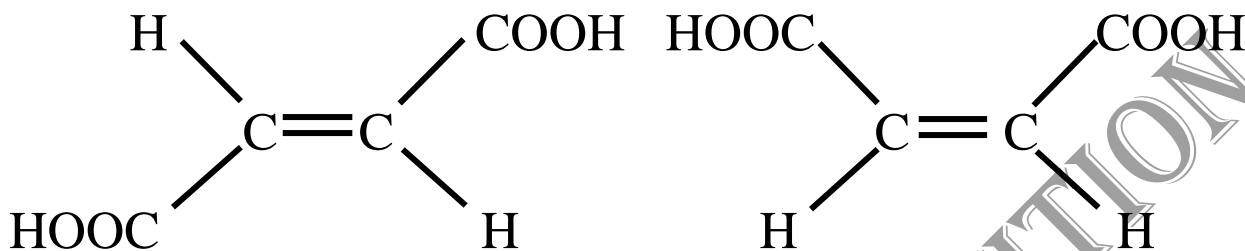


Stereoisomerism

Such isomers which differ in the orientation of atoms or groups in space are called stereoisomers and this phenomenon is called Stereoisomerism. Stereoisomers have same connectivity of atoms and groups but remarkably differ in their physical, chemical and biological properties. For example,



Fumaric acid

M. P.=287⁰C

(Essential metabolite)

Maleic acid

M. P.=287⁰C

(Toxic & irritant)

Classification of Stereoisomerism

Stereoisomerism



(1) Configurational isomerism- Such stereo-isomers which differ in the configuration i.e. the spatial arrangement of atoms or groups are called Configurational isomer and this phenomenon is called Configurational isomerism.

Configurational isomerism arises due to non-interconvertibility of stereoisomers at room temperature. Since, these isomers are non-interconvertible, they can be separated using suitable physical or chemical methods.

Chirality

Louis Pasteur for the first time observed that, sodium ammonium tartrate (a salt of tartaric acid which is used in making wine) exists in two crystalline forms. He separated these two forms using a pair of tweezers. These two forms were the mirror image of each other.

A solution of these two forms was optically inactive, while the solutions of the individual forms were optically active.

Moreover, the specific rotations of these two forms were equal in magnitude, but opposite in sign.

These observations led to the birth of stereochemistry. In general, a compound containing n chiral carbon atoms can exist in 2^n stereoisomeric forms. These stereoisomers may be sub-divided into two groups i.e. enantiomers and diastereomers.

Enantiomers, Diastereomers and Meso form

If a compound contains two chiral atoms, it can exist in four stereoisomeric forms. Since the configuration at each chiral carbon may either be R or S, there will be four stereochemical possibilities i.e. RR, SS, RS, and SR. Here,

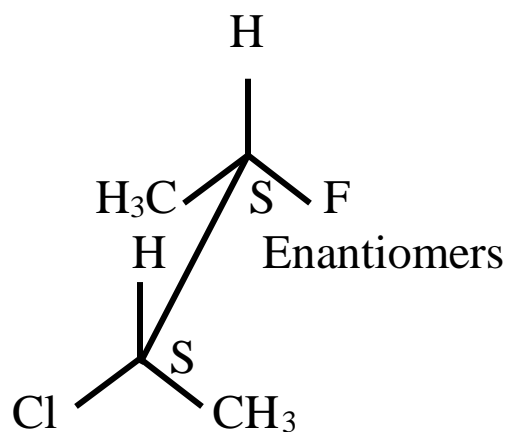
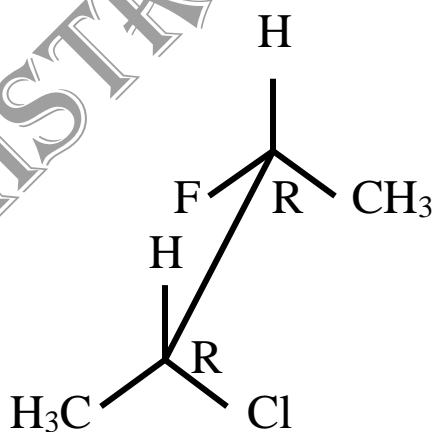
(i) The RR and SS stereoisomers are enantiomers.

(ii) The RS and SR stereoisomers are also enantiomers.

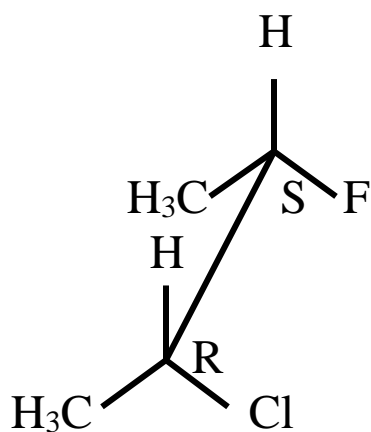
(iii) The RR stereoisomer is a diastereomer of both the RS and the SR stereoisomers.

(iv) The SS stereoisomer is a diastereomer of both the RS and SR stereoisomers.

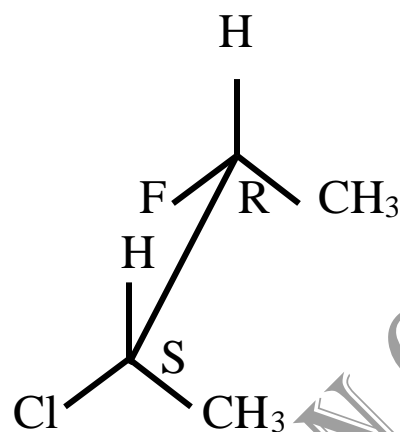
Let us consider, sawhorse projections of the four stereoisomers of 2-chloro-3-fluorobutane.



(R)-2-Chloro-(R)-3-fluorobutane (S)-2-Chloro-(S)-3-fluorobutan



(R)-2-Chloro-(S)-3-fluorobutane



(S)-2-Chloro-(R)-3-fluorobutane

Here,

(i) (R)-2-Chloro-(R)-3-fluorobutane and (S)-2-Chloro-(S)-3-fluorobutane are enantiomer of each other.

(ii) (R)-2-Chloro-(S)-3-fluorobutane and (S)-2-Chloro-(R)-3-fluorobutane are enantiomer of each other.

(iii) (R)-2-Chloro-(R)-3-fluorobutane is diastereomer of both (R)-2-Chloro-(S)-3-fluorobutane and (S)-2-Chloro-(R)-3-fluorobutane.

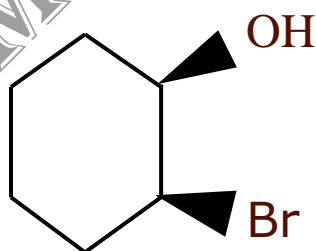
(iv) (S)-2-Chloro-(S)-3-fluorobutane is diastereomer of both (R)-2-Chloro-(S)-3-fluorobutane and (S)-2-Chloro-(R)-3-fluorobutane.

It is clear that, in case of enantiomers the configurations of atoms or groups are just opposite to each other at both the chiral centres i.e. C-2 and C-3.

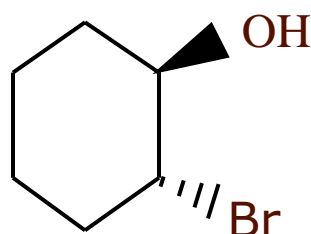
On the other hand, in case of diastereomers the configurations are opposite at only one of the two chiral centers.

Thus, the diastereomers are stereoisomers which are not mirror image that are not enantiomers of each other.

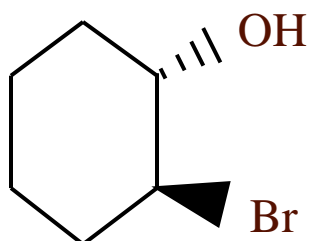
For example, let us consider following stereoisomers-



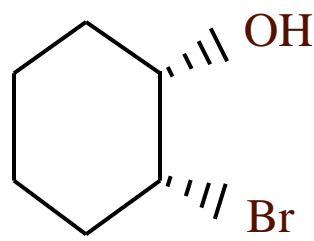
(I)



(II)



(III)

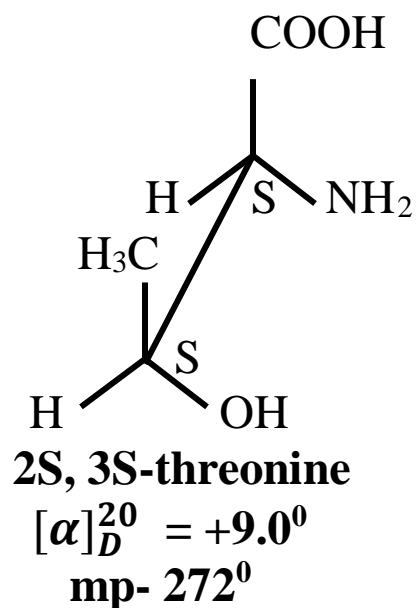
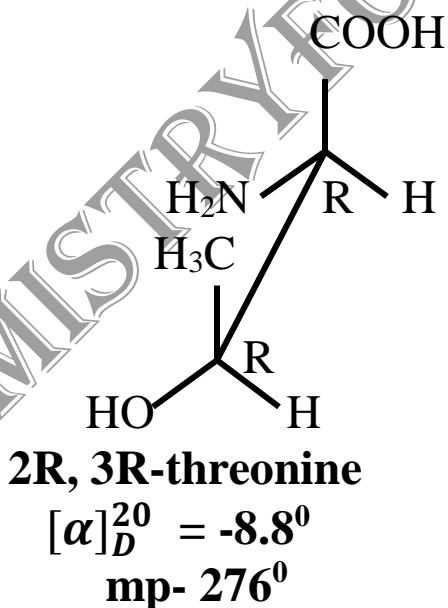


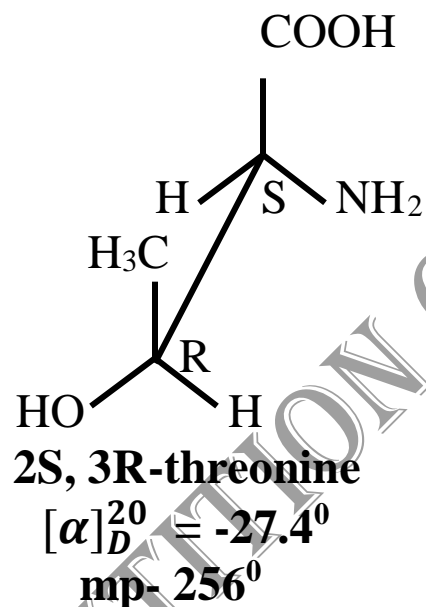
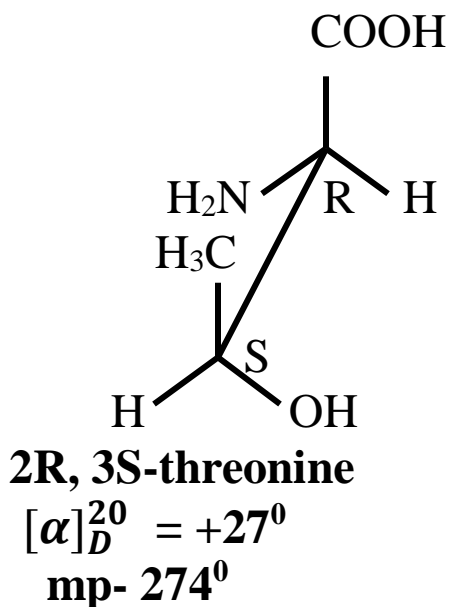
(IV)

Here,

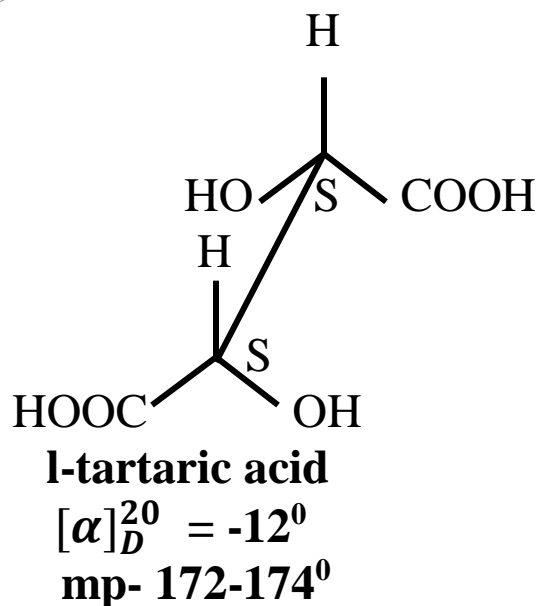
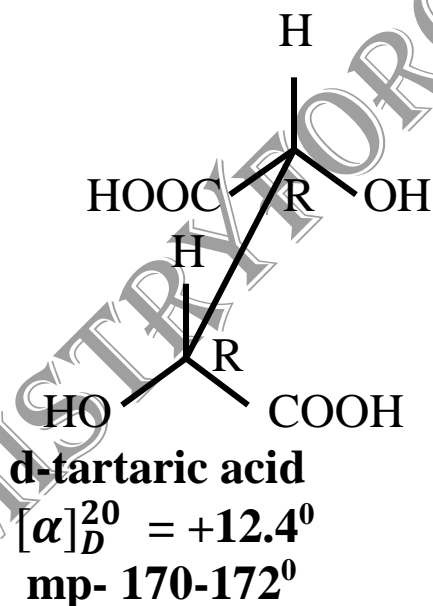
- (i) Stereoisomer (I) and (IV) are enantiomers of each other.
- (ii) Stereoisomer (II) and (III) are enantiomers of each other.
- (iii) Stereoisomer (II) and (III) are diastereomers of structure (I) and (IV).

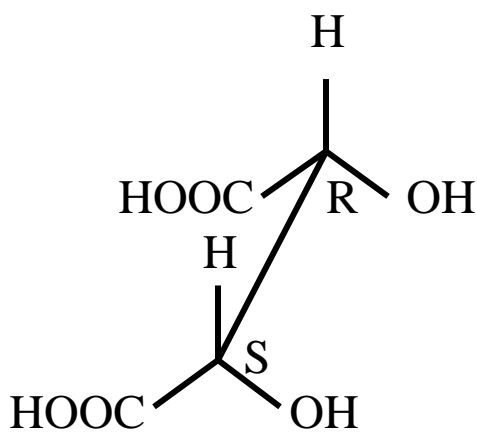
The optical rotations of the enantiomers are almost equal and opposite, but, there is no a priori relationship between the optical rotations of diastereomers. Unlike enantiomers, diastereomers have different physical properties i.e. melting points, boiling points, densities, etc. It can be shown by taking the example of naturally occurring stereoisomers of threonine (an amino acid).





Let us consider, tartaric containing two chiral carbon atoms. In general, a compound containing n chiral carbon atoms exists in 2^n stereoisomeric forms. Tartaric acid is an exception of this rule and has only three stereoisomeric forms.

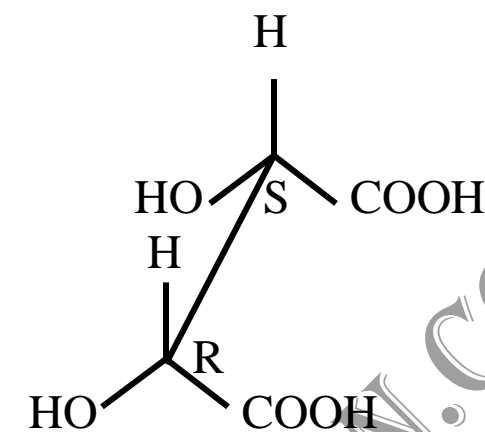




dl-tartaric acid

$$[\alpha]_D^{20} = 0^\circ$$

$$\text{mp- } 210\text{-}212^\circ$$



dl-tartaric acid

$$[\alpha]_D^{20} = 0^\circ$$

$$\text{mp- } 210\text{-}212^\circ$$

Here, last two structures appear to be mirror image of each other. However, the close inspection reveals that, they are not enantiomers but are same structure. It is called Meso or dl-tartaric acid. Imagine an axis lying half way of C₂ and C₃ in H-C₂-C₃-H plane of the left hand structure, if the structure is rotated by 180° around this axis a new orientation is obtained which is identical to the right hand structure.

Furthermore, there is an internal plane of symmetry in meso tartaric acid that bisects the molecule in two equal parts. This situation arises because H, OH, and COOH groups on C₂ occupy mirror image positions with respect to those on C₃.

Such stereoisomers which contain two or more chiral centers and an internal plane of symmetry are called meso compounds. They are not optically active due to internal compensation, even though they contain chiral atoms.