Chapter 5
Enantiomerism

第五章 对映异构

Sec 1 Introduction

Sec 2 How to recognize the chirality?

Sec 3 How to express the configuration

Sec 4 Measurement of optical activity

Sec 5 How to name enantiomers?

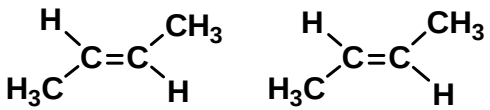
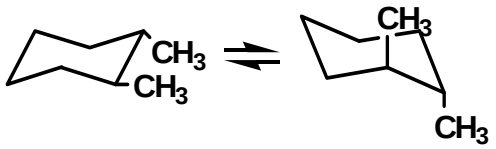
Sec 6 Stereoisomers with more than one C

Section 1 Introduction

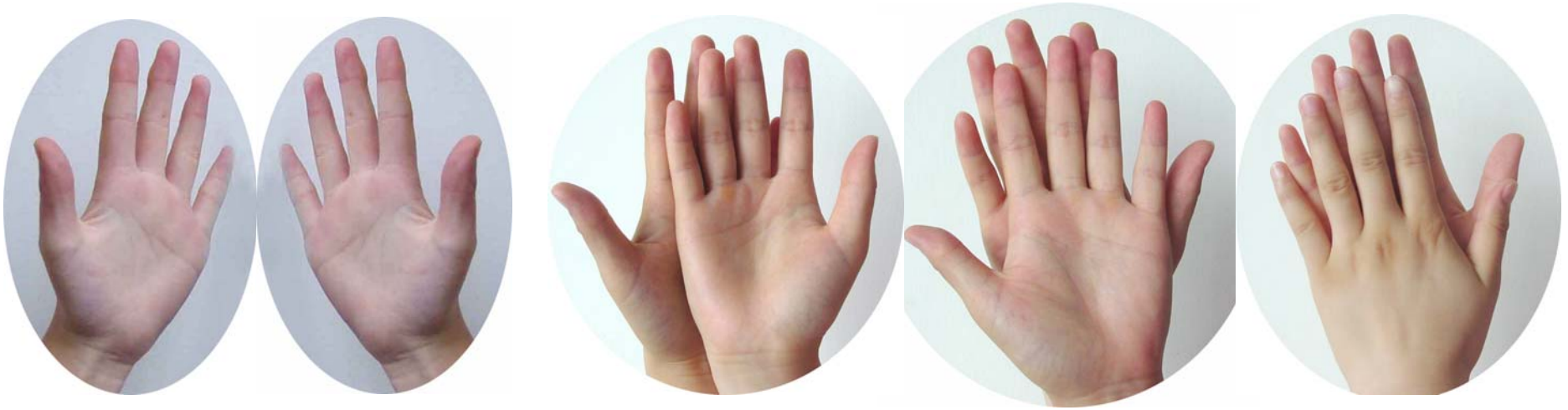
Ⅰ. Classification

CH_3-CH_2-CH_2-CH_3, CH_3-$CH(CH_3)$-CH_3

Isomerism *

- **Constitutional isomerism** 构造异构
  - **Skeletal isomerism**
  - **Positional isomerism**
    CH_2=CH-CH_2-CH_3, CH_3-CH=CH-CH_3
  - **Functional isomerism**
    CH_3-CH_2-OH, CH_3-O-CH_3
- **Stereo-isomerism** 立体异构
  - **Configurational isomerism** 构型异构
    - ***cis-trans***
      
    - **Enantiomerism** 对映异构
  - **Conformational isomerism** 构象异构
    

II. Conceptions: Chirality (手性)



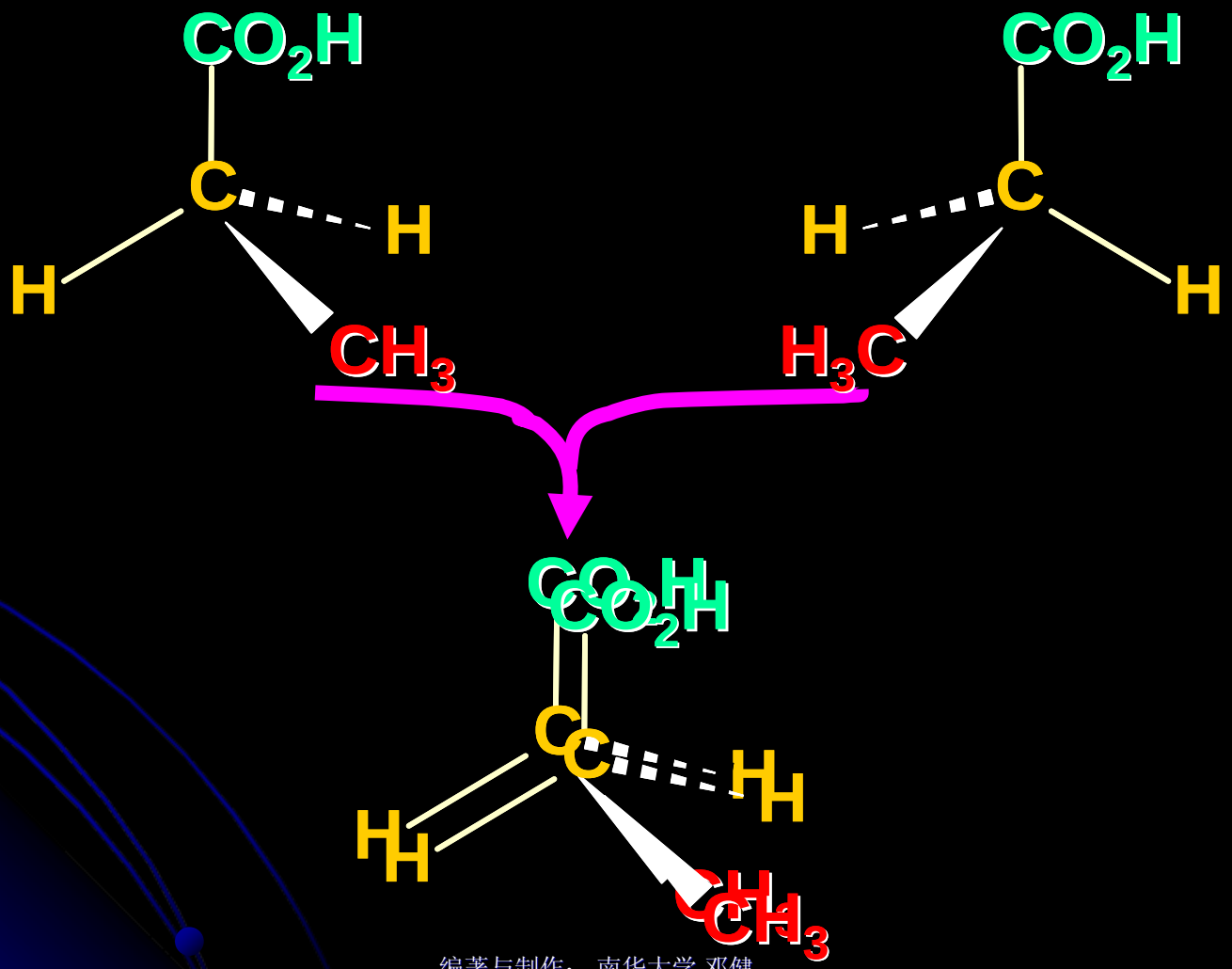
Chirality:

not superposable on their mirror images

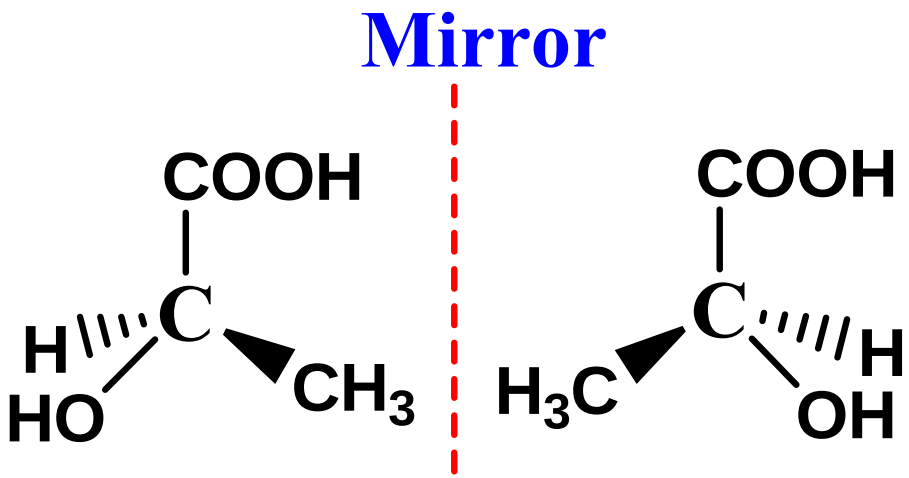
(Handedness 手性)

左右手互为镜像与实物关系(称为对映关系)，彼此又不能重合的现象称为手性.

Some of organic molecules are superposable on their mirror images.



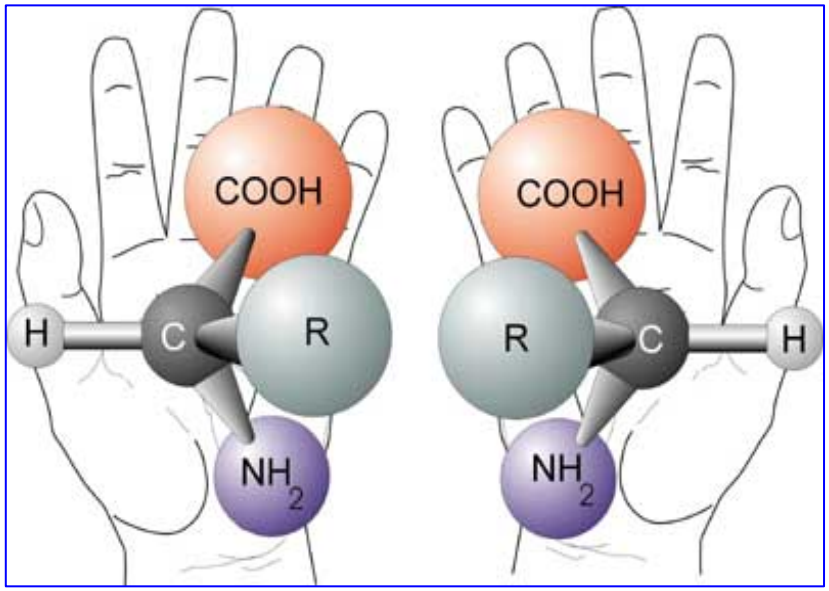
Look at the following molecules — the pair of lactic acid, are they identical?



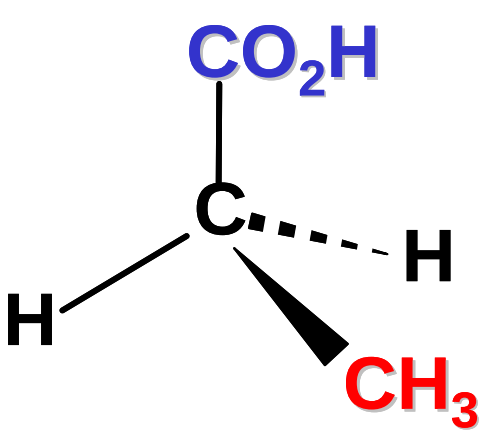
Lactic acid
(mirror image each other)

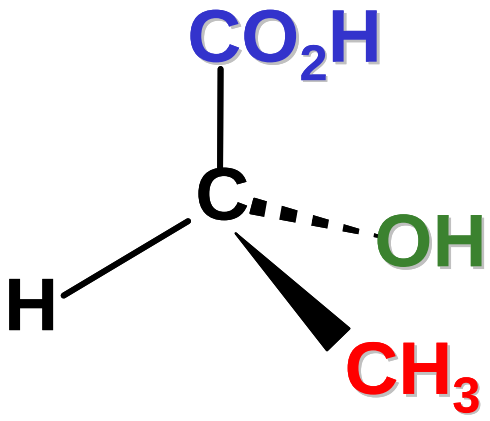
They are nonsuperimposable mirror images.
Each form exists independently.

Lactic acid are not superposable on their mirror images



A molecule that is not identical to its mirror image is a kind of stereoisomer called an enantiomer(对映体). Enantiomers are related to each other as a right hand is related to a left hand.





Close examination of propanoic acid and lactic acid reveals that lactic acid possesses a carbon with four different attached groups (CH_3, OH, H, CO_2H); there is no such carbon in propanoic acid. This special carbon with four different bonded groups is called a stereocenter or chiral carbon atom (手性碳 *).

Sec 2 How to recognize the chirality of a molecule?

I. To see if it is nonsuperposable on its mirror image;

II. To see if there is a single C*;

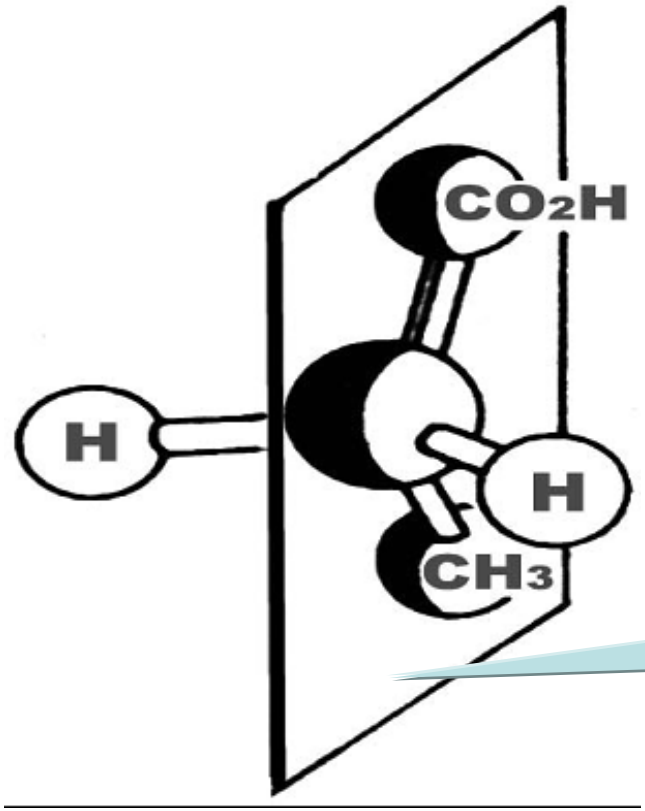
III. To find if there are some symmetry elements(对称元素)

*To see if there is a single C**

A molecule is chiral if it contains one chiral carbon atom (or chiral center). Compounds with a single chiral carbon atom always have one pair of enantiomers; each enantio-mer is a chiral molecule. We will see later that compounds with more than one chiral carbon atom have the possibility of more than one pair of enantiomers.

To find some symmetry elements

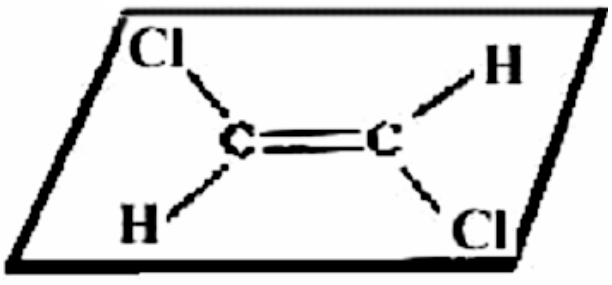
Plane of Symmetry (对称面, C_s)

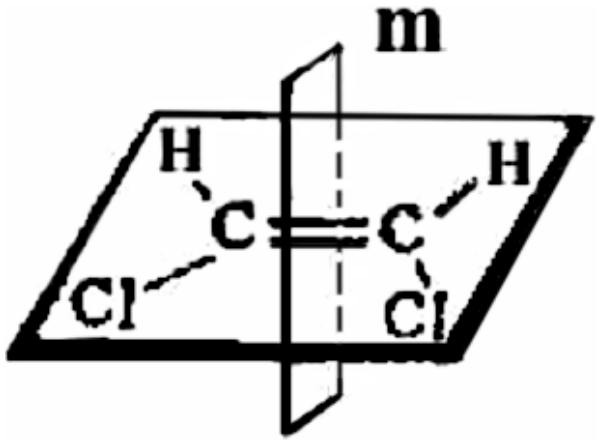


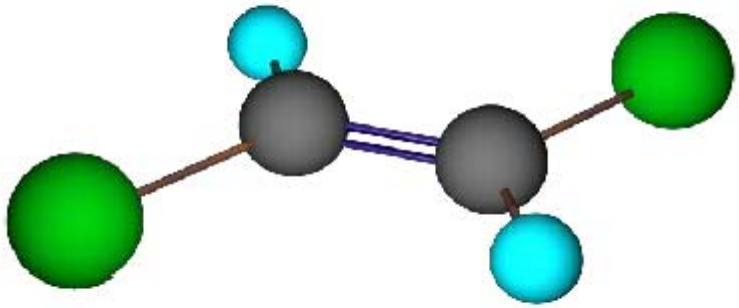
A compound is not chiral if it contains a plane of symmetry.

A plane of symmetry (C_s)

All atoms in a molecule are on a plane.







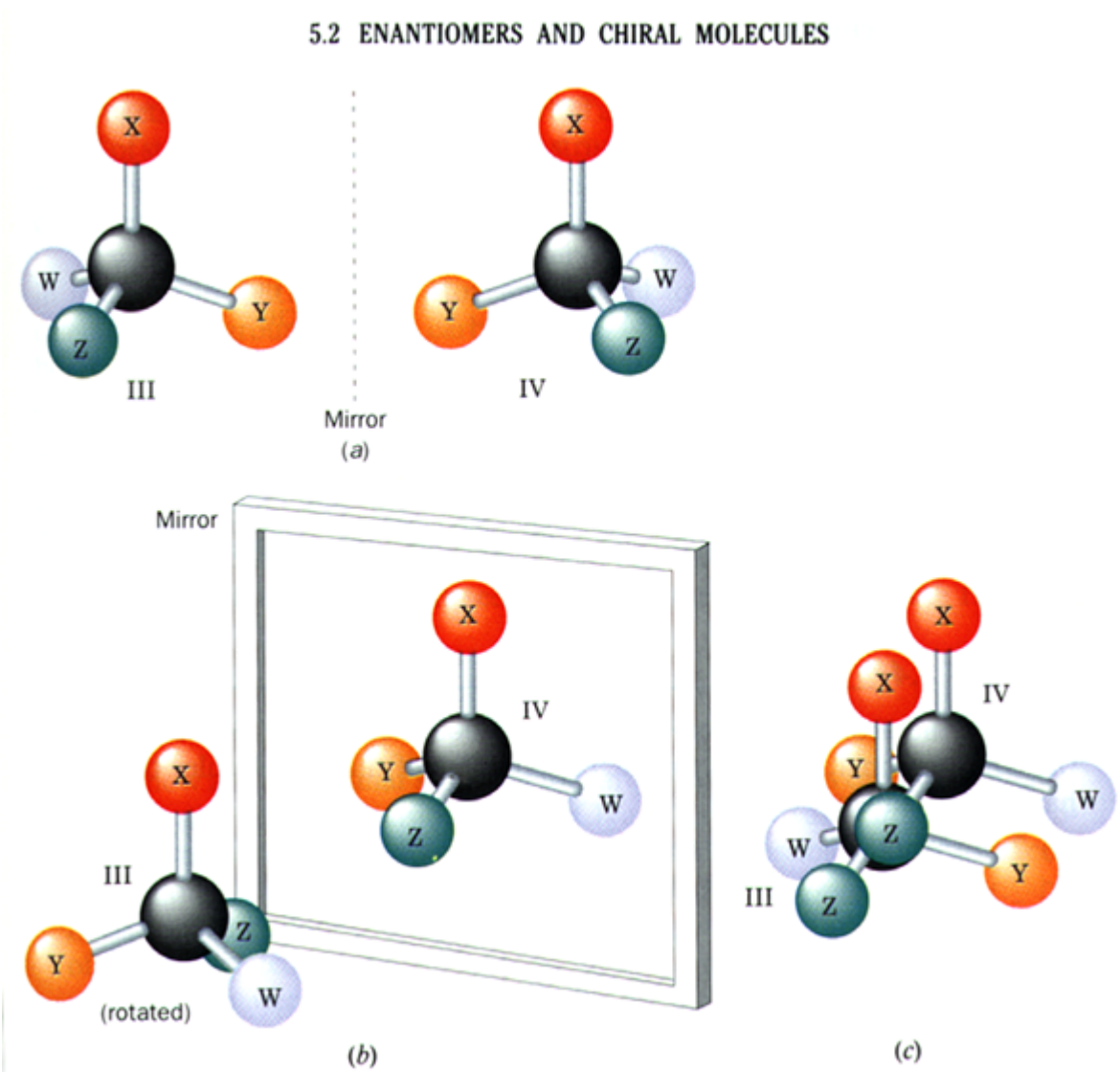
Section 3 How to express the configuration in three dimensions?

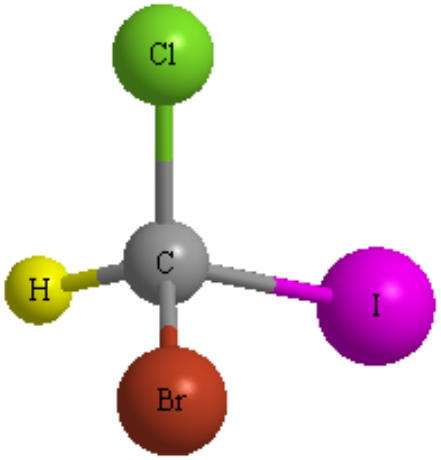
I. 3D models;

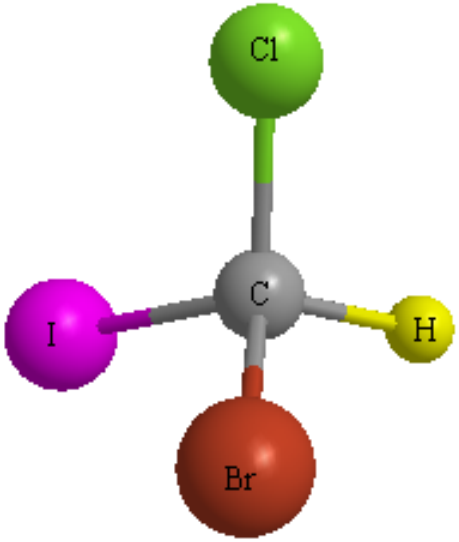
II. **Stereo Structure Formulas** *(wedges-dashes);*

III. Fischer projection formulas.

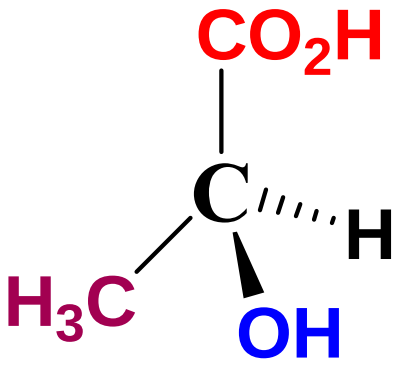
Ⅰ. 3D Models

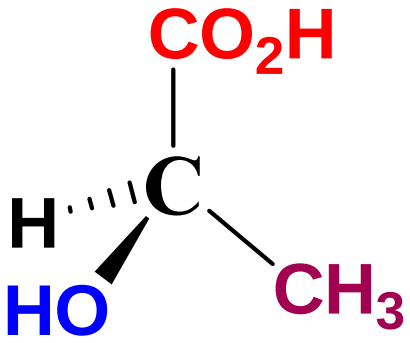

5.2 ENANTIOMERS AND CHIRAL MOLECULES
X
W
Y
Z
III
Mirror
(a)
X
W
Y
Z
IV
Mirror
X
IV
Y
W
Z
X
III
Z
Y
W
(rotated)
(b)
X
X
IV
Y
W
W
Z
III
Z
Y
(c)

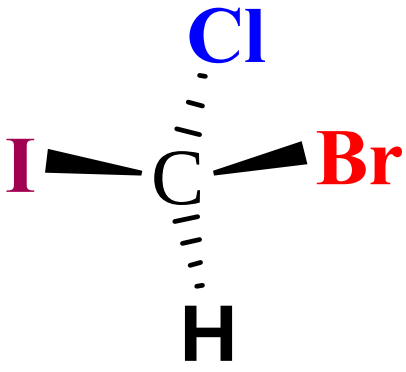

Cl
C
H
I
Br

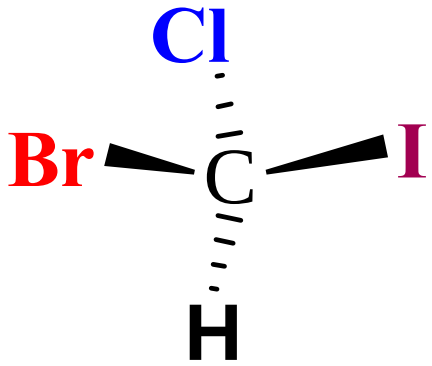

Cl
C
I
H
Br

Ⅱ. Stereo Structure Formulas *(wedges-dashes)*



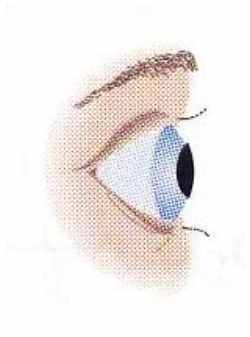


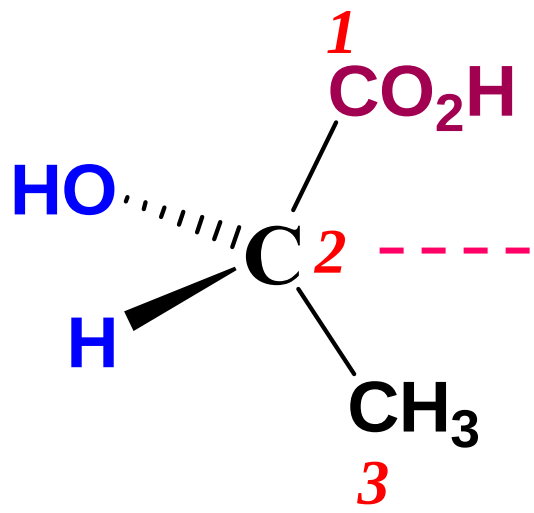


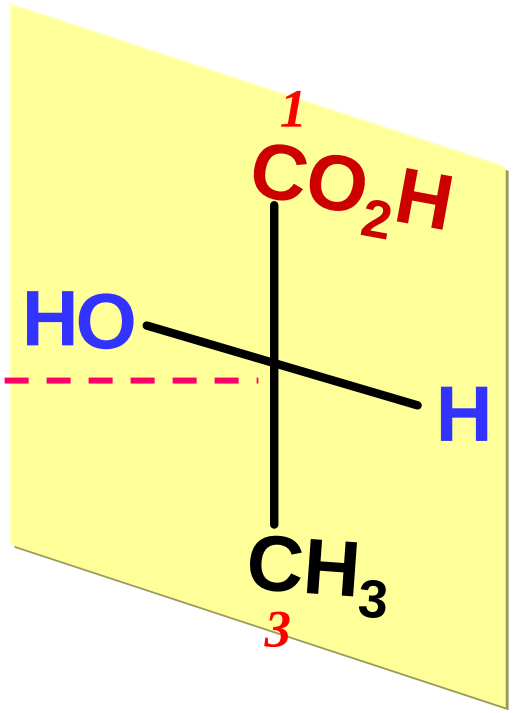


Ⅲ. Fischer Projection

In 1891, Emil Fischer suggested a two-dimensional representation called a Fischer projection to show the configuration of chiral molecules.

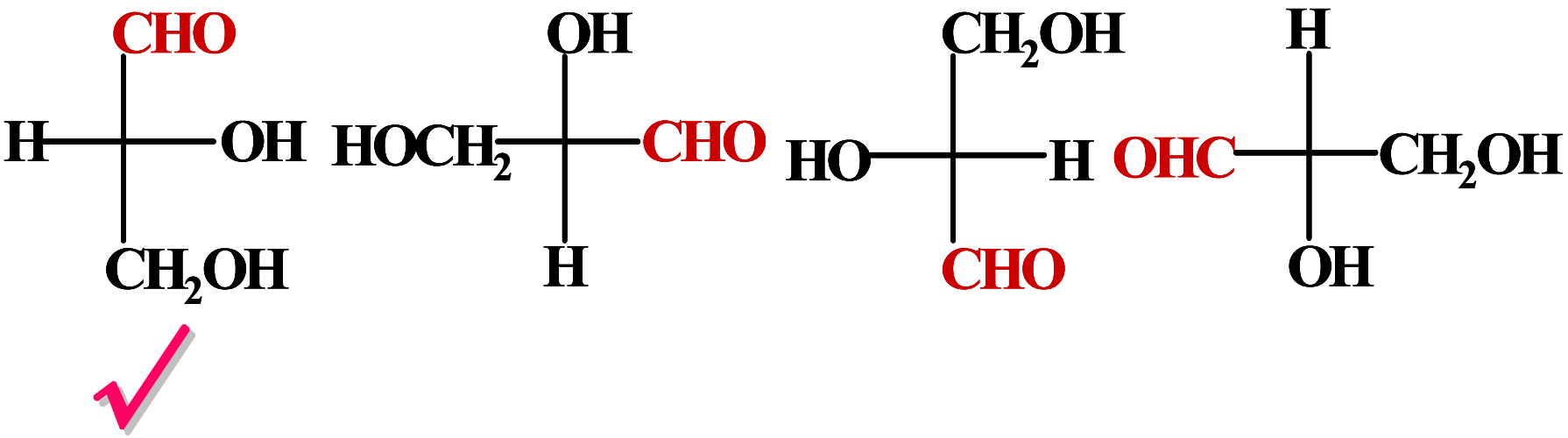






(+)-Lactic acid

书写Fischer投影式时，一般将主碳链放在竖直线上，把命名时编号最小的碳原子放在上端 (主链下行) 。

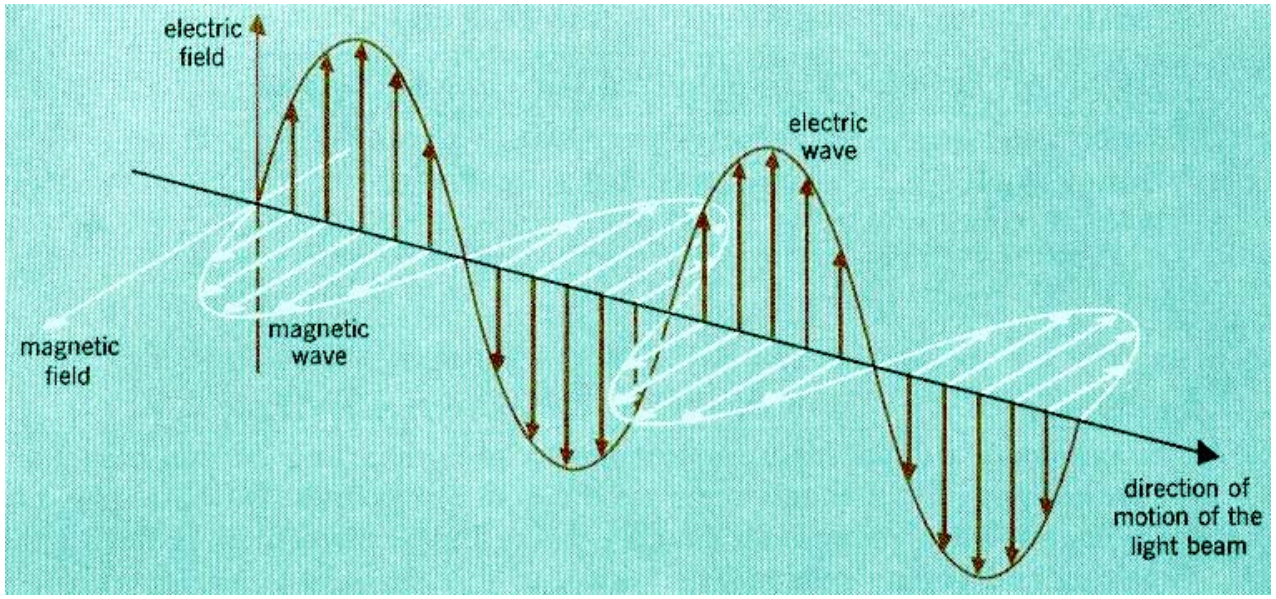


按此方式得到的为最严格的Fischer式，用D/L法命名时必须用这种Fischer式。

Sec. 4 Measurement of optical activity

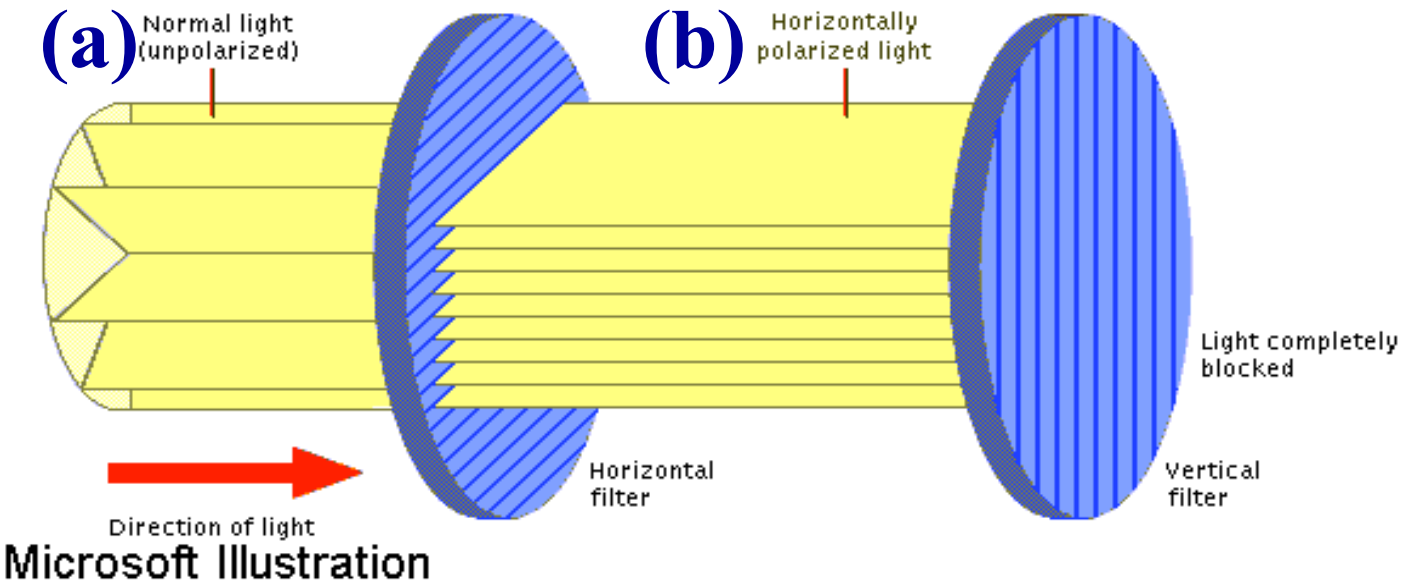
I. Plane-polarized light

A beam of ordinary light consists of electromagnetic waves that oscillate in an infinite number of planes at right angles to the direction of light travel.

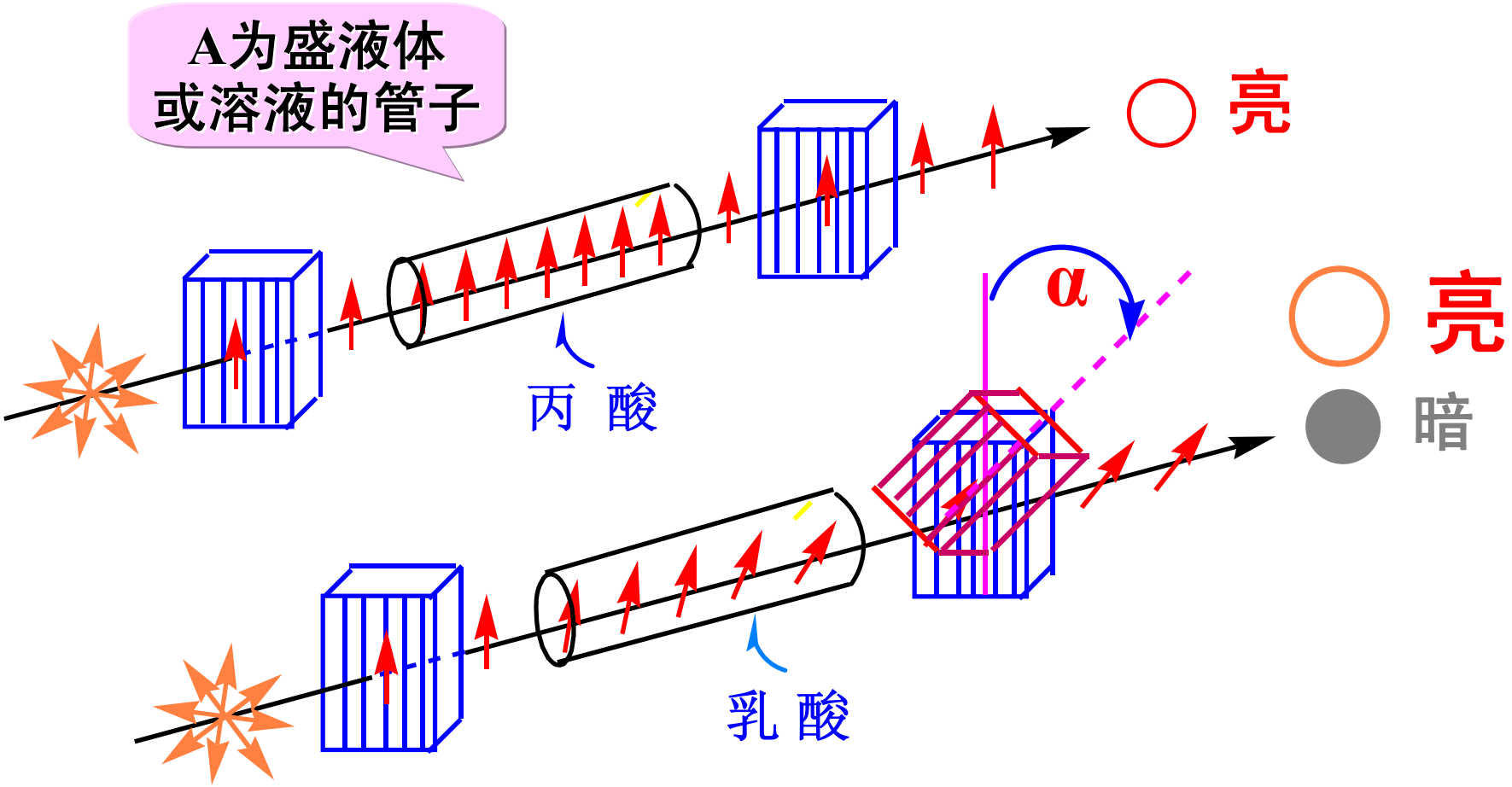


The oscillating electric and magnetic fields of a beam of ordinary light.

When a beam of ordinary light passes through a device called *a polarizer (起偏镜)*, only the light waves oscillating in a *single* plane pass through, and the light is said to be plane-polarized. Light waves in all other planes are blocked out.

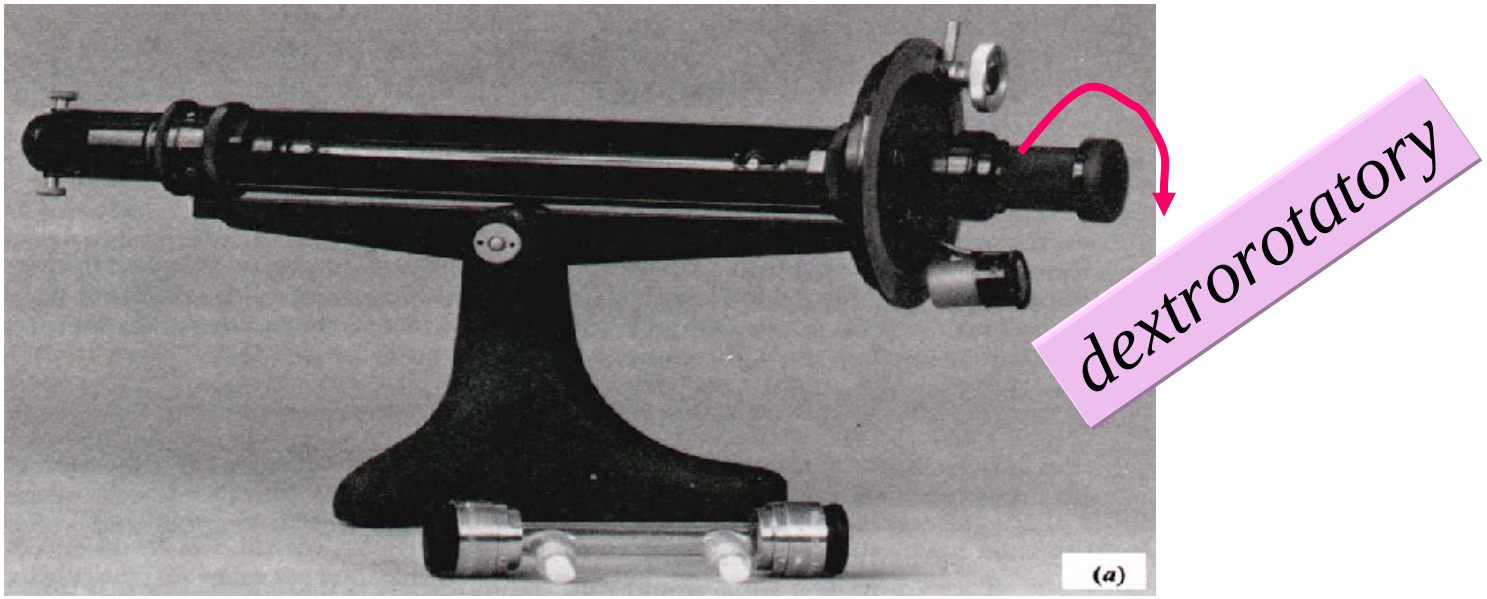


若使偏振光透过一些物质(液体或溶液)，有些物质如丙酸对偏光不发生影响，偏光仍维持原来的振动平面。但有些物质如乳酸，能使偏光的振动平面旋转一定的角度 α 。



II. The polarimeter 旋光仪

The one which rotate the plane of polarized light to the right is described as *dextrorotatory* (右旋), recordered as the (+) or *d*-. The other isomers which rotate the plane of polarized light to the left is described as *laevorotatory* (左旋), recorded as the (-) or *l*-.



The amount of rotation observed is denoted by α and is expressed in degrees.

III. Specific Rotation (比旋光度)

$$[\alpha]_D^t = \frac{\text{Observed rotation, } \alpha \text{ (°, degrees)}}{\text{Path length, } l \text{ (dm)} \times \text{Concentration, } C \text{ (g/mL)}} = \frac{\alpha}{l \times C}$$

α : observed rotation (degrees)

c: concentration of sample ($g \cdot mL^{-1}$)

l: length of sample tube (dm)

t : temperature

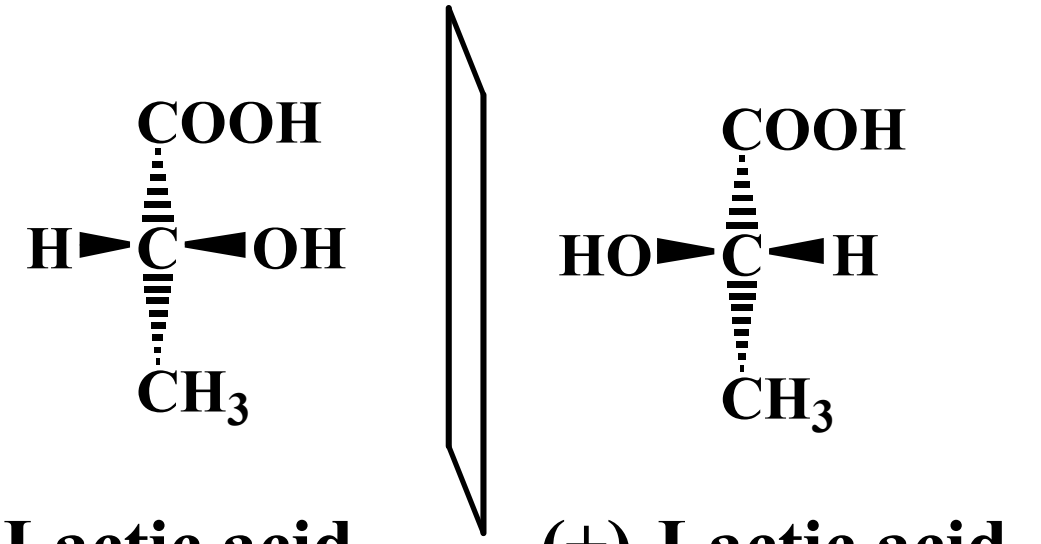
D : the light source used in polarimeter is the sodium D line (λ =589.6nm).

e.g: $[\alpha]_D^{20} = +98.3^o$ (C, 0.05, CH_3OH)

Racemate (外消旋物): **A mixture of equal amounts of enantiomers and they are optically inactive. (±) or *dl***

(Racemic mixture)

For example:



(-)-Lactic acid **(+)-Lactic acid**

***l*-Lactic acid** ***d*-Lactic acid**

$[\alpha]_D^{20}$ **-3.8°** **+3.8°**

(±)-Lactic acid $[\alpha]_D^{20}$ **0°**

Section 5

Nomenclature of Enantiomer

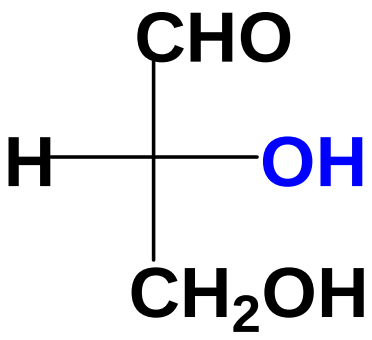
Although drawings provide visual representations of stereochemistry, they are difficult to translate into words. Thus, a verbal method for specifying the three-dimensional arrangement (the configuration) of substituents around a stereocenter is necessary.

Ⅰ. D/L system

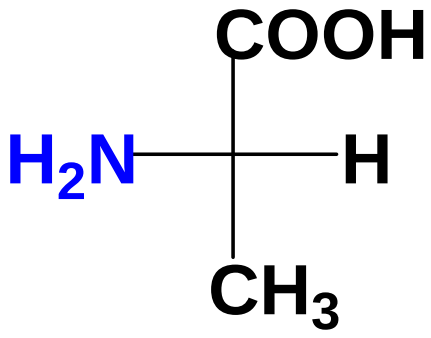
Ⅱ. R/S system

Ⅰ. D/L Representation: Relative Configuration

The Fischer projection of a compound can be oriented so that the most oxidized carbon is at the top, then if the —OH or —NH_2 lies on the right, the molecule is called "D"; if on the left, it is called "L".



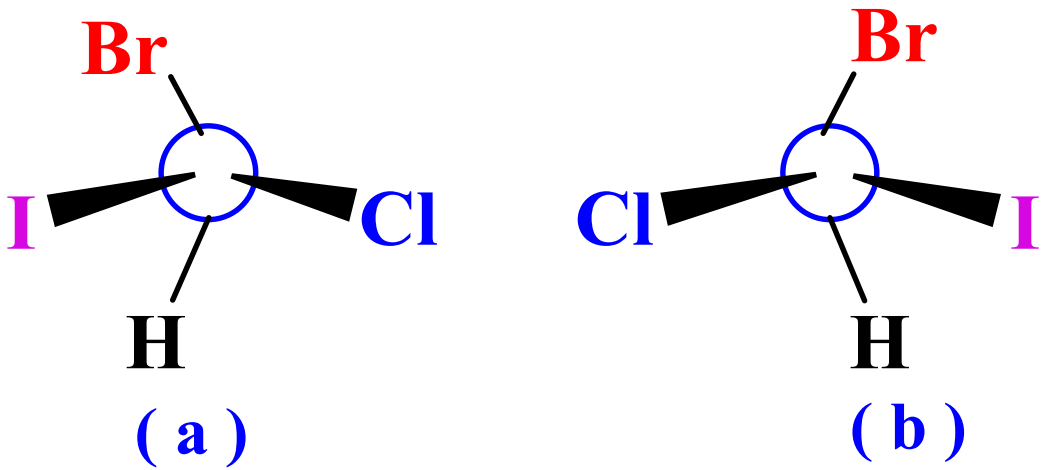
D-glyceraldehyde



L-alanine

Ⅱ. *R/S* Representation: Absolute Configuration

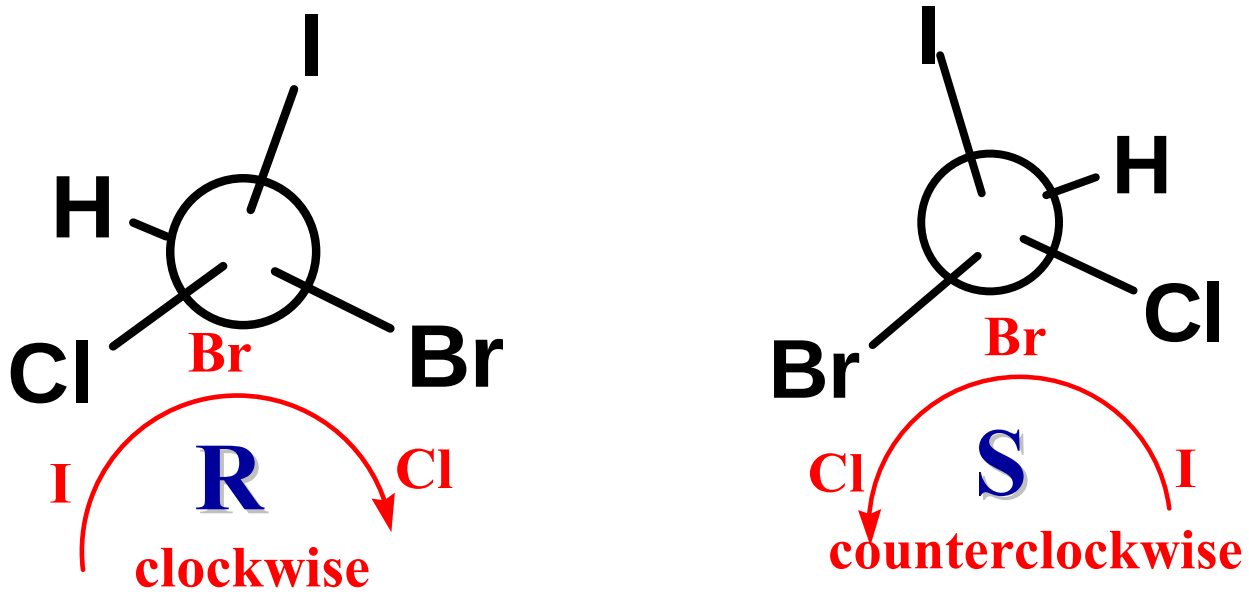
Step 1: **By a set of sequence rules, the groups connected to the chiral carbon are assigned priorities.**



Bromochloroiodomethane

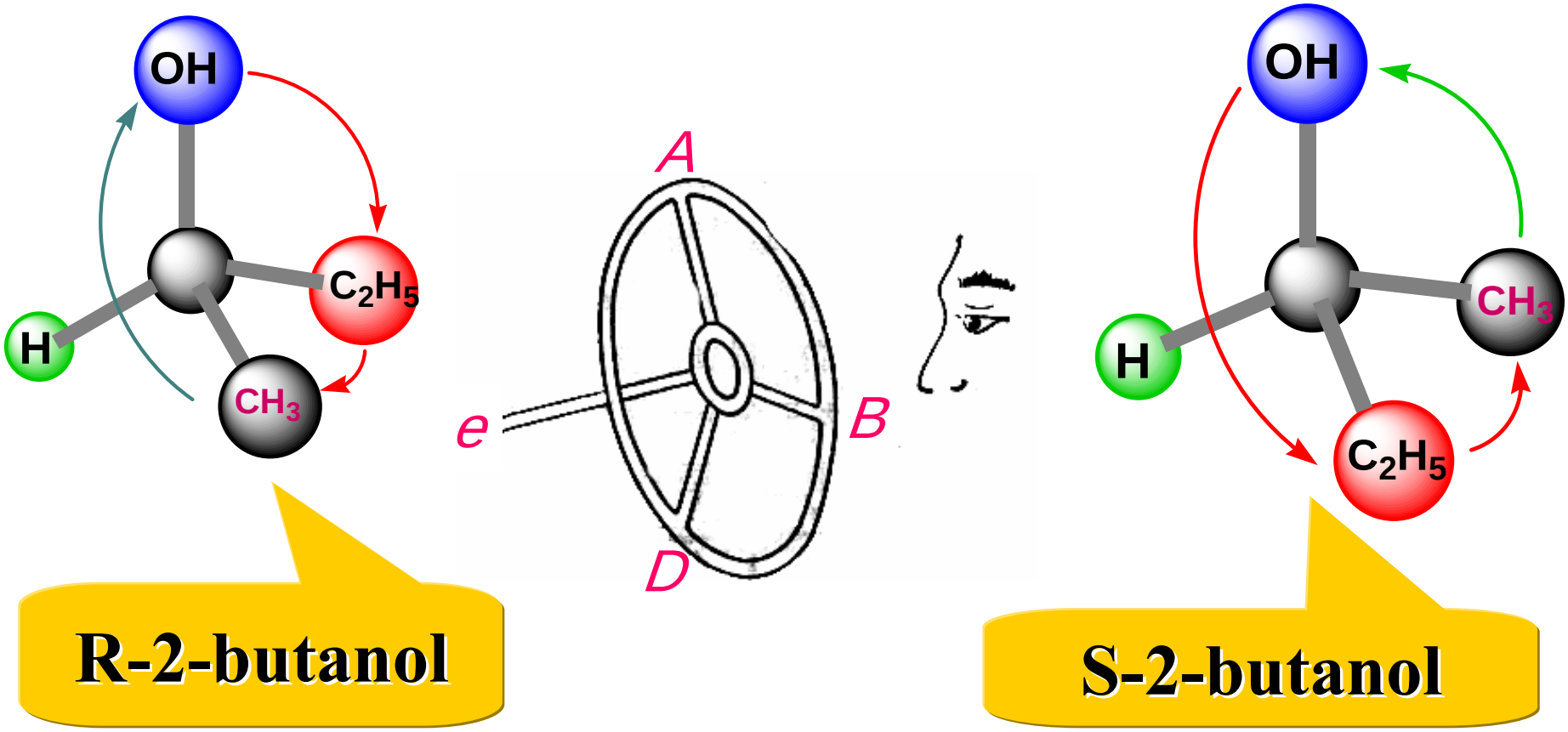
In the case of CHClBrI, the atom of higher number has higher priority, thus I, Br, Cl, H.

Step 2: **The molecule is then visualized such that the group of lowest priority is directed away from the observer. The remaining three groups are in a plane and project toward the observer. If the eye moves clockwise as it goes from the group of highest priority to the groups of second and third priority, the configuration is designated R (Latin, rectus, "right").**



If it moves in a counterclockwise direction, the configuration is designated S (Latin, sinister, "left")

R/S system 次序规则排次序, 方向盘上定构型。



SUPPOSE: a > b > c > d

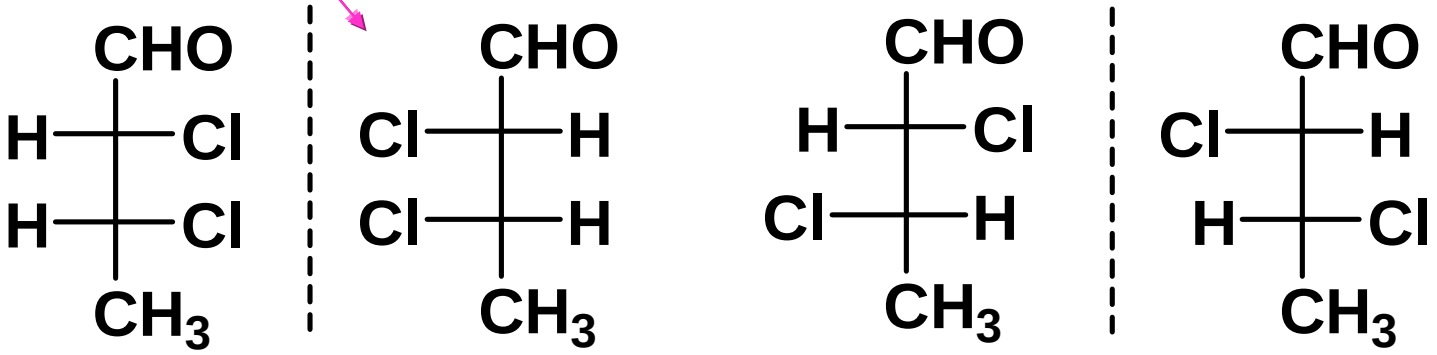
Section 6

Stereoisomers with 2 Chiral Carbon Atoms

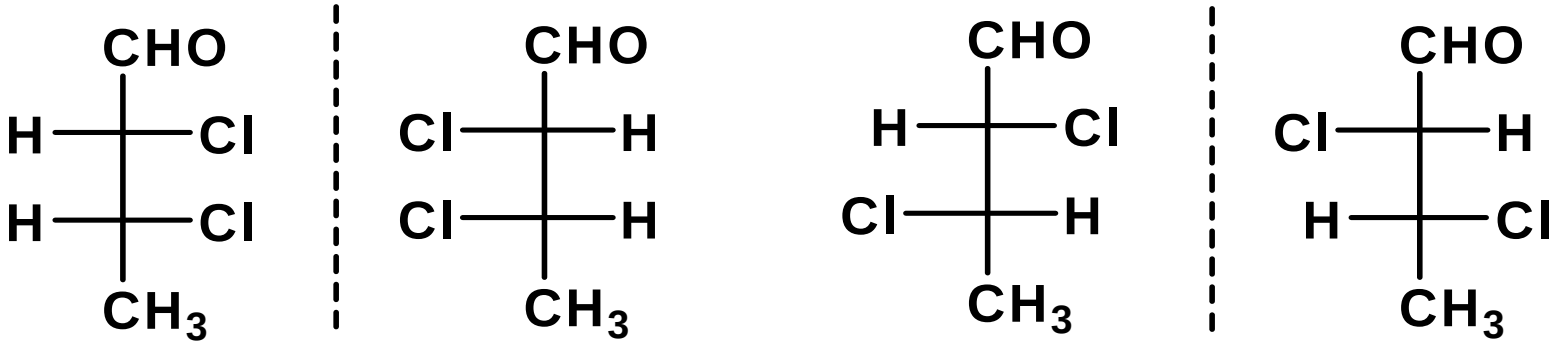
Ⅰ. Molecules with Two Dissimilar Chiral Carbon Atoms

2,3-Dichlorobutanal

mirror



(a) (b) (c) (d)



2S,3R ***2R,3S*** ***2S,3S*** ***2R,3R***

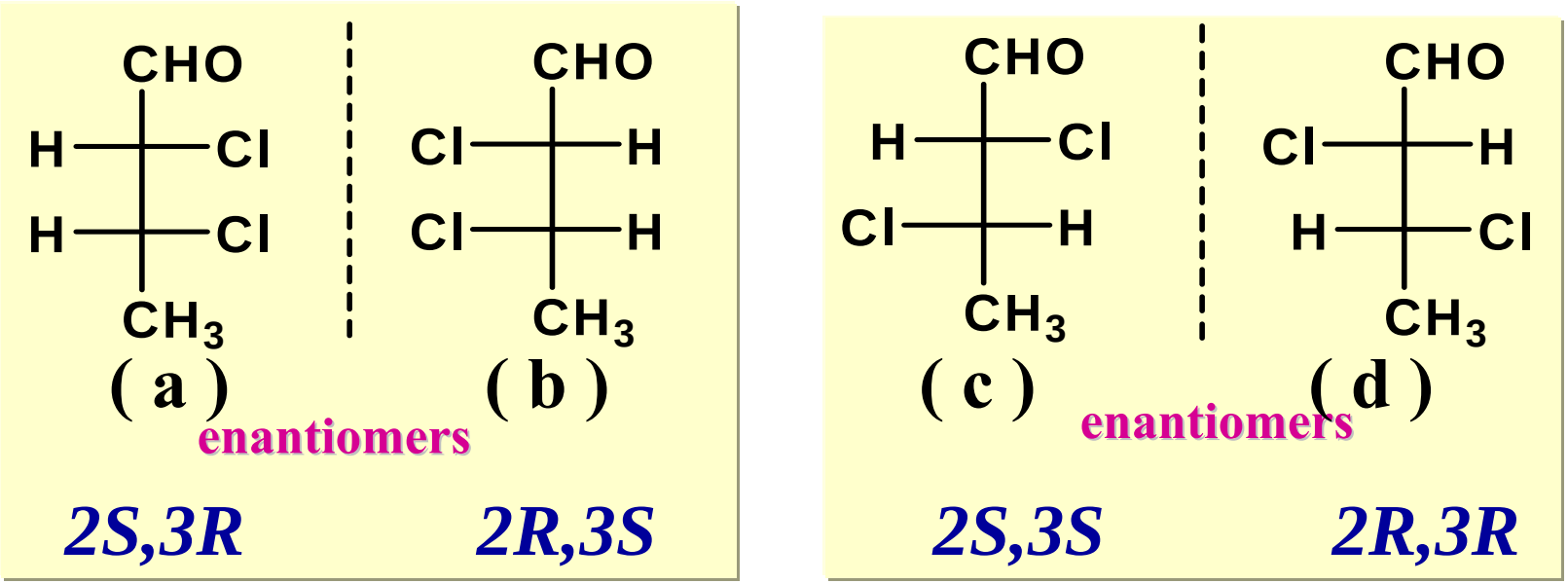
enantiomers **enantiomers**

(a) and (b) are nonsuperimposable mirror images pair and are a pair of enantiomers. And also (c) and (d).

The mixture of equal amounts of enantiomers (a) and (b), or (c) and (d), is called a racemic mixture (racemate also,外消旋物). Racemic mixtures are often denoted by the symbol (±) or (*R,S*) or *dl* to indicate that they show no optical activity (一对对映体的等量混合物称外消旋体,无旋光性).

What is the relationship between (a) isomer and (c)?

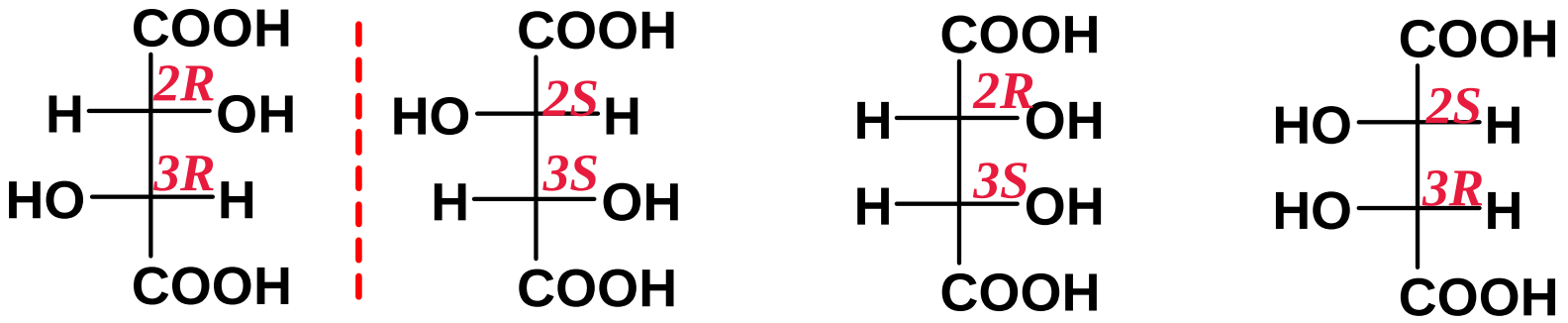
diastereomers



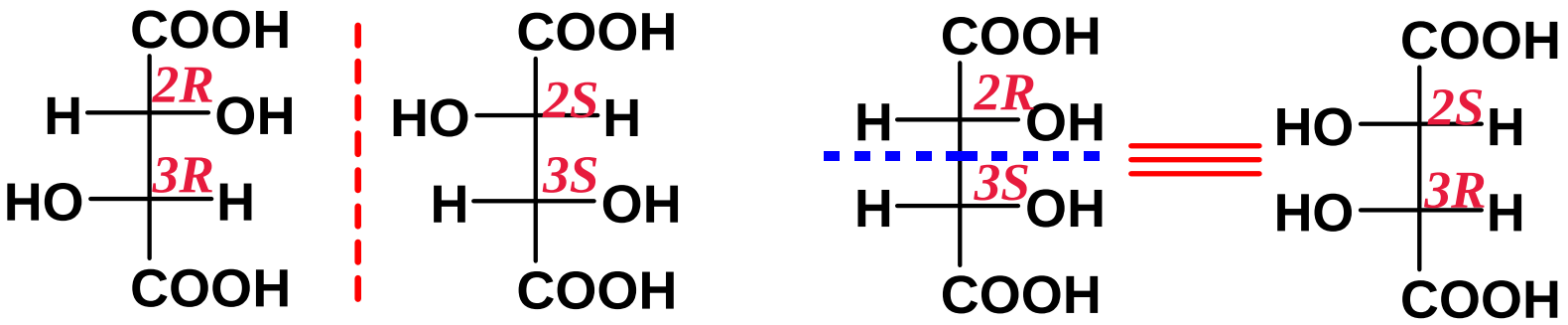
They are stereoisomers but not mirror images, and called diastereomers(非对映体). Diastereomers are stereoisomers that are not mirror images.

Ⅱ. Stereoisomers with two similar C*

Tartaric acid has two similar chiral carbons, C-2 and C-3. Each has 4 different bonded groups (-OH, -CO_2H, -$CHOHCO_2H$, -H).



The mirror image 2R,3R and 2S,3S structures are not identical and therefore represent an enantiomeric pair.



The compound (c) or (d) are achiral, yet contains stereocenters, is called meso compounds (meso form,内消旋体). The meso compounds are optically inactive, they do not rotate plane-polarized light. Thus, tartaric acid exists in 3 stereoisomeric forms.

Summary

1. **Basic concepts**

2. **Configuration expression**

   Newman projection; *Fischer P.F.*

3. **Nomenclature**

   ***D/L system*; *R/S system* (*hand curl method or steering wheel method*)**

4. **Recognize chirality: *Cs*; *Ci*; C***

5. **Optical activity:** $[\alpha]_D^t = \alpha / l \cdot C$

6. **Enantiomers of cyclic compounds**

Additional Questions (page 119)

5-1 Explain the following concepts:

5-2 Compare the dextrorotatory and levorotatory forms of …

5-3 The compound cortisone (500mg) is dissolved into 100ml …

5-5 How many chiral atoms are there in each of the …

5-6 Identify the same configuration from the following…

5-7 In the following compounds, which have the meso forms?…

5-8 Assign the following compound R or S ? Draw the Fischer…

5-9 Which of the following structures represent meso compounds?

5-10 Determine the *R* or *S* configuration of each of the following…

5-11 Name each of the following compounds, …

5-12 For each set of the following compounds, …