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Optical activity W. What connection, if any, will be optically active? Optical activity: Which of the following molecules is optically active? Chapter 7 : The issue of stereoimimia related to optical activity 1. Given that (R)-2-bromobutan has a certain rotation -23.1o , what is a specific rotation (S)-2-bromobutan? 2. Using data from zu1, what is optical purity and % composition of the mixture (R)- and (S)-2-bromobutan, whose particular rotation was found to be 18.4o ? 3. What about a mixture whose specific rotation was discovered - 9.2o? Answer..... Chapter 7 : Stereochemisty optical activity in depth Consider that (S)-bromobutan has a certain rotation of 23.1o and (R)-bromobutan has a certain rotation -23.1o Question: Determine the optical purity of the racial mixture. Answer: Specific rotation as well, a fellow racer is expected to be 0, since the effect of one enantiomer undo another, a molecule for the molecule. Optical purity, % - 100 per mixture / pure sample - 100 (0) / 23.1o - 0% question: Identify the enantiometric excess of the racing mixture. A: One would expect the R and S to be 50%. ee% - 100 (RH-C) / (RRS) - 100 (50-50) / (50-50) - 0% Let's consider something a little more complicated..... The question is: Which isomer dominates and what is the optical purity of the mixture, (R)- and (S)-bromobutan, whose specific rotation has been established ,9.2o? Answer: A negative sign indicates that R enantiomer is dominant. Optical purity, % - 100 per mixture / pure sample - 100 (-9.2) / -23.1o - 40%, which indicates a 40% excess of R over S! The question is: What is the percentage of the mixture? Answer: 60% of residues that are optically inactive must be equal amounts as (R)- and (S)-bromobutan. Exceeding 40% is all so a total of 70% (R) and 30% (S). Try a similar problem. © Dr Ian Hunt, Department of Chemistry Problem No. 527 Draw structure (2R,3S) 2-bromo-3-chlorobutan using wedges and dash. Also draw a projection of Fisher. SolutionIt's two separate problems. Many tutorials describe how to mentally transform the zigzag (wedge/dash) structures Fisher predictions, but I have never met a student who can do it without mistakes. So you have to convert the name ((2R,3S) 2-bromo-3-chlorobutan) into a zigzag structure, and then convert the name into a Fisher projection. Never try to convert a zigzag structure directly into a Fisher projection. To draw a zigzag structure, first draw a structure with each halogen (the highest priority of substintents) as a wedge, see We've drawn the R/S configuration and then adjusted it as needed. Why wedges? Because it puts hydrogen as a dash, so R/S is easy to assign. With two wedges, the structure (2R, 3R). So the 2R position is OK and we just switch the wedge to the C-3 in the dash, and the structure is correct (2R,3S). To draw a projection of Fisher, we do something similar - arbitarily draw the structure, check the R/S, and then adjust as needed. In the structure below, I drew (arbitorno) 2S,3S, but we need 2R,3S, so I just switch the C-2 and we have the right structure. Problem Details Problem No. 744 After the sample optically clean (S)-2-ethyl-cycloaxakin dissolves into an aqueous solution within a few hours, a significant loss of optical activity is observed. Explain. Problem solution number 532 Let's work through a chiral resolution. Write down the structure of the specified connection in each box. Turn on the stereochemity. Why can I split (R,R) and (R,S) salt? SolutionThe starter material (2-aminomobutan) is racemic; it has an equal number of R and S enantiomers. Enantiomers have the same chemical and physical properties, so we cannot separate them using common laboratory methods such as recrystalization, chromatography, etc. but diastereomers can have different properties, and we can use this fact to separate otherwise inseparable compounds. Adding optically pure acid to the amin produces a diastereometric mixture of salts that can be separated. Adding a base (NaOH) breaks salt and allows us to isolate pure R or S amin. We can separate (R,R) and (R,S) salts because they are diastereomers and therefore have different chemical and physical properties. Details of the problem of Chirality and optical activity Chiral Stereoisomers Cis/trans or E/isomers, formed alkenes are not the only example of stereoisomers. To understand the second example of stereoisomers, it would be useful to start by looking at a pair of hands. For all practical purposes, they contain the same substintents of four fingers and one thumb on each hand. If you clap them together, you will find even more similarities between the two hands. Thumbs are attached at about the same point on the hand; well below the point where the fingers start. The second fingers on both hands are usually the longest, then the third fingers, then the first fingers, and finally the little fingers. Despite their many similarities, there is a fundamental difference between a pair of hands that can be observed trying to place your right hand in the left glove. Your hands have two important properties: (1) each hand is a mirror image of the other, and (2) these mirror images are not superimposed. The mirror image of the left hand looks like the right hand, and vice versa, as shown in the picture below. Objects with a similar (literally, with your hand). Those that don't say that achiral. The gloves are chiral. (It is difficult, if not impossible, to place the right glove on the left hand or left glove on the right hand.) Mittens, however, are often achiral. (Either mittens can fit on any hand.) The legs and shoes are both chiral, but the socks are not. In 1874, Jacobus van't Hoff and Joseph Le Bel recognized that a compound that contains one tetraethral carbon atom with four different substints can exist in two forms that are mirror images of each other. Consider the CHFClBr molecule, for example, which contains four different substints to the tetraedral carbon atom. The image below shows one possible location of these substints and a mirror image of this structure. Under the convention, hard lines are used to represent bonds that lie in the paper plane. Wedges are used for bonds that come out of the plane of paper to the viewer; the dotted line describes the bonds that go after the paper. If we turn the molecule on the right at 180 around the ch-link, we get the structure shown on the right in the image below. These structures differ in that they cannot be superimposed on each other, as shown in the picture below. CHFClBr is a chiral molecule that exists in the form of a pair of stereoisomers that are mirror images of each other. Typically, any tetraethral atom that carries four different substints is a stereo center or stereogenic atom. However, the only criterion of chirality is the neoproblem nature of the object. The test for achirality is the presence of a mirrored plane inside the molecule. If there is a plane in the molecule that will cut it into two symmetrical halves, it is achira. Therefore, the absence of such a plane indicates that the molecule is chiralna. Connections containing a single stereo center always chirp. Some connections containing two or more stereo centers are achirals because of the symmetry of the relationship between stereo centers. The set-top box en- often means make, or reason to be, as in the threat. It is also used to strengthen the term to make it even stronger, as in revitalizing. Thus, it is not surprising that a pair of stereoisomers, which are mirror images of each of them, are called enantiomers. They are literally compounds that contain parts that are forced to be opposite each other. Stereoisomers, which are not mirror images of each other, are called diastereomers. The prefix dia- is often used to refer to opposite directions or across as diagonally. Cis/trans isomers 2-buten, for example, are stereoisomers, but they are not mirror images of each other. As a result, they are diastereomers. The difference between enantiomers on the macroscopic scale If could analyze the light that moves towards you from the lamp, you would find electrical and magnetic magnetic this radiation oscillating in all planes parallel to the path of light. However, if you have analyzed the light that has passed through the polarizer, such as Nicole's prism or the lens of polarized sunglasses, you will find that these vibrations are now limited to a single plane. In 1813, Jean Baptiste Biot noticed that flat-polarized light rotates either to the right or left when it passes through single quartz crystals or acacia solutions of tartare acid or sugar. Because they interact with light, substances that can rotate the plane of polarized light are said to be optically active. Those that rotate the plane clockwise (right) are said to be dextrorotor (from Latin dexter, right). Those that rotate the plane counterclockwise (left) are called left-rotational (from Latin laevis, left). In 1848, Louis Pasteur noted that sodium ammonium tartrate forms two different types of crystals that are mirror images of each other, just as the right hand is a mirror image of the left hand. Separating one type of crystal from another with a pair of tweezers, he was able to prepare two samples of this compound. One of them was dextrorotor when dissolved in an aqueous solution, the other was lebrotor. Because optical activity remained after the compound was dissolved in the water, it could not have been the result of the macroscopic properties of the crystals. Therefore, Pasteur came to the conclusion that in the structure of this compound should be some asymmetry, which allowed it to exist in two forms. Once the techniques were developed to determine the three-dimensional structure of the molecule, the source of the optical activity of the substance was recognized: Compounds that are optically active contain molecules that are chiral. Chirality is a molecule property that is the result of its structure. Optical activity is a macroscopic feature of the collection of these molecules, which arises from the way they interact with light. Connections such as CHFClBr that contain a single stereo center are the easiest to understand. One enantiomer of these chiral compounds is dextrorotor; another levorotatory. To decide whether the compound should be optically active, we look at evidence that the molecules are chiral. The tool by which optically active compounds are studied is the polarimeter shown in the image below. Imagine a horizontal line that runs through a zero coordinate system. According to the convention, negative numbers are placed on the left and positive numbers to the right of zero. Thus, it is not surprising that the leukotor compounds are shown with negative sign (-)and dextrorotor compounds with a positive sign (+am). The angle through which the enantiomer rotates light, depends on four quantities: (1) the wavelength of light, (2) the length of the cell through which light passes, light, concentration of the optically active joint in the solution through which light passes, and (4) the specific rotation of the compound, which reflects the relative ability of the compound to rotate flat-polarized light. The specific rotation of the dextrorotatoric glucose isomer is written as follows: when the spectrum of sunlight was first analyzed by Joseph von Fraunhofer in 1814, he observed a limited number of dark bands in this spectrum, which he called A-H. We now know that band D in this spectrum is the result of the absorption by sodium light atoms, which has a wavelength of 589.6 nm. The D in the symbol for a particular rotation indicates that it is the light of this wavelength that has been studied. 20 indicates that the experiment was done at 20C. It rotates the light clockwise. Finally, the magnitude of this measurement indicates that when studying the solution of this compound with a concentration of 1.00 g/ml in a 10-centimetre cell, it rotated light at 3.12. The amount of rotations observed by a pair of enantiomers is always the same. The only difference between these compounds is the direction in which they rotate the planes of polarized light. Thus, the specific rotation of the left-leaning isomer of this link is -3.12. The difference between enantiomers on the molecular scale A strategy, which is based on Latin terms for the left (sin) and the right (rectus), was designed to distinguish between a pair of enantiomers. Arrange four substints to reduce the atomic number of atoms attached to the stereo. (The subcharge with the highest atomic number receives the highest priority.) For example, substints in 2-bromobutans will be listed in order: Br zgt; CH3 and CH2CH3 zgt; H. When two or more substintents have the same priority, such as the CH3 and CH2CH3 groups in 2-bromobutane, keep working down the substant chain until you find the difference. In 2-bromobutan we give the CH2CH3 group a higher priority than the CH3 group, because the next point down the chain is the CH3 group in the CH2CH3 subprint and the H atom in the CH3 group. Thus, the four substints on the 2-bromobutan will be listed in the order: Br zgt; CH2CH3 zgt; H. View the enantiomer with a direction that puts the substitute with the lowest priority as far away from the eyes as possible. In the following example, this involves rotating a counterclockwise molecule around the CCH2CH3 connection and tilting it slightly around the axis that lies in the paper plane. When this is done, the substitution that has the lowest priority is hidden from view. Track the path that binds the subs officers in reducing the order of priority. If the path curves to the right clockwise the rectum molecule or R enantiomer. If it curves to the left it is sinister or s enantiomer. In this example, the path curves to the left, so this enantiomer is (S)-2-bromobutan stereoisomer. It is important to recognize that the system (R)/(S) is based on the structure of a single molecule, and the system is based on the macroscopic behavior of a large collection of molecules. The most complete description of the enantiomer combines aspects of both systems. Enantiomer, analyzed in this section, is best described as (S)-----2-bromobutan. There is an enantiomer (S) because of its structure and (-) enantiomer because enantiomer samples with this levorotatory structure; they rotate the plane of polarized light clockwise. Note that the optical rotation sign does not correlate with the absolute configuration. Return to the Organic Theme Review page organic chemistry: Structure and Nomenclature hydrocarbon structure and nomenclature of hydrocarbons (en) Isomers Reaction of Alkanes, Alkenes and Alkines Hydrocarbons Oil and Coal Chirality and Optical Activity Periodic Table (en) Periodic Table Glossary Cool Applets Gen Chem Topic Review (en) General Chemistry Site. optical activity practice problems pdf

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