

Optical Isomers (Enantiomers)

Louis Pasteur carefully analyzed crystals of sodium ammonium tartrate ($\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_6$). There were two types of crystals whose structures were mirror images of each other! There was no way to rotate the one type of crystal so it would have the same structure as the other type of crystal. He carefully separated the two types of crystals. If crystals of the one type were dissolved in water, the solution rotated polarized light clockwise. A water solution of the other type of crystal rotated polarized light counterclockwise.

The tartrate ions in one kind of crystal are mirror images of the tartrate ions in the other kind of crystal. There is no way to rotate the one kind of tartrate ion so its atoms are arranged the same way as the atoms in the other kind of tartrate ion.

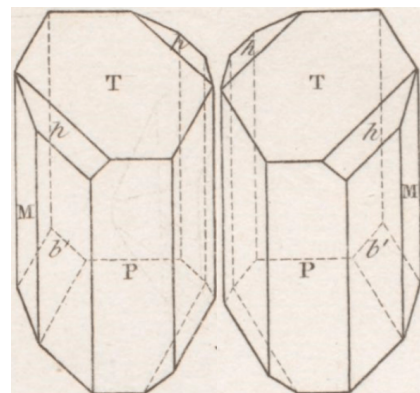
When the crystals are dissolved in water, the tartrate ions rotate polarized light. The tartrate ions are *optically active*. Since the one kind of ion rotates light one way while the other kind rotates light an equal amount the other way, these tartrate ions are *optical isomers*. Optical isomers are also called *enantiomers*. That term is derived from the Greek word *enantios* (ἐναντίος) which means *opposite*.

Consider a glove designed for the right hand. Its mirror image looks like a glove for the left hand. Such a glove can't be rotated to look like its mirror image. The tartrate ions described above have the same property. There is no way to rotate one of those ions so it will look like its mirror image. Each ion is *chiral* (KY rəl).¹

The word *chiral* comes from the Greek word *cheir* (χείρ) which means *hand*. Since a right-handed glove can't be rotated to look like its mirror image, it has *handedness* or *chirality*.²

Contrast the *chirality* of a right-handed glove with the *achirality* of a spoon. A spoon can be rotated so it looks like its mirror image. It is *achiral*. It lacks chirality (handedness).³

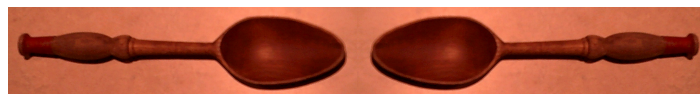
Bromochlorofluoromethane (CHBrClF) is a chiral molecule. Its central carbon atom has four different types of atoms attached to it. In the model shown, hollow spheres represent each atom. Charcoal gray is for carbon (C); dark red is for bromine (Br); green is for chlorine (Cl); yellow is for fluorine (F); and light gray is for hydrogen (H).



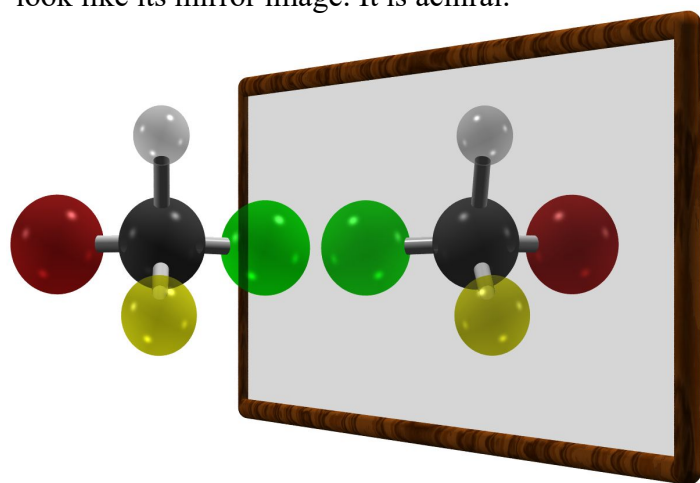
Pasteur drew these crystals of sodium ammonium tartrate.



The left glove is a mirror image of the right glove. There is no way to rotate the right glove so it would look like its mirror image. It is chiral.



The spoon on the right is a mirror image of the spoon on the left. The spoon on the left can be rotated to look like its mirror image. It is achiral.



A molecule of CHBrClF is chiral. A computer drew this image of a model of CHBrClF being reflected in a mirror. The model of CHBrClF cannot be rotated to look like its mirror image. Because of its chirality, CHBrClF exists in two forms. The model shows the form (*S*)- CHBrClF . Its mirror image is (*R*)- CHBrClF . Chemists use the letters *S* and *R* to specify the spatial arrangement of atoms around a carbon atom.

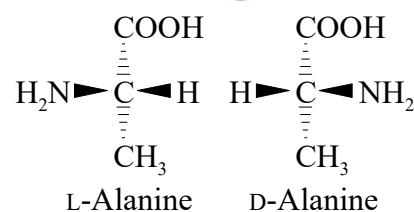
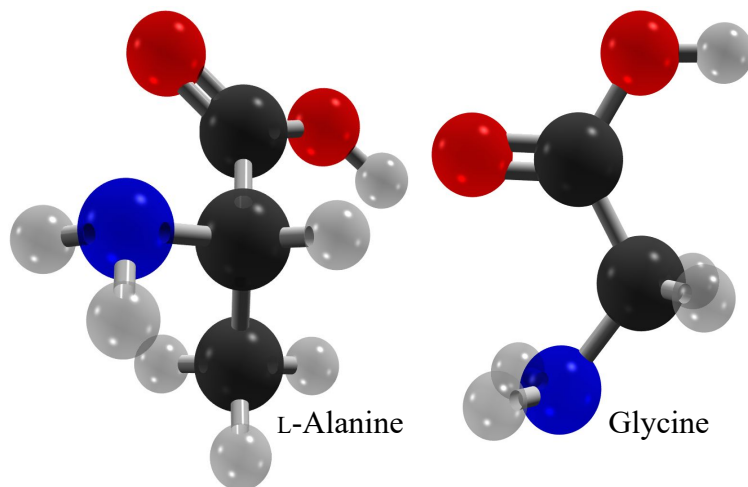
Because of the spatial arrangement of the four atoms bonded to the carbon, there is no way to rotate a molecule of CHBrClF so it will look like its mirror image.⁴ The carbon atom is a *chirality center*. In general, a carbon bonded to four different atoms or groups of atoms will be a chirality center.

To the right are models of the amino acids L-alanine and glycine. Light red is for oxygen (O), and blue is for nitrogen (N). In L-alanine, the central carbon is bonded to four different kinds of atoms or groups of atoms. Although two of the atoms are carbon, they belong to different types of groups. The top carbon belongs to a carboxyl group (COOH), and the bottom carbon belongs to a methyl group (CH₃). The central carbon is a chirality center since it is bonded to four different kinds of atoms or groups of atoms. L-Alanine is chiral.

Glycine has a carbon that is bonded to four atoms. However, two of those atoms are solitary hydrogen atoms. So only three different kinds of atoms or groups of atoms are bonded to that carbon. Glycine is achiral since it can be rotated to look like its mirror image. Of the 20 common amino acids used to make proteins, glycine is the only one that is not chiral.

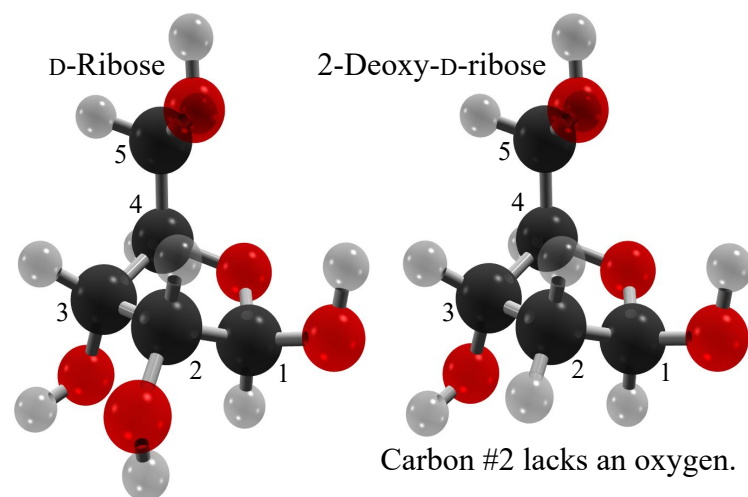
Alanine occurs in two forms: L and D. The D form of alanine is a mirror image of the L form. The chiral amino acids used to make proteins are all L-amino acids. If a mixture of forms were used to make a protein, then that protein's special design would be disrupted. Many proteins contain a special structure called an *alpha* (α) *helix*. The α helix would be distorted if D-amino acids were mixed with its L-amino acids.

Just as amino acids can exist in D or L forms, so can sugars. The special sugar D-ribose is used to help build RNA. The special sugar 2-deoxy-D-ribose is used to help build DNA. The special sugar D-glucose (blood sugar) provides energy to cells in the body. Since a solution of D-glucose rotates polarized light to the right (clockwise), it is *dextrorotatory* and is called *dextrose*. The common sugar sucrose is formed by joining molecules of D-glucose and D-fructose. Since a solution of D-fructose rotates polarized light to the left (counterclockwise), it is *levorotatory* and has been called *levulose*. Most sugars produced by biological organisms are of the D form and are said to be *right-handed*. Most biologically produced amino acids are of the L form and are said to be *left-handed*.⁵



The lower carbon of glycine isn't a chirality center since two atoms of hydrogen bond to it. Since glycine can be rotated to look like its mirror image, it is not chiral. The other 19 common amino acids in proteins are chiral L-amino acids.

These perspective structures of alanine use solid wedges to show bonds coming out of the page. They use dashed wedges to show bonds going behind the page.



When the carbons of these sugars are in DNA or RNA, a *prime* (') is written after their numbers. The carbons are then numbered 1', 2', 3', 4', and 5'.

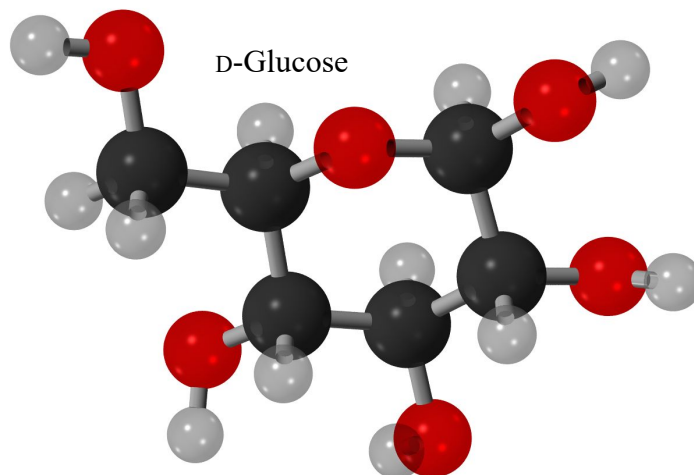
In the laboratory of Harold Urey in 1953, Stanley Miller used a specially designed apparatus to make amino acids from a gaseous mixture of ammonia (NH_3), water (H_2O), methane (CH_4), and hydrogen (H_2). Such experiments produce a mixture of both L and D forms of amino acids. In contrast, living things have the ability to make only the L-amino acids as they produce amino acids for proteins.

Each protein contains many L-amino acids joined together in a specially designed way. The design plan is stored in DNA. Molecular machines copy the design plan from DNA to RNA. Other miniature molecular machines read the RNA. They use the information from the RNA to join amino acids in the right sequence to make proteins.

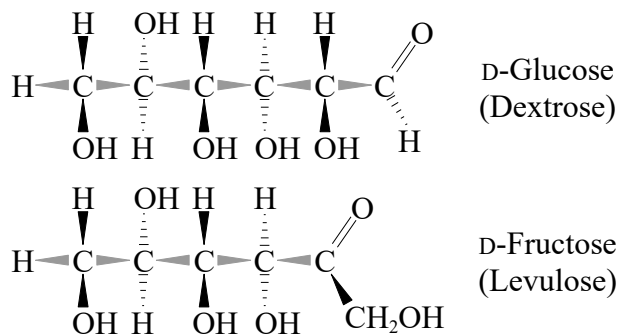
Both DNA and RNA are made from chiral sugars. Proteins are made from chiral amino acids. Chirality is an integral feature of living things. Why are DNA and RNA made from D forms of sugars? Why are proteins made from L forms of amino acids?

Scientific experiments demonstrate that natural chemical reactions do not produce sugars that are *only* of the D form or amino acids that are *only* of the L form. Those who hold to the philosophy of naturalism have not been able to find a satisfactory explanation for the origin of the special chirality found in living things. However, there is a satisfying and logical explanation for the origin of the chirality in DNA, RNA, and proteins: "In the beginning was the Word, and the Word was with God, and the Word was God. The same was in the beginning with God. All things were made by him; and without him was not any thing made that was made."

"For of him, and through him, and to him, are all things: to whom *be* glory for ever. Amen."



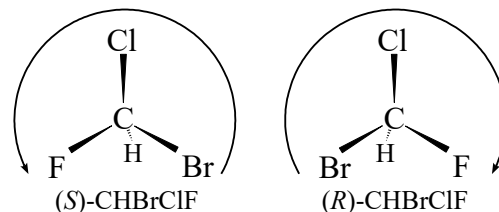
Chemists use the symbols (+) and (-) to state the direction a chiral substance rotates polarized light. Suppose someone looks through a polarizer filter at polarized light that has passed through a solution of D-glucose. By rotating the polarizer filter, it can be seen how the light has been rotated. Since D-glucose rotates light to the right, it is D-(+)-glucose. Since D-fructose rotates light to the left, it is D-(-)-fructose.



These perspective structures show open-chain forms of D-glucose and D-fructose. The molecular model at the top of the page shows a ring form of D-glucose. Both D-glucose and D-fructose can exist as rings or as open chains. In water, most molecules of these sugars exist as rings. In the open-chain form, parts of the molecule on opposite sides of a bond can rotate about that bond. After enough rotations about various bonds, different parts of the molecule may meet and join together to make a ring form of the sugar.

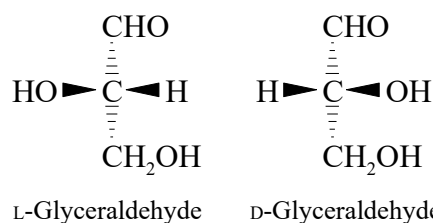
- For a 2-D example, consider this symbol: p. The "p" cannot be rotated in a plane so it looks like its mirror image (q). However, the symbol "p" is not truly chiral. In 3-D, a "p" can be flipped over to look like its mirror image.
- In 4-D, a glove or other 3-D chiral object might be able to be rotated to look like its mirror image. However, only three space dimensions are available to us. So we cannot rotate a chiral object to look like its mirror image.
- The statement about the achirality of a spoon is based upon its overall design. Small asymmetric features in the spoon would keep it from being truly achiral. For example, in the wooden spoon pictured, it seems highly unlikely that the wood grain is perfectly symmetric. Also, the cellulose in wood is formed by joining many chiral D-glucose units into a long polymer. At the microscopic level, a wooden spoon is chiral.

- The two forms of CHBrClF are (S)-CHBrClF and (R)-CHBrClF. The model shown on the first page is (S)-CHBrClF. In order of *decreasing* atomic number, the atoms around the C are Br, Cl, F, and H. If the model is rotated so the H is behind the C, then the Br, Cl, and F will be arranged in a *counterclockwise* way around the C. Its mirror image will then have the Br, Cl, and F arranged in a *clockwise* way around the C. In general, to determine the type of chirality around a C, the atoms around it are first listed in order of *decreasing* priority. Lower atomic numbers have lower priority. If two atoms are the same, then atoms bonded to them are analyzed to determine which group of atoms has the lower priority. The atoms are then rotated so the atom or group with the lowest priority is behind the C. If the three remaining atoms or groups are oriented in a *counterclockwise* way in order of decreasing priority, then the type of chirality is S. If their orientation is *clockwise*, then the type of chirality is R.



The Latin word *rectus* is related to the word *right* and can be translated as *right*. In this sense, *right* may mean *proper* or *correct*. It does not refer to the side that is opposite *left*. The Latin word *dexter* can mean *right* in that sense. Two antonyms of *dexter* are *laevus* and *sinister* which can both mean *left*. In view of the meaning of *rectus*, it is interesting that R and S are said to come from *rectus* and *sinister*.

- The D/L system is based on the simple sugar *glyceraldehyde*. Chiral sugars and amino acids are categorized as D or L depending on whether they are related to D-glyceraldehyde or L-glyceraldehyde. Textbooks state that when the D/L system was developed, it was not known which form of glyceraldehyde was dextrorotatory and which form was levorotatory. It is now known that D-glyceraldehyde is *dextrorotatory* and L-glyceraldehyde is *levorotatory*. Thankfully, the letters D and L were assigned correctly to the two different forms of glyceraldehyde. Although the D/L system is not as general as the R/S system, the D/L system works well for sugars and amino acids by giving the same letter to compounds with similar configurations. That does not always happen with the R/S system. The D/L and R/S systems are connected at glyceraldehyde. Do you see how D-glyceraldehyde has the R configuration around its central carbon while L-glyceraldehyde has the S configuration?



In the CHO group, there is a double bond between the C and the O. When the atoms around the central C are analyzed using the R/S system, the order of decreasing priority is OH (or HO), CHO, CH₂OH, and H. Can you mentally rotate these structures so H is behind the central C?

In these models of glyceraldehyde, the atom with the lowest priority (H) is behind the central C. The curved arrows show the orientation of the OH, CHO, and CH₂OH groups. To see why the S form of glyceraldehyde is L-glyceraldehyde, first consider the H that is mostly hidden by the central C in the model of (S)-glyceraldehyde. Mentally rotate the model a small amount about a vertical axis until that H is completely behind the central C. The OH will have rotated forward a bit. Think about where the OH is, and continue rotating the model until the H is at that location. Once that is done, the OH will have rotated to the left side of the C, and the atoms around the C will be arranged like the structure of L-glyceraldehyde shown above. A similar process shows that (R)-glyceraldehyde is D-glyceraldehyde.

