

The stabilization is only possible if the planes defined by the sp^2 bonding units of the carbonyl C and N atoms are coplanar as shown.

If the two bonding units are not coplanar, the $2p_z$ orbitals of the O, C and N atoms would not all overlap as shown for the hybrid.

This means that rotation about the peptide bond is restricted.

As a result of the lack of free rotation, *cis* and *trans* peptide bonds are possible as follows:

The peptide bond in proteins is in the *trans* form. This form is more stable because there is less steric interaction between R groups of adjacent a.a..

Fig 6-4 shows a representation of a polypeptide chain with planar peptide groups.

Fig 6-4 also indicates that only the single bonds to the α - carbon atoms in the polypeptide backbone are free to rotate.

Thus it is rotation about these bonds which gives rise to the conformations of proteins.

Angles of rotation about the C_{α} -C and C_{α} -N bonds are referred to by the letters Ψ (psi) and Φ (phi) respectively as shown in the handout figure.

$\Psi = 180^\circ$ when adjacent peptide planes are coplanar with N_1 and N_2 *trans* to the C_α -C bond.

$\Phi = 180^\circ$ when adjacent peptide planes are coplanar with carbonyl C_1 and C_2 *trans* to the N- C_α bond.

The handout figure shows an amino acid with Ψ and Φ angles of 180° .

Let's also define positive and negative angles of rotation.

While looking along a bond from one atom to another, a clockwise rotation of the farthest atom corresponds to a positive rotation.

Rotation of carbonyl C_2 (farthest atom) about the C_α in the direction shown in the figure corresponds to a positive rotation.

Rotation of N_1 (farthest atom) about the C_α in the direction shown in the figure corresponds to a positive rotation.

If the Φ and Ψ angles are constant throughout a polypeptide chain, the polypeptide will have the shape of a helix.

A given set of Φ and Ψ angles will determine the type of helix, i.e., n , the number a.a. per turn, p , the pitch, and d , the distance traversed by one a.a. along the helix axis.

The handout figure defines n , p and d .

The same n can result from other angles of Φ and Ψ as shown below

For a given value of Φ and different values of Ψ , helices of different n will result as represented below

Not all values of Φ and Ψ are equally favorable because of steric interactions within the polypeptide chain.

When $\Phi = 0^\circ$ and $\Psi = 180^\circ$, there is a large steric interaction between adjacent carbonyl O atoms as shown in the handout figure.