7.4

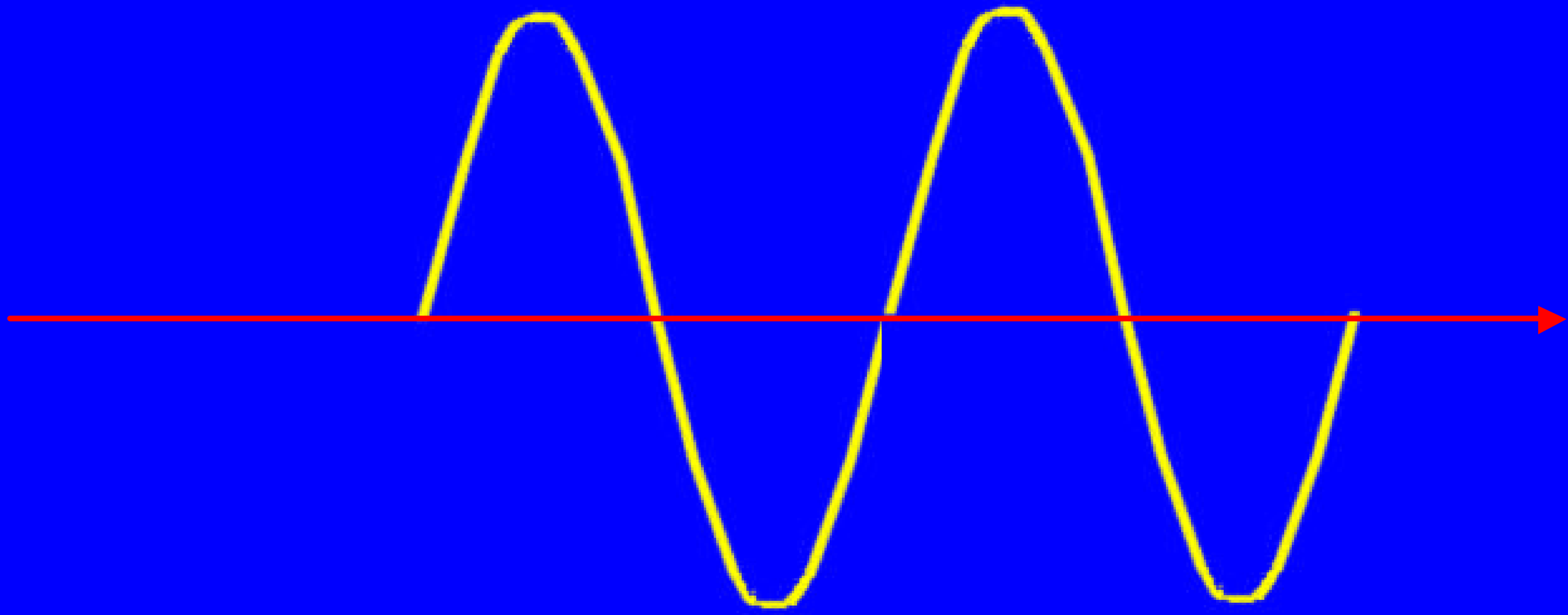
Properties of Chiral Molecules: Optical Activity

Optical Activity

A substance is optically active if it rotates the plane of polarized light.

In order for a substance to exhibit optical activity, it must be chiral and one enantiomer must be present in excess of the other.

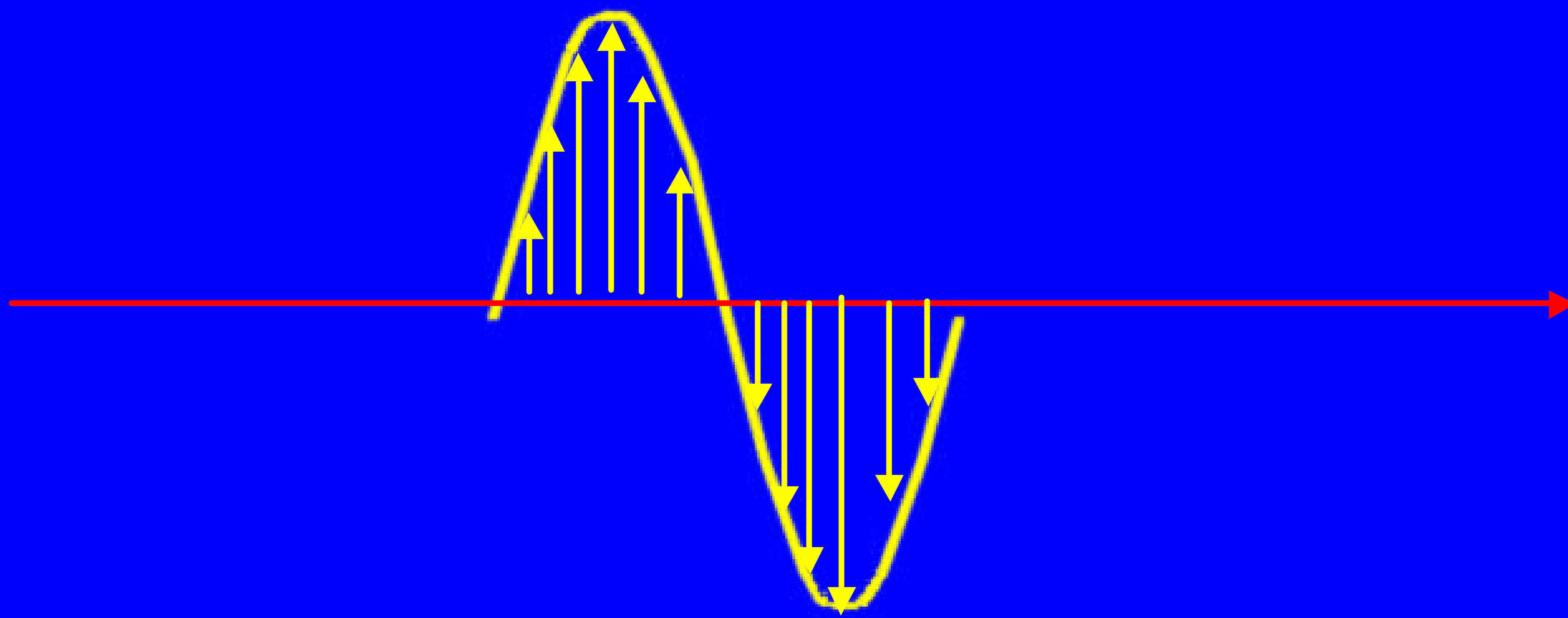
Light



has wave properties

periodic increase and decrease in amplitude of wave

Light

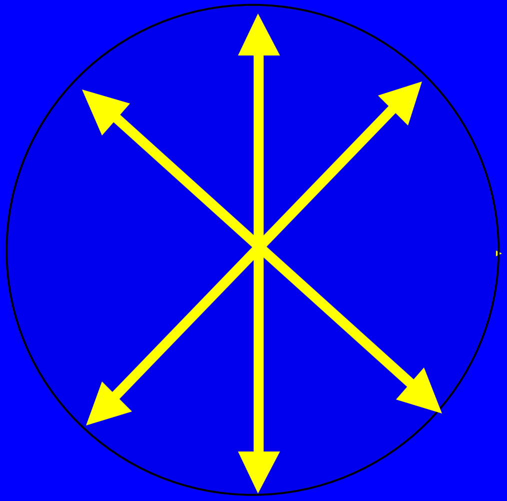


optical activity is usually measured using light having a wavelength of 589 nm

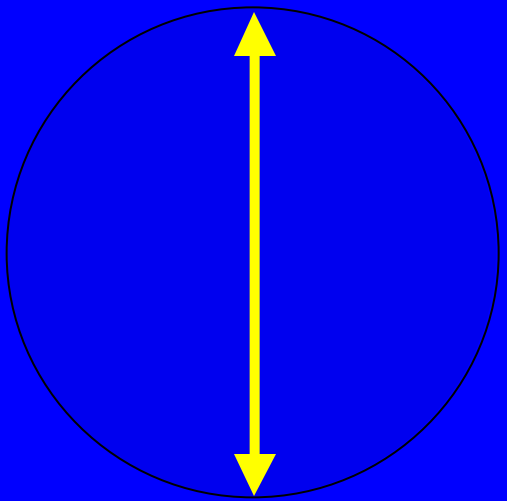
this is the wavelength of the yellow light from a sodium lamp and is called the D line of sodium

Polarized light

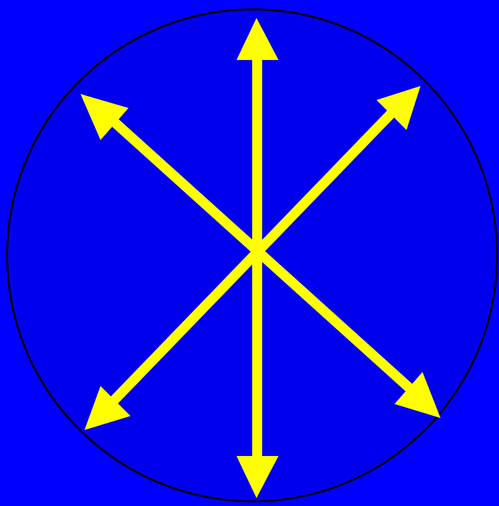
ordinary (nonpolarized) light consists of many beams vibrating in different planes



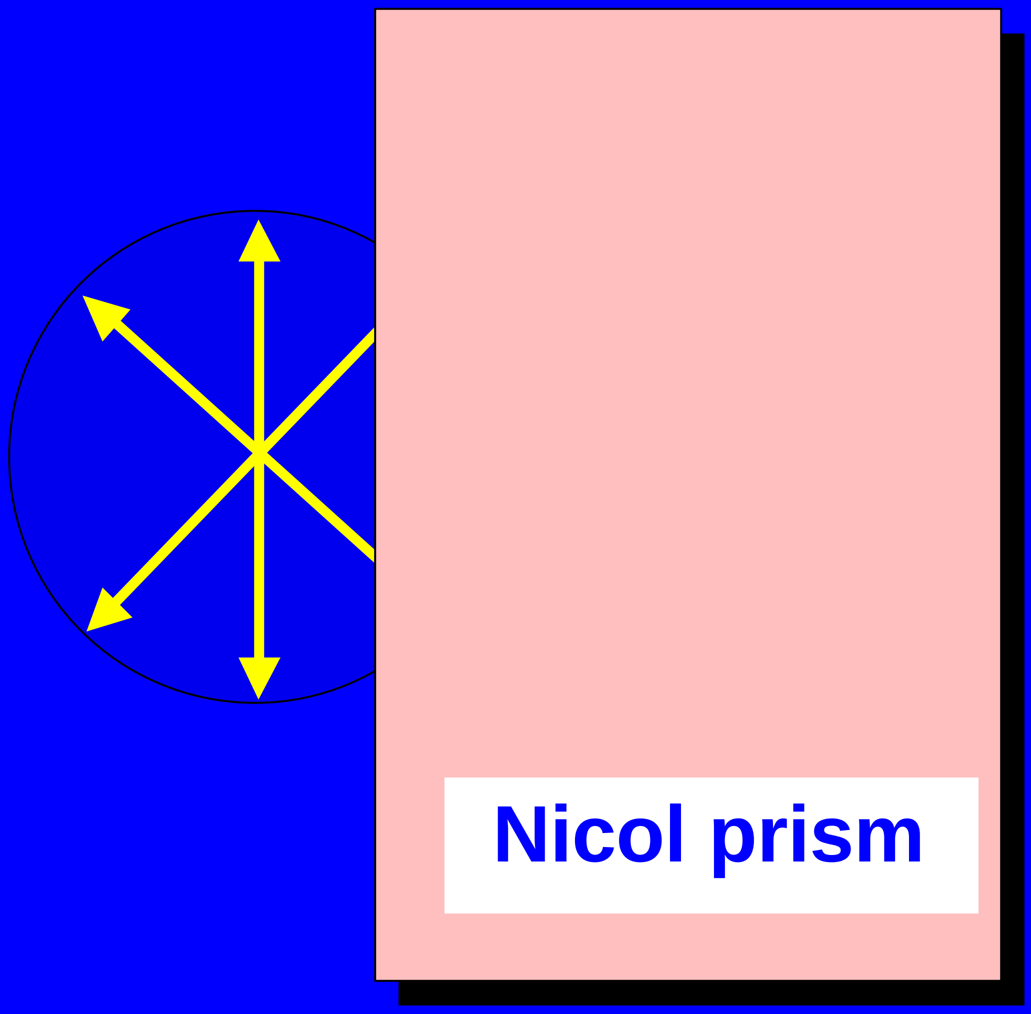
plane-polarized light consists of only those beams that vibrate in the same plane



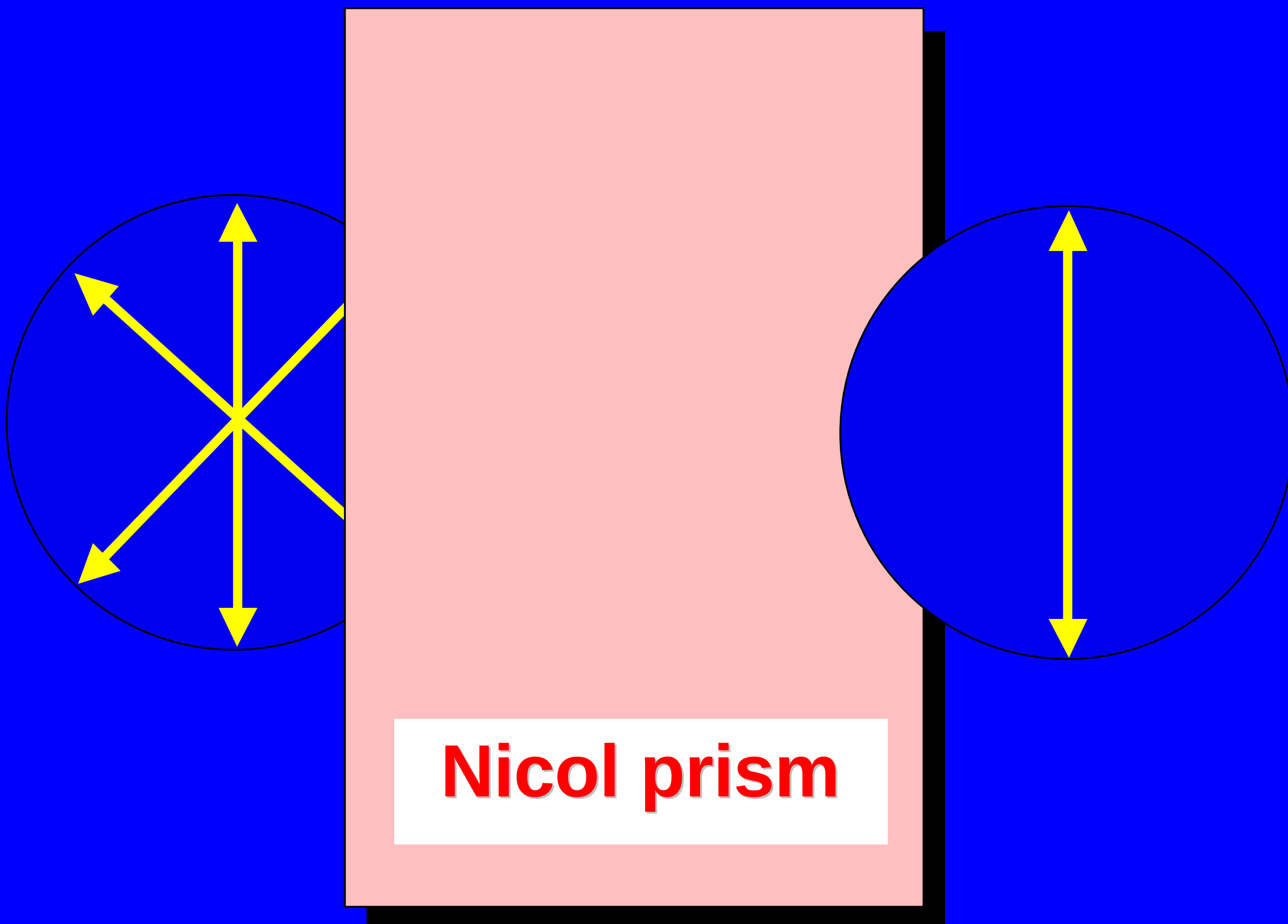
Polarization of light



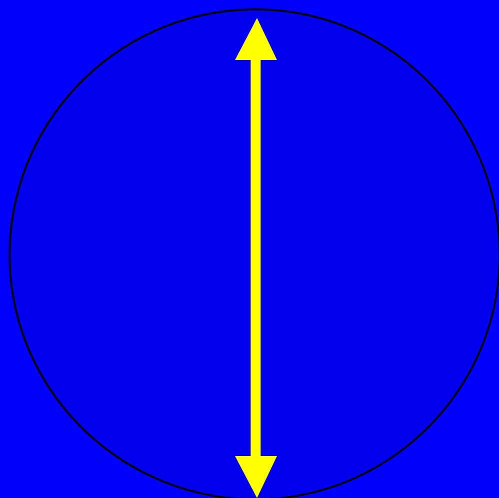
Polarization of light



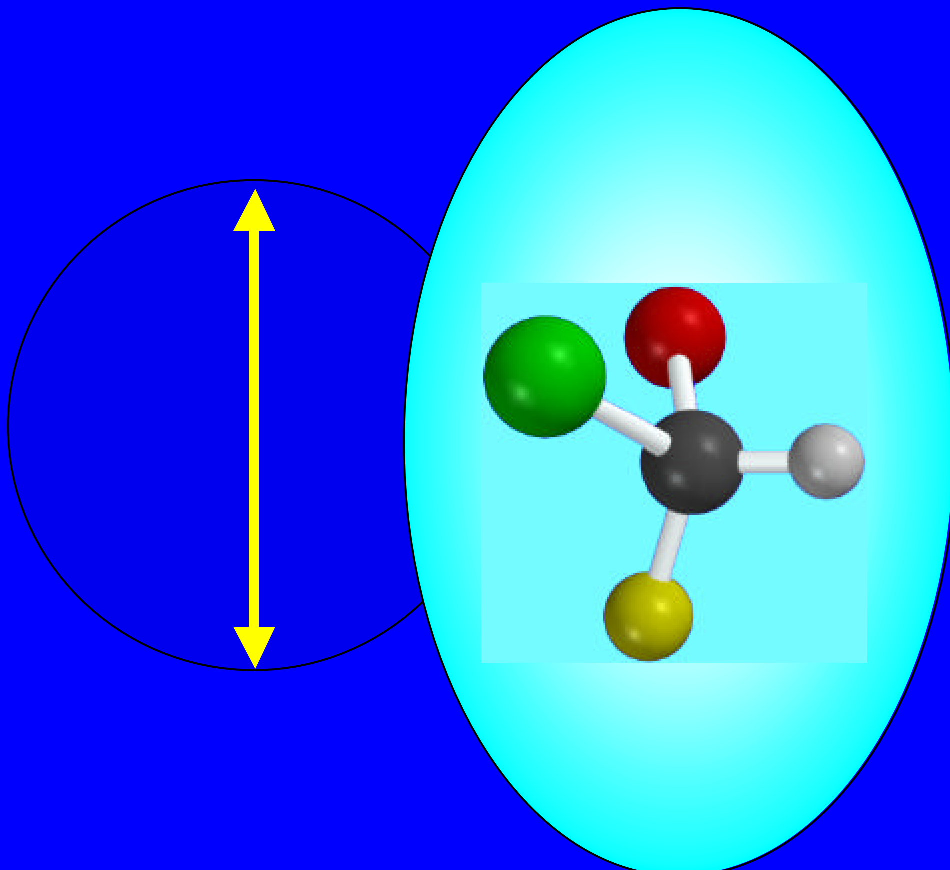
Polarization of light



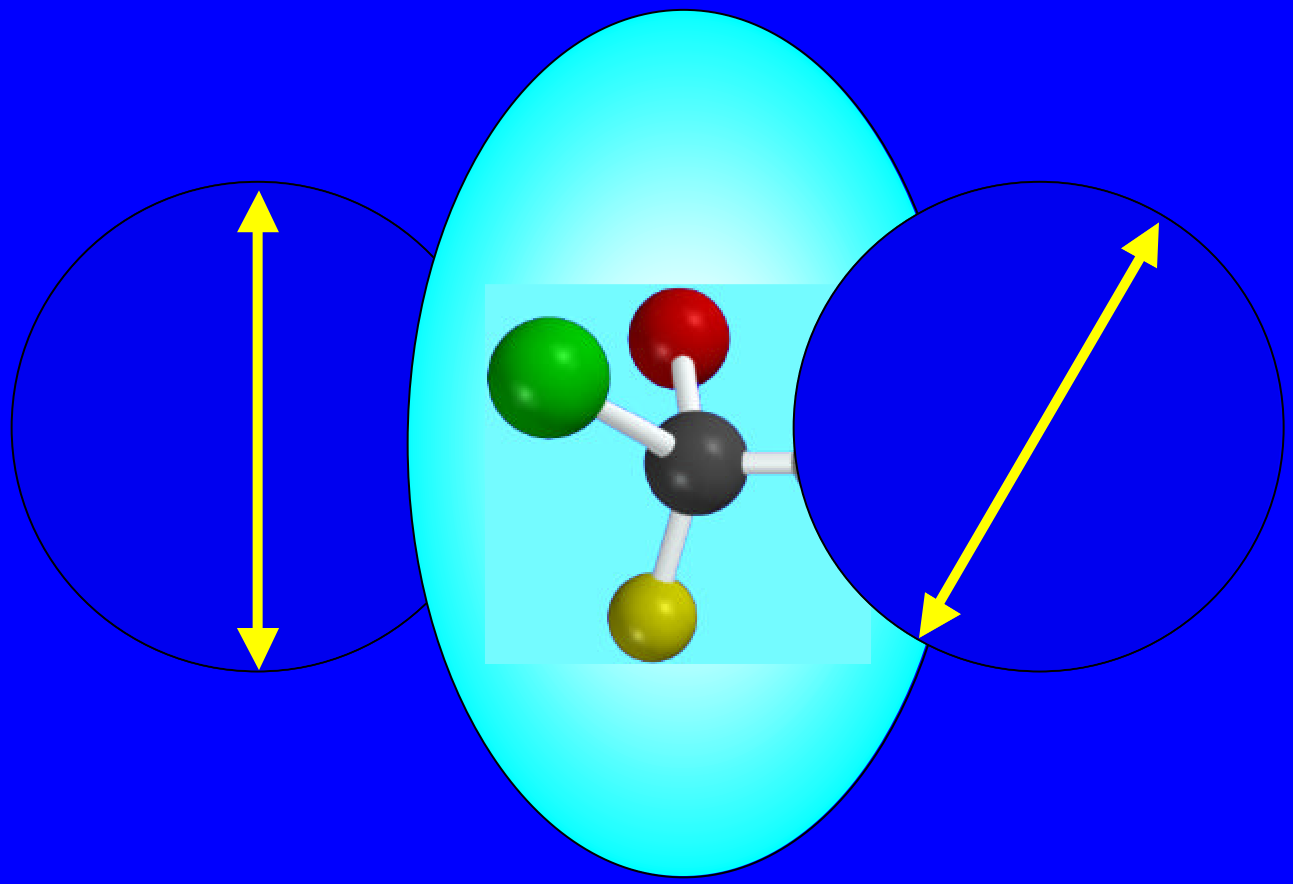
Rotation of plane-polarized light



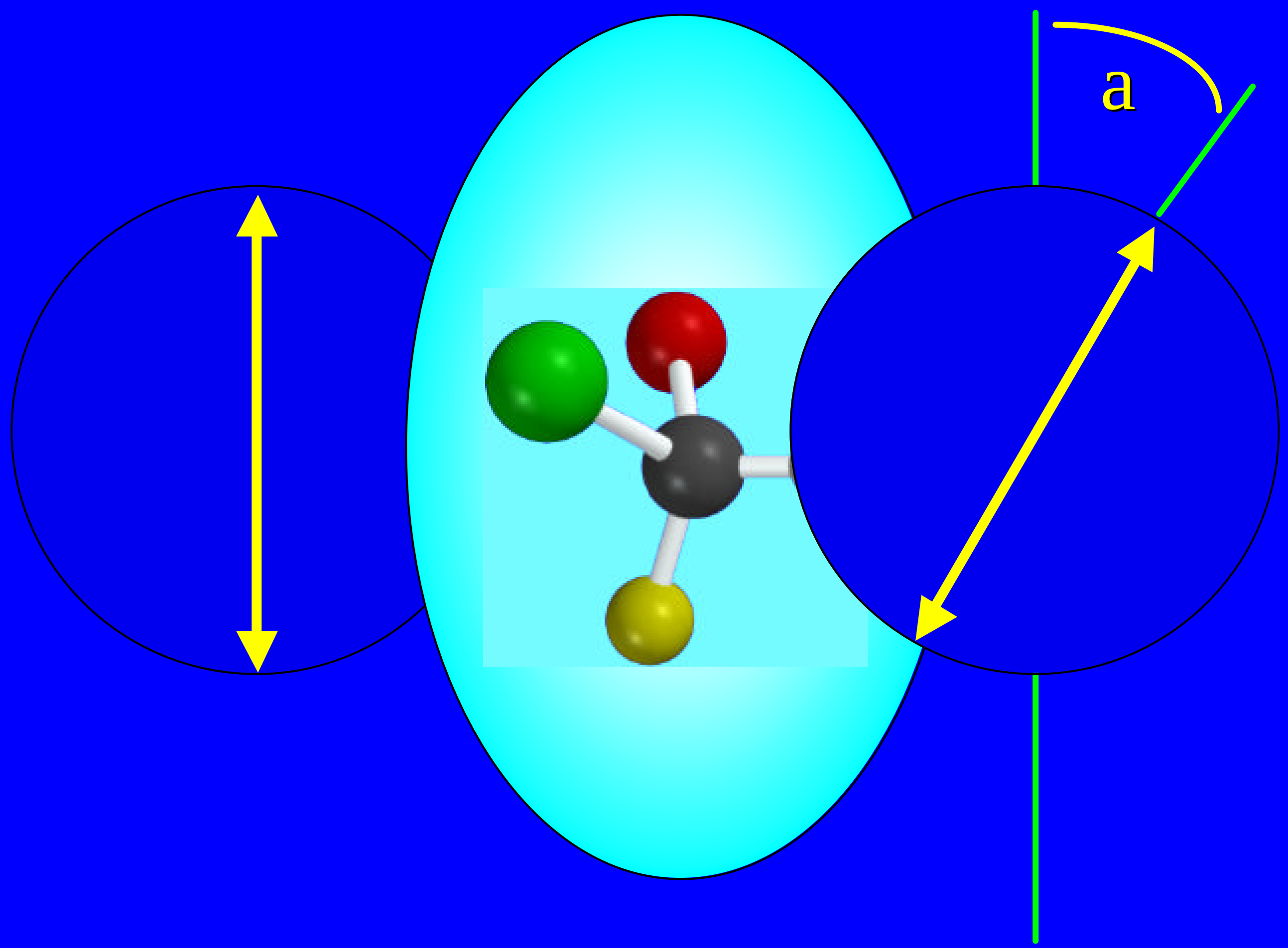
Rotation of plane-polarized light



Rotation of plane-polarized light



Rotation of plane-polarized light



Specific rotation

observed rotation (α) depends on the number of molecules encountered and is proportional to:

path length (l), and
concentration (c)

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concentration (c)

therefore, define specific rotation [α] as:

$$[\alpha] = \frac{100\,\alpha}{c\,l}$$

concentration = g/100 mL
length in decimeters

Racemic mixture

a mixture containing equal quantities of enantiomers is called a *racemic mixture*

a racemic mixture is <u>optically inactive</u> ($\alpha = 0$)

a sample that is optically inactive can be either an achiral substance or a racemic mixture

Optical purity

an optically pure substance consists exclusively of a single enantiomer

enantiomeric excess =

% one enantiomer – % other enantiomer

% optical purity = enantiomeric excess

7.5
Absolute
and
Relative Configuration

Configuration

Relative configuration compares the arrangement of atoms in space of one compound with those of another.

Absolute configuration is the precise arrangement of atoms in space.

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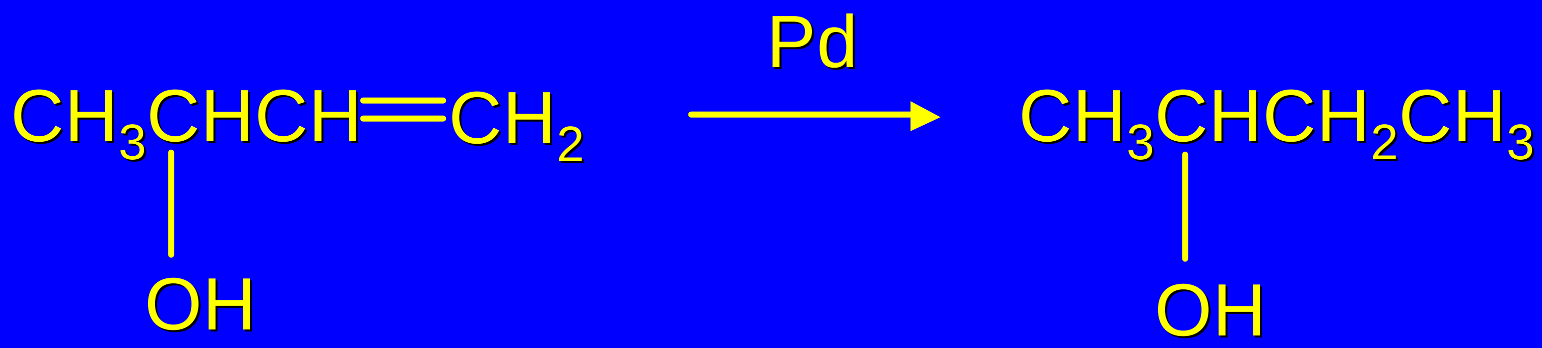
Relative configuration compares the arrangement of atoms in space of one compound with those of another.

until the 1950s, all configurations were relative

Absolute configuration is the precise arrangement of atoms in space.

we can now determine the absolute configuration of almost any compound

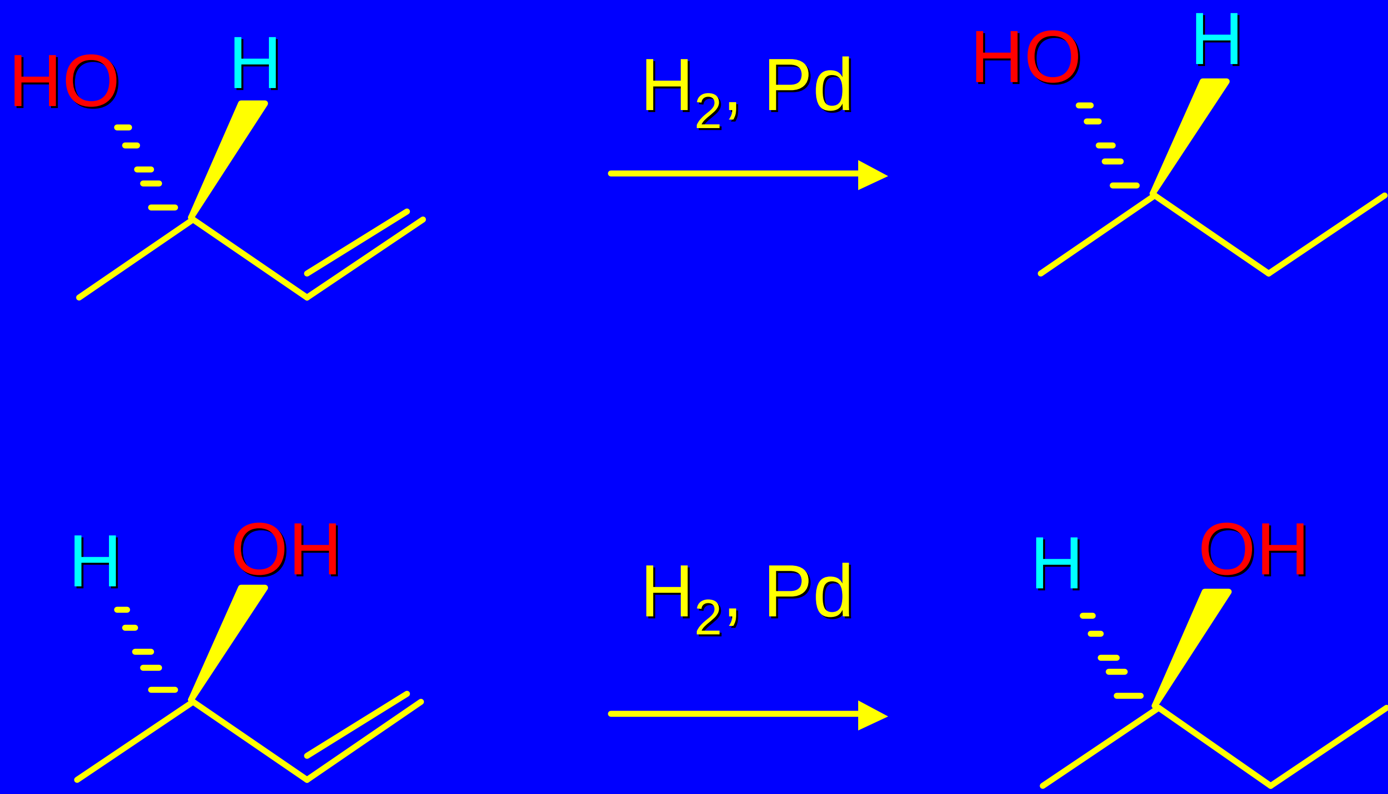
Relative configuration



[α] + 33.2° [α] + 13.5°

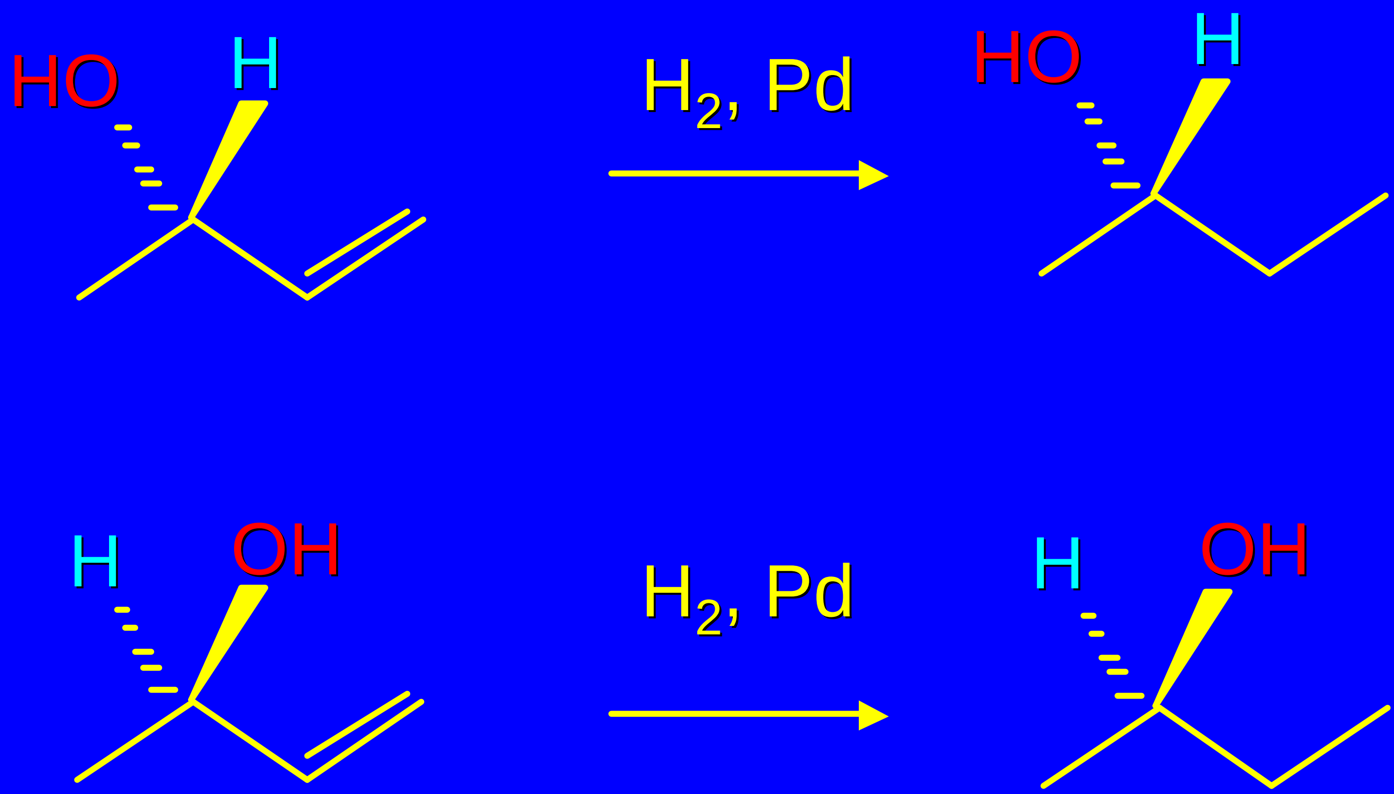
No bonds are made or broken at the stereogenic center in this experiment. Therefore, when (+)-3-buten-2-ol and (+)-2-butanol have the same sign of rotation, the arrangement of atoms in space is analogous. The two have the same relative configuration.

Two possibilities



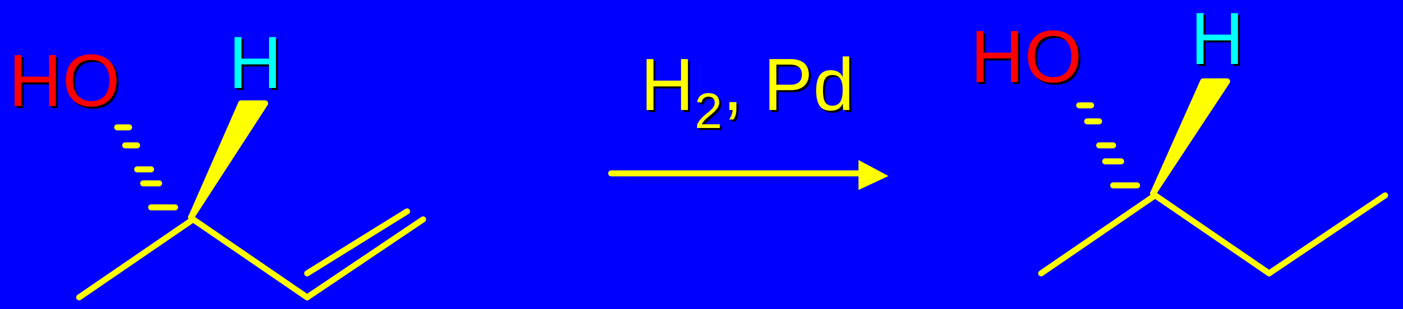
But in the absence of additional information, we can't tell which structure corresponds to (+)-3-buten-2-ol, and which one to (–)-3-buten-2-ol.

Two possibilities

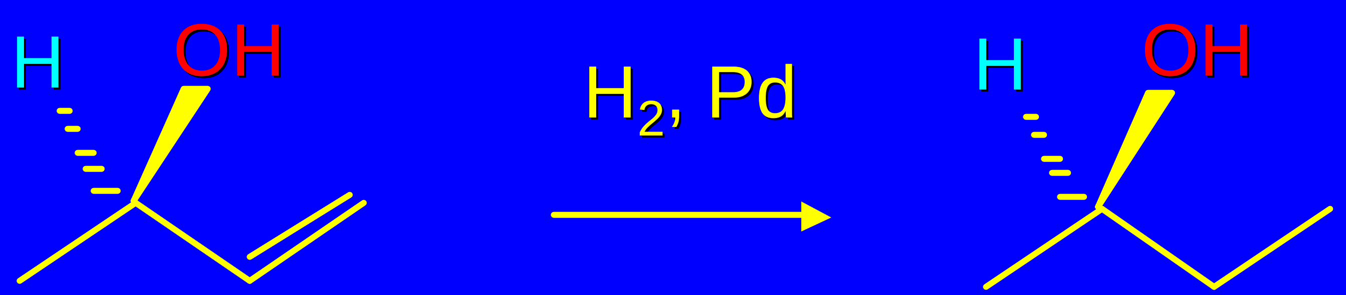


Nor can we tell which structure corresponds to (+)-2-butanol, and which one to (–)-2-butanol.

Absolute configurations

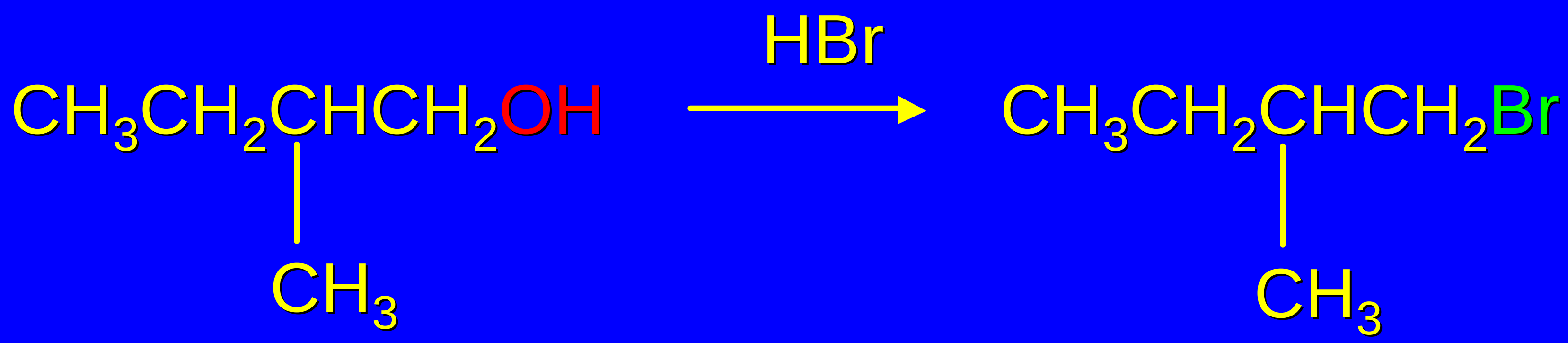


[α] +13.5° [α] +33.2°



[α] –13.5° [α] –33.2°

Relative configuration



[α] -5.8° [α] + 4.0°

Not all compounds that have the same relative configuration have the same sign of rotation. No bonds are made or broken at the stereogenic center in the reaction shown, so the relative positions of the atoms are the same. Yet the sign of rotation changes.