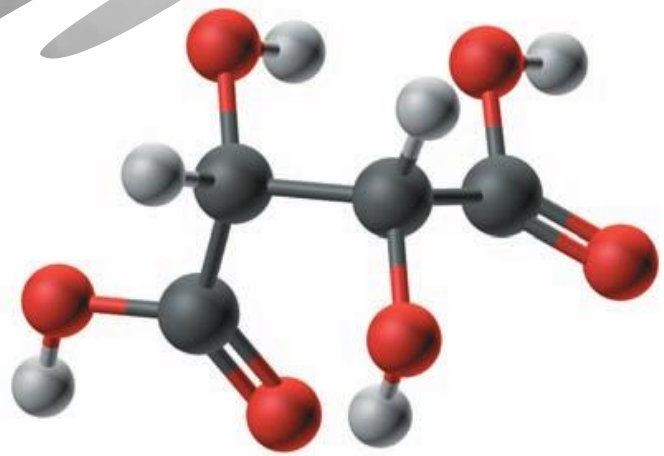
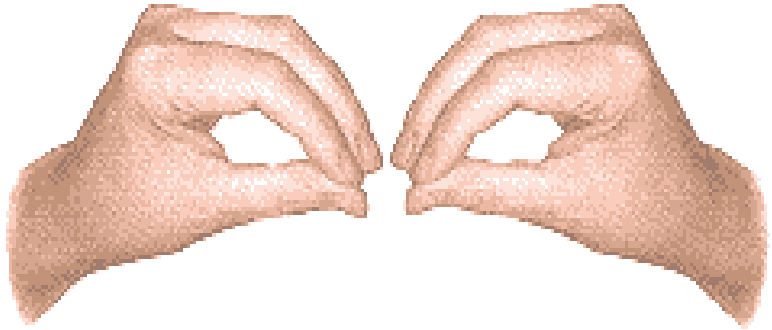
西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

Chapter 6

Chirality: The Handedness of Molecules





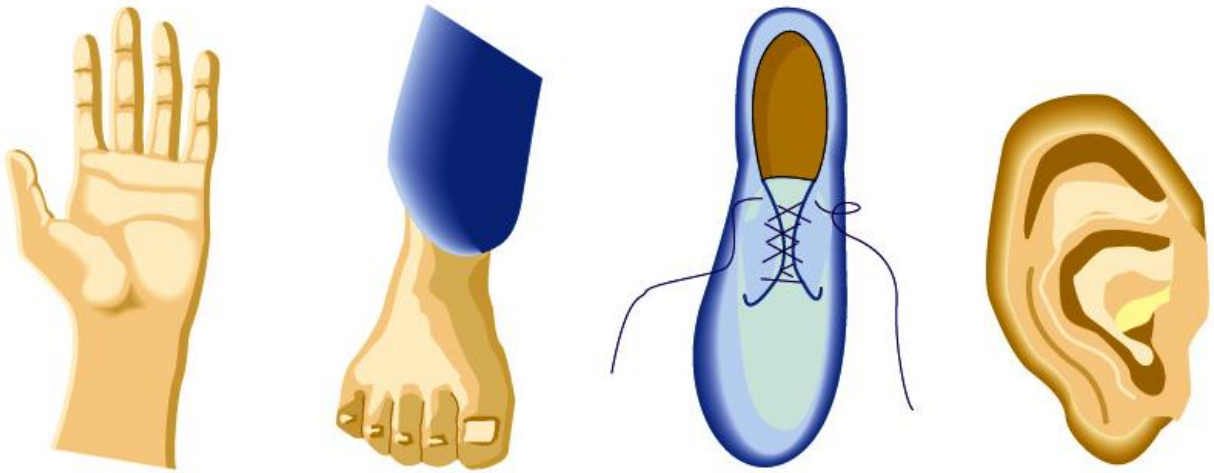
(a)

6.1 What Are Stereoisomers and Enantiomers?

6.2 How Do We Designate the Configuration of a Stereocenter?

6.3 What Is the 2^n Rule?

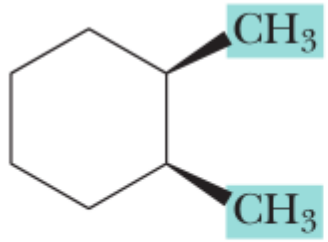
6.4 How Is Chirality Detected in the Laboratory?



chiral objects

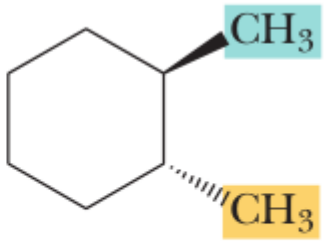
6.1 What Are Stereoisomers（立体异构体） and Enantiomers（对映体）?

Stereoisomers Isomers that have the same molecular formula and the same connectivity, but different orientations of their atoms in space.

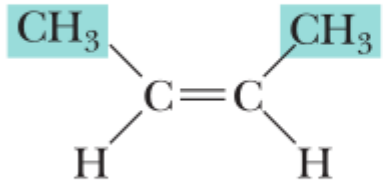


cis-1,2-Dimethyl-cyclohexane

and

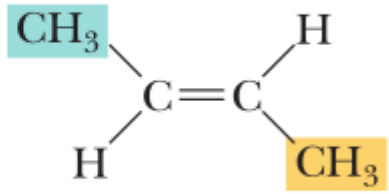


trans-1,2-Dimethyl-cyclohexane



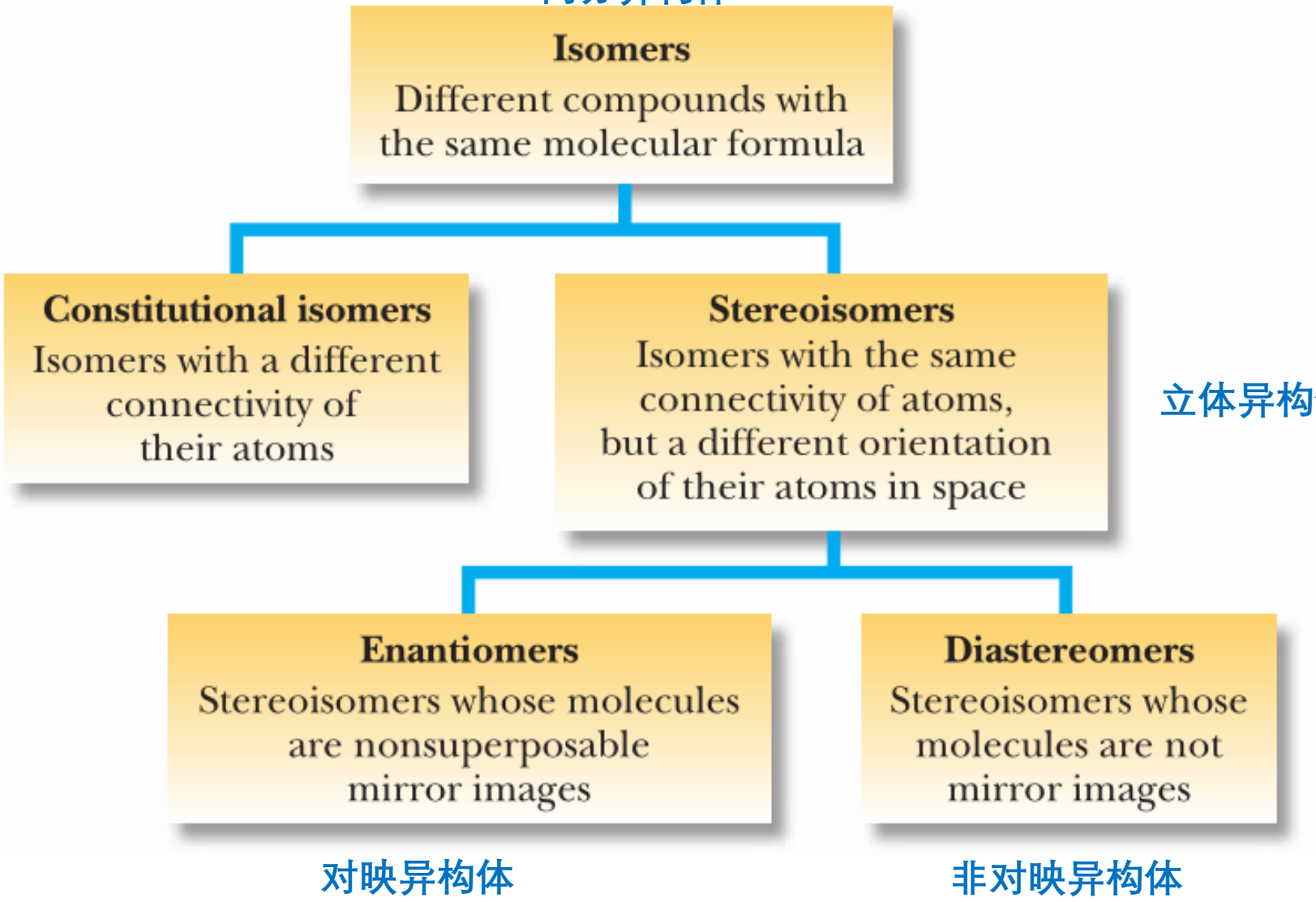
cis-2-Butene

and



trans-2-Butene

同分异构体



构造异构体

立体异构体

对映异构体

非对映异构体

异构体分类：

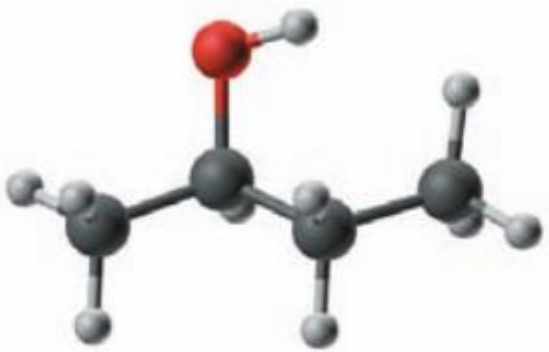
- 同分异构
  - 构造异构
    - 碳链异构
    - 官能团异构
    - 官能团位置异构
  - 立体异构
    - 构象异构
    - 构型异构
      - 顺反异构
      - 对映异构（旋光异构）

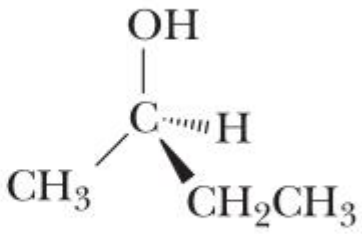
Enantiomers（对映体） Stereoisomers that are nonsuperposable mirror images; the term refers to a relationship between pairs of objects.

手性碳（不对称碳）

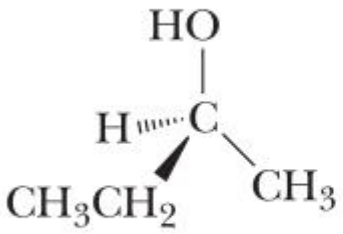
the four different "groups" bonded to this carbon are —H, —OH, —CH_3, and —CH_2CH_3

2-Butanol

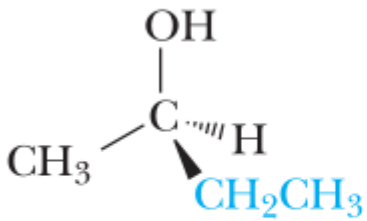




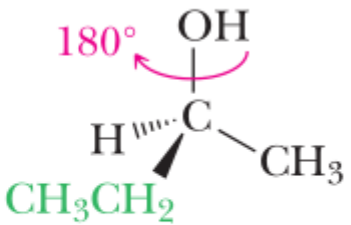
Original



Mirror image

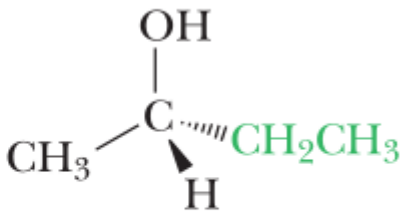


The original molecule



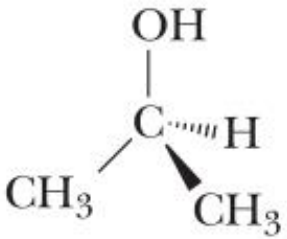
The mirror image of the original molecule

rotate about the C—OH bond by 180°



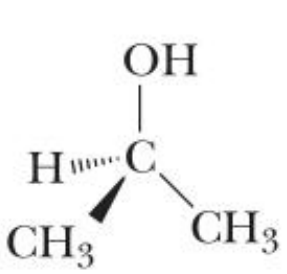
The mirror image rotated by 180°

Chiral（手性） From the Greek cheir, meaning hand; objects that are not superposable on their mirror images.

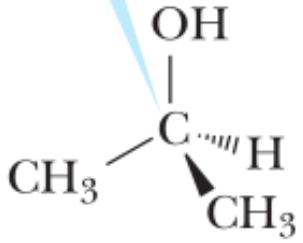


Original

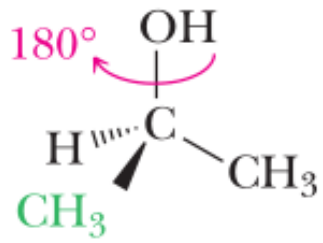
Mirror image



every single group on this atom matches up with the corresponding groups in the mirror image (i.e., they are superposable)

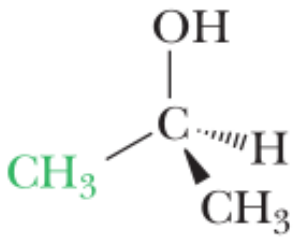


The original



The mirror image

rotate about the C—OH bond by 120°



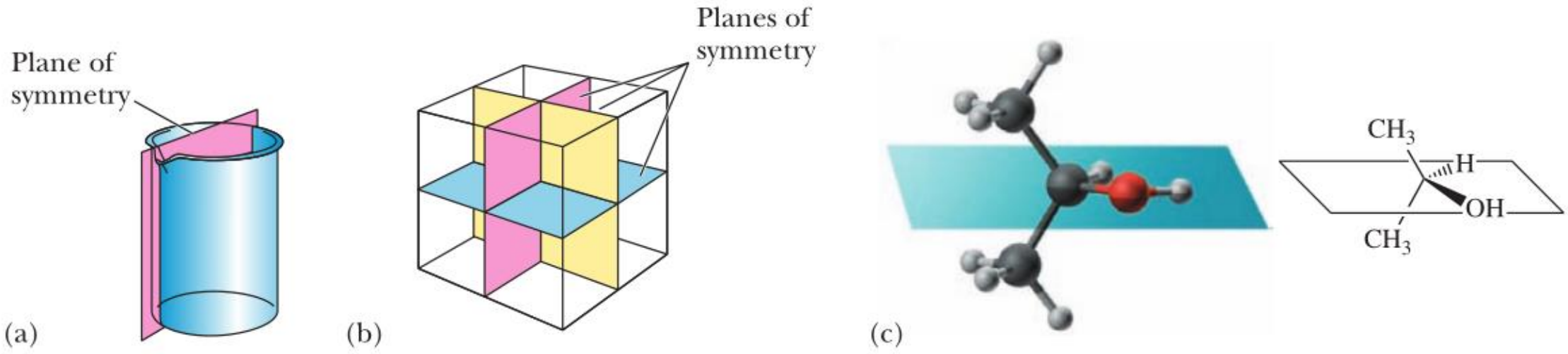
The mirror image rotated by 180°

Achiral（非手性） An object that lacks chirality; an object that has no handedness and is superposable on its mirror image.

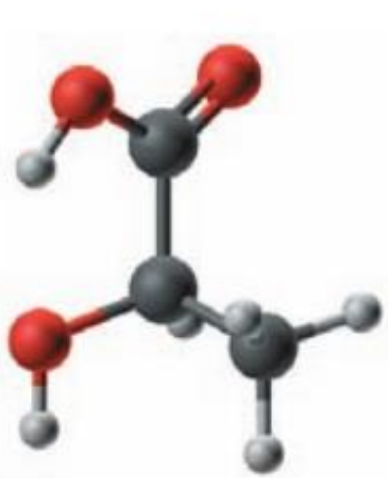
Plane of symmetry（对称面） An imaginary plane passing through an object and dividing it such that one half is the mirror image of the other half.

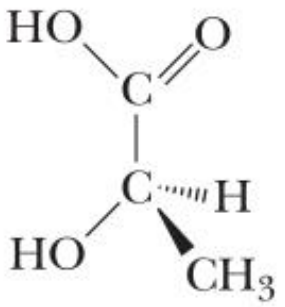
Chiral center（手性） An atom, such as carbon, with four different groups bonded to it.

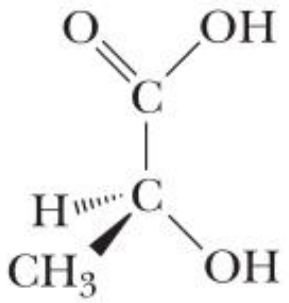
Stereocenter（立体中心） An atom at which the interchange of two atoms or groups of atoms bonded to it produces a different stereoisomer.

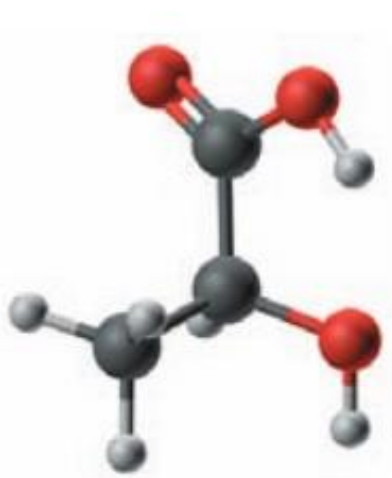


乳酸



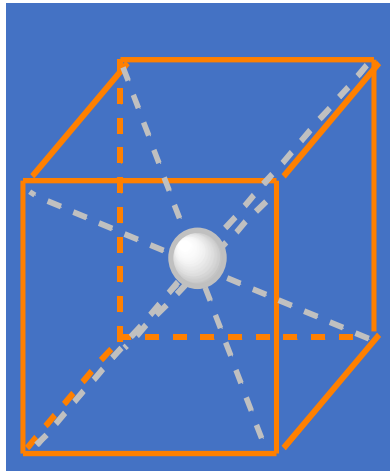


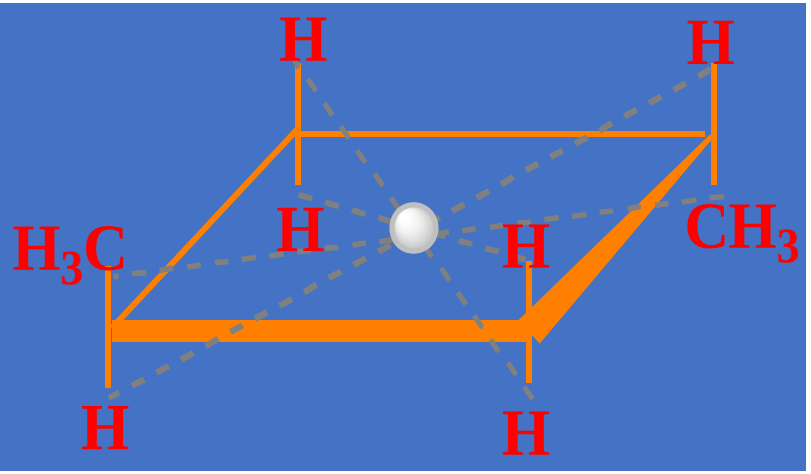




对称中心

设想分子中有一个点，从分子中任一个原子出发，向这个点作一直线，再从此点将直线延长出去，则在与该点前一段等距离处，可遇到一同样的原子，该点称为分子的对称中心。





小结:

※ 凡具有对称 面、对称中心的分子，都是非手性分子。

※ 有无对称轴，对分子是否有手性无决定作用。

※ 当分子中只有一个C* ，分子一定有手性。

※ 当分子中有多个手性中心时，要借助对称因素。无对称面，又无对称中心的分子，可基本断定是手性分子。

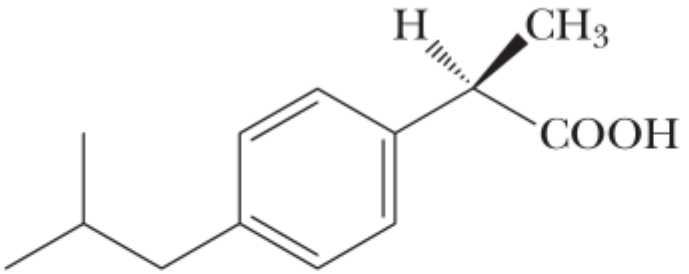
※ 互为镜像的两种构型的异构体称为对映异构体。

※ 分子的手性是存在对映体的必要和充分条件。

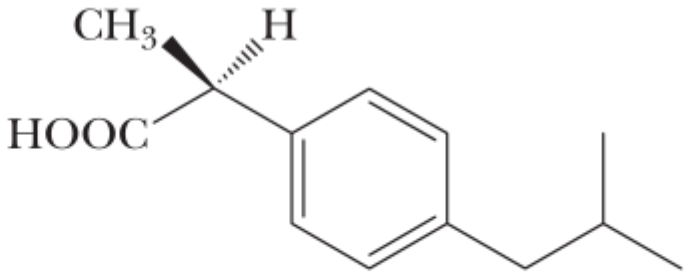
※ 手性分子必有互为镜像的对映异构体。

※ 对映异构体之间的转变必须通过断裂分子中的化学键并交换基团的空间位置。

6.2 How Do We Designate the Configuration of a Stereocenter?

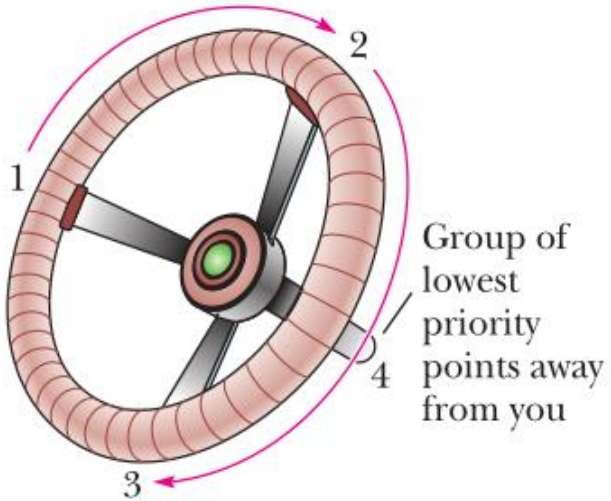


The inactive enantiomer of ibuprofen



The active enantiomer
布洛芬

R,S system A set of rules for specifying the configuration about a stereocenter.



R From the Latin *rectus*, meaning right; used in the R,S system to show that the order of priority of groups on a stereocenter is clockwise.

S From the Latin *sinister*, meaning left; used in the R,S system to show that the order of priority of groups on a stereocenter is counterclockwise.

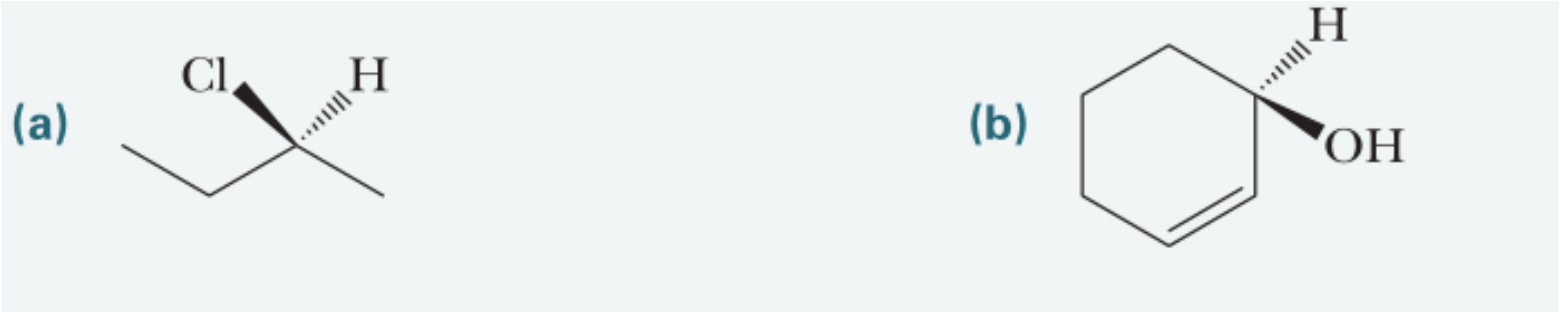
To assign an R or S configuration to a stereocenter,

1. Locate the stereocenter, identify its four substituents, and assign a priority from 1 (highest) to 4 (lowest) to each substituent.

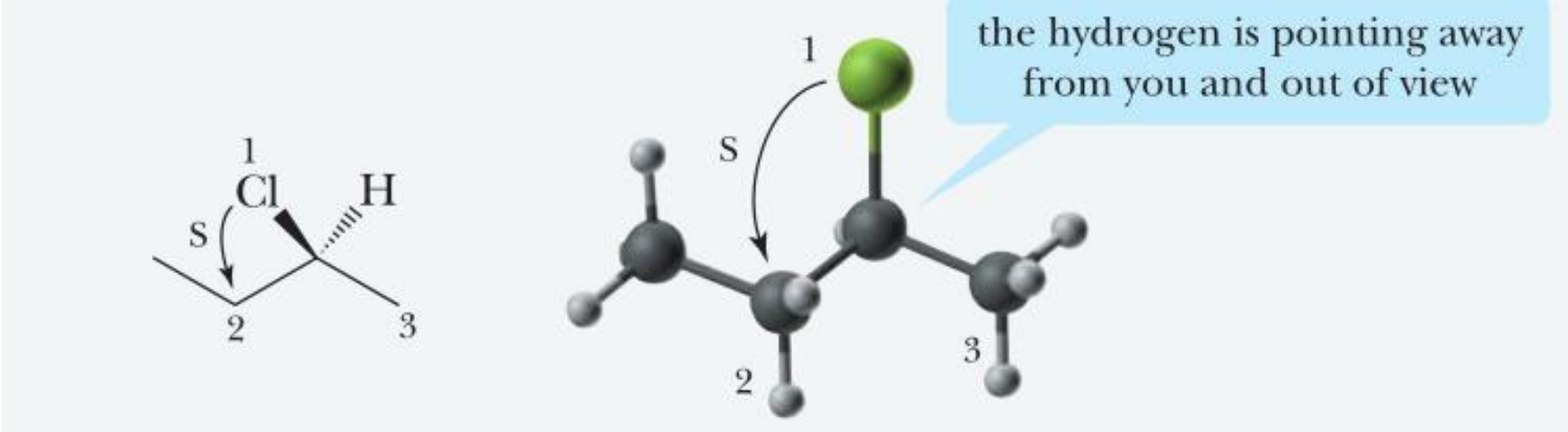
2. Orient the molecule in space so that the group of lowest priority (4) is directed away from you, as would be, for instance, the steering column of a car. The three groups of higher priority (1–3) then project toward you, as would the spokes of a steering wheel.

3. Read the three groups projecting toward you in order, from highest priority (1) to lowest priority (3).

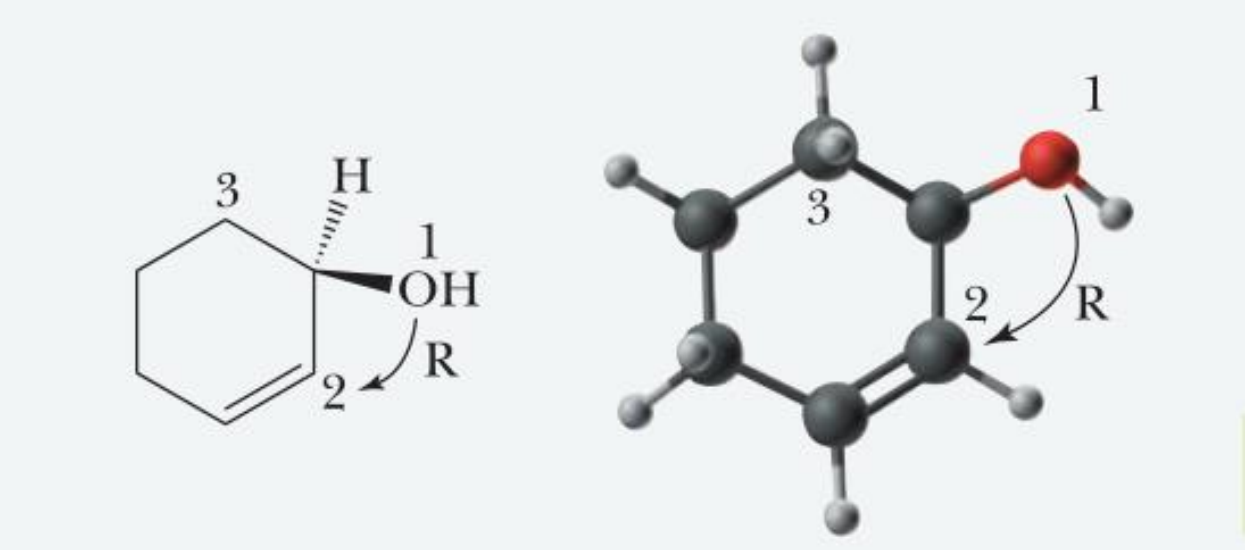
4. If reading the groups proceeds in a clockwise direction, the configuration is designated R (Latin: rectus, straight, correct); if reading proceeds in a counterclockwise direction, the configuration is S (Latin: sinister, left). You can also visualize this situation as follows: Turning the steering wheel to the right equals R, and turning it to the left equals S.



(a) The order of priority is -Cl > -CH_2 CH_3 > - CH_3 > -H. The group of lowest priority, H, points away from you.Reading the groups in the order 1, 2, 3 occurs in the counterclockwise direction, so the configuration is S.



(b) The order of priority is -OH > -CH=CH > - CH_2CH_2 > -H. With hydrogen, the group of lowest priority, pointing away from you, reading the groups in the order 1, 2, 3 occurs in the clockwise direction, so the configuration is R.

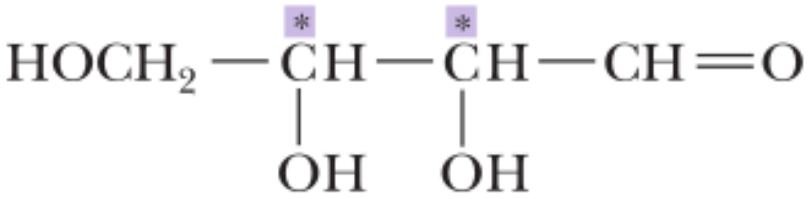


6.3 What Is the 2^n rule?

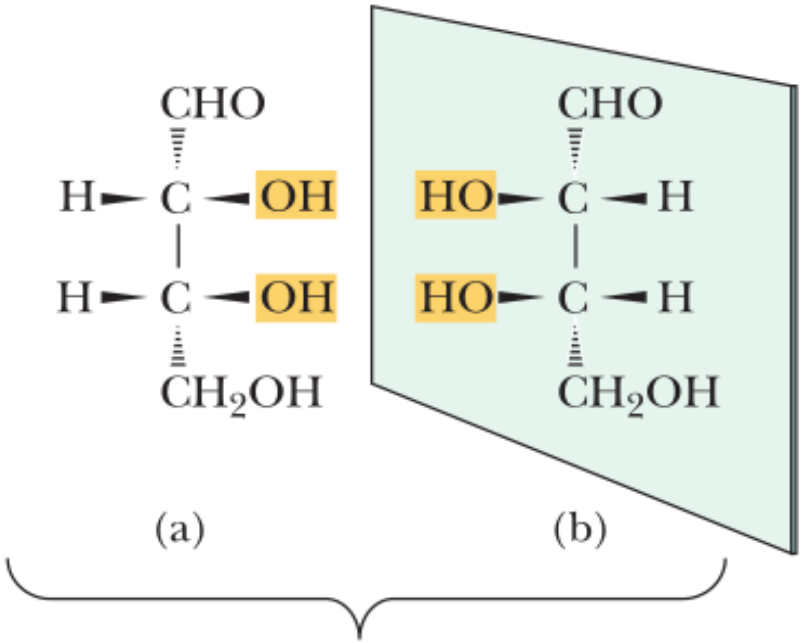
To generalize, for a molecule with n stereocenters, the maximum number of stereoisomers possible is 2^n .

A. Enantiomers and Diastereomers（对映体和非对映体）

Diastereomers(非对映异构体) Stereoisomers that are not mirror images of each other; the term refersto relationships among objects

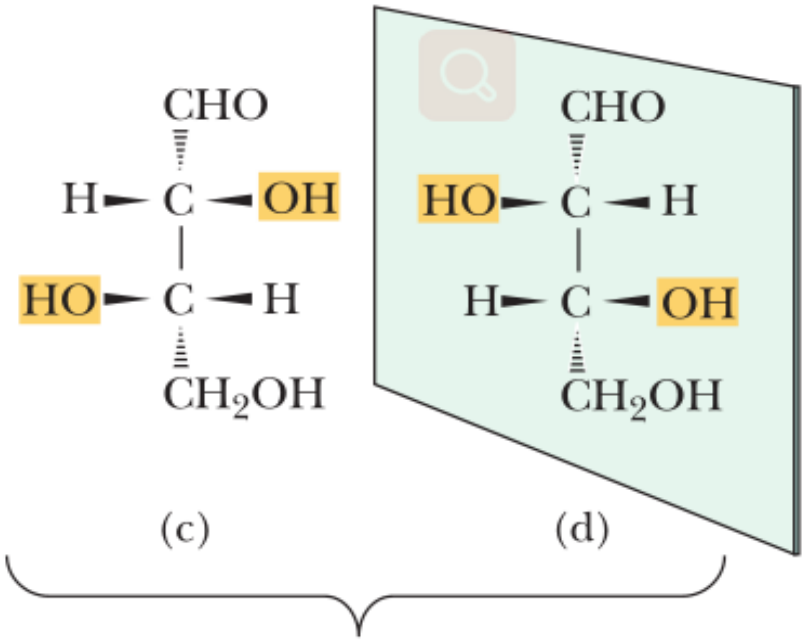


2,3,4-Trihydroxybutanal



(2R,3R) (2S,3S)

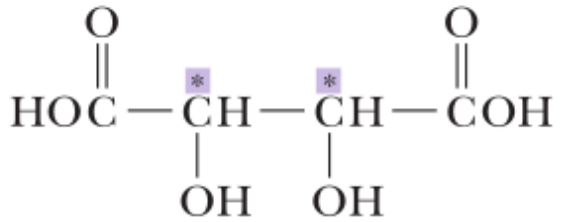
赤藓糖



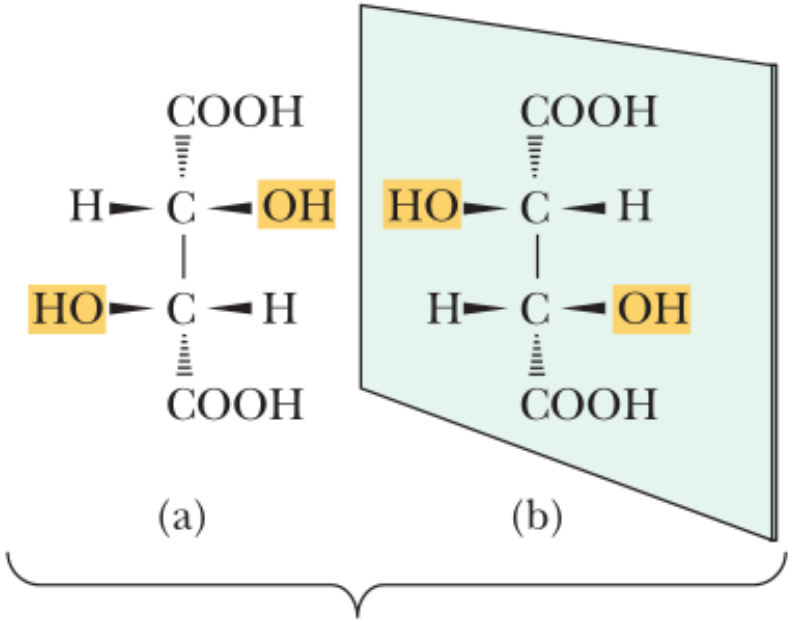
(2R,3S) (2S,3R)

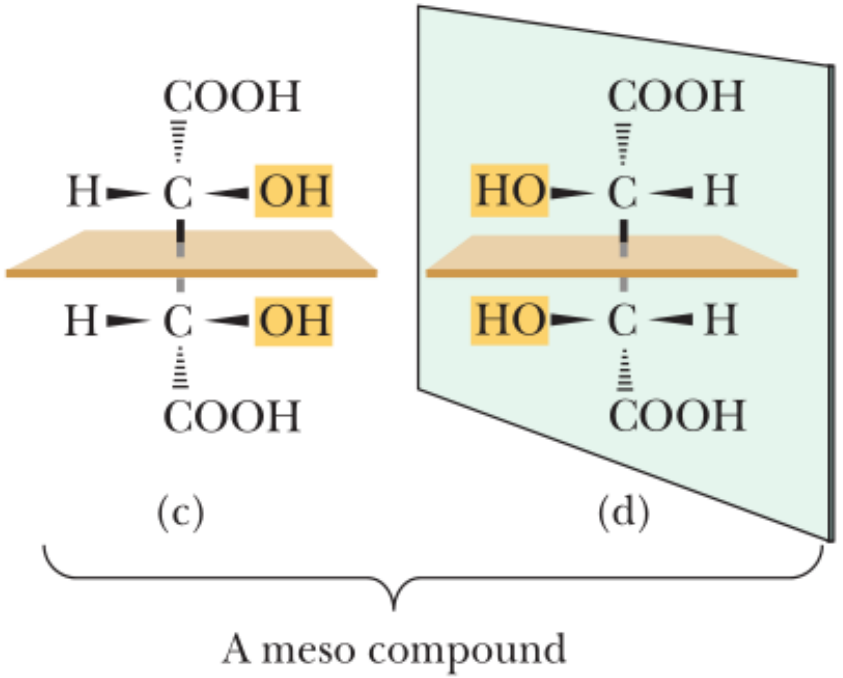
苏阿糖

B. Meso Compounds（内消旋化合物）



2,3-Dihydroxybutanedioic acid
(tartaric acid)





Meso compound （内消旋体） An achiral compound possessing two or more stereocenters.

6.4 How Is Chirality Detected in the Laboratory?

Polarimeter（偏振光） An instrument for measuring the ability of a compound to rotate the plane of polarized light.

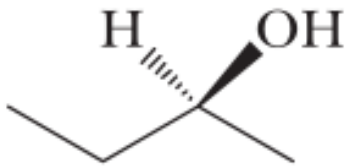
observed rotation （旋光度）The number of degrees through which a compound rotates the plane of polarized light.

Specific rotation（比旋光度） Observed rotation of the plane of polarized light when a sample is placed in atube 1.0 dm long at aconcentration of 1.0 g/mL.

$$\text{Specific rotation} = [\alpha]_{\lambda}^{T} = \frac{\text{Observed rotation (degrees)}}{\text{Length (dm)} \times \text{Concentration}}$$

Dextrorotatory （右旋） Rotating the plane of polarized light in a polarimeter to the right.

Levorotatory （左旋）0Rotating the plane of polarized light in apolarimeter to the left.



(*S*)-(+)-2-Butanol

$[\alpha]_D^{25}$ + 13.52°

(*R*)-(−)-2-Butanol

$[\alpha]_D^{25}$ −13.52°

Racemic mixture（外消旋体） A mixture of equal amounts of two enantiomers.

Optically inactive （非光学活性） Showing that a compound or mixture of compounds does not rotate the plane of polarized light.

	mp	$[\alpha]_D$(水)	溶解度 (g/100ml)	p*Ka*1	p*Ka*2
(+)-酒石酸	170℃	+12.0	139	2.98	4.23
(-)-酒石酸	170 ℃	-12.0	139	2.98	4.23
(±)-酒石酸	206 ℃	0	20.6	2.96	4.24
meso-酒石酸	140 ℃	0	125	3.11	4.80

外消旋体与内消旋体:

- 共同之处是：二者均无旋光性，但本质不同。
- 外消旋体：是混合物，可拆分出一对对映体。
- 内消旋体：是单一化合物，不能拆分。

酒石酸 HOOC-C*H(OH)-C*H(OH)-COOH

作 业

6. 17、6.19(a.b.c)、6.21、6.23、6.25、6.36

P197: 4、5

回答问题：

如何拆分一对对映异构体