Limits on Rotation in Amides

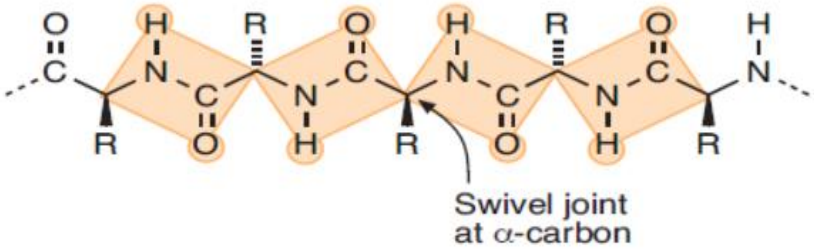
We do not have as many degrees of freedom as we have bonds. One type of bond in the backbone does not rotate freely. The amide bonds are held in a planar orientation due to orbital overlap between the π-orbitals of the SP_2 hybridized atoms of the carbonyl group and the π-orbital of the SP_2 hybridized amine group (Stryer, chapter 3.2.2). This distributed π-orbital system resists rotation, as the orbital overlap would have to be broken. The distributed nature of the system also makes the amide bond resistant to hydrolysis.

The amide group will prefer to have all atoms connected to it in the same plane as the amide bond (no rotation). This can result in a 'cis' or 'trans' configuration. Due to steric and electronic reasons the 'trans' configuration is the predominant form for the amide bond. Figure 3 shows the two possible planar configurations. Note the steric clash between the side chain groups in the 'cis' form.

Figure 3. Planar amide bonds.

So we can look at a polypeptide chain as a series of planar structures connected by swivel joints at the α-carbons of each amino acid residue. The two atoms of each amide bond and the four atoms connected to them are coplanar for each individual amide bond. Any two planar amide groups share a common atom – the α-carbon of an amino acid residue.

Figure 4. Polyamide with planar amide bonds indicated.



These swivel joints have two connections that can rotate freely. Like a universal joint in the drive train of a car, these two circular (cylindrical) rotations can allow for a fully spherical range of motion. We will consider each of these two rotating bonds separately.

The Ramachandran Angles

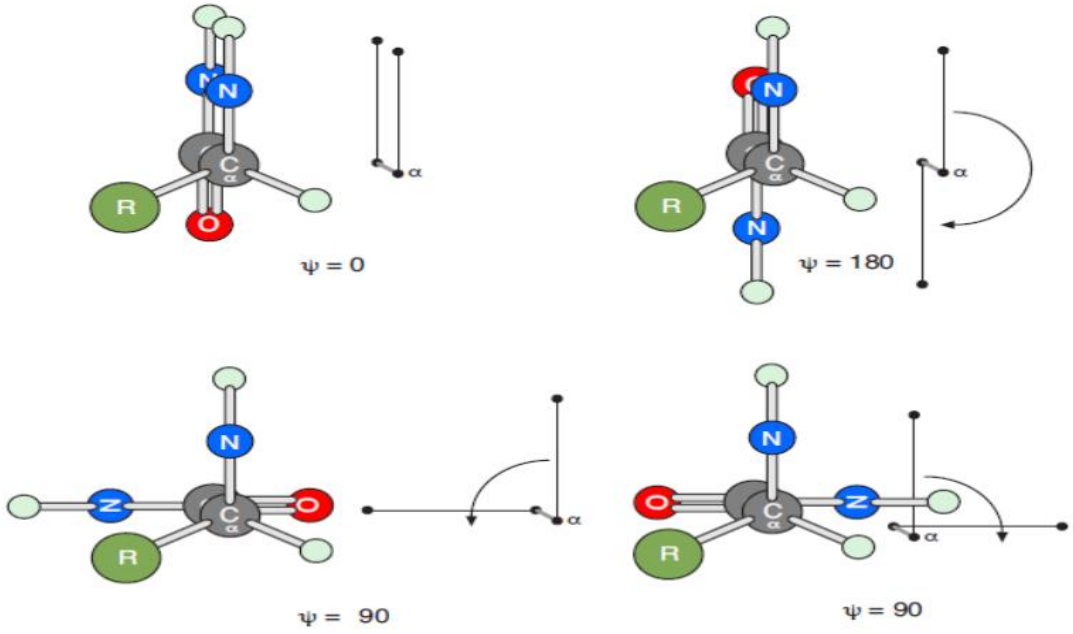
Each residue will have two bonds that can rotate freely. These two angles define the conformation of that residue in a protein and are called the Ramachandran angles, ψ (psi) and ϕ (phi).

The ψ (psi) Angle

The bond from the α-carbon to the carbonyl group (at the C-terminus) of the amino acid residue can rotate and turn the whole plane of the amide group, which includes the carbonyl carbon, in a 360-degree range. This angle is measured by looking along that bond with the carbon of the carbonyl group in the rear and the α-carbon to the front. We measure the apparent angle between the two bonds to nitrogen that you can see coming out of the axis of the $C_\alpha \rightarrow C_{(C=O)}$ bond. This angle is labeled ψ (psi) and is measured from −180° to +180° with the positive direction being when you turn the rear group clockwise so that the rear nitrogen bond is clockwise of the front nitrogen bond (or when you turn the front group counterclockwise so that the rear nitrogen bond is clockwise of the front.)

Figure 5. The ψ (psi) angle in an amino acid residue. (In these examples ϕ = 180°)

Figure 6. The ψ (psi) angle seen along the $C_\alpha \rightarrow C_{(C=O)}$ axis. (In these examples ϕ = 180°)

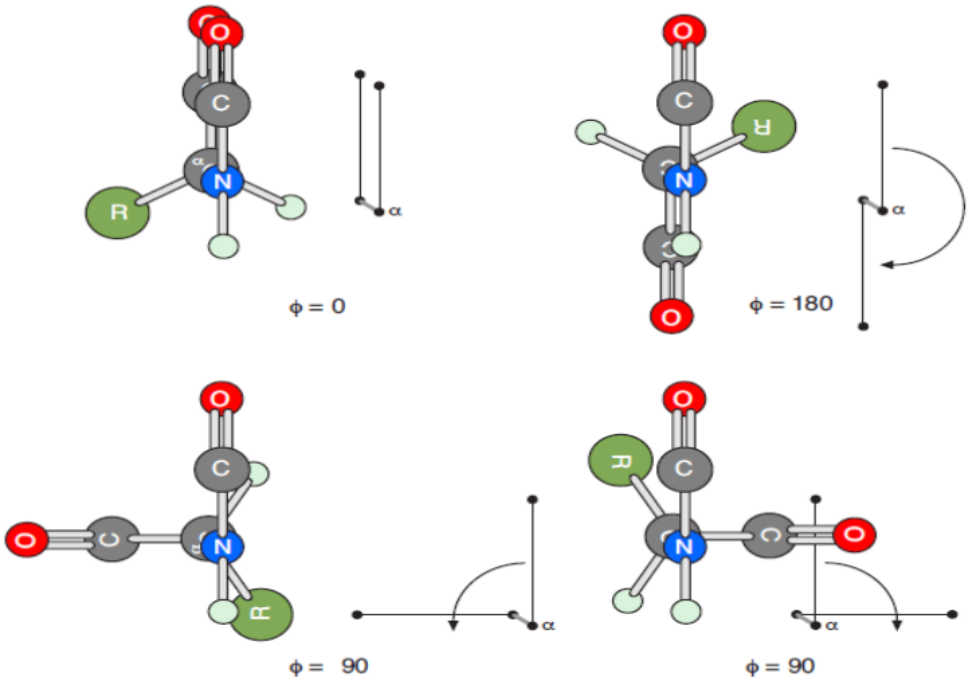


The ϕ (phi) Angle

The bond from the nitrogen (at the N-terminus) to the α-carbon of the amino acid residue can rotate and turn the whole plane of the other amide group, which includes the nitrogen, in a 360-degree range. This angle is measured by looking along that bond with the nitrogen atom in front and the α-carbon to the rear. We measure the apparent angle between the two bonds to the carbonyl carbons that you can see coming out of the axis of the N→C_α bond. This angle is labeled ϕ (phi) and is measured from −180° to +180° with the positive direction being when you turn the rear group clockwise so that the rear carbonyl bond is clockwise of the front carbonyl bond (or when you turn the front group counterclockwise so that the rear carbonyl bond is clockwise of the front.)

Figure 7. The ϕ (phi) angle in an amino acid residue. (In these examples ψ = 180°)

Figure 8. The ϕ (phi) angle seen along the N→C_α axis. (In these examples ψ = 180°)



The Ramachandran Plot

We can vary ψ from -180° to 180° and we can vary ϕ from -180° to 180° (that is 360° of rotation for each). But many combinations of these angles are almost never seen and others are very, very common in proteins.

Let us plot the values of ψ vs. the values of ϕ for an example globular protein. We will obtain a data set for the positions of each atom in space. We can get such data from one