Polarimetry

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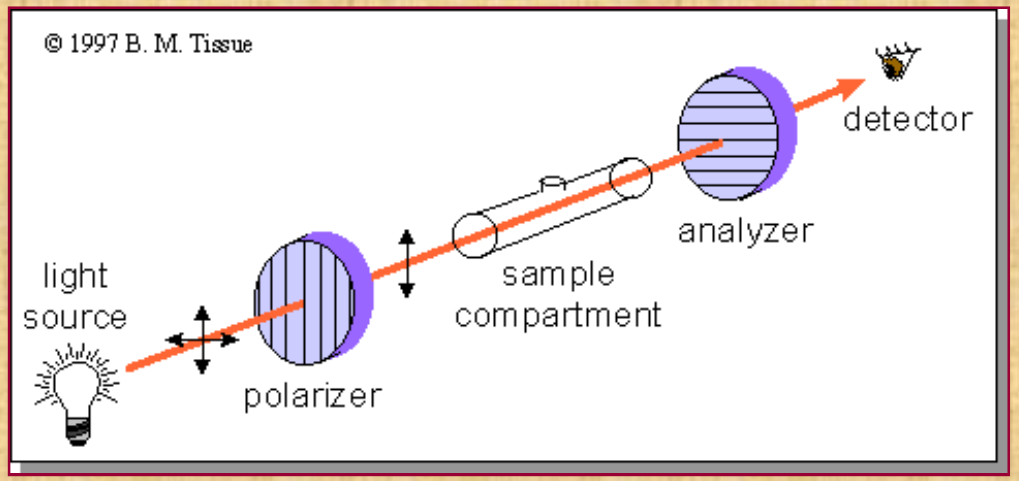
Polarimetery

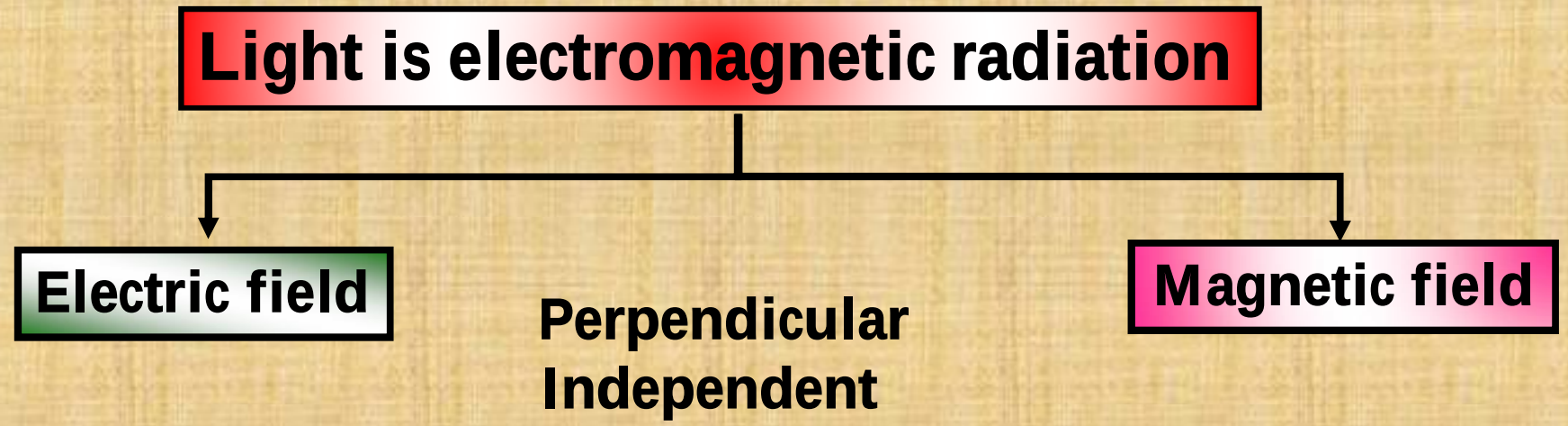
- **Definition**
- **Plane polarized light**
- **Chirality**
- **Optical activity**
- **Enantiomers**
- **Specific rotation**
- **Examples**
- **Polarimeter**



Polarimetery

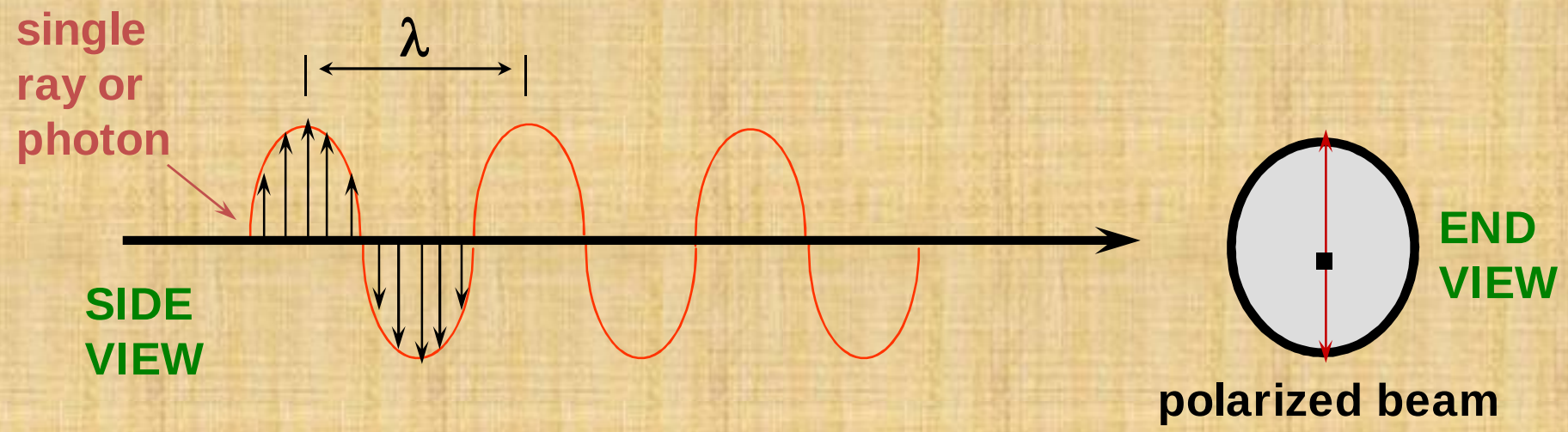
A sensitive, nondestructive technique for measuring the optical activity exhibited by inorganic and organic compounds

LIGHT BEAM


Light is electromagnetic radiation
Electric field
Magnetic field
Perpendicular
Independent

PLANE-POLARIZED LIGHT BEAM

Is light that has an electric vector that oscillates in a single plane. Plane-polarized light arises from passing ordinary light through a polarizer.

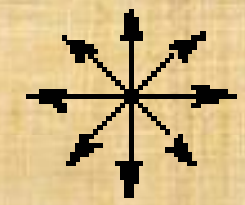


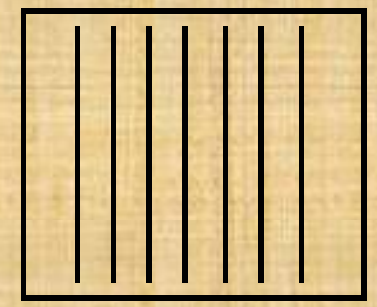
Electric field of a single photon

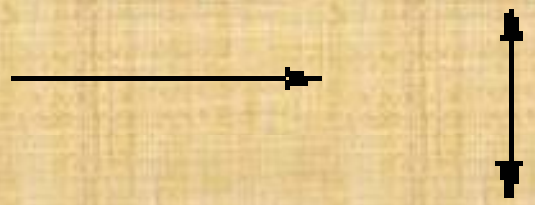
PLANE-POLARIZED LIGHT BEAM

A beam of unpolarized light

Prism
Or lens
(plane polarizer)







ordinary light, oriented in many different directions

filter

plane-polarized light parallel to filter

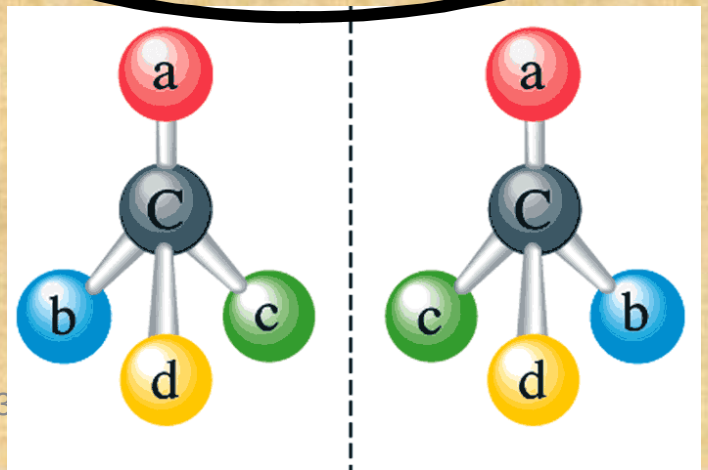
Causes light to vibrate within particular planes.

Objects

Chiral

no plane of symmetry

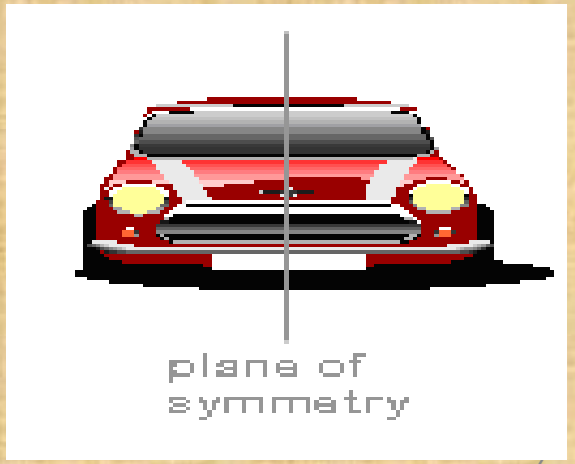
not superimposable on its mirror image.



Achiral

plane of symmetry

superimposable on (identical to) its mirror image



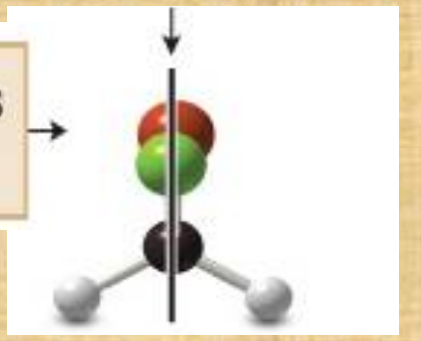
Plane of Symmetry

- **A plane of symmetry is a mirror plane that cuts the molecule in half, so that one half of the molecule is a reflection of the other half.**

CH_2BrCl

plane of symmetry

Aligning the C–Cl and C–Br bonds in each molecule.

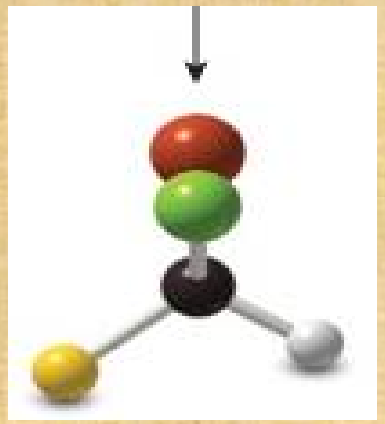


This molecule has **two identical halves.**

CH_2BrCl is **achiral.**

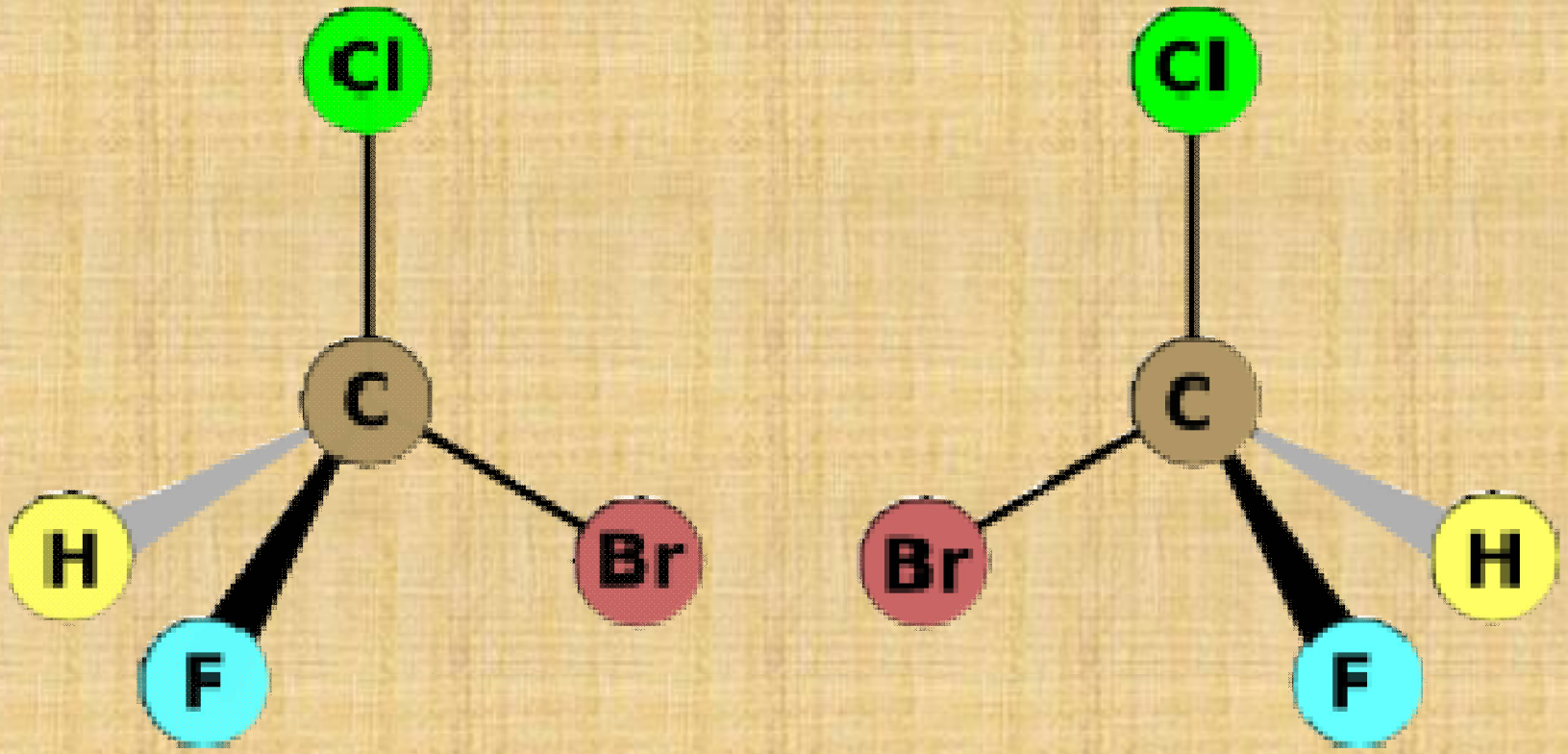
CHBrClF

NO plane of symmetry



CHBrClF is **chiral.**

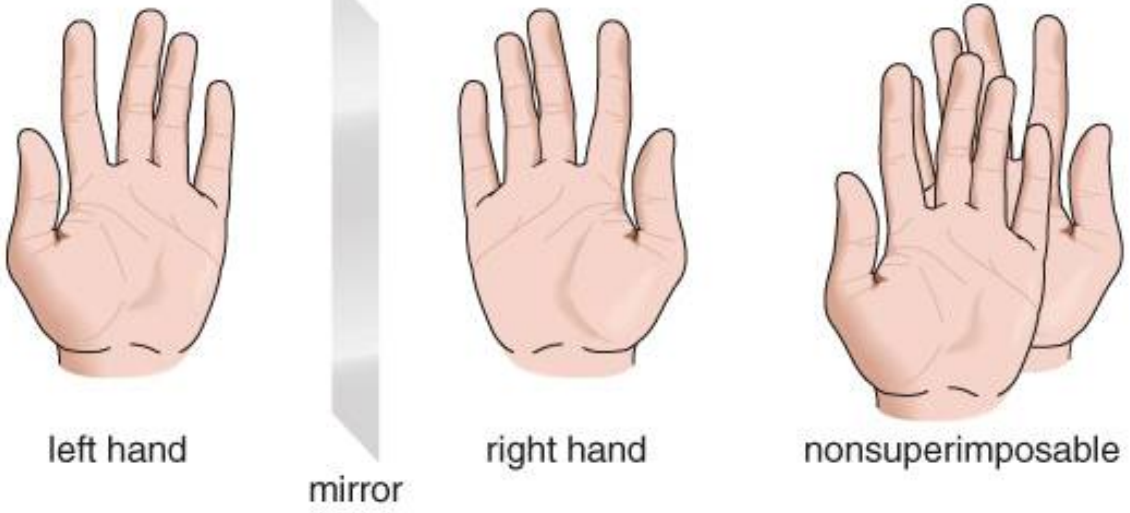
Example of Chiral molecules



Chirality or Handedness

Stereoisomerism optical isomers3.swf

- **Although everything has a mirror image, mirror images may or may not be superimposable.**
- **Some molecules are like hands. Left and right hands are mirror images, but they are not identical, or non superimposable.**



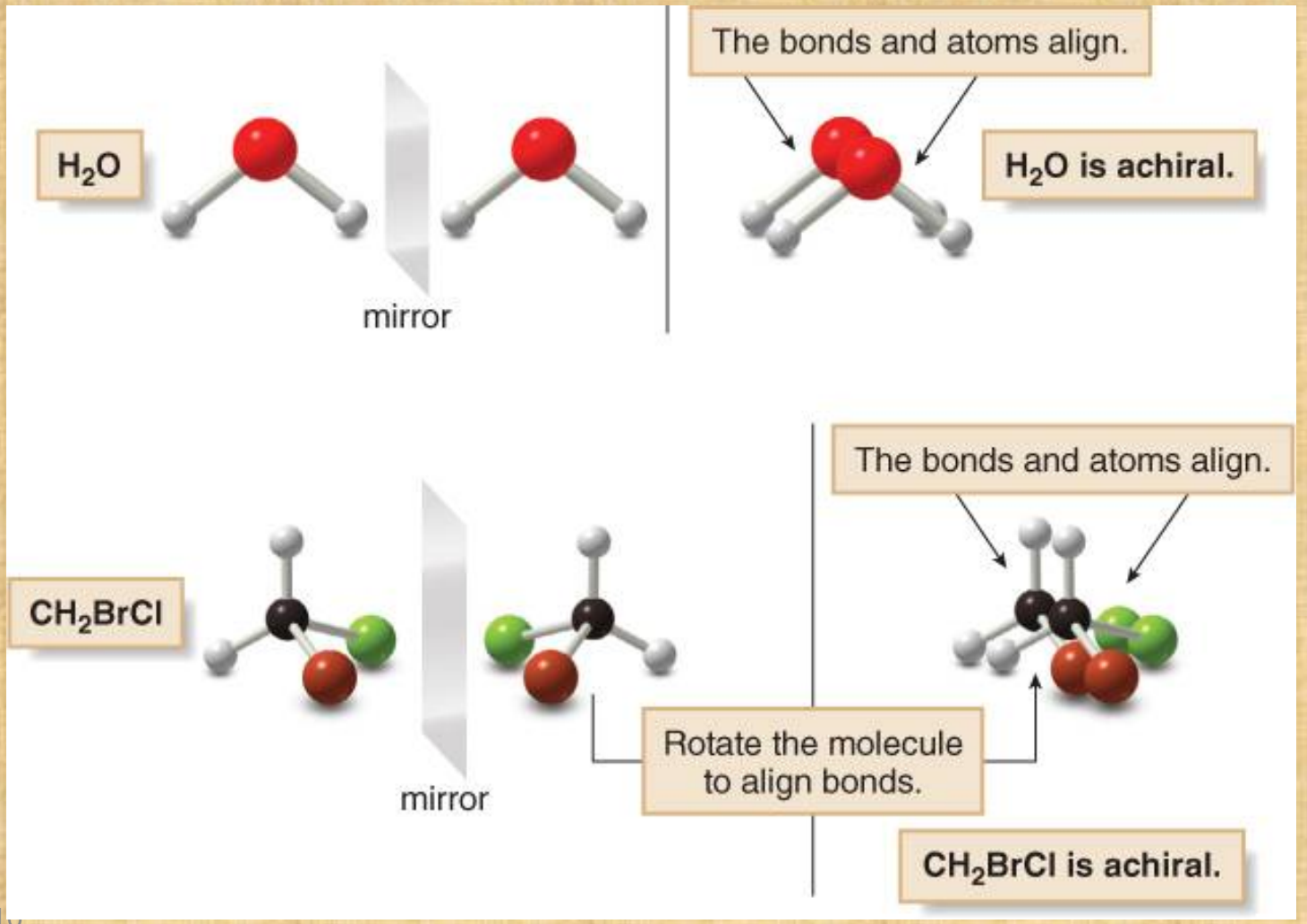
- A molecule (or object) that is *not* superimposable on its mirror image is said to be *chiral*.

Achiral Objects and Molecules

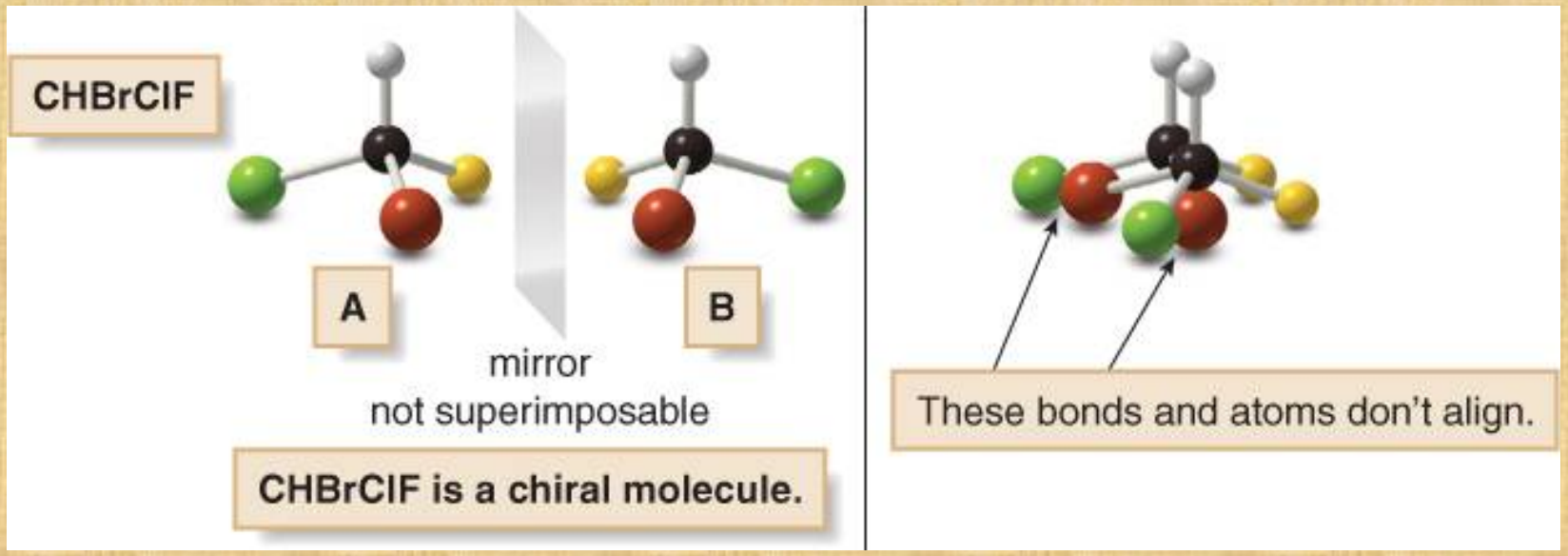
- **Other molecules are mirror images that are superimposable**
- **Two socks from a pair are mirror images that are superimposable.**
- **A molecule or object that is superimposable on its mirror image is said to be achiral.**

Achiral Molecules

- **Do these molecules contain a Plane of Symmetry (Mirror Plane)?**

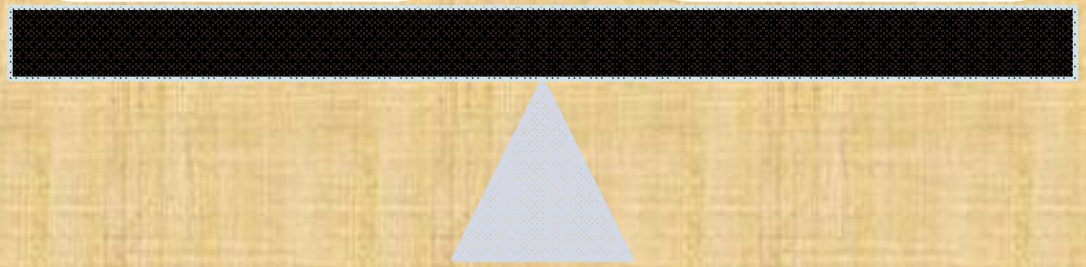


Chiral Molecules



- **A and B are stereoisomers—specifically, they are enantiomers.**
- **A carbon atom with four different groups is a tetrahedral stereogenic center.**

Achiral	v.s	Chiral
A molecule with no stereogenic centers		do not contain a plane of symmetry
contain a plane of symmetry		With one stereogenic center



Properties of Chiral molecules

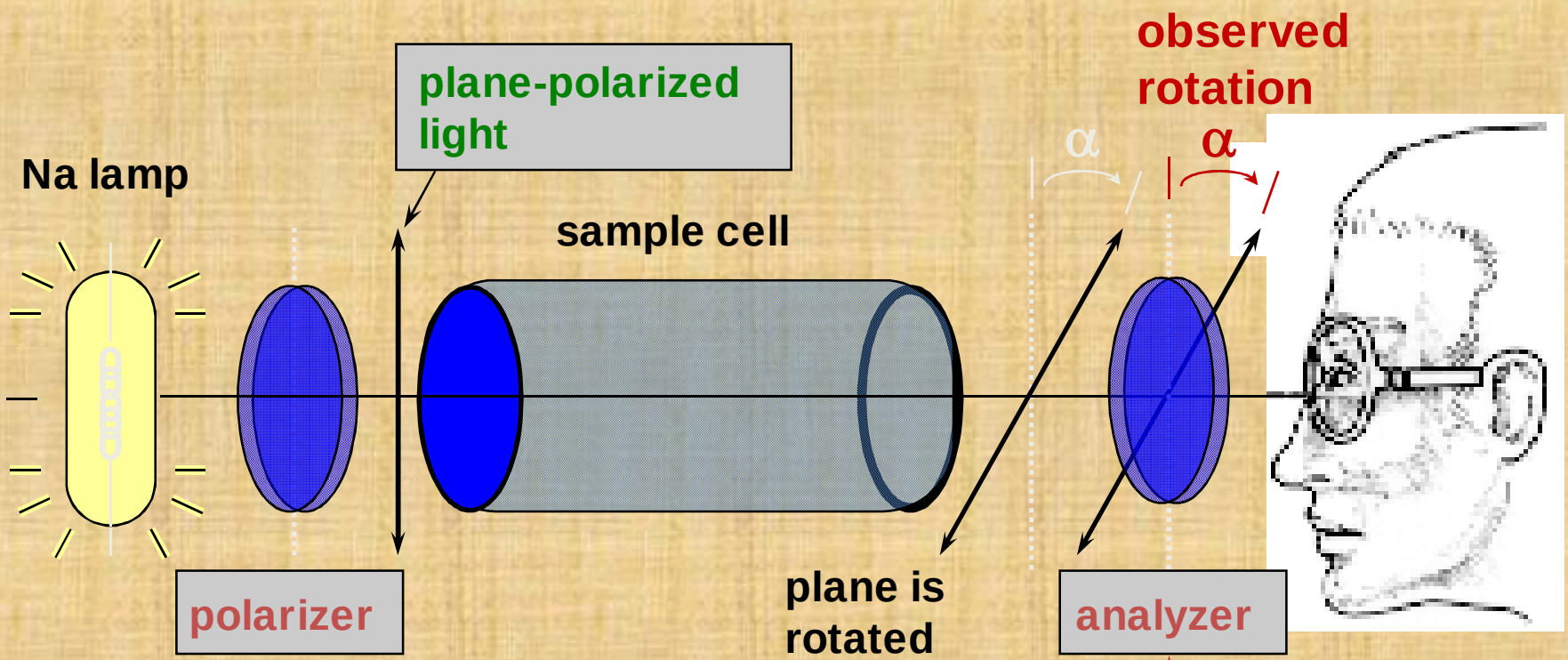
- Exist in the form of stereoisomers (mirror images), enantiomers
- Tetrahedral atoms with 4 different substituents are stereogenic atoms
- Lack a plane of symmetry
- Nonsuperimposable
- Single stereo-center molecules are always chiral.

Physical Properties of Stereoisomers

- **Enantiomers have identical physical properties, except for how they interact with plane-polarized light.**

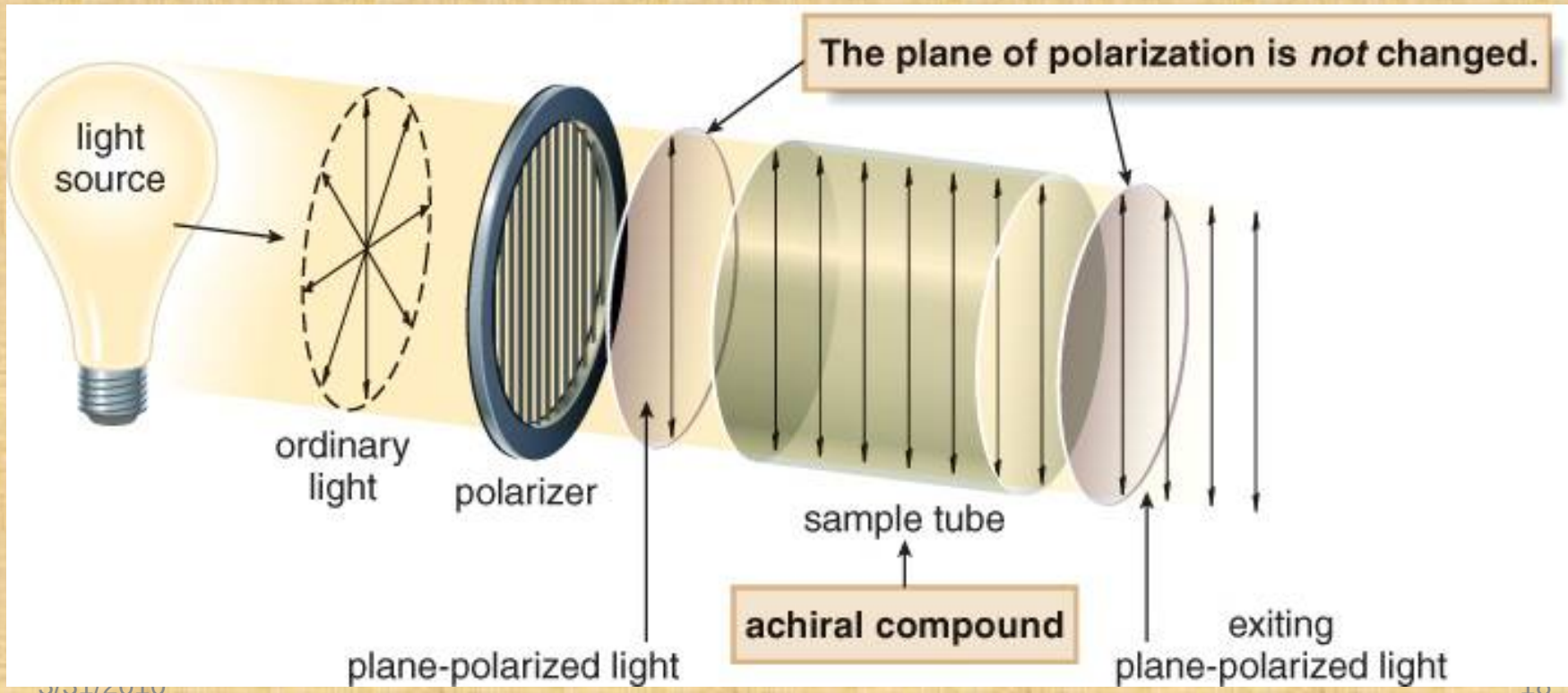
POLARIMETER

The instrument used to determine whether a substance is optically active and to measure the direction and degree of optical rotation.



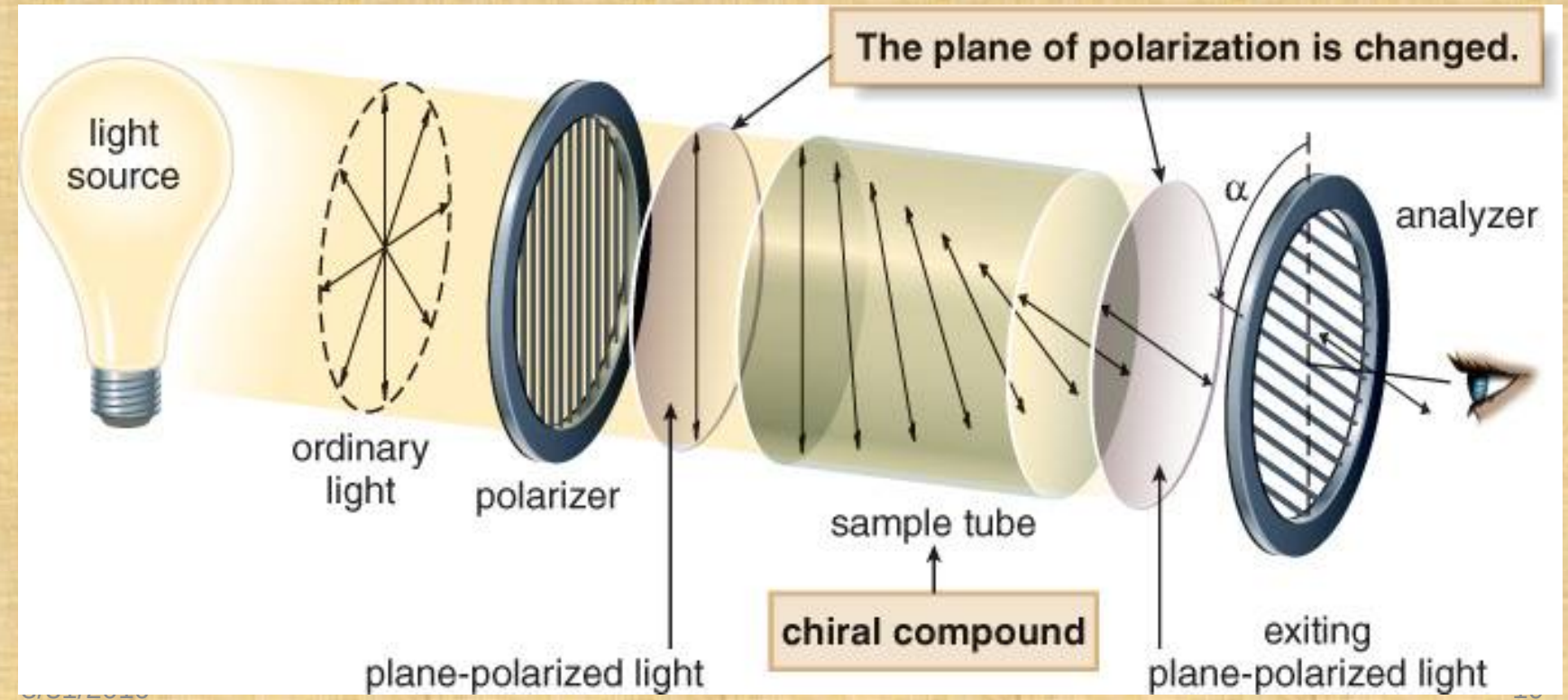
Polarimeter

- **With achiral compounds, the light that exits the sample tube remains unchanged.**
- **A compound that does not change the plane of polarized light is said to be optically inactive.**

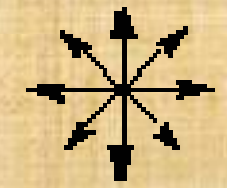


Optically Active Compounds

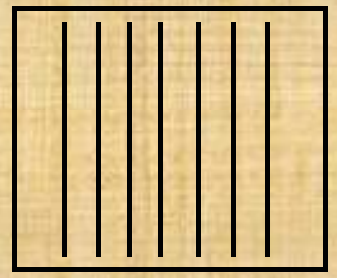
- **With chiral compounds, the plane of the polarized light is rotated through an angle α. The angle α is measured in degrees (^{0}), and is called the observed rotation.**
- **A compound that rotates polarized light is said to be optically active.**



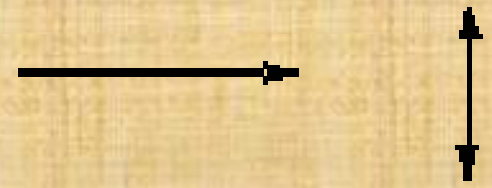
Optical activity



ordinary light, oriented in many different directions

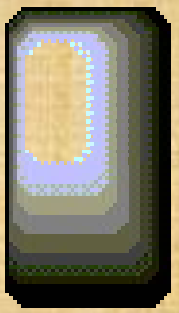


filter



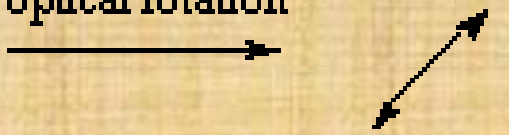
plane-polarized light parallel to filter

plane-polarized light



optically active sample

optical rotation

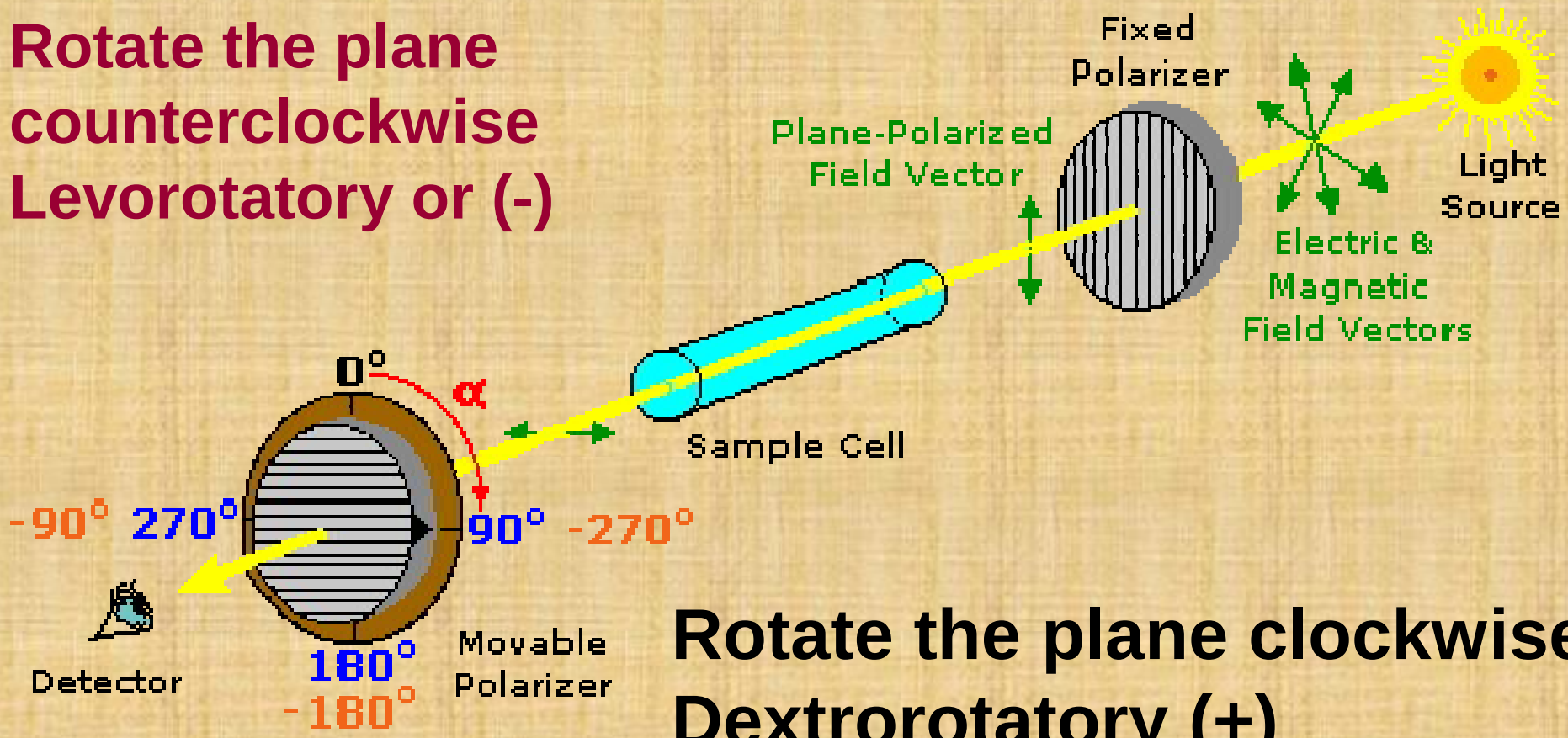


rotated plane-polarized light

Optical activity

Rotating plane-polarising light.swf

Rotate the plane counterclockwise Levorotatory or (-)



Rotate the plane clockwise Dextrorotatory (+)

Optically active

TYPES OF OPTICAL ACTIVITY

Dextrorotatory

Rotates the plane of plane-polarized light to the right.

Levorotatory

Rotates the plane of plane-polarized light to the left.

Rotation of Polarized Light

- **Two enantiomers rotate plane-polarized light to an equal extent but in opposite directions. Thus, if enantiomer A rotates polarized light $+5^0$, the same concentration of enantiomer B rotates it -5^0.**

Racemates

- **An equal amount of two enantiomers is called a racemate or a racemic mixture.**
- **A racemic mixture is optically inactive. Because two enantiomers rotate plane-polarized light to an equal extent but in opposite directions, the rotations cancel, and no rotation is observed.**

TABLE 5.1 The Physical Properties of Enantiomers A and B Compared

Property	A alone	B alone	Racemic A + B
Melting point	identical to **B**	identical to **A**	may be different from **A** and **B**
Boiling point	identical to **B**	identical to **A**	may be different from **A** and **B**
Optical rotation	equal in magnitude but opposite in sign to **B**	equal in magnitude but opposite in sign to **A**	0°

Factors affecting optical rotation

Structure of the substance

Concentration

Path length

Temperature

Specific Rotation

is a standardized physical constant for the amount that a chiral compound rotates plane-polarized light.

$$\text{specific rotation} = [\alpha] = \frac{\alpha}{l \times c}$$

α = observed rotation (°)
l = length of sample tube (dm)
c = concentration (g/mL)

[dm = decimeter
1 dm = 10 cm]

Optical activity7.swf

Specific rotation α

$$[\alpha]_D^t = \frac{\alpha}{cl}$$

α = observed rotation

c = concentration (g/mL)

l = length of cell (dm)

D = yellow light from sodium lamp (589 nm)

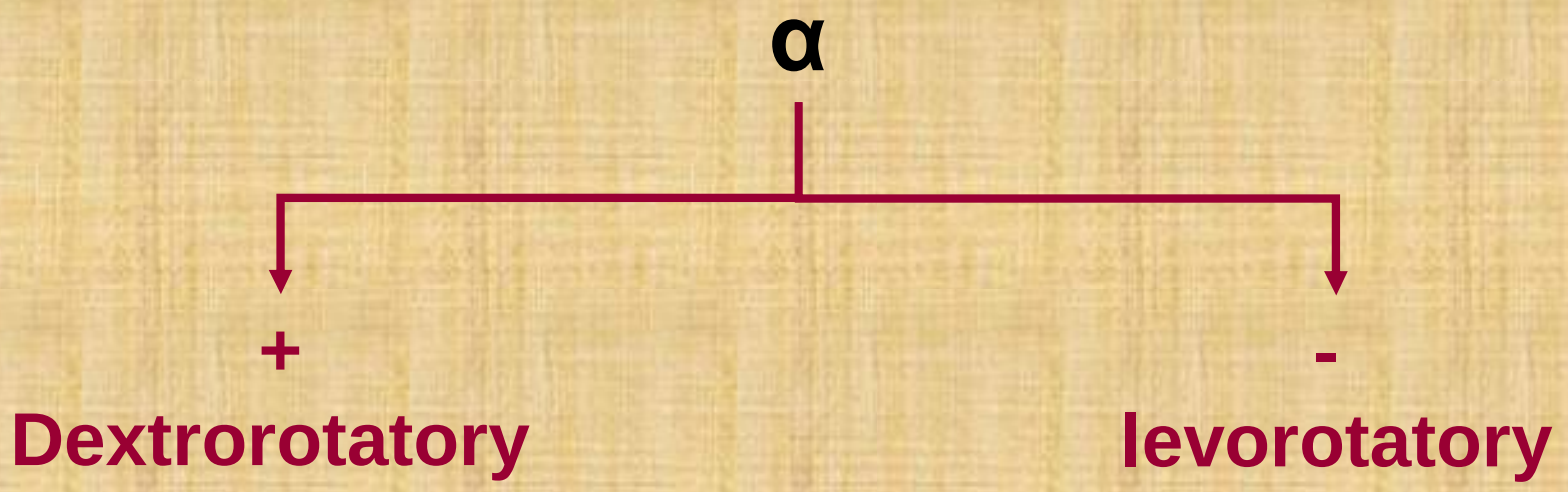
t = temperature (25 ^{0}C)

α → Specific rotation

α → Optical purity = % one enan. - % other enan.

Specific rotation α

Rotation per decimeter of a solution containing 1g/cm^3 at a temperature of 25ºC for the yellow D line of sodium.



Optical Purity

- **Enantiomeric excess (optical purity) is a measurement of how much one enantiomer is present in excess of the racemic mixture. It is denoted by the symbol *ee*.**

  ***ee* = % of one enantiomer - % of the other enantiomer.**

- **Calculating ee - If a mixture contains 75% of one enantiomer and 25% of the other, the enantiomeric excess is 75% - 25% = 50% ee.**
- **50% ee means that there is a 50% excess of one enantiomer over the racemic mixture.**
- **The enantiomeric excess can also be calculated if the specific rotation [α] of a mixture and the specific rotation [α] of a pure enantiomer are known.**

***ee* = ([α] mixture/[α] pure enantiomer) x 100.**

SPECIFIC ROTATIONS OF BIOACTIVE COMPOUNDS

COMPOUND	$[\alpha]_D$
cholesterol	-31.5
cocaine	-16
morphine	-132
codeine	-136
heroin	-107
epinephrine	-5.0
progesterone	+172
testosterone	+109
sucrose	+66.5
β-D-glucose	+18.7
α-D-glucose	+112
oxacillin	+201

Sample problem

- A pure enantiomer has an observed optical rotation of -0.82^{o} when measured in a one dm tube at a concentration of 0.3 g/10 mL. Calculate the specific rotation for this molecule.

- For this sample, the **apparent** specific rotation is:
- $[\alpha] = (-0.82^{o}) / (0.03\ g/mL \times 1.0\ dm)$
- $[\alpha] = -27.3^{o}\ g^{-1}\ mL\ dm^{-1}$

Sample problem 9.2

- The specific rotation for a pure enantiomer is known to be $-39^{o}\ g^{-1}\ mL^{-1}\ dm^{-1}$. A sample containing both enantiomers is found to have an observed rotation of -0.62^{o} in a one dm tube at a concentration of 3.5 g/100 mL. What is the optical purity of the sample?

Solution 1

$[\propto] = (-0.62^{o})/(0.035\ g/mL \times 1.0\ dm)$

$[\propto] = -17.7^{o}\ g^{-1}\ mL\ dm^{-1}$

$x(-39^{o}) + (1-x)(+39^{o}) = -17.7^{o}$

$(-39x) + 39 - 39x = -17.7$

$-78x = -56.7$

$x = 0.726$

The mixture contains 72.7% of the (-) enantiomer and 27.3 % of the (+)enantiomer.

Optical purity = ee = 72.7-27.31 = 45%

Solution 2

ee **= ([α] mixture/[α] pure enantiomer) x 100.**

$[\propto] = (-0.62^{o})/(0.035\ g/mL \times 1.0\ dm)$

$[\propto] = -17.7^{o}\ g^{-1}\ mL\ dm^{-1}$

[α] pure enantiomer= -39°

ee **= (-17.7 °/-39°) x 100**

ee **= 45%**