§3 立体化学

立体化学基础

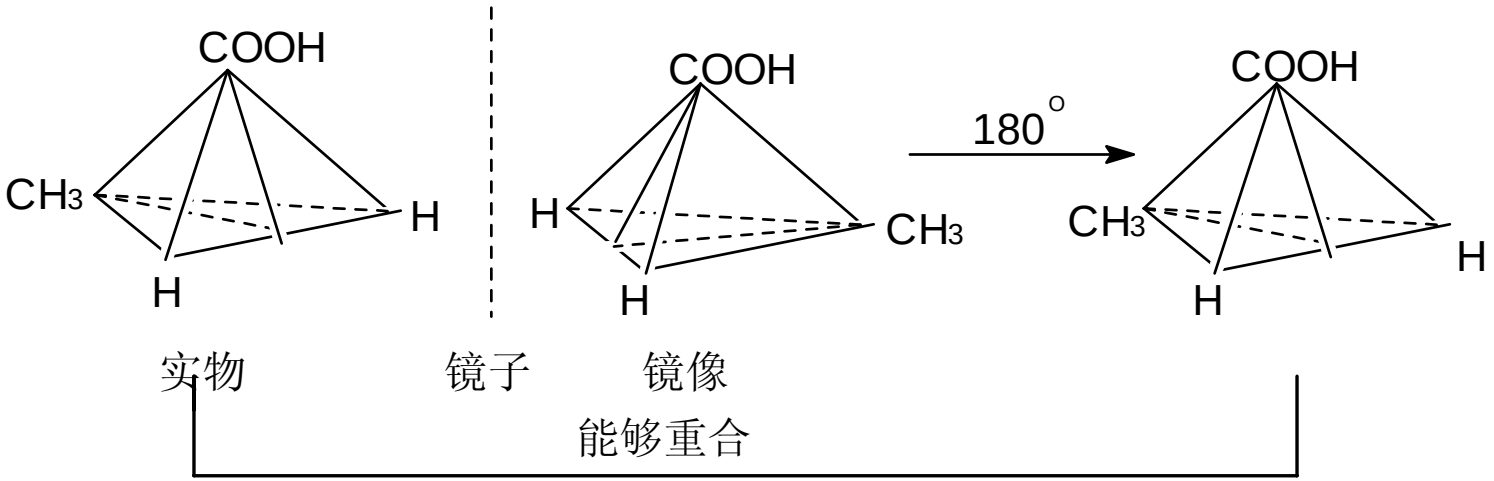
§3.1 对称因素与手性分子

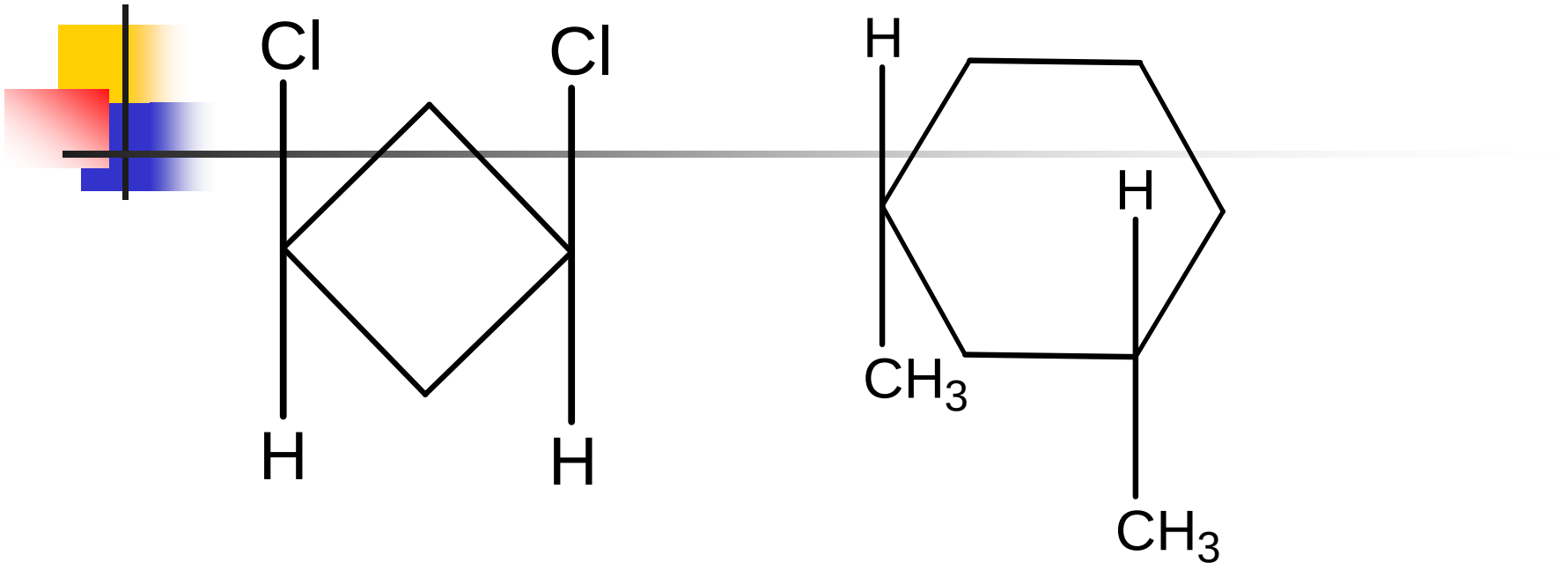
1. 对称因素

A.对称面

分子中有一平面将分子一分两半，两部分互为镜像关系，该平面称为对称面，用σ表示。

CH_3CH_2COOH

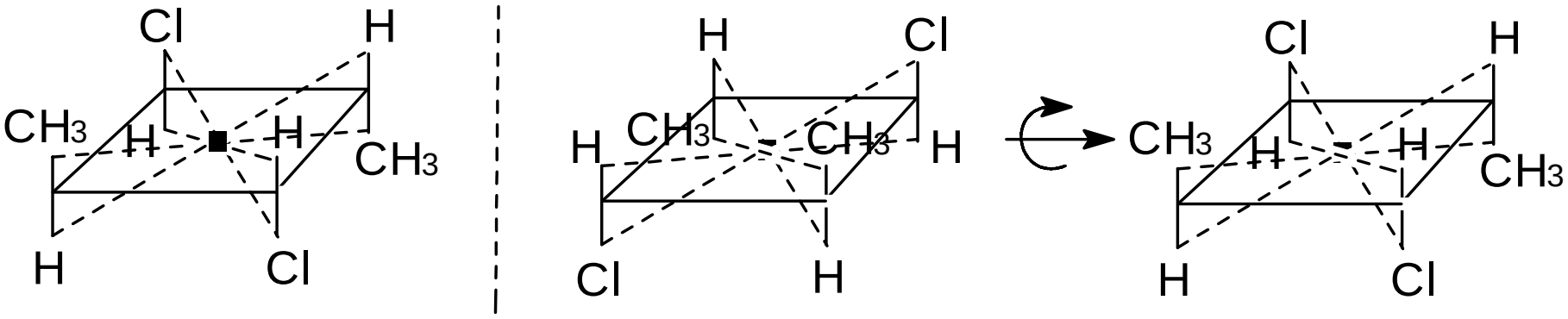




结论：如果分子中存在对称面，那么该分子的镜像可以与实物重合。

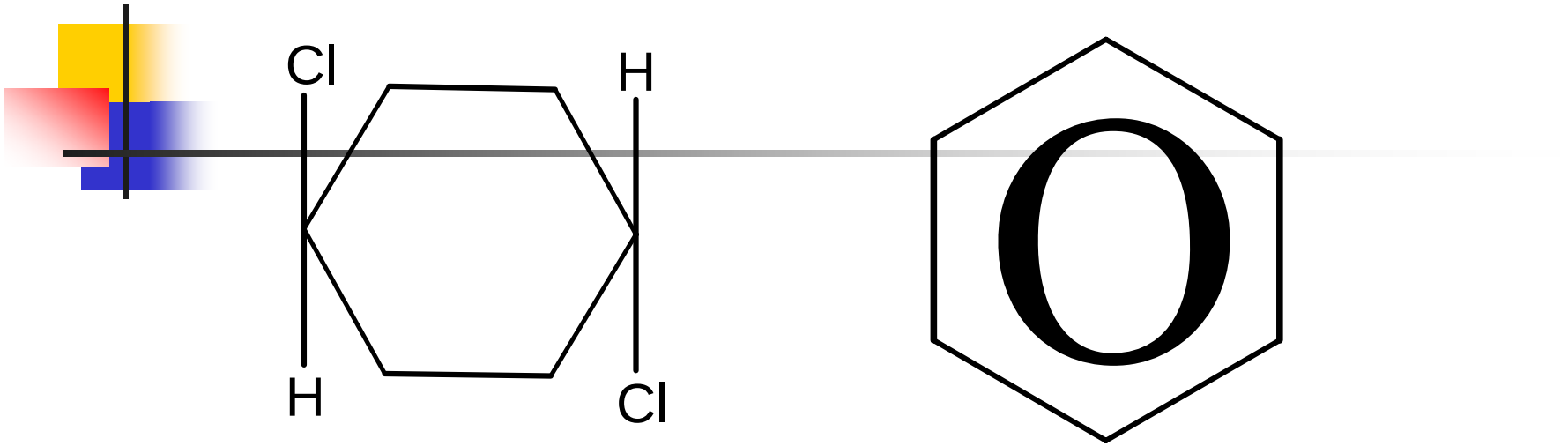
B.对称中心

在分子中可找到某一个点，通过该点任意向两端作射线，距离该点相等的距离有相同的原子或基团，则该点称为该分子的对称中心。用*I*表示.



实物　　镜子　　镜像

能够重合　（对称中心）



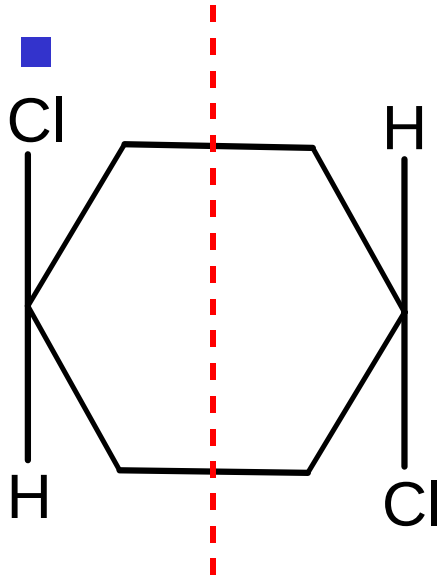
结论：如果分子中存在对称中心，该分子的镜像可以与实物重合。

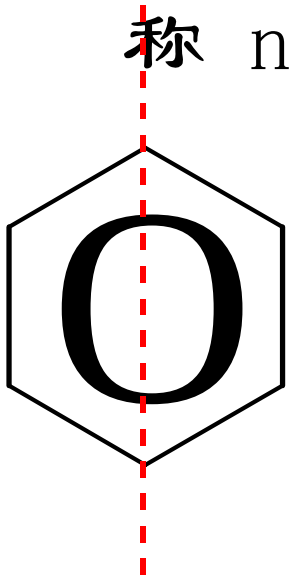
C.对称轴

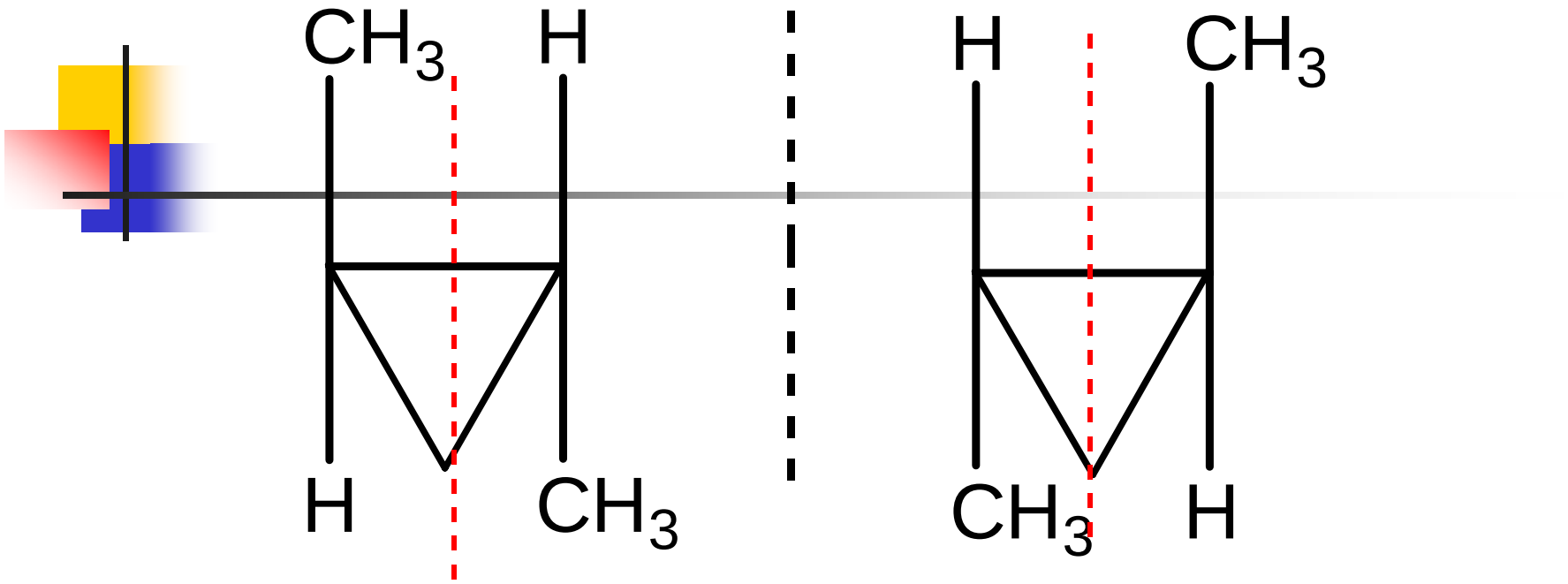
- 在分子中可找到某条直线，分子绕该直线旋转一定角度后可与原分子重合，则该直线称为该分子的对称轴。用*Cn*表示. 其中：

$$n = \frac{360^0}{\text{旋转的角度}}$$

称 n 重对称轴



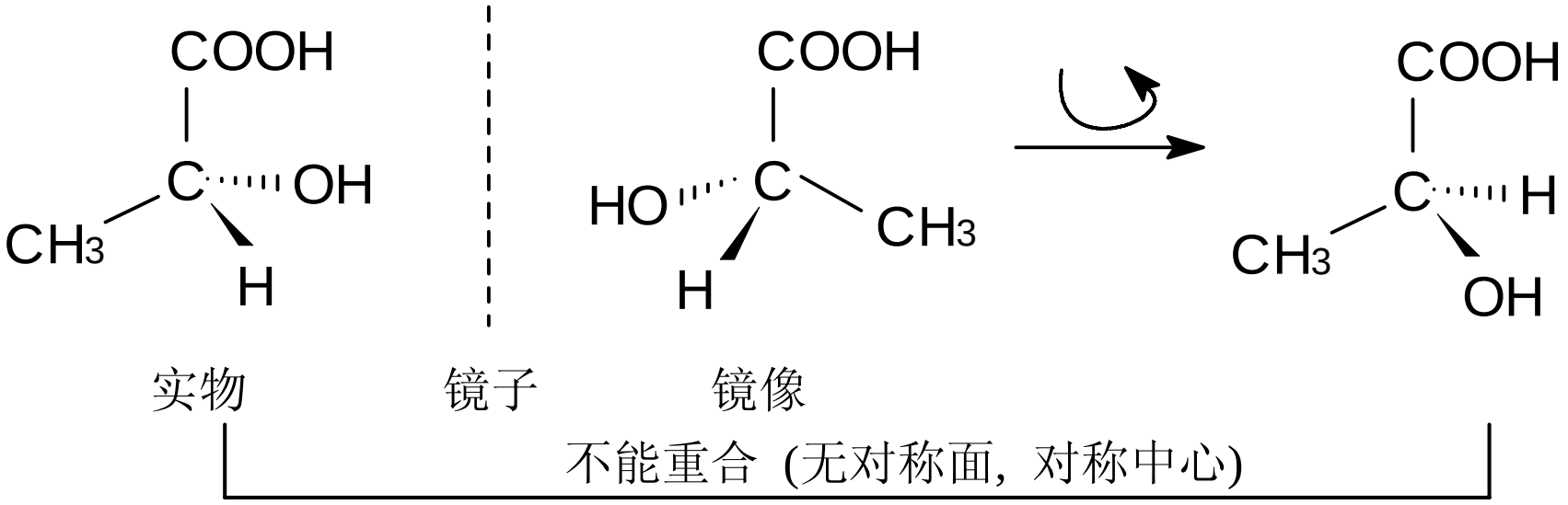




结论：虽然分子中存在C2对称轴，但该分子的镜像却不可以与实物重合。

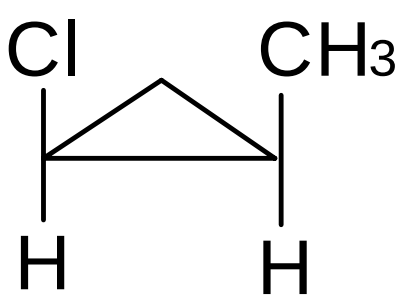
2.手性及手性分子

- 手性:不对称性
- A. 手性分子
- a. 实例 :乳酸

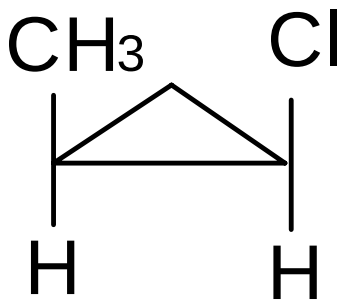


1-氯-2-甲基环丙烷

cis

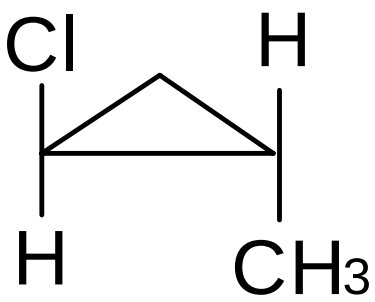


实物

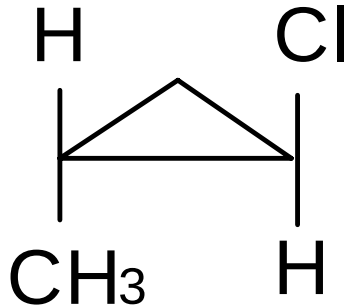


镜像

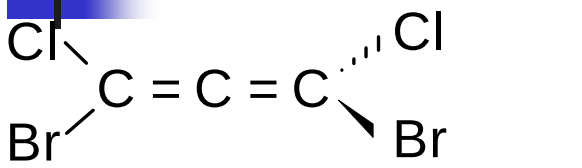
trans

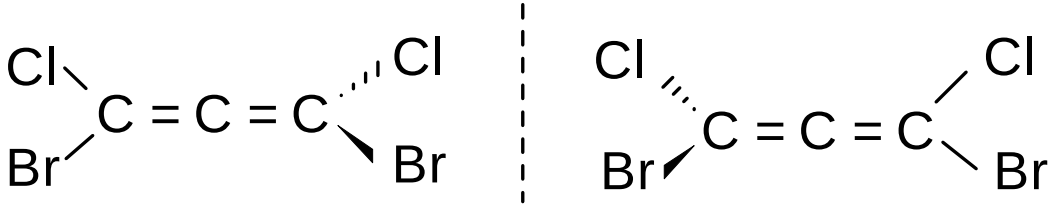


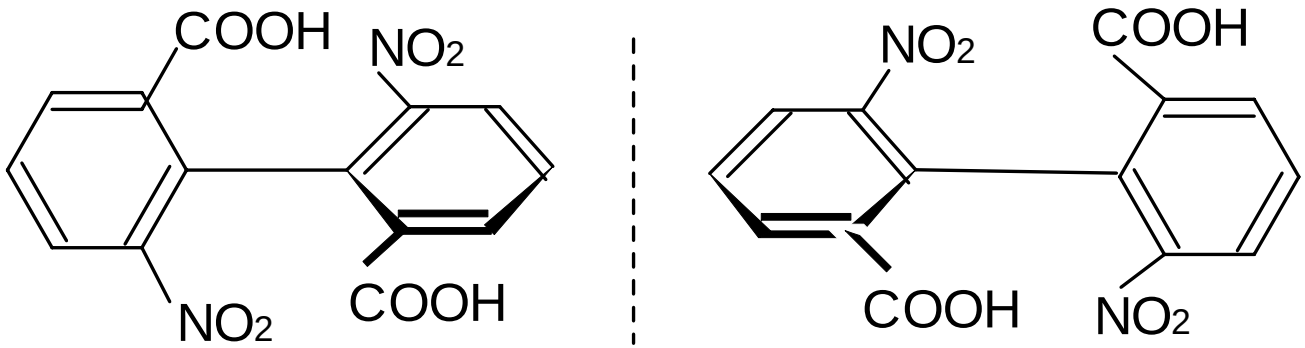
实物



镜像


Cl
Cl
Br
Br

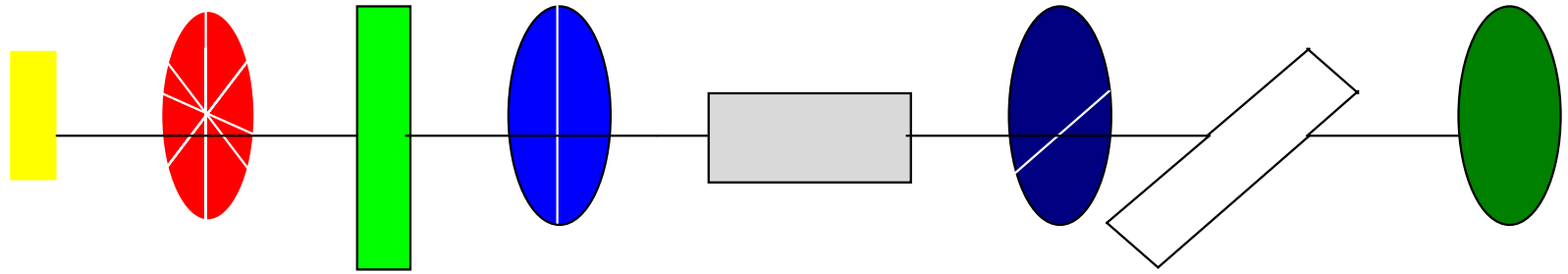

Cl
Cl
Br
Br
Cl
Cl
Br
Br


COOH
NO2
NO2
COOH
NO2
COOH
COOH
NO2

- b. **手性分子**：实物与镜像不能重合的分子是手性分子，即-不对称的分子.
- 实物与镜像的关系为对映关系。
  实物与镜像互为**对映(异构)体**。

- c. **手性分子产生的条件**：既无对称面
  也无对称中心

2. 手性分子的物理性质——旋光性



光源　　尼可尔棱镜(起偏器)　　手性分子溶液　　尼可尔棱镜(检偏器)　　读数 右旋 (+) 左旋 (-)

旋光测定示意图

- 比旋光度 $[\alpha]^{t}_{\lambda} = \alpha / (c\ l)$

  α 测得的旋光度 + 或 −

  c 溶液浓度 (g/ml)

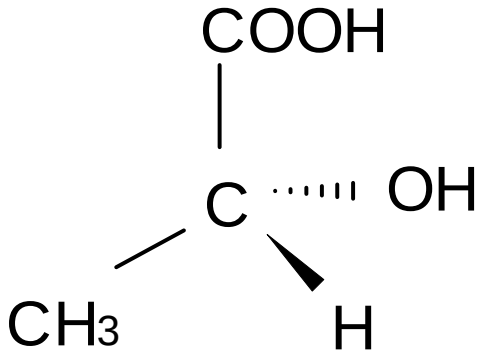
  l 旋光管长度 (10cm)

  t 温度 通常为25 °C

- λ 波长 通常为Na光源(5893A°)
- 即D光源

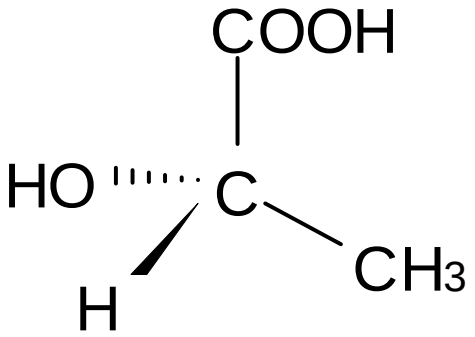
§3.2 构型及构型的平面表达

- **1. 构型：分子中的原子或基团在空间的特定排布方式称为构型**



构型 I

$[\alpha]^t_\lambda = +3.8°$



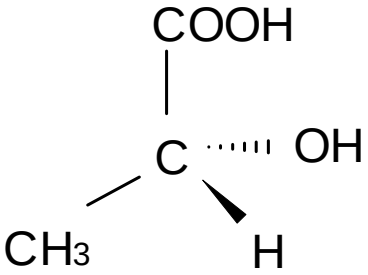
构型 II

$[\alpha]^t_\lambda = -3.8°$

实物　　镜像

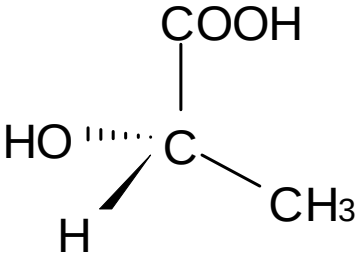
2、对映(异构)体及外消旋体

- A,对映体:



构型 I

$[\alpha]^{t}_{\lambda}$= +3.8°



构型 II

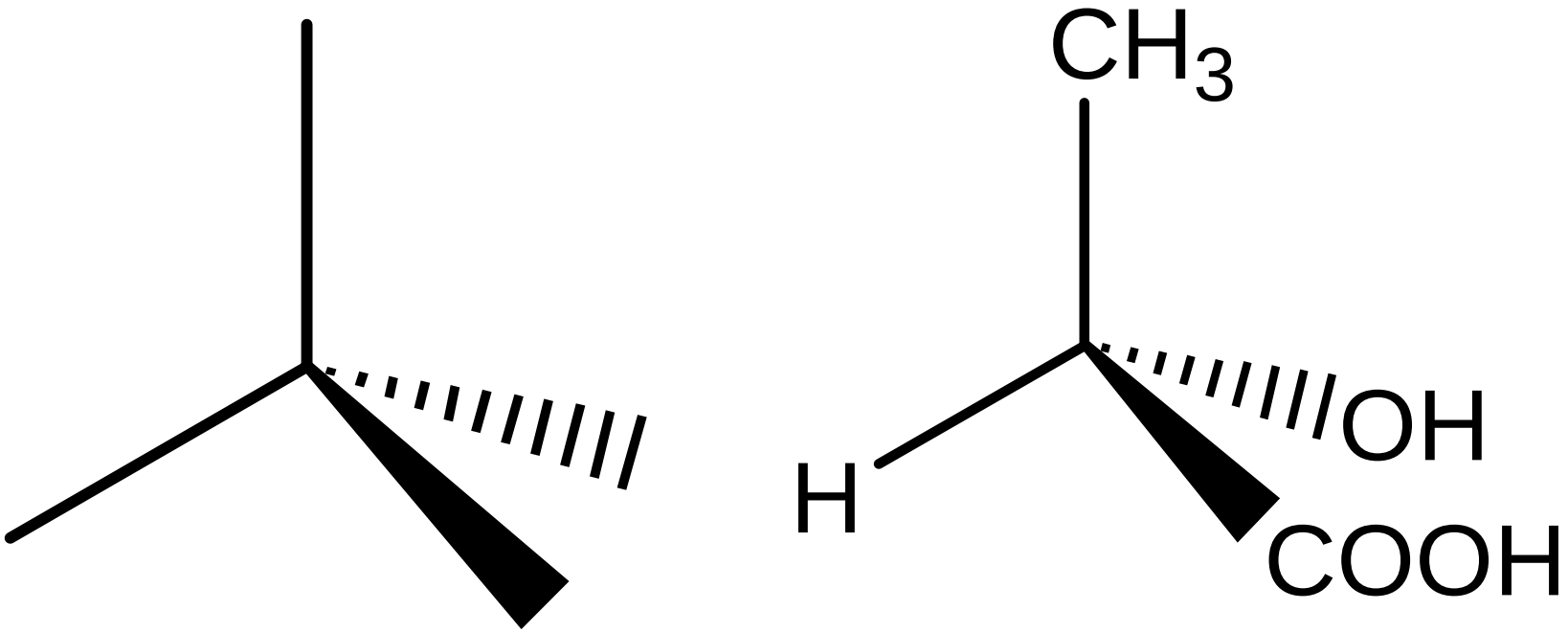
$[\alpha]^{t}_{\lambda}$= -3.8°

实物　　镜像

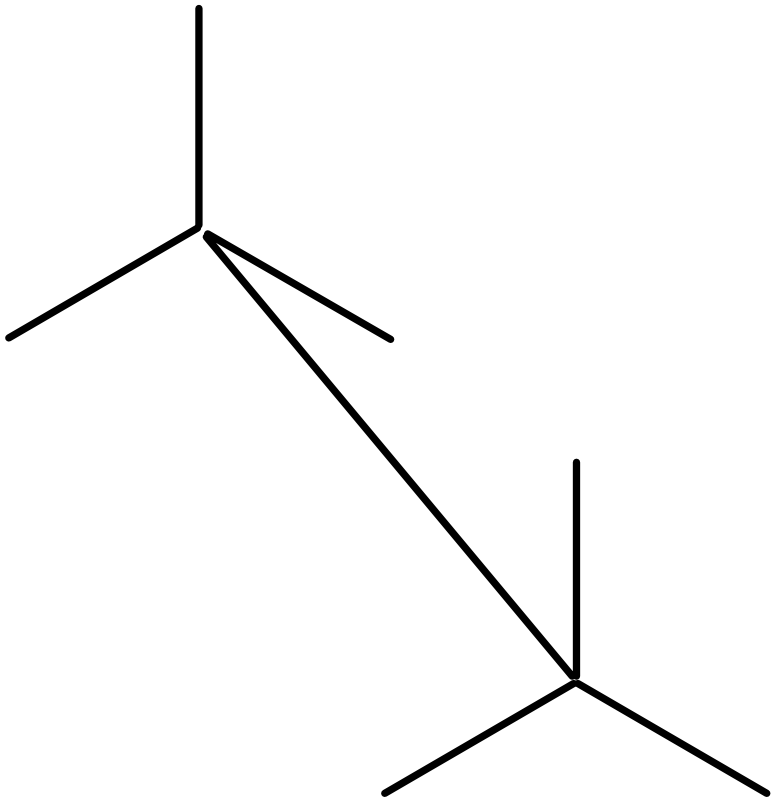
- B,外消旋体:
- 等量对映体的混合物

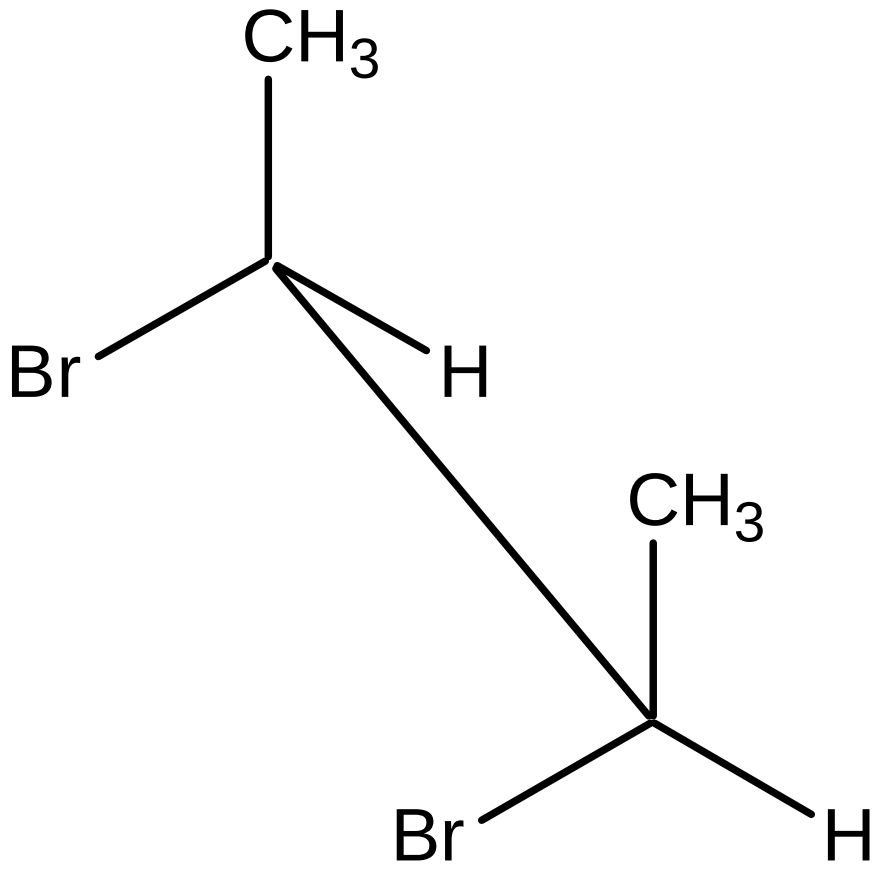
3、构型的平面表达

- A, 伞形式：

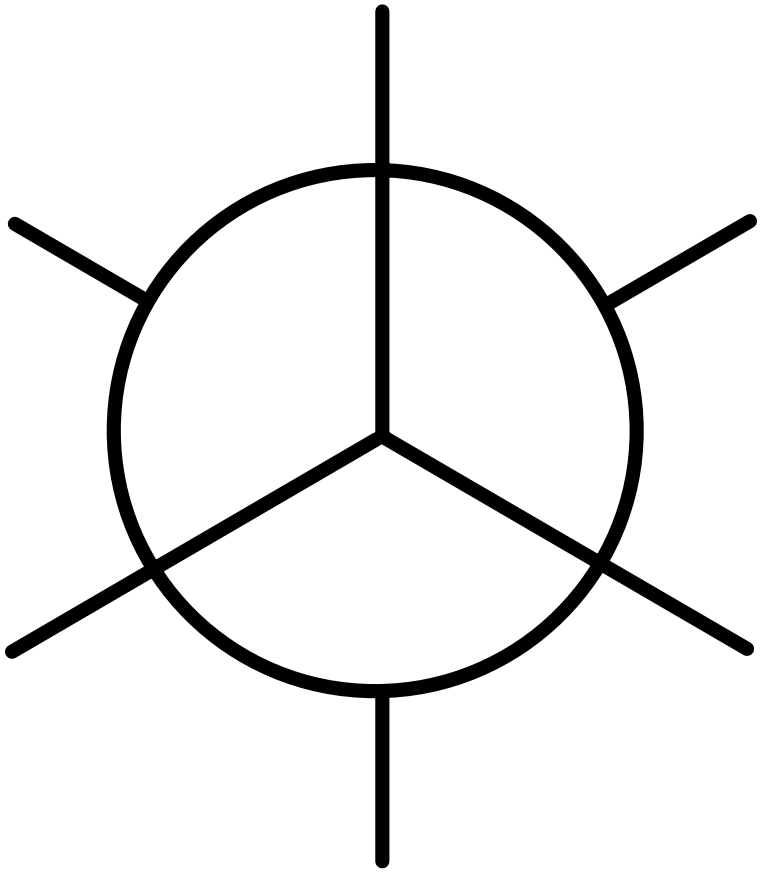


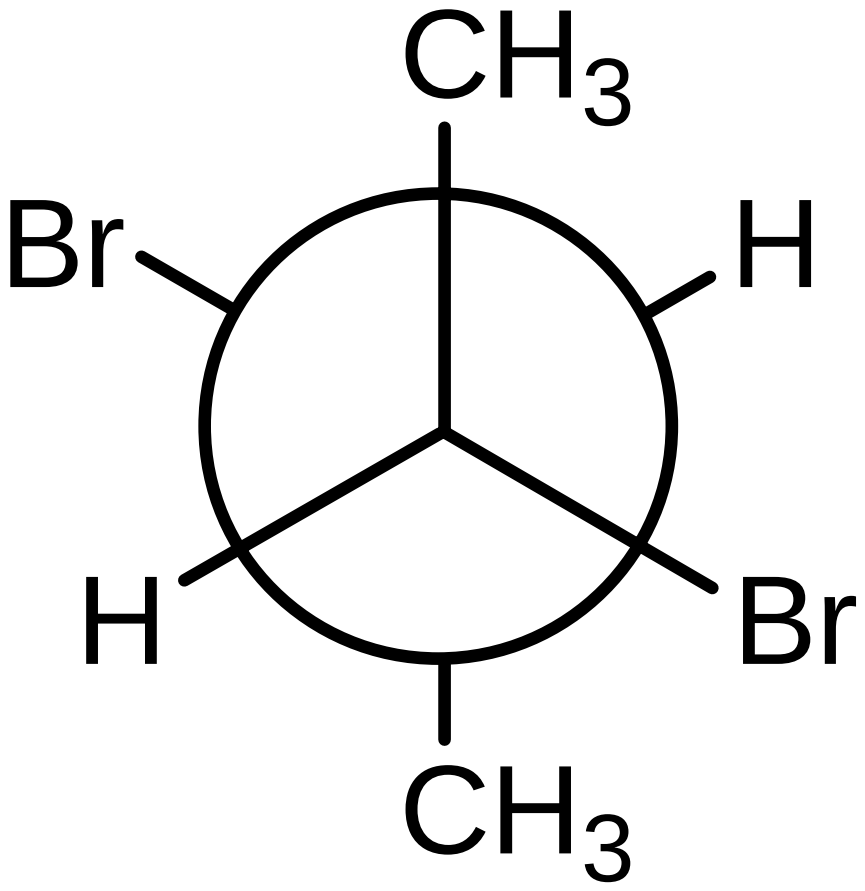
B. 锯架式：





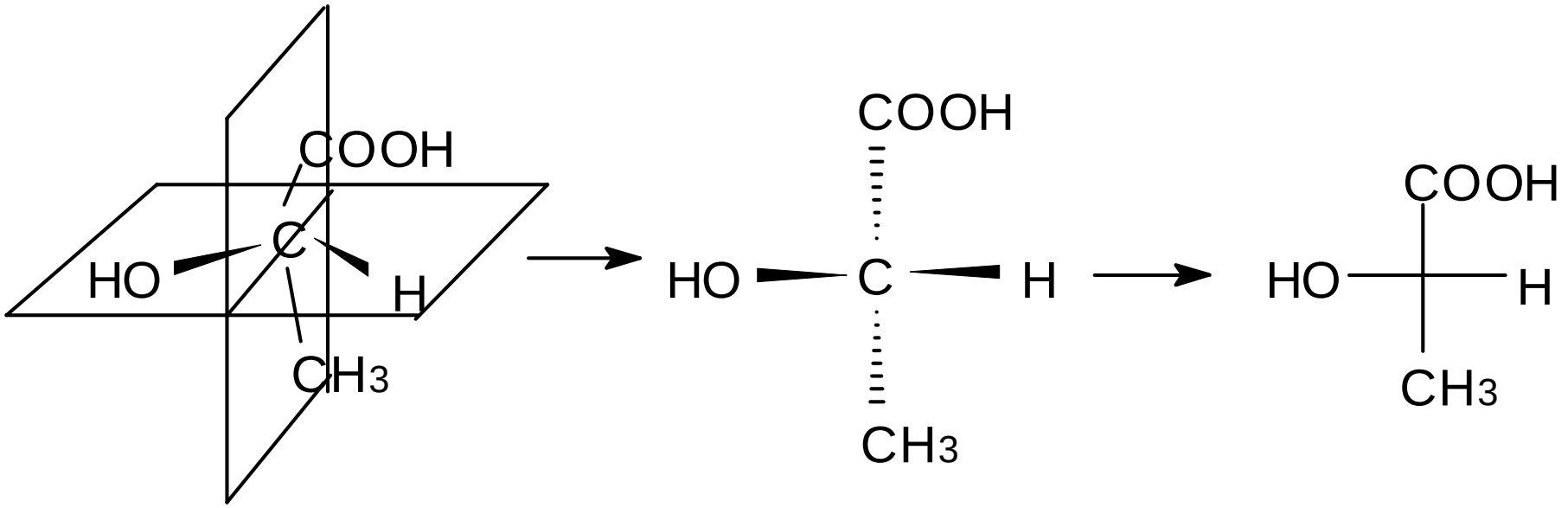
C. 纽曼式：





D,Fischer投影式

a,Fischer投影式：



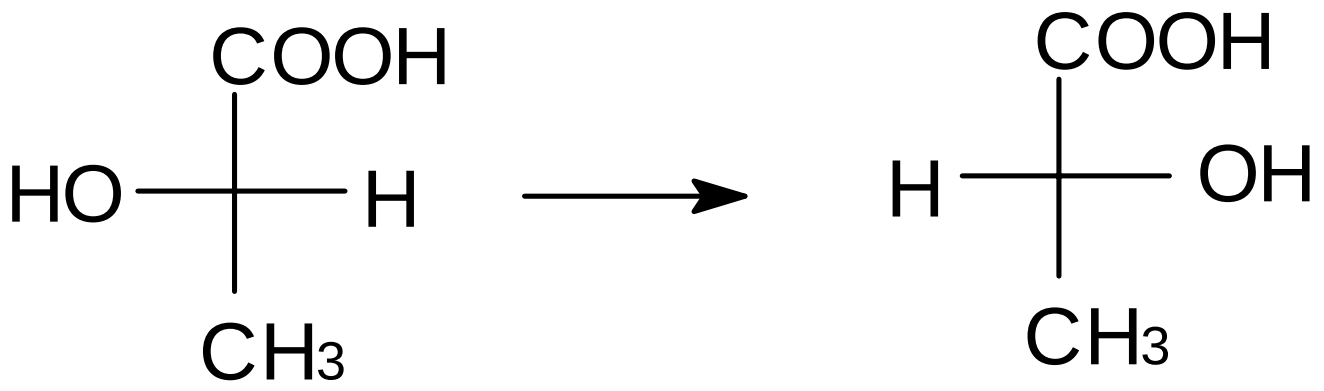
1)十字型交叉点为手性碳；

2)横线表示向前；竖线表示向后

3)一般把含碳基团写在竖线上，氧化态高的写在上

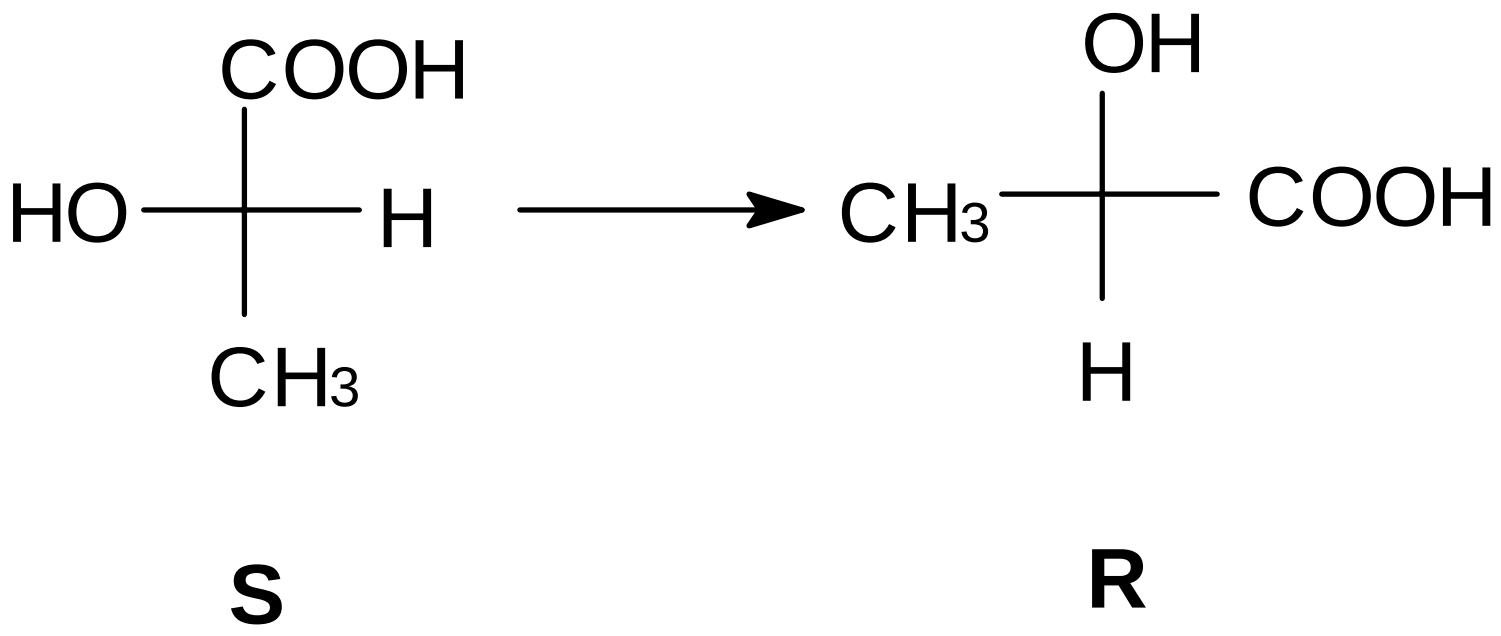
6. Fischer投影式的规则

- 1)交换两个基团，变为对映体

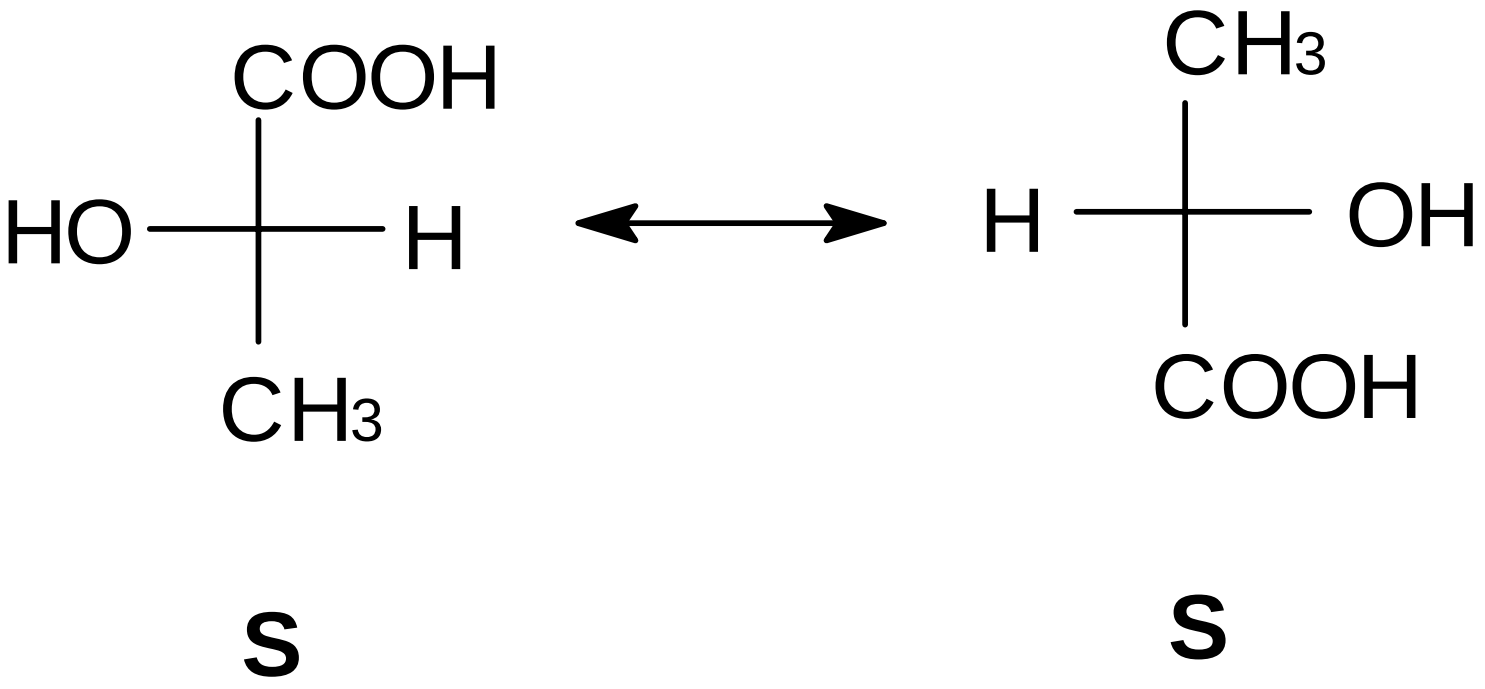


S　　R

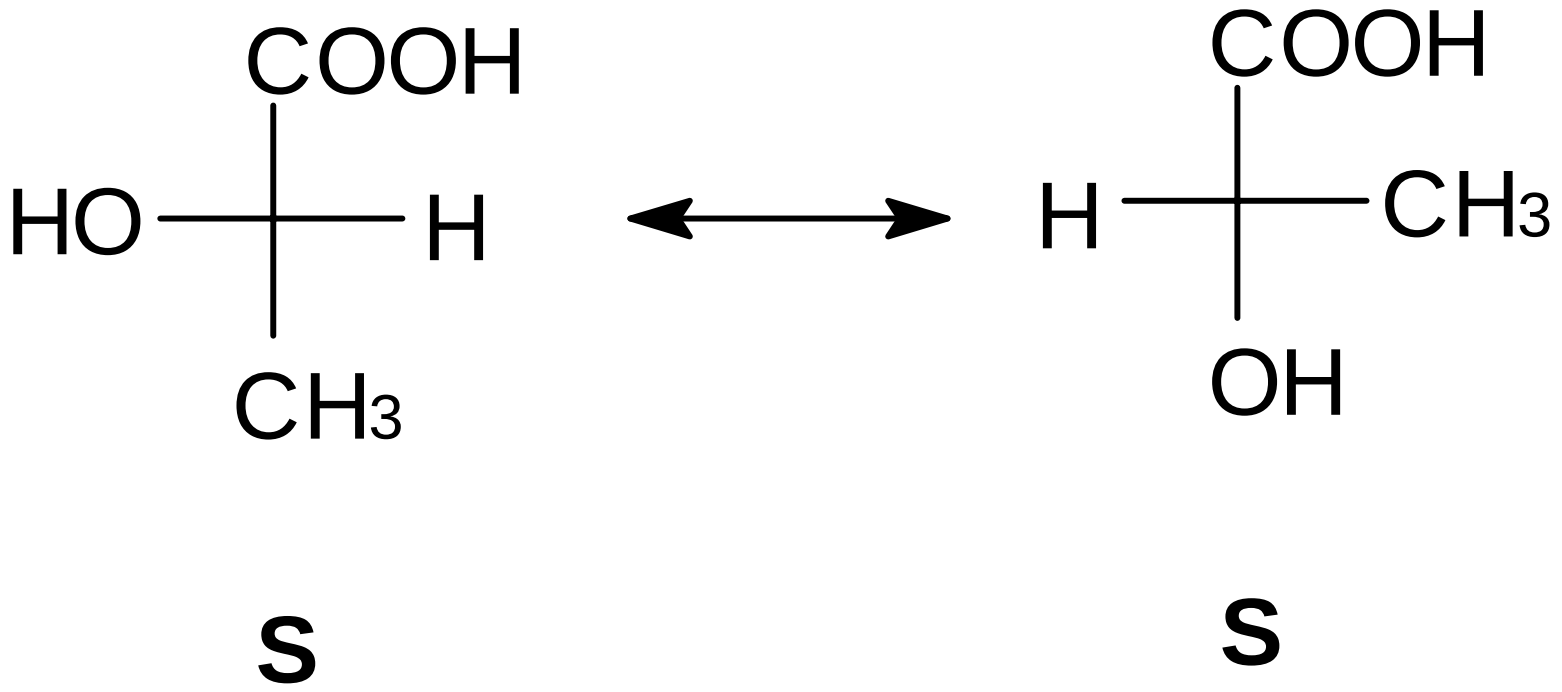
- 2)面内旋转90°，或面外翻转180°变为对映体



- 3l面内旋转180°，构型不变



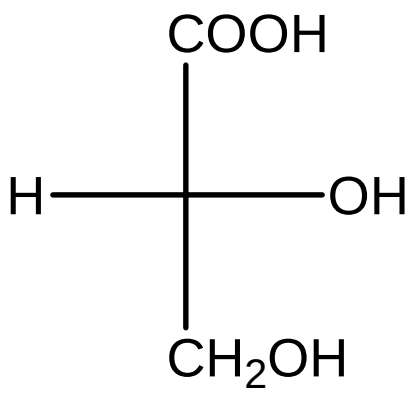
4)固定一个基团不动，按次序交换另三个基团，构型不变；



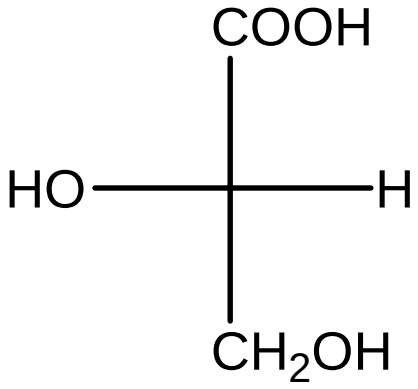
S　　S

§3.3 构型的标识

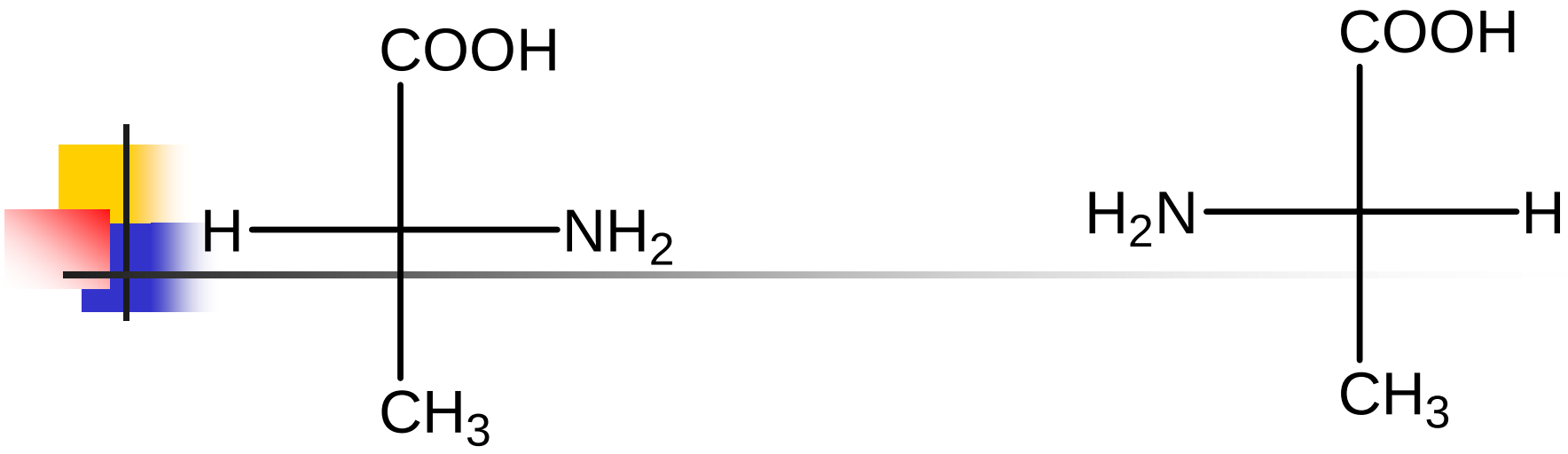
1. D/L 构型标识法：



D-甘油酸

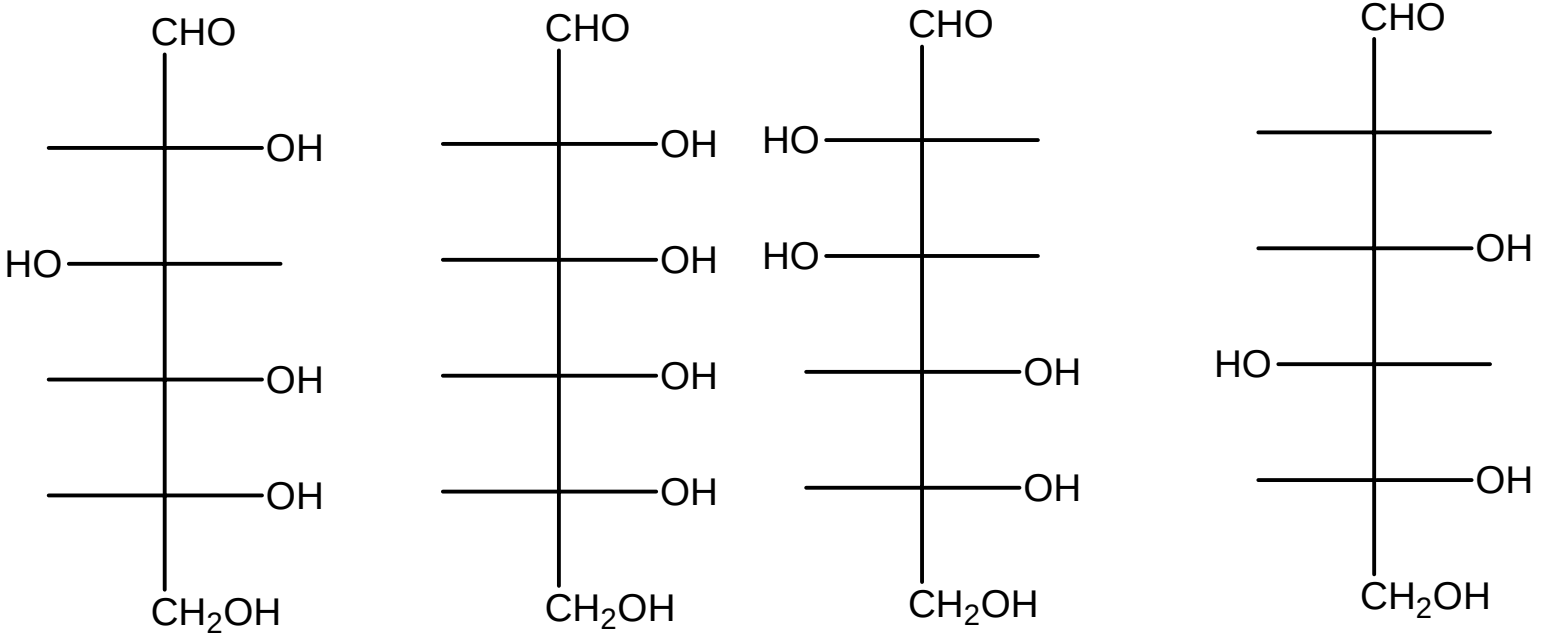


L-甘油酸

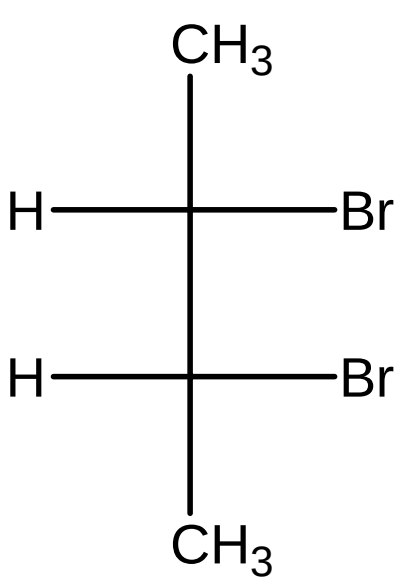

COOH
H
NH2
CH3
COOH
H2N
H
CH3

D-丙氨酸

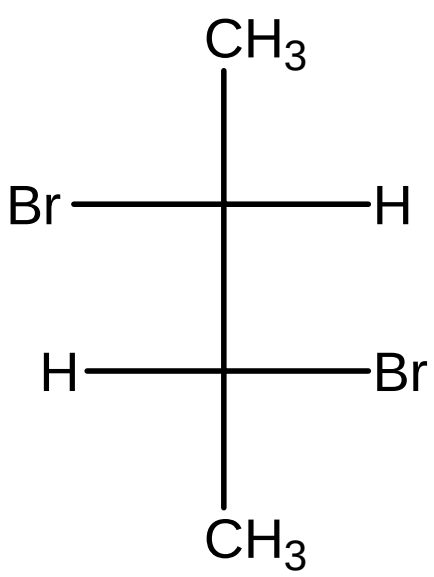
L-丙氨酸

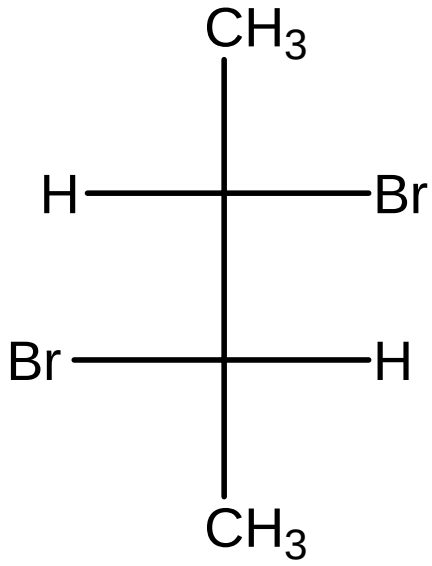

CHO
OH
HO
OH
OH
CH2OH
CHO
OH
OH
OH
CH2OH
CHO
HO
HO
OH
OH
CH2OH
CHO
OH
HO
OH
CH2OH

2. 赤式/苏式 构型标识法：

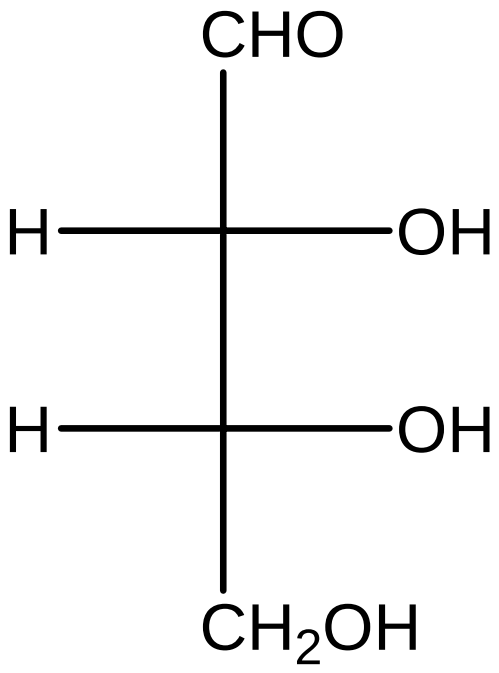


赤式

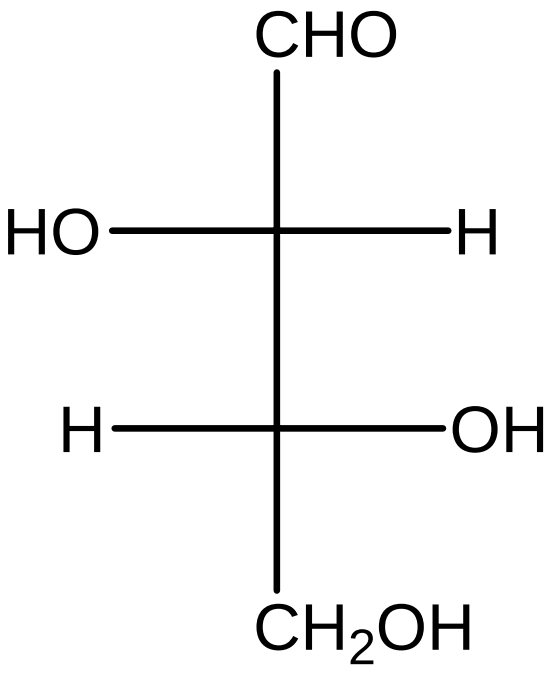




苏式



赤藓糖



苏阿糖

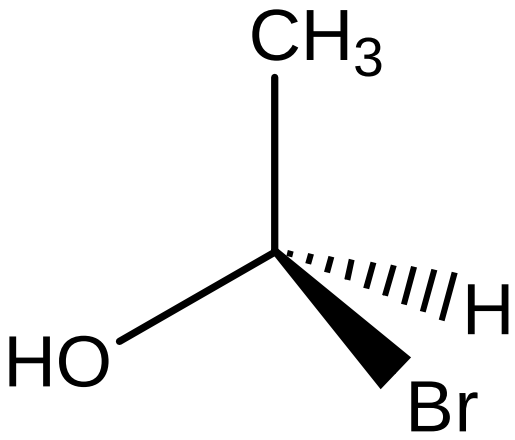
3. R/S 构型标识法(IUPAC)：

A.规定：(1)把基团按一定的定序规则定序。

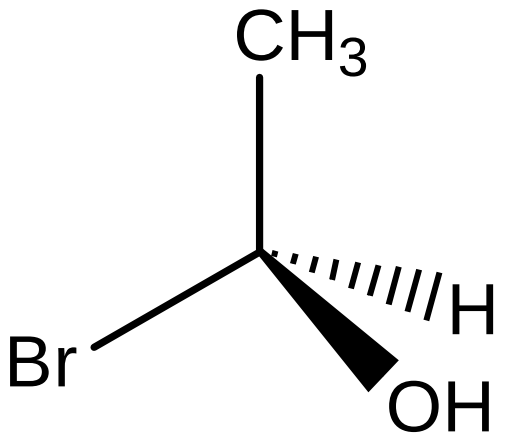
(2)朝向最小基团，按由大到小看另三个基团，若为顺时针则定义该手性碳的构型为 R 构型；反之，若为逆时针则定义该手性碳的构型为 S 构型。

如：

若按一定的定序规则：　Br > OH >CH_3 > H

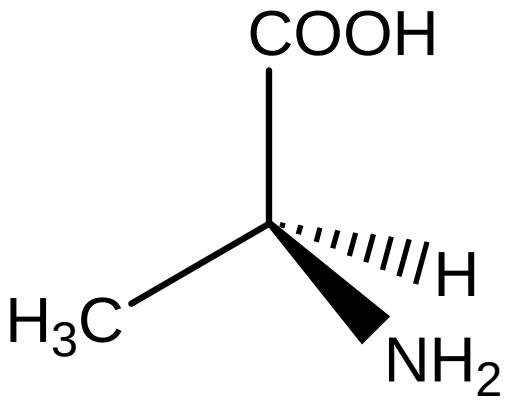


R



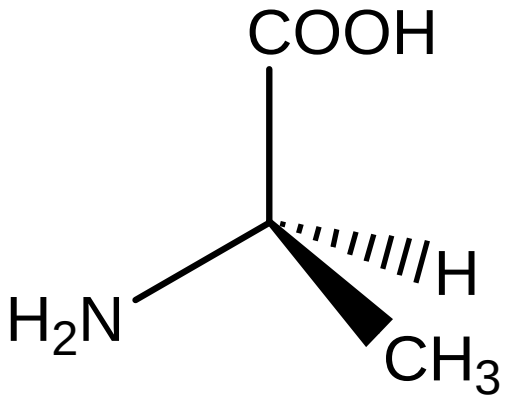
S

若按一定的定序规则：NH_2 >COOH >CH_3 > H



S-丙氨酸

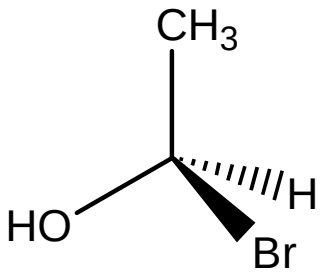
L-丙氨酸



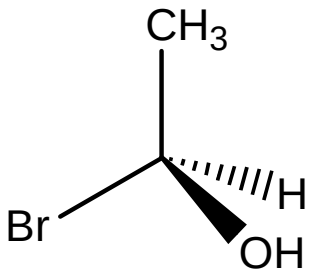
R-丙氨酸

D-丙氨酸

若按一定的定序规则： Br > OH >CH_3 > H

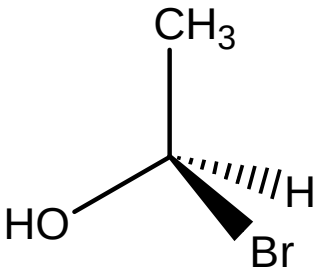


R

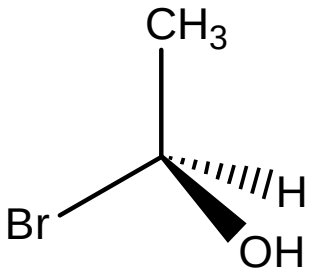


S

若按一定的定序规则： OH > Br >CH_3 > H



S

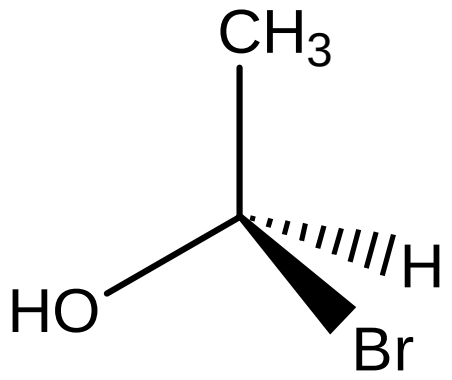


R

B.定序规则：

1，若一个手性碳上连有四个不同的原子，则原子序数大的优先。

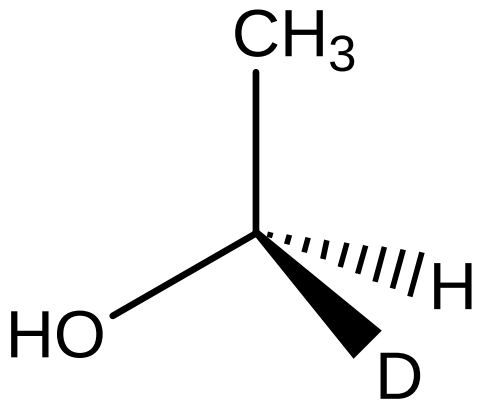
如：



Br > OH >CH_3 > H

2，若一个手性碳上连有原子序数相同的原子，则原子量大的优先。

如：

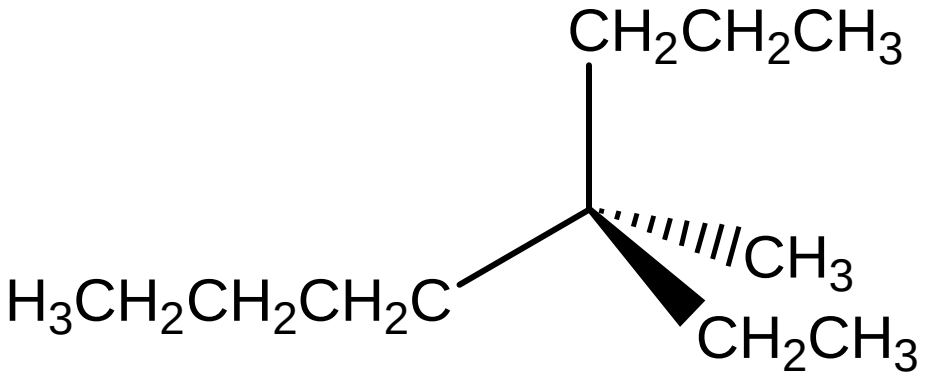


OH >CH_3 > D > H

R

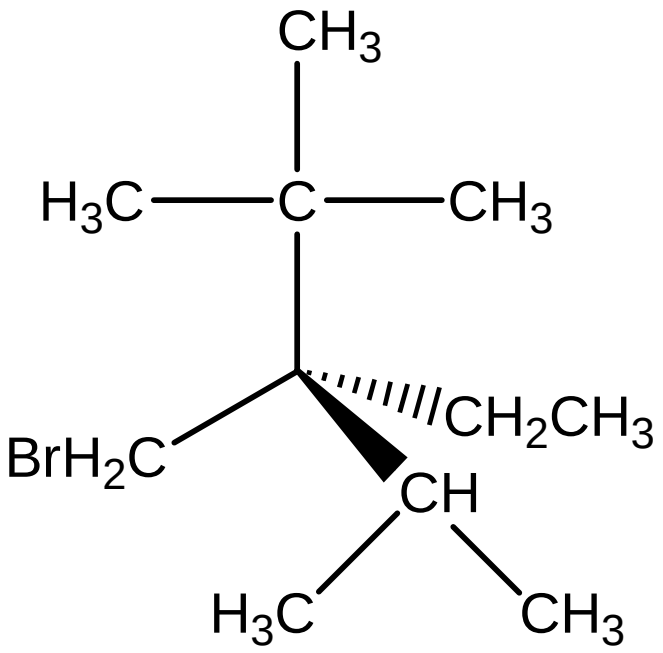
3，若一个手性碳上连有原子序数相同的原子，且原子量也相同，则按规则 1，2，次序地比较下一个所连的原子。

如：

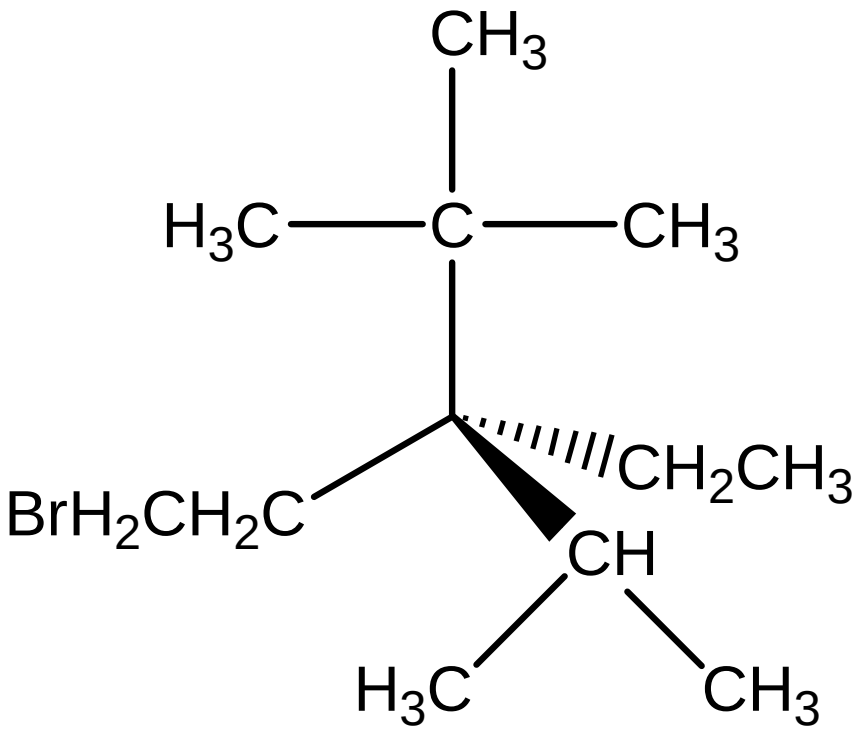


R

一个较大的原子序数比多个较小的原子序数优先



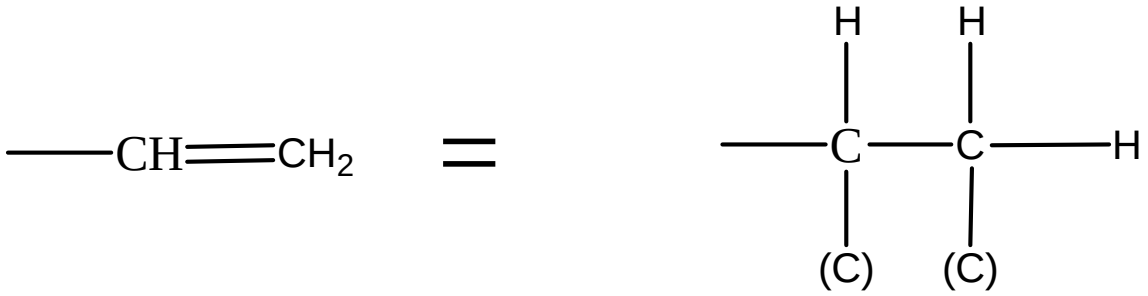
R

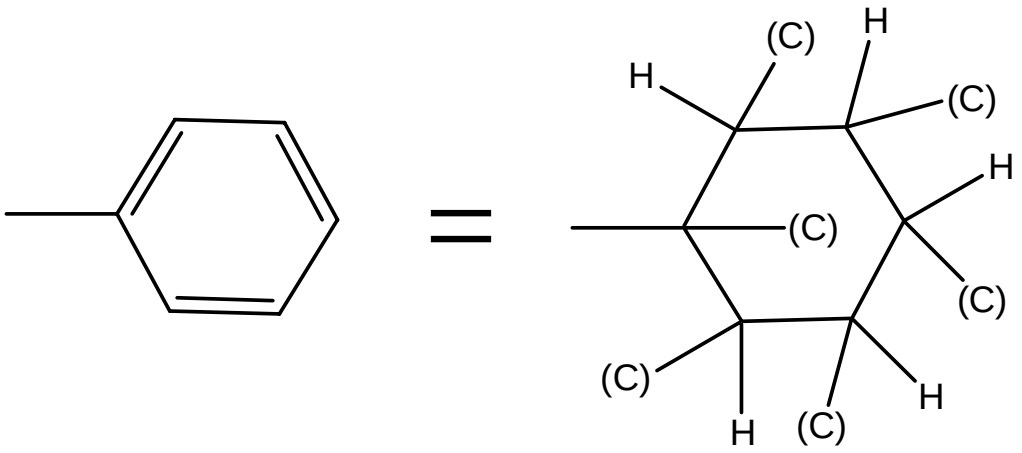

CH3
H3C
C
CH3
CH2CH3
BrH2CH2C
CH
H3C
CH3

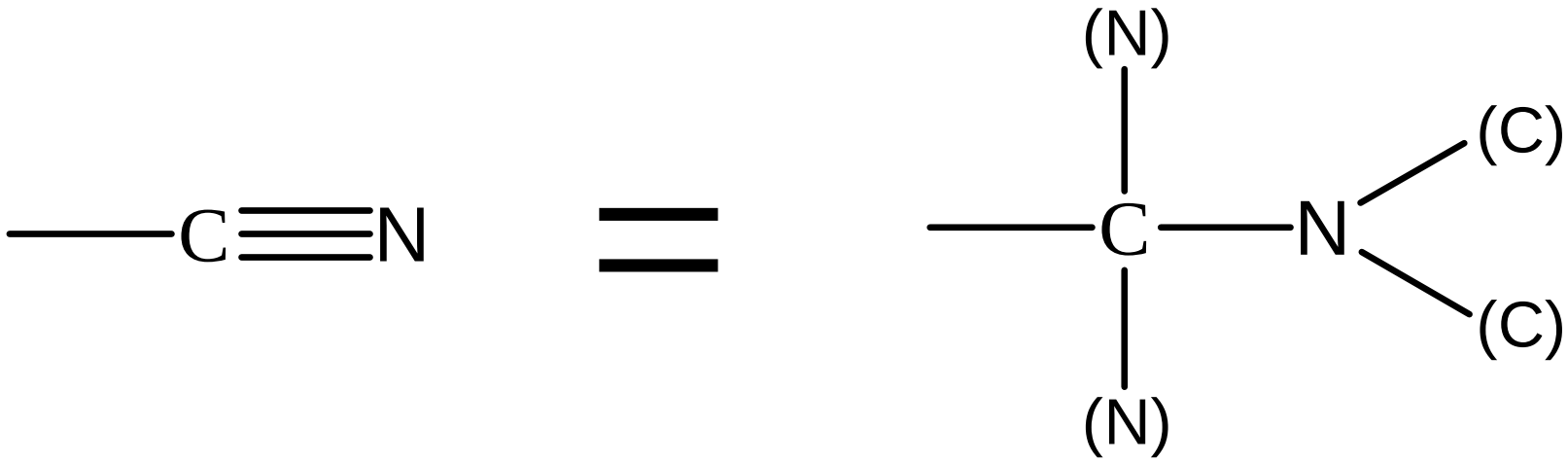
?

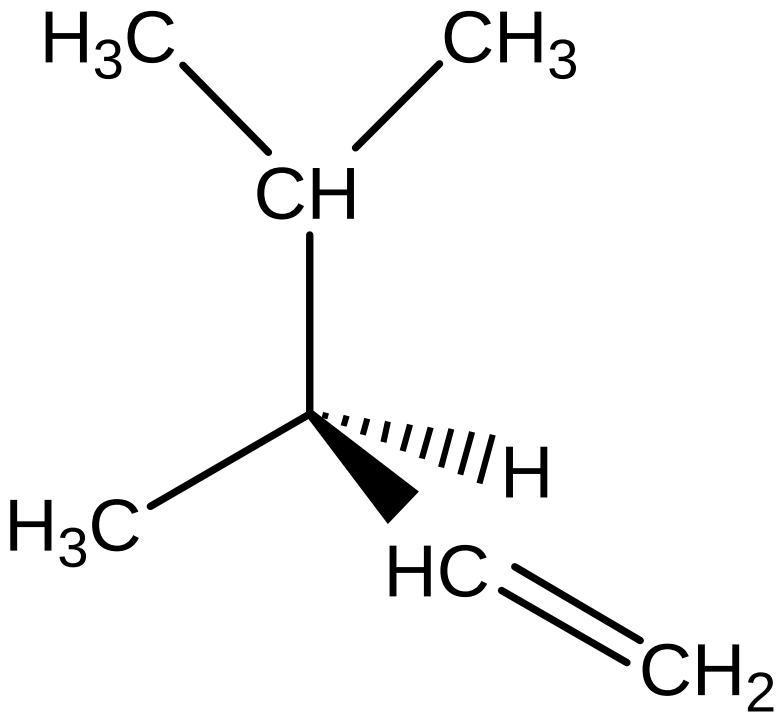
4，若一个手性碳上连有双键或三键，可将其拆开后比较。

如：





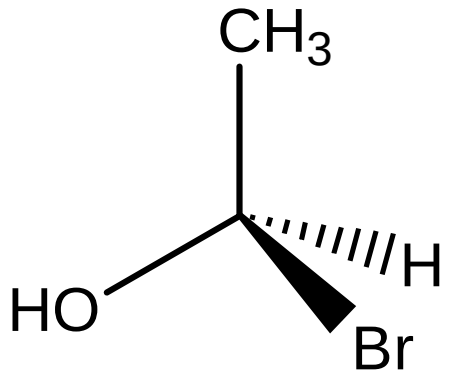

C
N
(N)
(C)
C
N
(C)
(N)


H3C
CH3
CH
H
H3C
HC
CH2

?

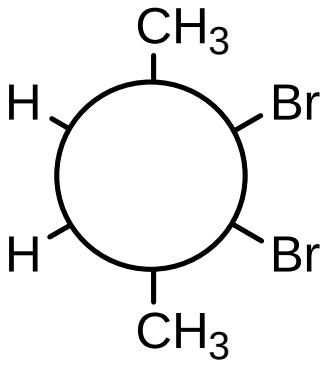
§3.4 构型在各种表达式中的标识

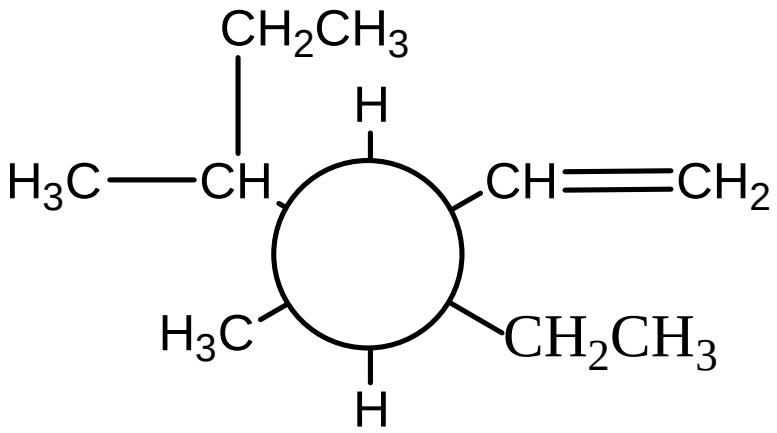
1，构型在飞楔式中的标识：

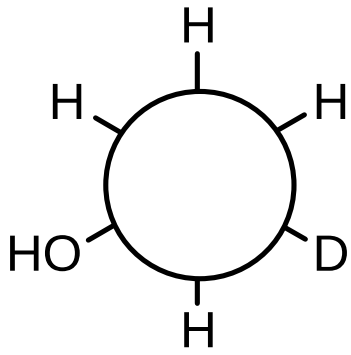


Br > OH >CH_3 > H

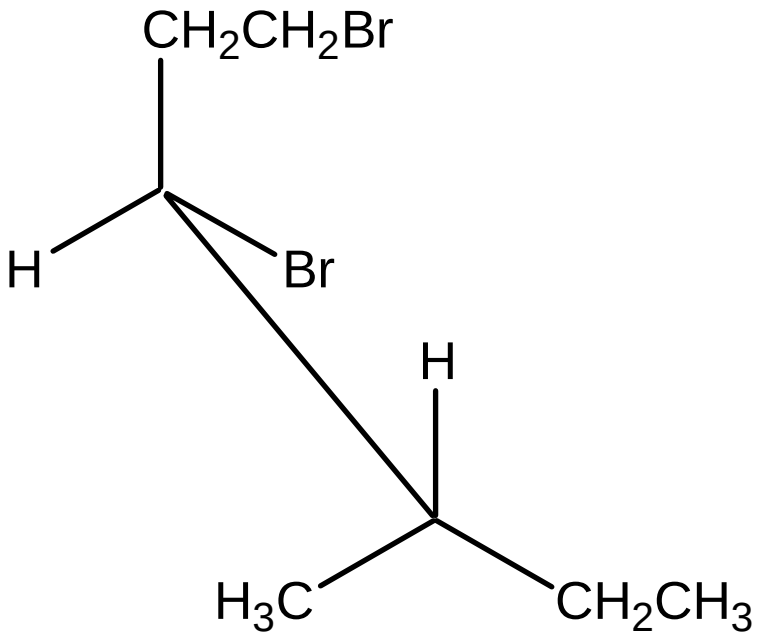
2， 构型在Newman投影式中的标识：

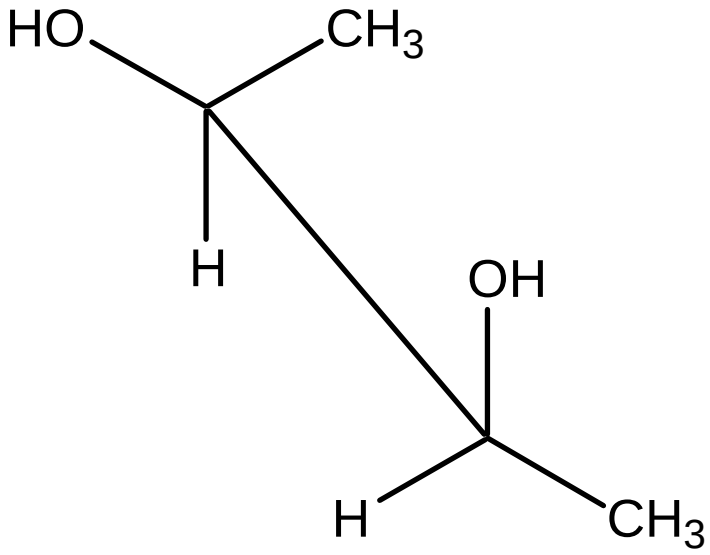




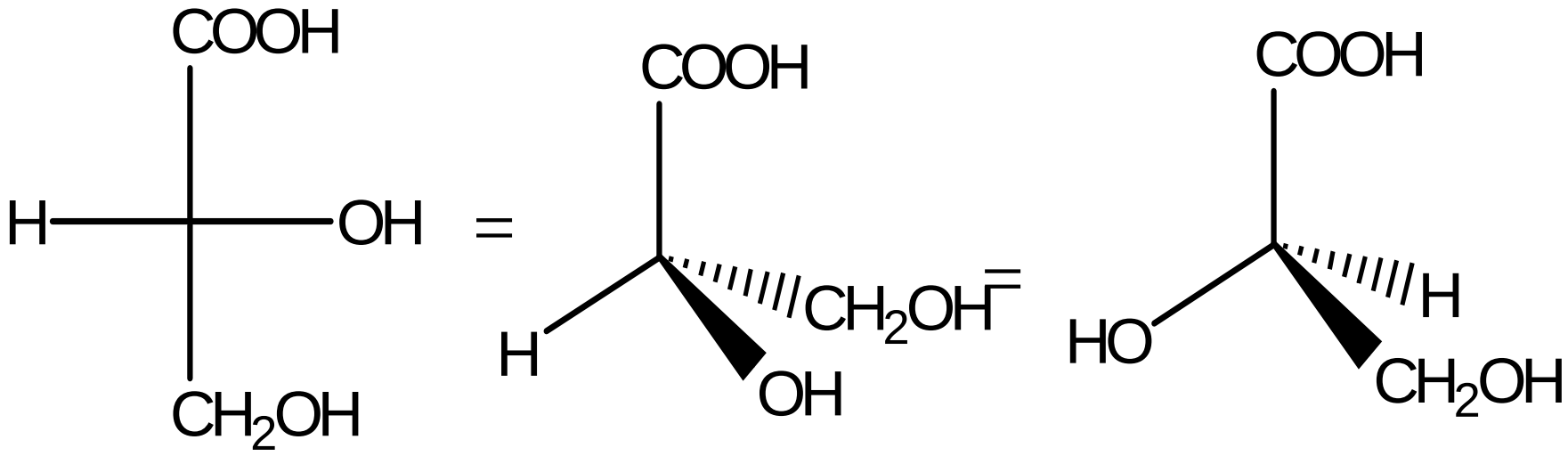


3，构型在锯架式中的标识：

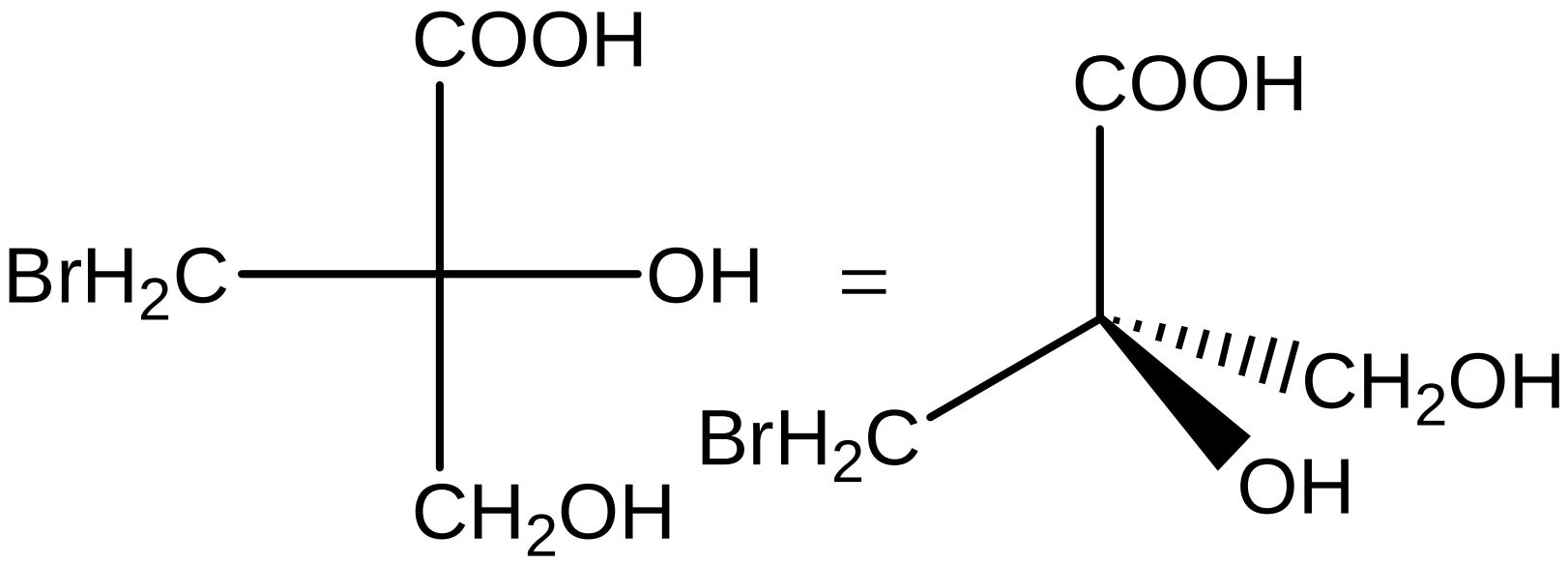




4，构型在Fischer投影式中的标识：



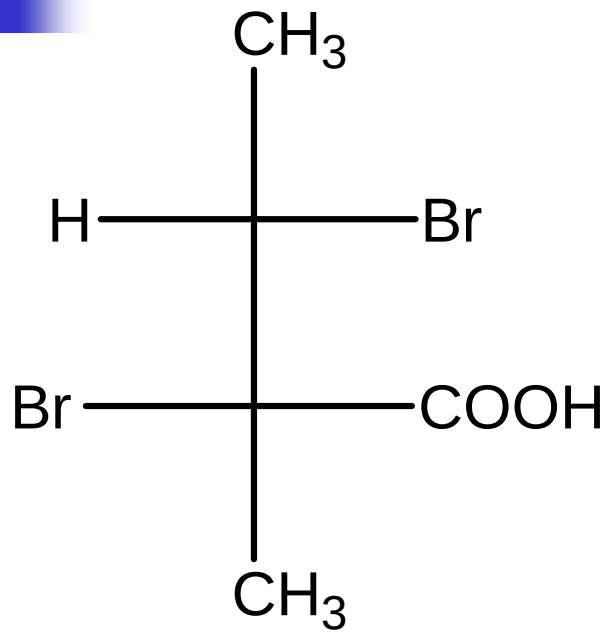
D-甘油酸

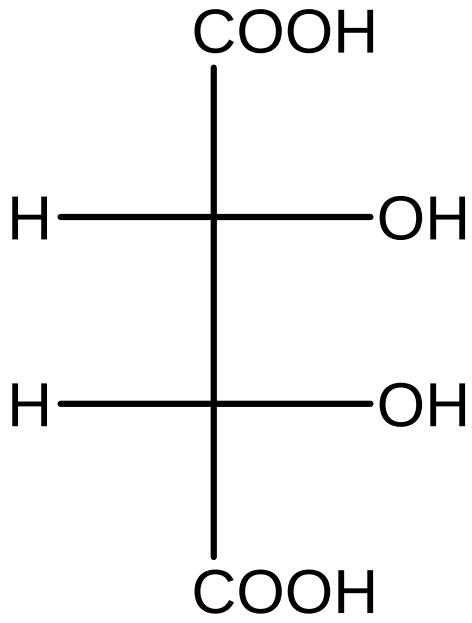

COOH
BrH2C
OH
CH2OH
=
COOH
CH2OH
BrH2C
OH

总结：

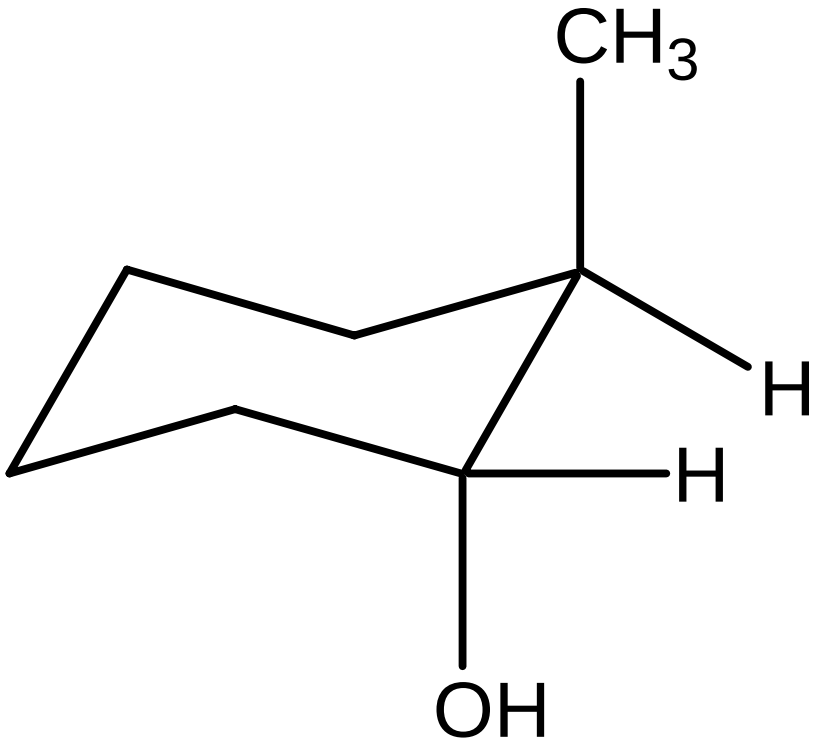
A. 在Fischer投影式中，当最小基团在横键时，在Fischer投影式中的标定方向与实际标定方向相反，即顺时针则定义该手性碳的构型为 S 构型；反之，若为逆时针则定义该手性碳的构型为 R 构型。

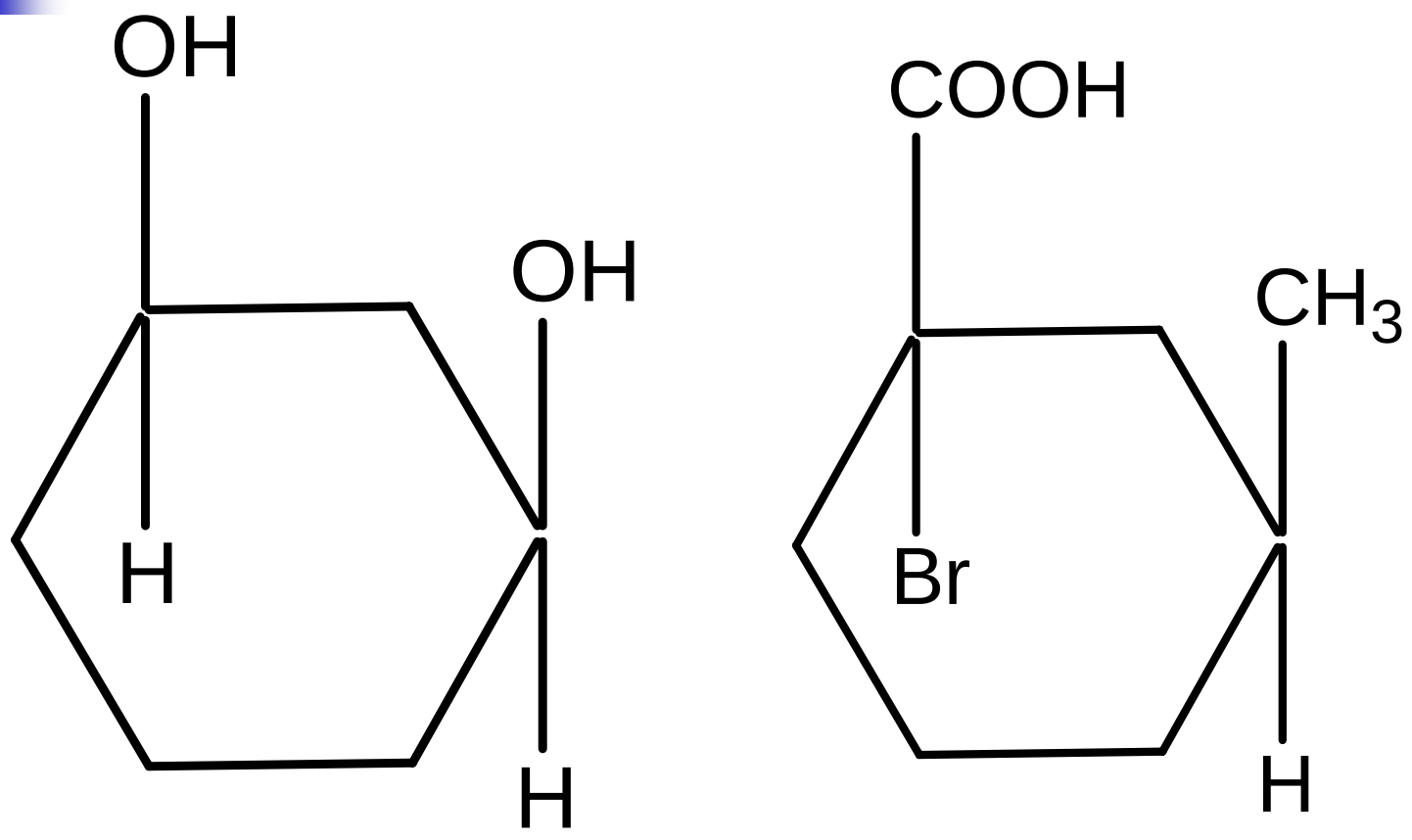
B. 在Fischer投影式中，当最小基团在竖键时，在Fischer投影式中的标定方向与实际标定方向相同。


CH3
H
Br
Br
COOH
CH3


COOH
H
OH
H
OH
COOH

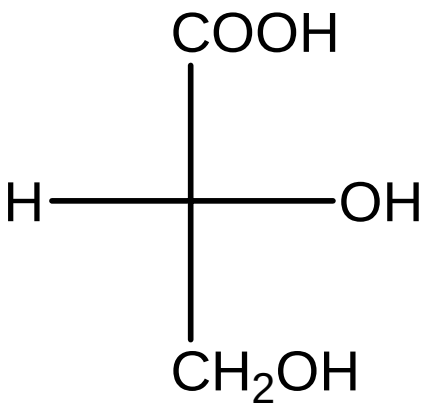
5，构型在其它表达式中的标识：



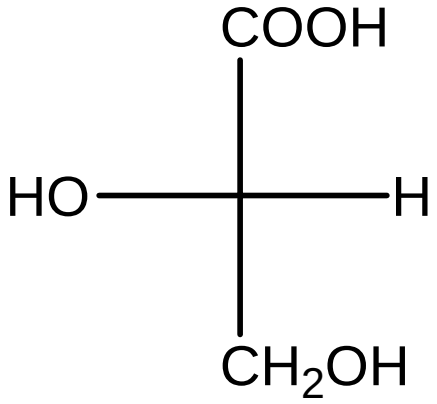

OH
OH
H
H
COOH
CH3
Br
H

§3.5 手性化合物的旋光性及旋光度的测量

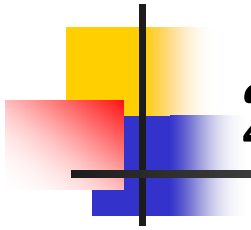
- 1，手性化合物的旋光性



(-)-甘油酸



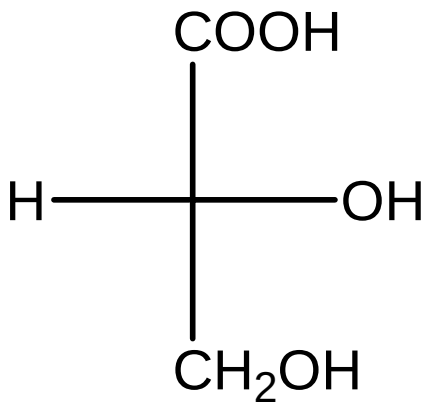
(+)-甘油酸



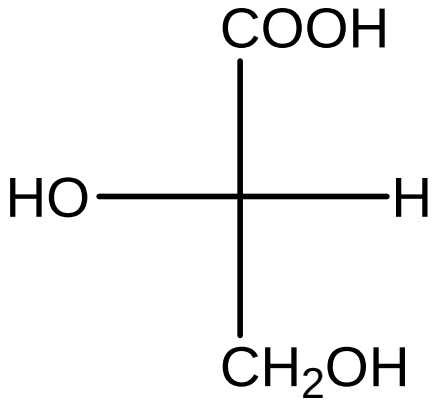
2，旋光度的测量

§3.6 外消旋体及内消旋体

- 1，**外消旋体：等量的对映异构体的混合物**

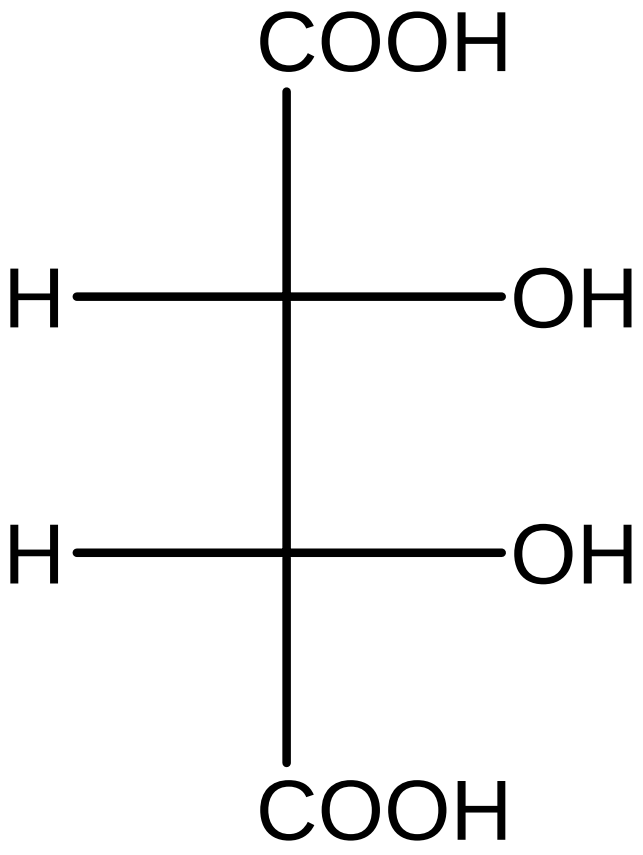


(-)-甘油酸



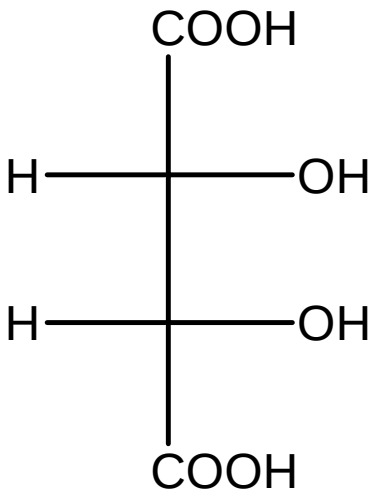
(+)-甘油酸

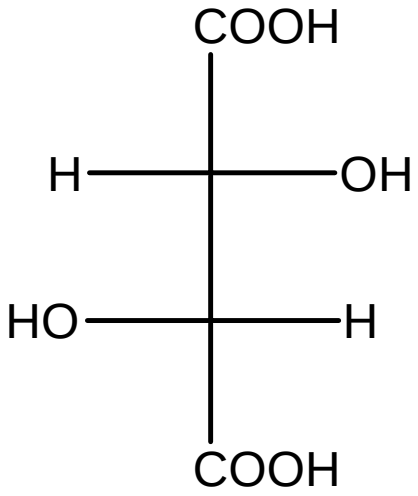
2，内消旋体：

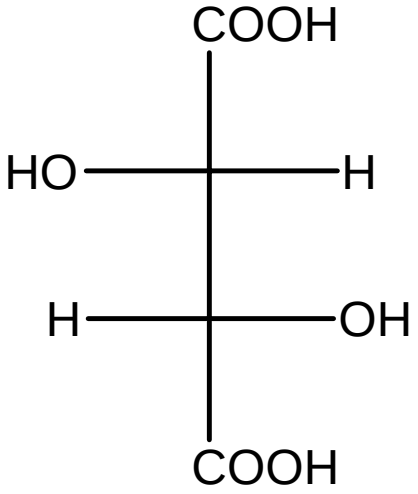


§3.7 含有两个手性碳的化合物

- 1，含有两个相同手性碳的化合物







2，含有两个不相同手性碳的化合物