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PROTEINS

THE PEPTIDE BOND

The peptide bond, shown above enclosed in the blue curves, generates the basic structural unit for proteins.

The carbon and nitrogen atoms are both hybridized sp$^2$ and they are connected by a $\sigma$ bond.

In addition to the $\sigma$ bond, there is a resonance which allows the unshared electrons of the nitrogen to overlap the p orbitals of the CO (carbonyl) group, giving rise to an effective $\pi$ bond which, combined with the sp$^2$ planarity of the carbon and nitrogen atoms, holds the whole peptide bond in a plane.

In these pictures we have added the oxygen atom and shown the two p orbitals which lie in the plane of the paper in color. Note how one of the oxygen p orbitals overlaps one of the carbon sp$^2$ orbitals to form a $\sigma$ bond. We have also added dashed circles to represent the p orbitals on each of the three atoms which are directed out of the plane of the paper. See how the p orbital of the central carbon atom overlaps the p orbitals of both of the other atoms, forming $\pi$ bonds with each of them. We have also added the hydrogen atom shown in gray. If the top of the hydrogen is clipped off, that is due to printing limitations; the real atom is spherical.

Rigid amide plane outlined in green

The dashed curve indicates the resonance between the carbon-oxygen and the carbon-nitrogen $\pi$ bonds. This is what gives the amide structure its planar rigidity.

Rotatable bonds by which the amide structure connects to other amide structures to form the backbone of the protein.
PROTEINS

AMIDE PLANES

Now, for clarity, we show the amide plane in blue.

In proteins, two amide planes are joined by a mutual bond to a carbon atom, called the $C_\alpha$ atom. Each amide plane can rotate about its bond to the $C_\alpha$ atom. The angle of rotation between the N and the $C_\alpha$ is named $\phi$ (phi) and the angle of rotation between the $C_\alpha$ and the C atom is called $\psi$ (psi).

Multiple amide planes can be joined to form polypeptide chains.

In proteins, polypeptide chains also form larger units, of which two of the most important varieties are $\alpha$ helices and $\beta$ sheets. Two additional effects, however, beyond the peptide bond are important in determining the structure of these forms. These effects are steric hindrance and hydrogen bonding.
PROTEINS

AMIDE PLANES

In real proteins the hydrogen atoms in the amide plane are often replaced by amino acids. This is what gives proteins their great variety and effect.

In proteins, the C\textsubscript{\alpha} atom has an amino acid residue connected to it.

The amino acid residues are fairly large molecular fragments, which push away from each other by steric hindrance, causing the polypeptide chain to rotate around the single bonds connecting the C\textsubscript{\alpha} atom.

Where have amino acids been observed in nature, besides in proteins?

We have shown that the amide planes are connected via a C\textsubscript{\alpha} atom with two rotational degrees of freedom. Explain why this fact shows that the C\textsubscript{\alpha} atom only has single bonds.

Look for examples of spirals in the natural world, as well as spiral objects constructed or drawn by humans. Describe the spirals, especially noting whether they are right handed or left handed.
Two important structural features of proteins are \(\alpha\)-helices and \(\beta\)-sheets.
The amino acid residues force the peptide planes to twist so as to minimize the steric hindrance.

In the picture below the amide planes are shown in green.

Is the \(\alpha\)-helix right handed or left handed?

In the picture below a certain type of bonding is represented by the dotted lines. You should be able to deduce what kind of bonding that is and describe what effect it has on the structure of the alpha helix.
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AMALAYSE

The next six pictures show human pancreatic alpha amalayse, which is an essential enzyme for digesting starch. We are using this protein molecule to demonstrate the interplay of several different forms of bonding in one molecule.

First examine the backbone structure of the molecule in picture 1. Locate the helices.

What kind of bonding holds the backbone together? Why would ionic bonding not work?

In picture 2 you can trace the backbone by following the spectral sequence of colors. Starting at a, you can follow the backbone to b (or vice-versa).

Picture 3, in ribbon form, makes the helices stand out clearly. You can also find several beta sheets near the bottom of the molecule.

Each colored patch represents an amino acid. In figure 3, count the number of amino acids that make up the different helices.
PROTEINS

PROTEIN STRUCTURE

Picture 4 is a ball and stick representation which makes the individual atoms stand out. The colors are differentiated according to the individual amino acids.

Why is it valuable for chemists, teachers and students to be able to view several different forms of the molecule?

The space filling representation in picture 5 helps to see the overall shape of the molecule. It is also colored according to the amino acids.

In picture 6 the backbone is printed in blue, the oxygen atoms (which show the associated water molecules) in red, the disulfide bonds in orange and the ligands in gray and white. You can also locate the chloride and calcium ions.

Each amylase molecule contains several hundred waters. What kind of bonding connects the waters to the rest of the amylase?
This is called the ribbon view, of human pancreatic alpha amylase, and is useful to show the linear arrangement, or backbone, of the amino acids.
This view superimposes the atomic ball and stick view on top of the ribbon view and is perhaps most useful to get an impression of the actual complexity of the molecule.

Locate the calcium ion in the above picture. It is shown in black.
Each amylase molecule contains one doubly charged calcium ion, Ca\(^{2+}\). Find the calcium ion in picture 99.

What, in terms of the atomic structure of calcium, makes it natural for the ion to be doubly charged?

We know from experiment that the calcium ion in amylase is doubly charged. Otherwise, which would be more unlikely, Ca\(^+\) or Ca\(^{2+}\)?

Suppose the calcium ion in amylase were given two electrons, what effect would you expect this to have on the structure of the molecule?

In picture 99, count the number of bonds shown between Ca\(^{2+}\) and other atoms in the molecule. From the number of bonds alone, explain why these cannot be covalent bonds.
This is a picture showing the local linkage of the disulfide bridge in the human pancreatic alpha amylase molecule.
This is a picture of the locality of the chloride ion in human pancreatic alpha amylase.

Why is the chloride ion only singly charged, when we know that the calcium ion is doubly charged?
These pictures exhibit the location of various substructures in the human pancreatic alpha amylase molecule.
This page shows eight views of the human pancreatic alpha amylase ribbon structure, successively rotated through 45 degrees.

Print out the picture on the right. From a fairly close distance you may be able to superimpose the images by crossing your eyes. Then you will see a 3-D image of the molecule. This is usually easier for older people than for young people.
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VIEWS OF AMALAYSE