

Optical isomerism & Chirality

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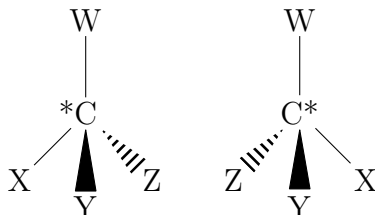
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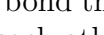
1 Introduction

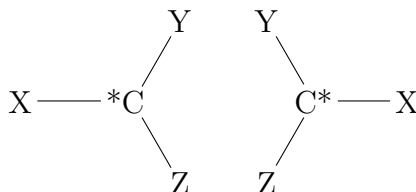
Optical isomerism is a type of stereoisomerism. It can be observed as the isomerism that exists when the mirror image of a molecule is not superimposable on itself.

2 Theory

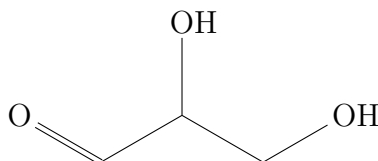
The simplest form of chirality can be seen in a molecule where four different atoms or groups of atoms are connected to one carbon atom, acting as the chiral centre. This central carbon atom usually has an asterisk adjacent to it to denote its asymmetric nature, here you can see two chiral molecules:



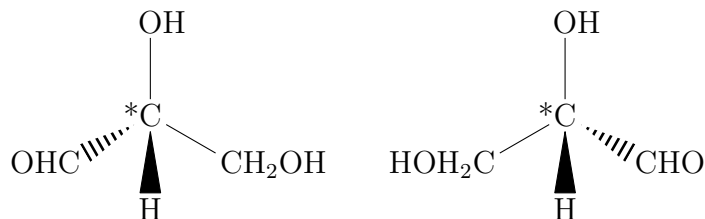
In the diagram shown above, the  bond denotes a bond that is in front of the paper. The  bond denotes a bond that is behind the paper, and the  bond denotes a bond that is in the plane of the paper. These molecules are mirror images of each other, but are not the same exact molecule. It is easier to observe this difference by looking up from the bottom of these molecules:



No matter how much you rotate these molecules, they cannot be superimposable on each other, thus making them isomers. One common example of an organic molecule with a chiral centre is glyceraldehyde, systematically known as 2,3-dihydroxypropanal:



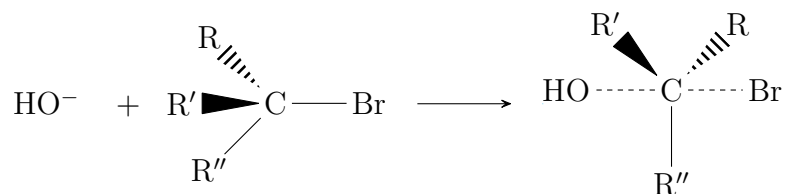
Looking purely at the carbon in the middle of the chain which has a hydroxyl group attached to it, we can observe the chirality that exists.



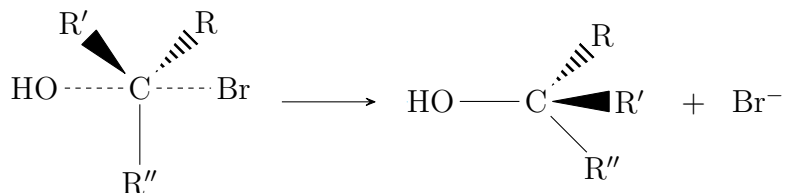
These mirror images are not superimposable due to the fact that there are 4 distinct groups attached to the central carbon. Both of these compounds are distinct mirror images of each other and are optically active. These mirror images are given prefixes that denote the optical rotation they cause. The molecule on the left is formally called D-glyceraldehyde, because it has the 'D-' prefix, which is a short form of 'Dextro-', which indicates that the molecule rotates light clockwise.

The molecule on the right is called L-glyceraldehyde, it has the 'L-' prefix which is a short form of 'Laevo-' which denotes that the molecule rotates light anti-clockwise. These two molecules are called enantiomers. These molecules are virtually identical in terms of their physical properties as well as the way they react chemically. The only way to differentiate between the two molecules is to observe the way they rotate plane-polarised light. Both enantiomers have equal and opposite rotational effect on plane-polarised light. It therefore stands to reason that a one to one mixture of both enantiomers will not be optically active (does not rotate the plane of plane polarised light).

This is true, and there is a specific name given to mixtures of both enantiomers: a racemic mixture. The clockwise rotation caused by one enantiomer is balanced by the anticlockwise rotation caused by the other enantiomer. Knowledge of the compositions of mixtures of two enantiomers can be used to determine whether reactions are undergoing S_N1 mechanisms or S_N2 mechanisms. Consider the following S_N2 mechanism:

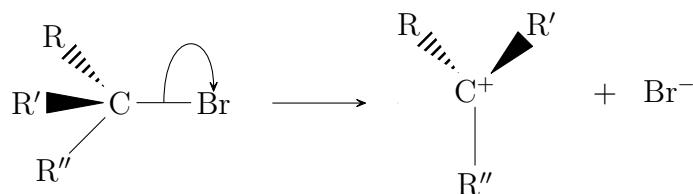


The bonds represented with the dashes show the intermediate bonds:

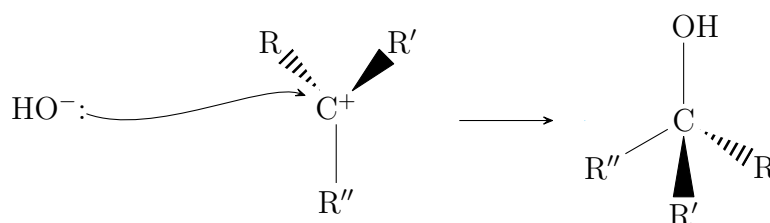


The three R groups bonded to the chiral centre get turned inside out during the reaction. This is called inversion of the configuration. As you can see, this reaction can only produce one enantiomer, since the nucleophile attacks from one side only.

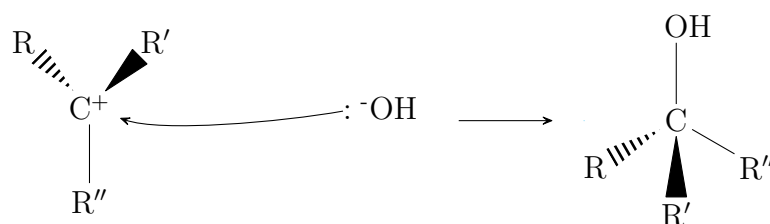
Now consider the following S_N1 mechanism:



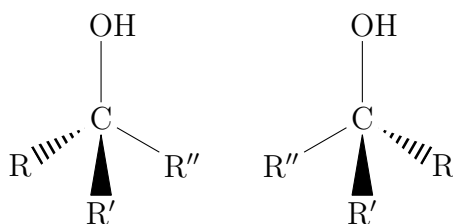
The carbo-cation produced is planar, meaning that it can get attacked from both sides of the plane by a nucleophile:



or:



Now by looking at the molecules side by side we can see that they are mirror images of each other, and are therefore enantiomers:



Since the likelihood of a nucleophile attacking from one side of the planar molecule is just as likely as the nucleophile attacking from the other side of the molecule, the mixture of products is a racemic mixture. This means that if the solution is undergoing an S_N1 reaction mechanism, the product would not be optically active. However, if the solution is undergoing an S_N2 reaction, the product would be optically active.