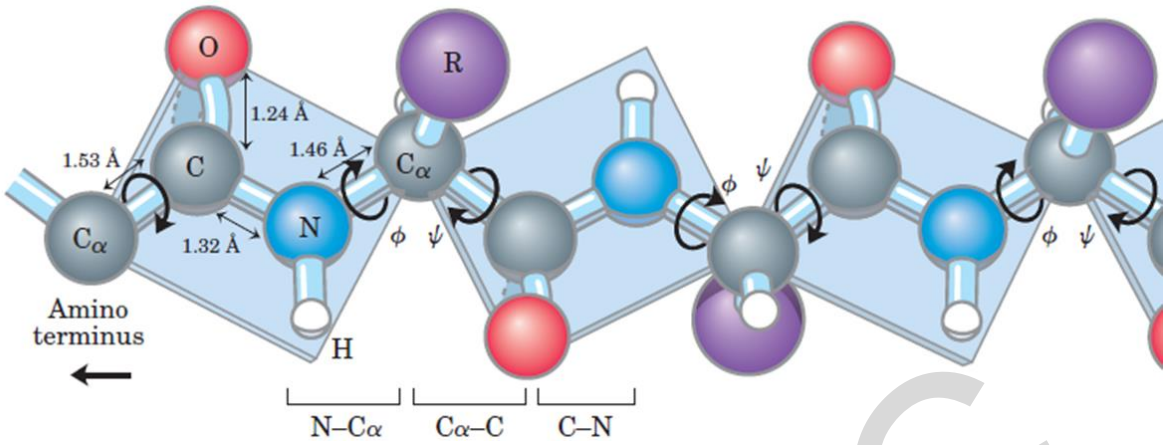
1. Carbonyl oxygen
2. Carbonyl carbon
3. Amide nitrogen
4. Hydrogen linked to amide nitrogen (or amide/peptide hydrogen)
5. $C\alpha_n$ (Cα of first/previous amino acid residue)
6. $C\alpha_{n+1}$ (Cα of next amino acid residue)



Three resonance contributors

From these findings **Pauling and Corey** concluded that the peptide C–N bonds are unable to rotate freely because of their **partial double-bond character**. Rotation is permitted about the N–Cα and the Cα–C bonds. The backbone of a polypeptide chain can thus be pictured as a series of **rigid planes** with consecutive planes sharing a common point of rotation at Cα. The rigid peptide bonds limit the range of conformations that can be assumed by a polypeptide chain.

"In nutshell, sharing of electrons between carbonyl oxygen (more electro-negative than amide nitrogen) and amide nitrogen, a sort of resonance occurs imparting a partial double bond character to peptide bond. Due to this partial double bond character, rotation is prohibited about this bond. Restricted rotation ceases the flexibility of peptide bond and makes it rigid. Rigid nature of peptide bond in turn causes co-planarity of all six atoms associated with this bond."



Because of the free rotation about N–Cα and the Cα–C bonds, there exist certain torsion angles or dihedral angles in the peptide back bones. By convention, the torsion angles resulting from rotations at C*α* are labelled **φ** (phi) about the N–Cα bond and **ψ** (psi) about the Cα–C bond. The third dihedral angle, **ω** (omega), is not often considered. This is the torsion angle about peptide bond where rotation is constrained or prohibited.

Under fully extended conformation of polypeptide backbone, values of both **φ** and **ψ angles** can be defined as 180º. In this extended conformation, all peptide groups along with associated atoms remain in the same plane. But in aqueous solution at physiological pH, a polypeptide chain does not remain in fully extended condition and backbone usually becomes folded so as to achieve native three-dimensional conformation.

Suggested readings:

- Cox and Nelson: Lehninger's Principles of Biochemistry
- Murray, Granner, Mayes and Rodwell: Harper's Biochemistry
- Singh and Kumar: Animal Physiology and Biochemistry

Declaration