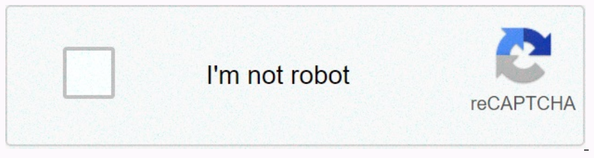

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R vs s configuration amino acids

March 13, 2016 Of Leah4sci Amino acids are biologically active molecules. 19 of the 20 common amino acids have a chiral alpha carbon, 2 amino acids (Leucine and Threonine) have another chiral center in their side chain. This video shows you how to find R/S for 3-D amino acids Find R/S and D/L for Amino Acid Fischer Projections Trick to Quickly Convert R/S to D/L Amino Acids (Look at YouTube: Amino Acid Chirality. Click cc bottom right of video transcription) Referenced in this video: Chirality/Stereochemistry Video Series < - See previous video: Polar, acidic and basic amino acids -> Watch Next Video: Zwitterion and Amino Acid Charge at Given pH value This is video 4 of the Amino Acids Series. Click for complete series + Practice Quiz and Cheat Sheet Have you grabbed the free Printable Cheat Sheet to follow along? CLICK HERE 1. Enter complete names for each of the following compounds, including the designation of stereochemistry: 1a) (3S,6R)-3-bromo-2,3,6,7,7-pentamethylnonan 1b) (2S,, 3S)-1,1-dichloro-2,3-dimethylcyclopropane 1c) (3R,4R)-4-chloro-3-fluoro-1,1-dimethylcyclohexane 2. All of the naturally occurring amino acids are called L because they have a stereochemistry that was historically correlated with a stereoiomer of glyceraldehyde, shown below. L-Glyceraldehyde and the natural amino acids all have S's absolute configuration. The two exceptions are glycine and cysteine. Beat their 3-dimensional structures and explain why they are different. Glycine does not have a stereo center (R = H). Cysteine has a sulfur substitute (R = CH2SH), but it has the same relative configuration as all the other L-amino acids. Due to the S-atom, the priority for the page group is higher than for the COOH group, which is different from all the other amino acids (where the page group priority falls between COOH and H). Chapter 27: Amino acids, peptides and proteins Amino acid Stereochemistry Stereochemistry was introduced in Chapter 7 and most recently revised for carbohydrates Here we will look at Fischer projections, D-, L-notation of amino acids It is a good idea to review the basics of these topics if you remember them before proceeding. Fischer projections are commonly used to represent amino acids. Remember that Fischer projections are typically drawn with the longest chain oriented vertically and with the more heavily oxidized C at the top. For the 20 α-amino acids that occur naturally in proteins, if we focus on α-center, a chirality center, and subtract the Fischer projection put the -CO2H group up, then the ammonium group, NH3+, will be on the left, making it like L-glyceraldehyde, where-OH is on the left (review?). That's why we have the L-amino acids. You can check this out using the 3D-JMOL images below: alanine tryptophan S-(-)-glyceraldehyde or L-glyceraldehyde questions Which of common amino acids are achiral? ANSWER R and S nomenclature are also used to define configuration at chirality centers. Are the L amino acids R- or S-? ANSWER NOTE: Although only the L-amino acid series are incorporated into natural proteins, D-amino acids also occur naturally. © Dr. Ian Hunt, Department of Chemistry The amino acids are all chiral, with the exception of glycine, whose side chain is H. As with lipids, biochemists use L and D nomenclature. All naturally occurring proteins from all living organisms consist of L amino acids. The absolute stereochemistry is related to L-glyceraldehyde, as was the case for triacylglycerides and phospholipids. Most naturally occurring chiral amino acids are S, with the exception of cysteine. As the chart below shows, the absolute configuration of the amino acids can be displayed with H pointed at the back, COOH groups pointing out to the left, the R group on the right, and the NH3 group upwards. You remember this with the ANAGRAM CORN. Figure: Stereochemistry of amino acids. Why do biochemistry still use D and L for sugars and amino acids? This explanation (taken from the link below) seems reasonable. In addition, however, chemists often have to define a configuration uniquely in the absence of a reference connection, and for this purpose, the alternative (R,S) system is ideal as it uses priority rules to specify configurations. These rules sometimes lead to absurd results when applied to biochemical molecules. For example, as we've seen, all the common amino acids are L because they all have exactly the same structure, including the location of the R group, if we just write the R group as R. But they don't all have the same configuration in the (R, S) system: L-cysteine is also (R)-cysteine, but all the other L-amino acids are (S), but this simply reflects the human decision to give a sulfur atom higher priority than a carbon atom , and does not reflect a real difference in configuration. Worse problems can sometimes occur in substitution reactions: sometimes inversion of configuration can result in no change in (R) or (S) prefix; and sometimes configuration retention can result in a change in the prefix. It follows that it is not only conservatism or lack of understanding of the (R.S) system that causes biochemists to continue with D and L: it's just that the DL system meets their needs much better. As mentioned, chemists also use D and L when they are appropriate for their needs. The explanation above as to why the (R,S) system is slightly used in biochemistry is thus almost the exact opposite of reality. This system is actually the only practical way to uniquely represent the stereochemistry of complicated molecules with multiple asymmetric centers, but it is inconvenient with regular series of molecules like amino acids and simple sugars. I told you to draw the correct stereochemistry of a molecule with 1 chiral C (S isomer for example), and I gave you substitutes, you can make it easy to follow R, S priority rules. But how would you draw the correct isomer for L isomer of the amino acid alanine? You could not do so without prior knowledge of the absolute configuration of the related molecule, L glyceraldehyde, or unless you remembered the anagram CORN. However, this disadvantage is more than compensated for by the fact that different L amino acids with the same absolute stereochemistry, can be labeled R or S, making this nomenclature unleet to biochemists. Contributors and Attributions Prof. Henry Jakubowski (College of St. Benedict/St. John's University) To name enantiomers of a compound unequivocally, their names must include the handness of the molecule. The method for this is formally called the R/S nomenclature. The method of uniquely assigning hand-raising of molecules was the origin of three chemists: RS Cahn, C. Ingold, and V. Prelog and as such is also often called Cahn-Ingold-Prelog rules. In addition to the Cahn-Ingold system, there are two ways to make an experimental determination of the absolute configuration of an enantiomer: X-ray diffraction analysis. Note that there is no correlation between the signs of rotation and the structure of a particular enantiomer. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction. However, for non-laboratory purposes, it is beneficial to focus on the R/S system. The sign of optical rotation, although different for the two enantiomers of a chiral molecule,at the same temperature, cannot be used to establish the absolute configuration of an enantiomer; This is because signs of optical rotation for a particular enantiomer can change when the temperature changes. The nomenclature right hand and left hand are used to name enantiomers a chiral connection. The stereo centers are marked as R or S. Consider the first image: A curved arrow is drawn from the highest priority (1) substitute to the lowest priority (4) substitute. If the arrow is pointing counterclockwise (left when it leaves at 12 o'clock), the stereo center configuration is considered S (Sinister → Latin= left). However, if the arrow is clockwise(Right when you leave at 12 o'clock), the stereo center is marked R (Rectus → Latin= right). R or S is then added as a prefix in parentheses to the name of the enantiomer interest. Example 1 (R)-2-Bromobutane (S)-2,3- Dihydroxypropanal Before applying the R and S nomenclature to a stereo center, the substitutes must be prioritised according to the following rules: First, check the atoms directly attached to the stereo center of the connection. A substitute with a higher the figure takes precedence over a substitute with a lower atomic number. Hydrogen is the lowest priority substitute because it has the lowest atomic number. When dealing with isotopes, the atom with the higher atomic mass gets higher priority. When visualizing the molecule, the lowest priority substitution should always point away from the viewer (a dotted line indicates this). To understand how it works or looks, imagine that a clock and a rod. Attach the rod to the back of the watch so that when looking at the face of the watch, the rod points away from the viewer in the same way that the lowest priority substitly should point away. Then drag an arrow from the highest priority atom to the second highest priority atom to the third highest priority atom. Because the fourth highest priority atom is located in the back, the arrow should look as if it goes across the face of a clock. If it goes clockwise, then it is an R-enantiomer; If it goes anticlockwise, it's an S-enantiomer. When looking at a problem with wedges and lines, if the lowest priority atom is not on the dotted line pointing away, the molecule must be rotated. Remember that wedges indicate coming towards the viewer. Lines indicate pointing away from the viewer. If there are two substitutes of the same rank, continue along the two substitute chains until there is a point of difference. First, determine which of the chains has the first connection to an atom with the highest priority (the highest atomic number). This chain has the highest priority. If the chains are the same, continue down the chain until a point of difference. For example: an ethylene substituent takes precedence over a methylertituent. When connecting the stereo center, both have a carbon atom that is equal in rank. Going down the chains, a methyl has only had hydrogen atoms attached to it, while ethyl has another carbon atom. The carbon atom on ethylene is the first difference point and has a higher atomic level than hydrogen; therefore ethylene takes precedence over methyl. If a chain is connected to the same type of atom two or three times, check to see if the atom to which it is connected has a larger atomic number than any of the atoms associated with the competing chain. However, if none of the atoms associated with the competing chain(s) in the same location has a larger atomic number: the chain, which is bound to the same atom several times, has the highest priority if one of the atoms connected to the competing chain has a higher atomic number: this chain has the highest priority. Example 2 A 1-methylethylerubstituent takes precedence over an ethylerubstituent. Ethyl is associated with the first carbon atom and has only one other carbon, while 1-methylethylene has two carbon atoms attached to the first; This is the first point of difference. Therefore, 1-methylethyl ranks higher priority over ethyl, as shown below: But remember, being double or triple bound to an atom means that the atom is connected to the same atom twice. In this case, follow the same method as above. Caution!! Remember that priority is determined by the first point of difference along the two similar substitute chains. After the first point of difference, the rest of the chain is irrelevant. When you see, firstly, the difference between similar substitute chains, you may encounter branching. If there is a branch, select the branch that has higher priority. If the two substitutes have similar branches, rank the elements within the branches until a point of difference. Once all your substitutes have been prioritized in the right way, you can now name/label the molecule R or S. Put the lowest priority substitute in the back (dotted line). Continue from 1 to 2 to 3. (it's useful to draw or imagine an arc arrow that goes from 1 - > 2 - >3) Find out if the direction from 1 to 2 to 3 clockwise or counterclockwise. i) If it's clockwise it's R. ii) if it's counterclockwise it's S. USE YOUR MODELING KIT: Models help visualize the structure. When using a model, make sure that the lowest priority points away from you. The direction from the highest priority is then determined to the lowest: clockwise (R) or counterclockwise (S). If you don't have a modeling kit: remember that the lines mean the bond goes into the screen and the wedges mean the bond comes off the screen. If the lowest priority bond doesn't point to the back, mentally rotate it, so it is. But it is very useful when learning organic chemistry to use models. If you have a model set, use it to help you resolve the following practice issues. Are the following R or S? Solutions S: I > Br > F > H. The lowest priority substitute, H, is already heading for the back. The turn left goes from I to Br to F, so it's an S. R: Br > Cl > CH3 > H. You have to change H and Br to place H, the lowest priority, in the back. Then, going from Br to Cl, ch3 is turning right, giving you an R. Neither R nor S: This molecule is achiral. Only chiral molecules can be named R or S.R: OH > CN > CH2NH2 > H. H, the lowest priority, must be switched to the back. Then, goes from OH to CN to CH2NH2, you turn right, gives you an R. (5) S: \(\ce{-COOH}\) > \(\ce{-CH_2OH}\) > \(\ce{C#CH}\) > \(\ce{H}\). When you go from \(\ce{-COOH}\) to \(\ce{-CH_2OH}\) to \(\ce{-C#CH}\), you then turn left, giving you an S configuration. References Schore and Vollhardt. Organic chemistry structure and function. New York:W.H. Freeman and Company, 2007. McMurry, John and Simanek, Eric. The basics of organic chemistry. 6. Ed. Brooks Cole, 2006. Contributors Ekta (UCD), Ifemayowa Aworanti (University of Maryland Baltimore Baltimore

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