Organic chemistry

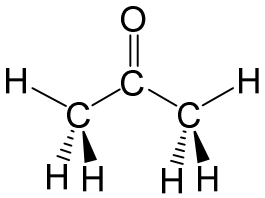
Chemistry of carbon:

All organic molecules contain C atoms.

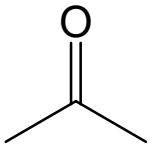
C is the only element able to:

- bind other C atoms forming chains and cycles
- bind H and many other heteroatoms (N, O, S, P, halogens, etc.)
- Form single, double or triple bonds.

Representation of organic molecules



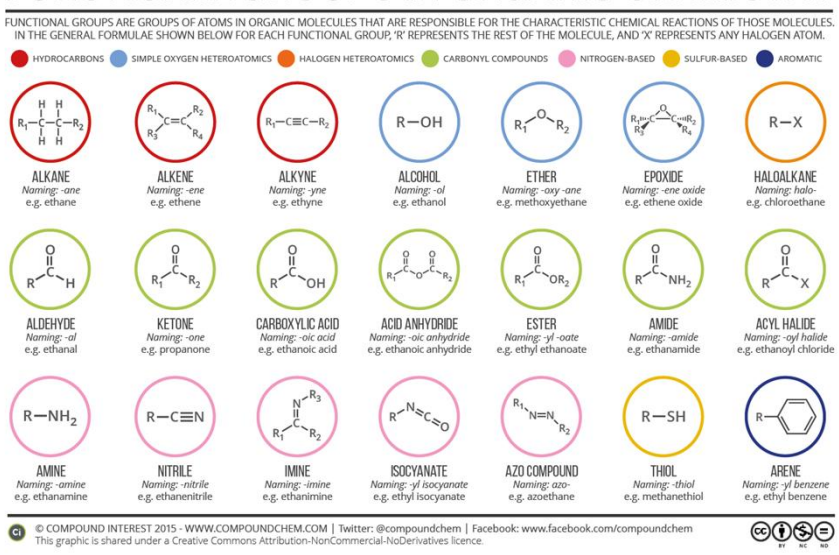
Structural formula



Bond-line formula

ball-and-stick

space-filling



Functional groups determine the chemical reactivity of the organic molecules.

Classification of organic molecules

Aromatic compounds

All the compounds that are follow the **Hückel's rule**

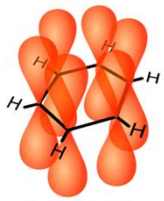
Aliphatic compounds

All the compounds that are not aromatic

Hückel's rule

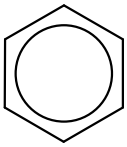
- Planar structure with sp^2 hybridization
- Extended π system, delocalized on the on the whole molecule and containing a number of electrons equal to 2n+1, where n in an integer ≥ 0

Sigma Bonds
sp^2 Hybridized orbitals



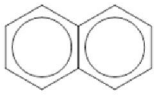
6 p_z orbitals

Benzene
n = 1

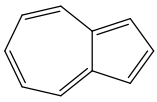


Classification of organic molecules

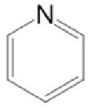
Aromatic compounds



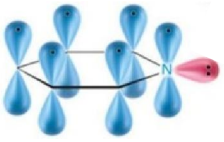
Naftalene
n = 2

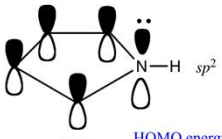


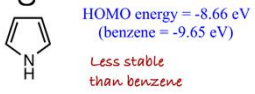
Azulene
n = 2



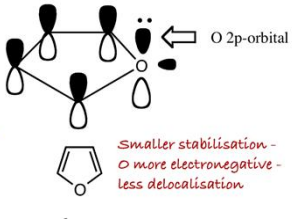
Pyridine
n = 2



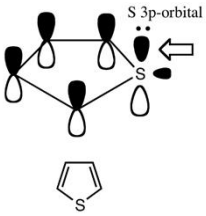




Pyrrole
n = 1



Furan
n = 1



Thiophene
n = 1

Nomenclature of organic molecules

IUPAC

Location – Prefix – Location – Parent – Suffix

↓

Name of the hydrocarbon with the same number of carbon atoms

N° C atoms	Alkane	Parent	Alkyl group
1	Methane	Meth-	Methyl
2	Ethane	Eth-	Ethyl
3	Propane	Prop-	Propyl
4	Butane	But-	Butyl
5	Pentane	Pent-	Pentyl
6	Hexane	Hex-	Hexyl

Nomenclature of organic molecules

IUPAC

Location – Prefix – Location – Parent – Suffix

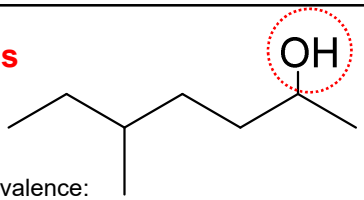
All the other functional group are included as prefixes

Derived from the functional group with the highest prevalence

The location of the functional groups in the parent chain must be reported.

Nomenclature of organic molecules

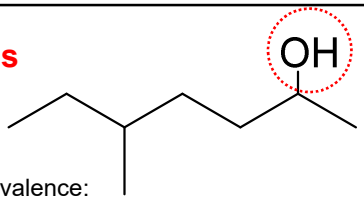
IUPAC



1. Find the functional group with the highest prevalence: bound to aliphatic or aromatic skeleton?

Prevalence	Functional group	Formula	Prefix	Suffix
1	Carboxylic acid	R-COOH	Carboxy-	-ic acid
2	Aldehyde	R-CHO	formyl-	-al
3	Ketone	R^1-CO-R^2	oxo-	-one
4	Alcohol, phenol	R-OH	hydroxy-	-ol
5	Amine	R-NH_2 R^1-NHR^2 R^1-NR^2R^3	amino- *N*-alkylamino- *N,N'*-dialkylmmino-	-amine -*N*-alkylamine -*N,N'*-dialkylamine
6	Halide	-X	fluoro- chloro- bromo- iodo-	----
7	Ether	R^1-OR^2	alkoxy-	----
8	Alkyne	C≡C	alkynyl-	-ine
9	Alkene	C=C	alkenyl-	-ene
10	Alkane	C-C	alkyl-	-ane

Nomenclature of organic molecules



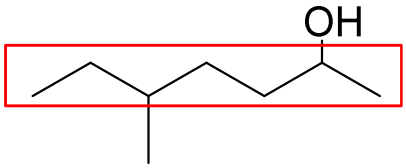
IUPAC

1. Find the functional group with the highest prevalence: bound to aliphatic or aromatic skeleton?

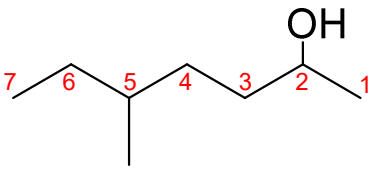
Priorità	Functional group	Formula	Prefix	Suffix
1	Acidi carbossilici	R-COOH	carbossi-	acido ...-oico
2	Aldeidi	R-CHO	formil-	-ale
3	Chetoni	R^1-CO-R^2	osso-	-one
4	Alcoli, Fenoli	R-OH	idrossi-	-olo
5	Ammine	R-NH_2 R^1-NHR^2 R^1-NR^2R^3	ammino- *N*-alchilammino- *N,N'*-dialchilammino-	-ammina -*N*-alchilammina- *N,N'*-dialchilammina
6	Alogenuri	-X	fluoro- cloro- bromo- iodo-	[mai]
7	Eteri	R^1-OR^2	alcossi-	[mai]
8	Alchini	C≡C	alchinil-	-ino
9	Alcheni	C=C	alchenil	-ene
10	Alcani	C-C	alchil-	-ano

Nomenclature of organic molecules

IUPAC – aliphatic compounds

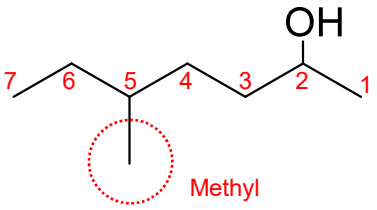


2. Find the longest C atom chain connected to the functional group with the highest prevalence
3. Enumerate the C atom chain in order to obtain the lowest numbers for location of the substituents.



Nomenclature of organic molecules

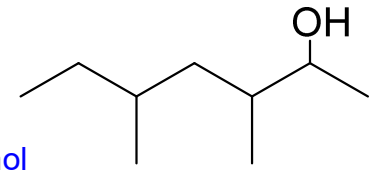
IUPAC – aliphatic compounds



4. Assign the proper name to each substituent depending on its chemical nature.
5. List the substituents in alphabetic order as prefixes.

5-methyl-2-eptanol

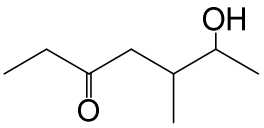
6. Use di-, tri-, tetra- etc. if identical substituents are present.



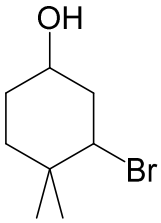
3,5-dimethyl-2-eptanol

Nomenclature of organic molecules

IUPAC – aliphatic compounds



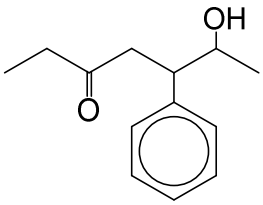
2-hydroxy-3-methyl-5-eptanone



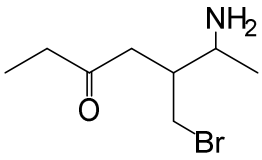
3-bromo-4,4-dimethyl-cyclohexanol

Nomenclature of organic molecules

IUPAC – aliphatic compounds



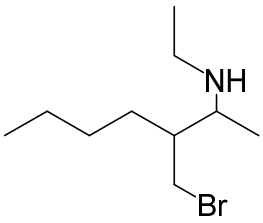
2-hydroxy-3-phenyl-5-eptanone



2-amino-3-(bromomethyl)-5-eptanone

Nomenclature of organic molecules

IUPAC – aliphatic compounds



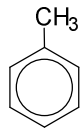
N-ethyl-3-(bromomethyl)-2-eptanamine

2-[4-(2-methylpropyl)phenil]propanoic acid

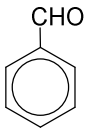
Nomenclature of organic molecules

IUPAC – aromatic compounds

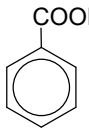
The name of benzene derivatives is formed starting from very common compounds:



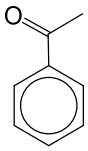
Toluene
(methylbenzene)



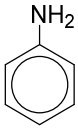
Benzaldehyde



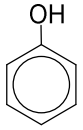
Benzoic acid



Acetophenone



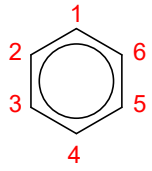
Aniline



Phenol

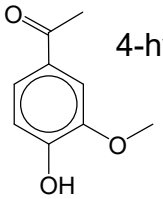
Nomenclature of organic molecules

IUPAC – aromatic compounds



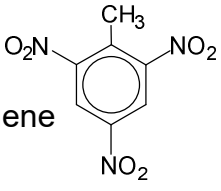
1. The substituent with the highest prevalence is placed in position 1.
2. Enumerate the C atom ring in order to obtain the lowest numbers for location of the substituents.

The name of benzene derivatives is formed starting from very common compounds:



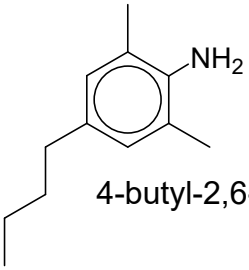
4-hydroxy-3-methoxybenzaldehyde

2,4,6-trinitrotoluene

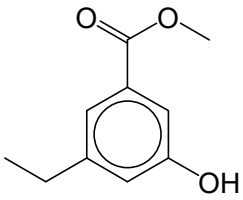


Nomenclature of organic molecules

IUPAC – aromatic compounds



4-butyl-2,6-dimethylaniline

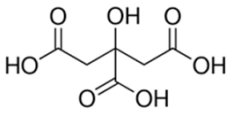


Methyl 5-ethyl-3-hydroxybenzoate

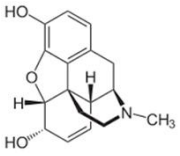
Nomenclature of organic molecules

Traditional

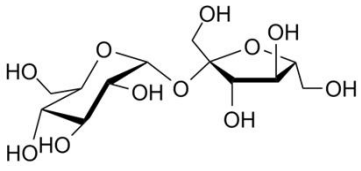
Many organic compounds have a traditional name, deriving from its natural source.



Citric acid



Morphine



Sucrose

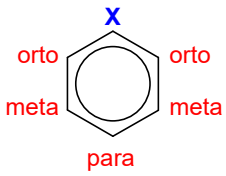
(2R,3R,4S,5S,6R)-2-[(2S,3S,4S,5R)-3,4-dihydroxy-2,5-bis(hydroxymethyl)oxolan-2-yl]oxy-6-(hydroxymethyl)oxane-3,4,5-triol

Nomenclature of organic molecules

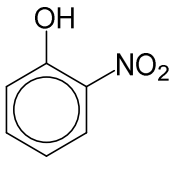
Carbon atoms	Common name	IUPAC name	Chemical formula	Common location or use
1	Formic acid	Methanoic acid	HCOOH	Insect stings
2	Acetic acid	Ethanoic acid	CH_3COOH	Vinegar
3	Propionic acid	Propanoic acid	CH_3CH_2COOH	Preservative for stored grains, body odour
4	Butyric acid	Butanoic acid	$CH_3(CH_2)_2COOH$	Butter
5	Valeric acid	Pentanoic acid	$CH_3(CH_2)_3COOH$	Valerian
6	Caproic acid	Hexanoic acid	$CH_3(CH_2)_4COOH$	Goat fat
7	Enanthic acid	Heptanoic acid	$CH_3(CH_2)_5COOH$	
8	Caprylic acid	Octanoic acid	$CH_3(CH_2)_6COOH$	Coconuts and breast milk
9	Pelargonic acid	Nonanoic acid	$CH_3(CH_2)_7COOH$	Pelargonium
10	Capric acid	Decanoic acid	$CH_3(CH_2)_8COOH$	Coconut and Palm kernel oil
11	Undecylic acid	Undecanoic acid	$CH_3(CH_2)_9COOH$	
12	Lauric acid	Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	Coconut oil and hand wash soaps
13	Tridecylic acid	Tridecanoic acid	$CH_3(CH_2)_{11}COOH$	
14	Myristic acid	Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	Nutmeg
15	Pentadecylic acid	Pentadecanoic acid	$CH_3(CH_2)_{13}COOH$	
16	Palmitic acid	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	Palm oil
17	Margaric acid	Heptadecanoic acid	$CH_3(CH_2)_{15}COOH$	
18	Stearic acid	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	Chocolate, waxes, soaps, and oils
19	Nonadecylic acid	Nonadecanoic acid	$CH_3(CH_2)_{17}COOH$	Fats, vegetable oils, pheromone
20	Arachidic acid	Icosanoic acid	$CH_3(CH_2)_{18}COOH$	Peanut oil

Nomenclature of organic molecules

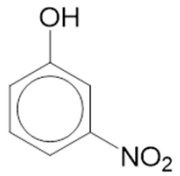
Traditional – aromatic compounds



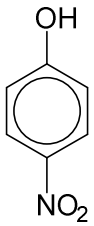
The name of benzene derivatives is formed starting from very common compounds:



o-nitrophenol



m-nitrophenol



p-nitrophenol

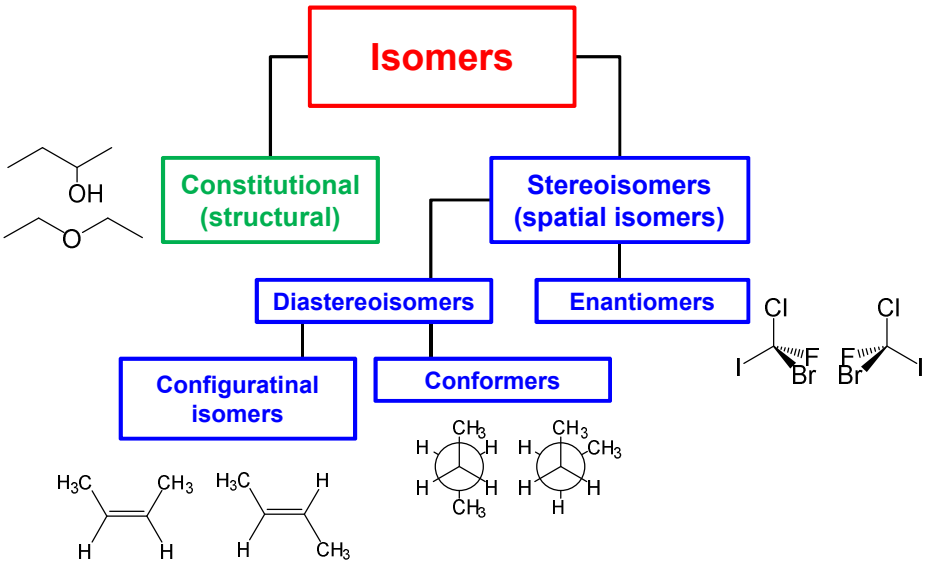
Isomers

Isomers are compounds with the same molecular formula (same molecular weight and same atomic composition) but with a **different molecular structure**.

They can differ by:

- How the atoms are connected within the molecule
- The spatial disposition of the atoms

Isomers



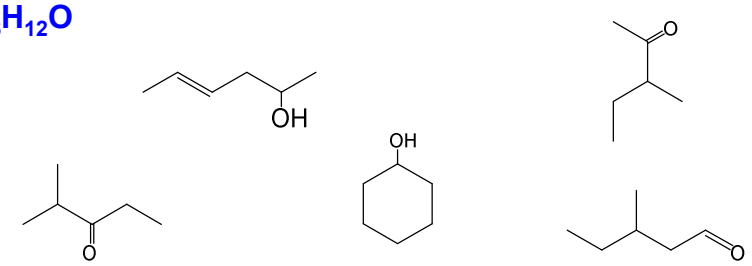
Constitutional isomers

They have the same formula but different connections between the atoms.

In other words, they have the same molecular formula but different structural formula.

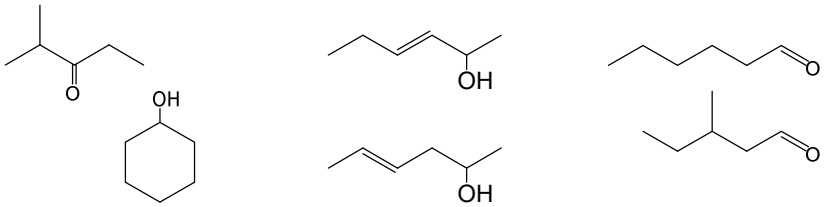
They have different physical and chemical properties, because of the different bonds between the atoms.

$C_6H_{12}O$



Constitutional isomers

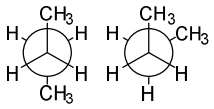
Functional group	Position	Chain
Contain different functional groups: different chemical reactivity and different physical properties.	Different position of multiple bonds or substituents on the carbon chain: different physical properties.	Presence of ramification on the carbon chain: different physical properties.



Stereoisomers

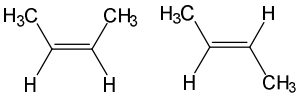
They have the same formula and the same connections between the atoms but they arranged in a different way in the space. For this reason, stereoisomers cannot superimpose.

Conformers

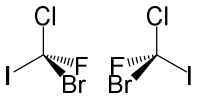


Differ only for rotation around a single bond.

Geometric isomers

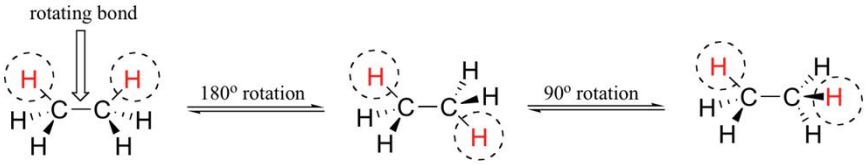


Enantiomers

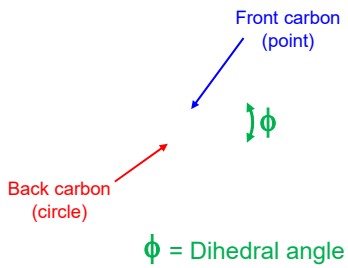


Cannot be interconverted without breaking bonds between the atoms.

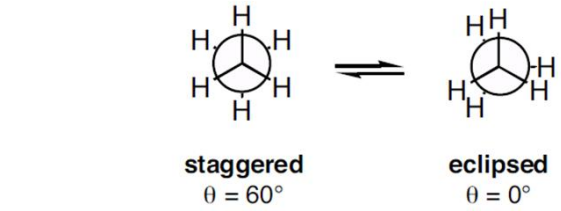
Conformers – Ethane

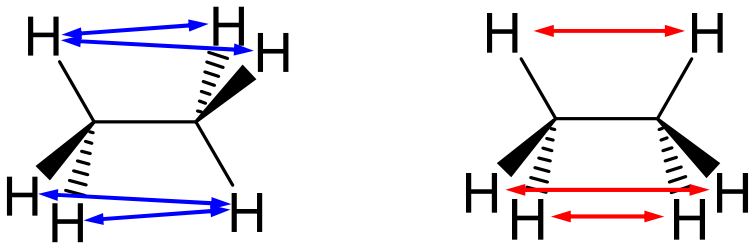


Newman projections

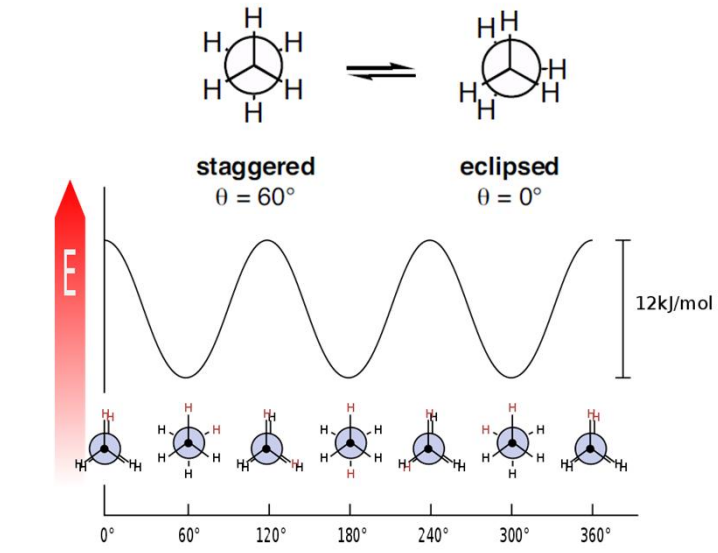


Conformers – Ethane

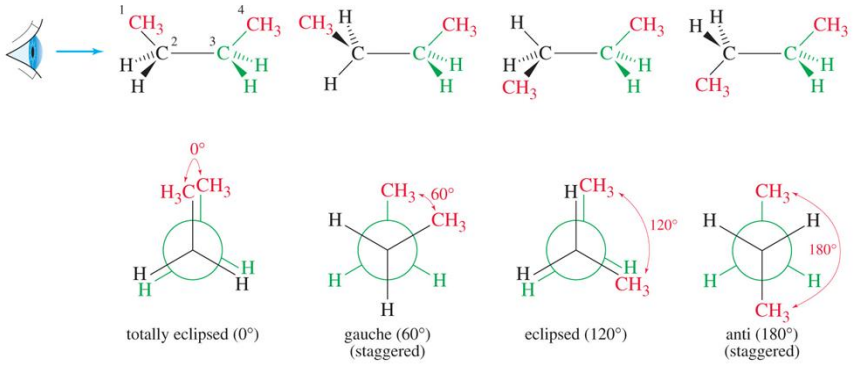




Conformers – Ethane

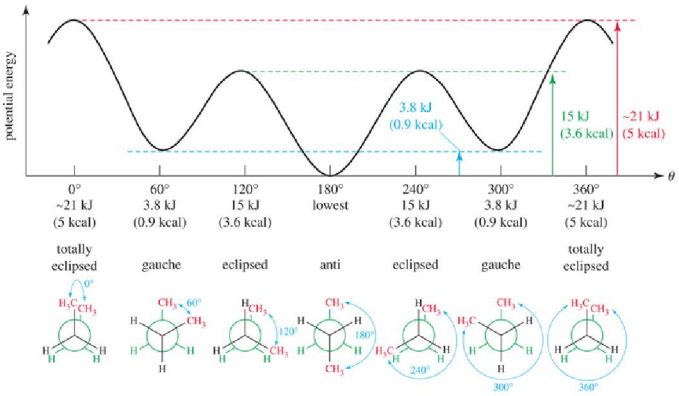


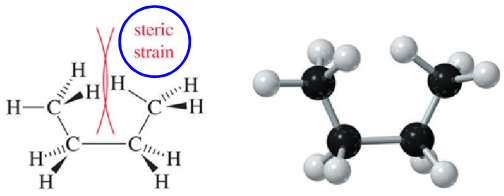
Conformers – Butane



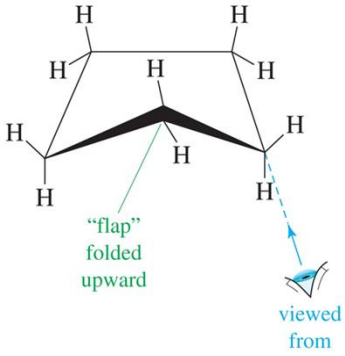
- Butane has two different staggered conformations: gauche (60° between the methyl groups) and anti (180° between the methyl groups).
- The eclipsed conformation where the dihedral angle between the methyl groups is 0° is referred to as *totally eclipsed*.

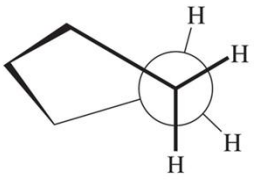
Conformers – Butane





Conformers – Cyclopentane

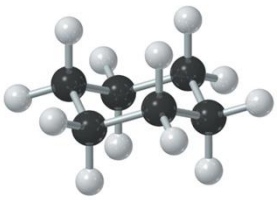




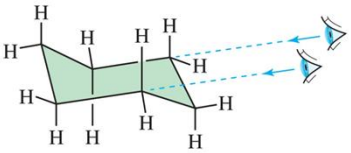
Newman projection showing relief of eclipsing of bonds

The conformation of cyclopentane is slightly folded, like the shape of an envelope. This puckered conformation reduces the eclipsing of adjacent methylene (CH_2) groups.

Conformers – Cyclohexane

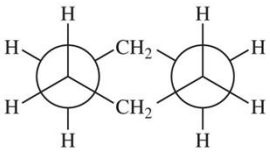


chair conformation



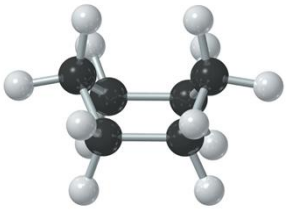
viewed along the "seat" bonds

All bounds are in "anti" configuration

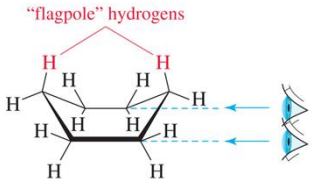


Newman projection

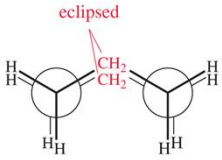
Conformers – Cyclohexane



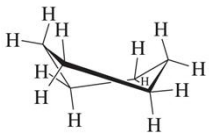
boat conformation



symmetrical boat

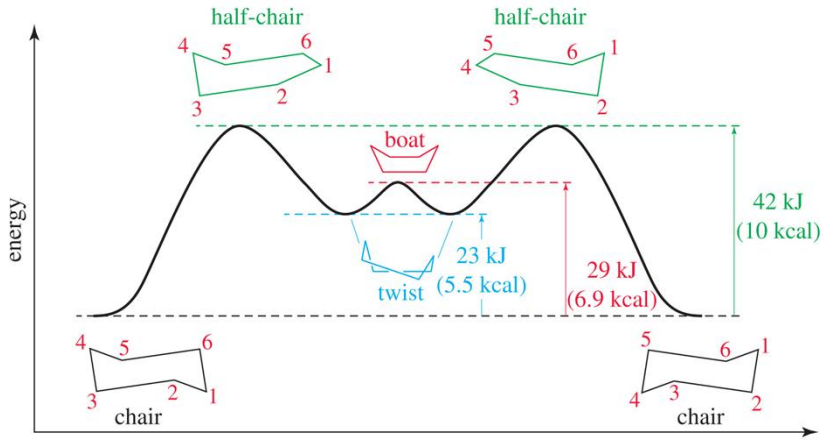


Newman projection

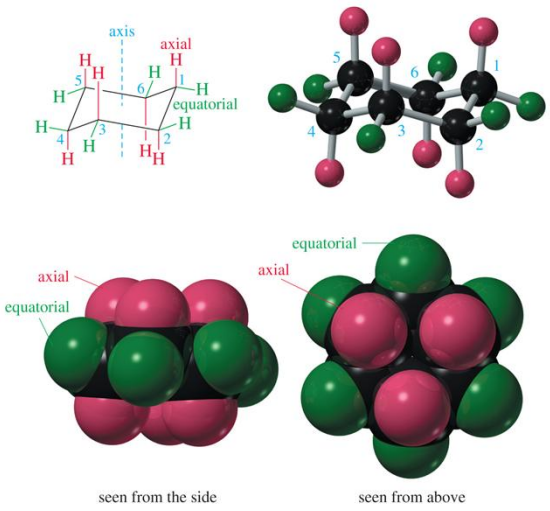


"twist" boat

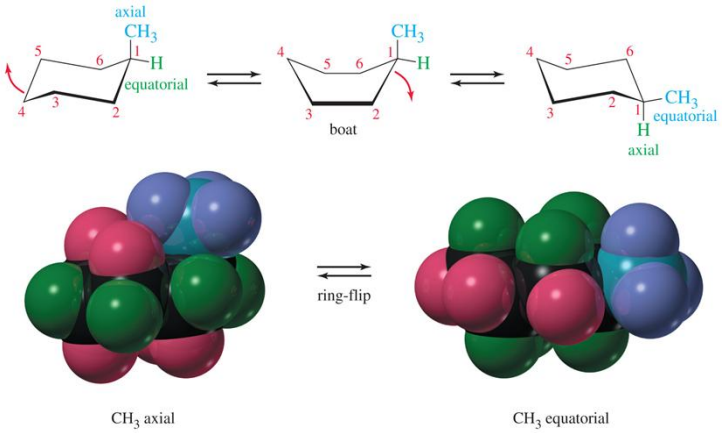
Conformers – Cyclohexane



Conformers – Cyclohexane

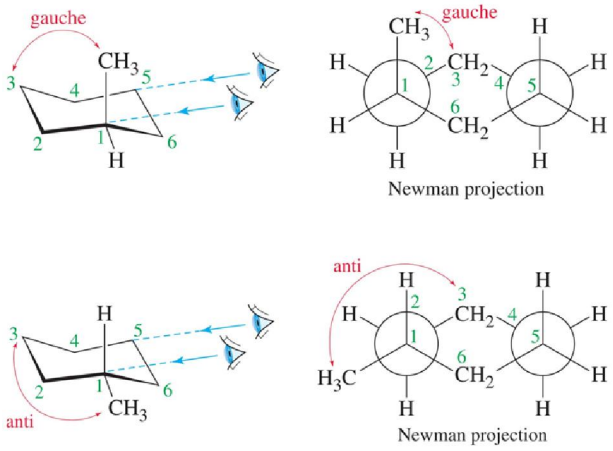


Conformers – Cyclohexane

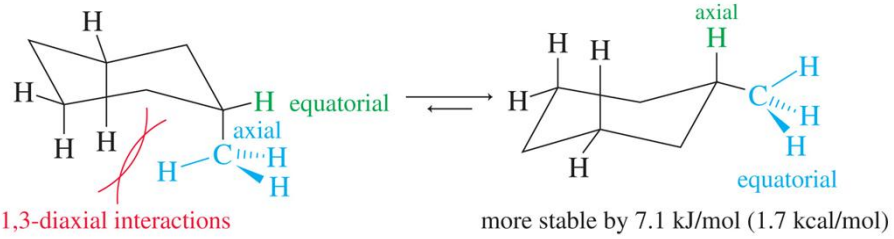


The most important result in chair conversion is that any substituent that is axial in the original conformation becomes equatorial in the new conformation.

Conformers – Cyclohexane



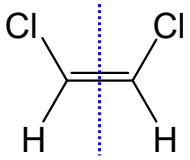
Conformers – Cyclohexane



The axial substituent interferes with the axial hydrogens on C3 and C5. This interference is called a *1,3-diaxial interaction*.

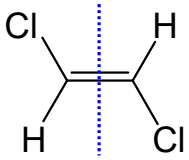
Configurational isomers

Cannot be converted into each other without breaking bonds within the molecule.



cis-1,2-dichloroethane

The substituents with the higher priority are on the same side of the double bond.



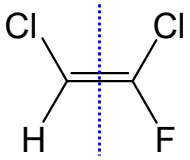
trans-1,2-dichloroethane

The substituents with the higher priority are on the opposite sides of the double bond.

Priority is determined on the basis of the atomic weight of the substituents.

Configurational isomers

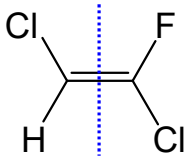
(*E*) – (*Z*) system is not ambiguous in the case of trisubstituted alkenes.



(*Z*)-1,2-dichloro-1-fluoroethane

Zusammen

The substituents with the higher priority are on the same side of the double bond.



(*E*)-1,2-dichloro-1-fluoroethane

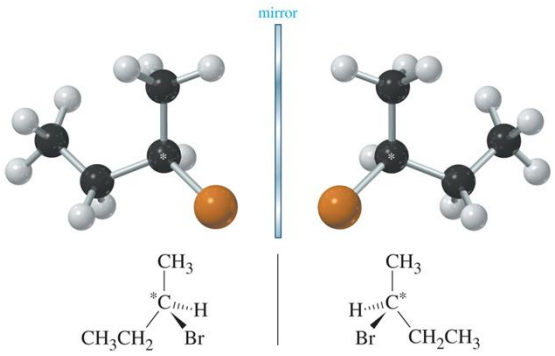
Entgegen

The substituents with the higher priority are on the opposite sides of the double bond.

Priority is determined on the basis of the atomic weight of the substituents.

Enantiomers

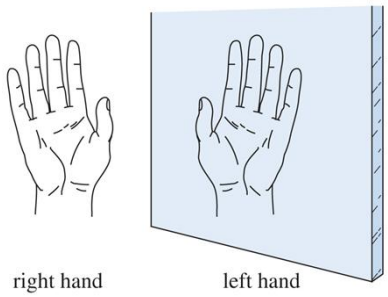
Non-superimposable mirror images



This property is called **CHIRALITY**

Enantiomers

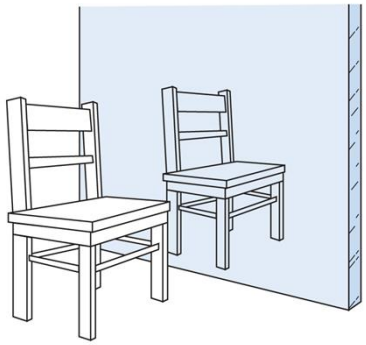
Chirality



Mirror-image object is different from the original object.

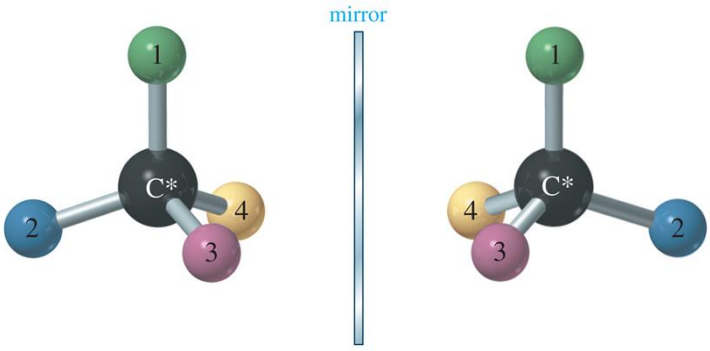
Enantiomers

Objects that can be superposed are **achiral**.

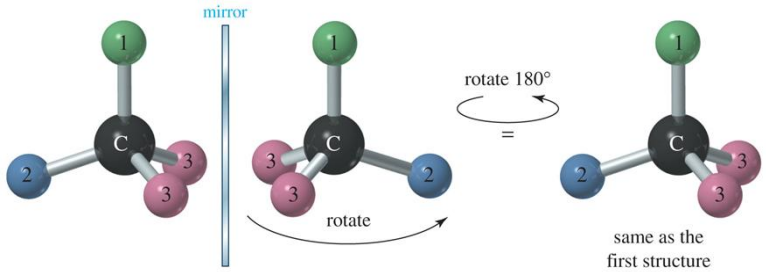


Chiral Carbons

Carbons with four different groups attached are chiral.
It's mirror image will be a different compound (enantiomer).



Achiral Compounds

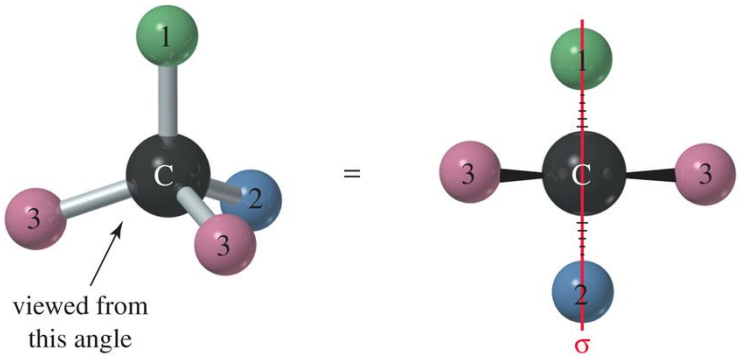


Take this mirror image and try to superimpose it on the one to the left matching all the atoms. Everything will match.

When the images can be superposed the compound is ***achiral***.

Enantiomers

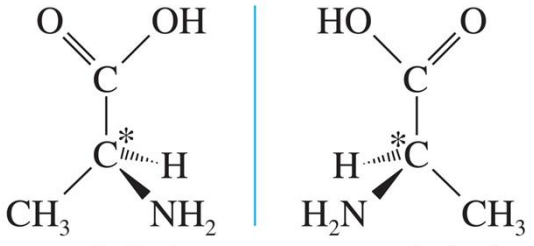
Planes of Symmetry



A molecule that has a plane of symmetry is ***achiral***.

Enantiomers – Absolute configuration

(*R*) and (*S*) Nomenclature



natural alanine unnatural alanine

- Different molecules (enantiomers) must have different names.
- Usually only one enantiomer will be biologically active.
- Configuration around the chiral carbon is specified with (*R*) and (*S*).

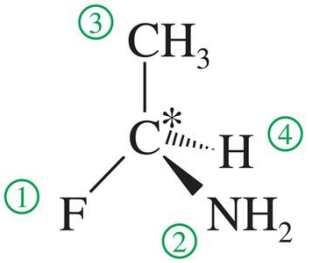
Enantiomers – Absolute configuration

Cahn–Ingold–Prelog Rules

- Assign a priority number to each group attached to the chiral carbon.
- Priority is assigned according to atomic number. The highest atomic number assigned is the highest priority #1.
- In case of ties, look at the next atoms along the chain.
- Double and triple bonds are treated like bonds to duplicate atoms.

Enantiomers – Absolute configuration

Assign Priorities



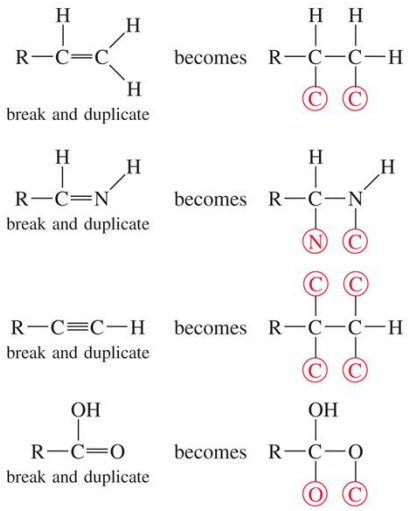
Atomic number: F > N > C > H

Once priorities have been assigned, the lowest priority group (#4) should be moved to the back if necessary.

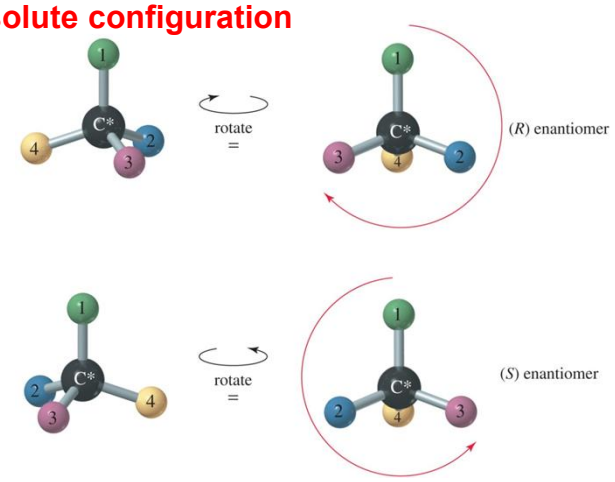
Enantiomers – Absolute configuration

Assign Priorities

Treatment of Multiple Bonds



Enantiomers – Absolute configuration

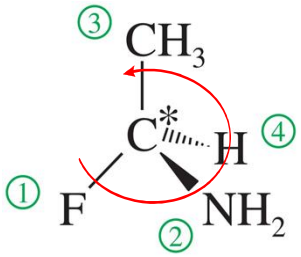


Assign (*R*) or (*S*)

- Working in 3-D, rotate the molecule so that the lowest priority group is in back.
- Draw an arrow from highest to lowest priority group.
- Clockwise = (*R*), Counterclockwise = (*S*)

Enantiomers – Absolute configuration

Assign (*R*) or (*S*)



Counterclockwise

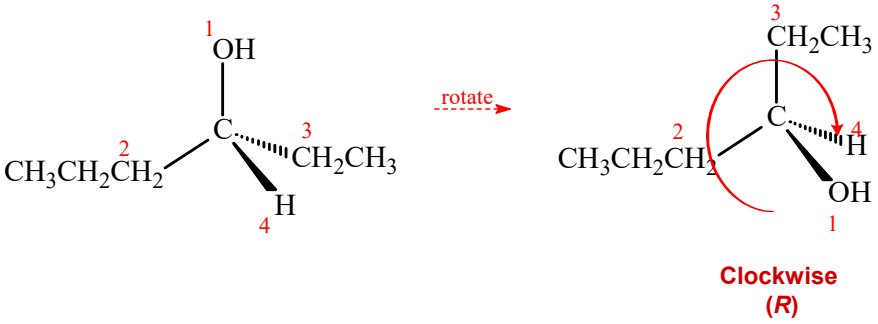
(*S*)

Draw an arrow from Group 1 to Group 2 to Group 3 and back to Group 1. Ignore Group 4.

Clockwise = (*R*) and Counterclockwise = (*S*)

Enantiomers

Example 1

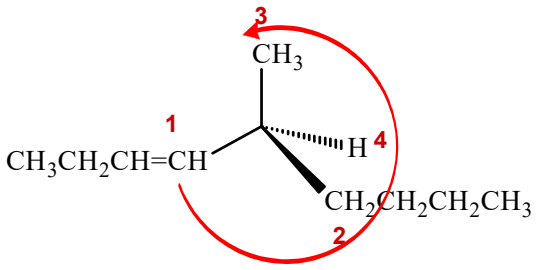


Clockwise
(*R*)

When rotating to put the lowest priority group in the back, keep one group in place and rotate the other three.

Enantiomers

Example 2

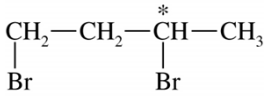


Counterclockwise
(*S*)

Enantiomers

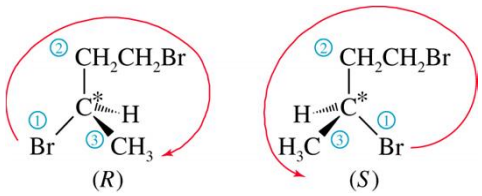
Problem 1

Draw the enantiomers of 1,3-dibromobutane and label them as (*R*) and (*S*). (Making a model is particularly helpful for this type of problem.)



Solution

The third carbon atom in 1,3-dibromobutane is asymmetric. The bromine atom receives first priority, the ($-CH_2CH_2Br$) group second priority, the methyl group third, and the hydrogen fourth. The following mirror images are drawn with the hydrogen atom back, ready to assign (*R*) or (*S*) as shown.

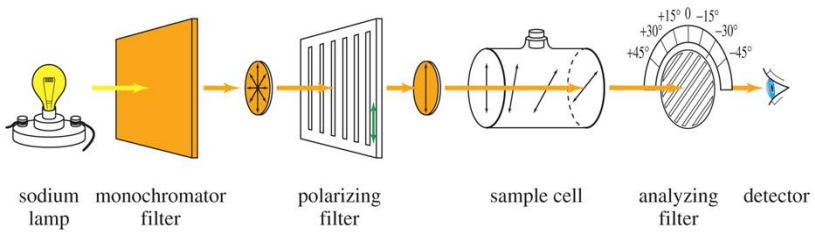


Enantiomers - Properties

- Same boiling point, melting point, and density.
- Same refractive index.
- Rotate the plane of polarized light in the same magnitude, but in opposite directions.
- Different interaction with other chiral molecules:
  - Active site of enzymes is selective for a specific nantiomer.
  - Taste buds and scent receptors are also chiral. Enantiomers may have different smells.

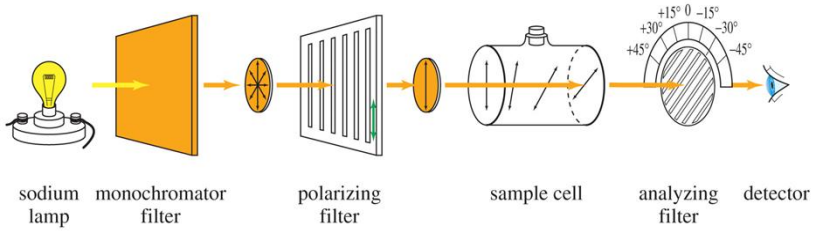
Enantiomers – Optical activity

- Enantiomers rotate the plane of polarized light in opposite directions, but same number of degrees.



Enantiomers – Optical activity

Polarimeter



Clockwise

Dextrorotatory (+)

Counterclockwise

Levorotatory (-)

Not related to (*R*) and (*S*)

Enantiomers – Optical activity

Specific rotation

Observed rotation depends on the length of the cell and concentration, as well as the strength of optical activity, temperature, and wavelength of light.

$$[\alpha] = \frac{\alpha \text{ (observed)}}{c \bullet l}$$

Where α (observed) is the rotation observed in the polarimeter, *c* is concentration in g/mL and *l* is length of sample cell in decimeters.

Enantiomers

Problem 2

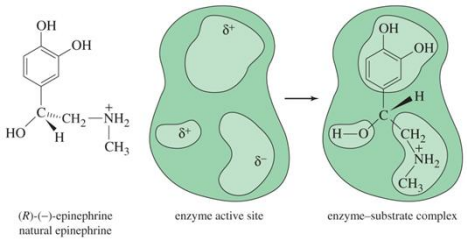
When one of the enantiomers of 2-butanol is placed in a polarimeter, the observed rotation is 4.05° counterclockwise. The solution was made by diluting 6 g of 2-butanol to a total of 40 mL, and the solution was placed into a 200-mm polarimeter tube for the measurement. Determine the specific rotation for this enantiomer of 2-butanol.

Solution

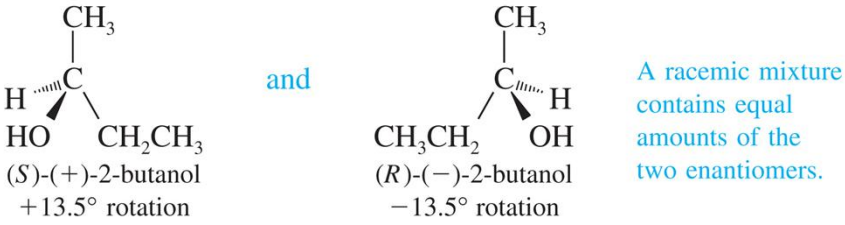
Since it is levorotatory, this must be (–)-2-butanol The concentration is 6 g per 40 mL = 0.15 g/ml, and the path length is 200 mm = 2 dm. The specific rotation is

$$[\alpha]_D^{25} = \frac{-4.05}{0.15 * 2} = -13.5°$$

Enantiomers – Biological discrimination



Enantiomers – Racemic mixtures



A racemic mixture contains equal amounts of the two enantiomers.

- Equal quantities of R- and S- enantiomers.
- Notation: (R,S) or (±)
- No optical activity.
- The mixture may have different boiling point (b. p.) and melting point (m. p.) from the enantiomers!

Enantiomers – Enantiomeric excess

Enantiomeric excess (ee) is defined as the absolute difference between the mole fraction of each enantiomer.

$$ee = | x_R - x_S |$$

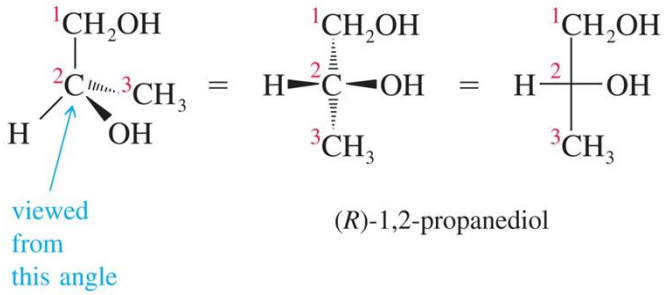
Example:
a sample with 70% of R isomer and 30% of S has an enantiomeric excess of 40%

ee can be determined by different analytical method (chiral GC, NMR) or simply measuring the specific rotation of the mixture (the specific rotation of the pure enantiomers must be known).

$$\text{optical purity (\%)} = \frac{[\alpha]_{observed}}{[\alpha]_{maximal}} \cdot 100$$

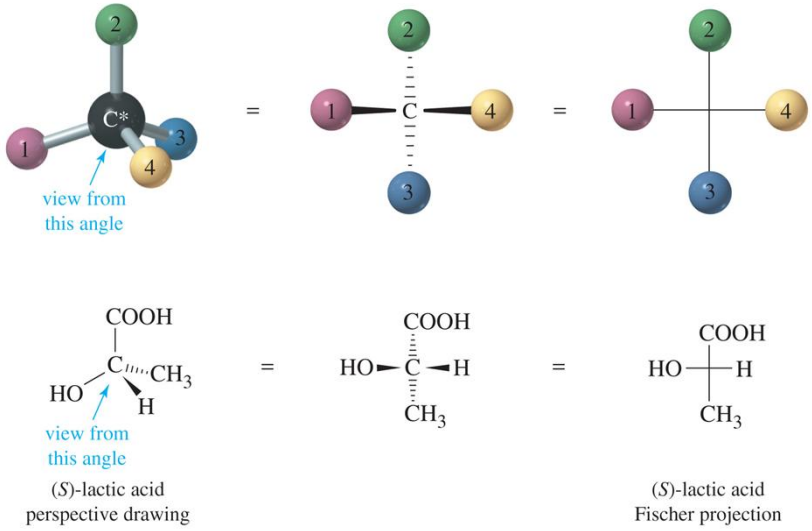
Enantiomers – Fisher projection

- Flat representation of a 3-D molecule.
- A chiral carbon is at the intersection of horizontal and vertical lines.
- Horizontal lines are forward, out-of-plane.
- Vertical lines are behind the plane.



(*R*)-1,2-propanediol

Enantiomers – Fisher projection



Enantiomers – Fisher projection

Fisher rules

- Carbon chain is on the vertical line.
- Highest oxidized carbon is at top.
- Rotation of 180° in plane doesn't change molecule.
- Do not rotate 90°!

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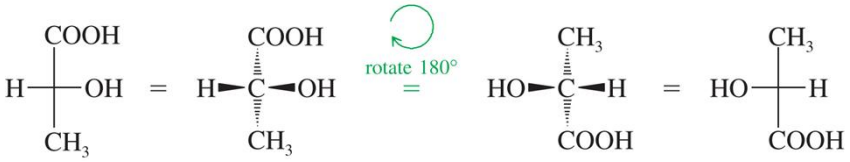

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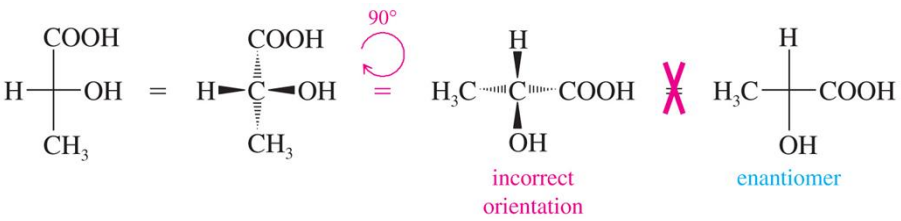
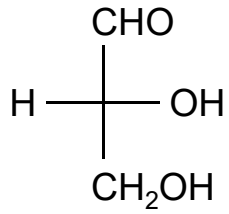


Enantiomers – Relative configuration

(*D*) or (*L*) nomenclature

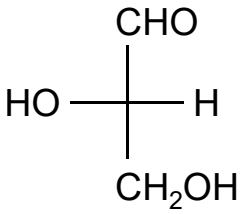
The D/L system (named after latin Dexter and Laevus, right and left) does this by relating the molecule to glyceraldehyde.



(R)-glyceraldehyde

(+)-glyceraldehyde

D-glyceraldehyde



(S)-glyceraldehyde

(-)-glyceraldehyde

L-glyceraldehyde

Enantiomers – Relative configuration

(*D*) or (*L*) nomenclature

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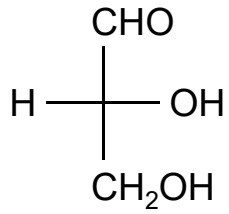
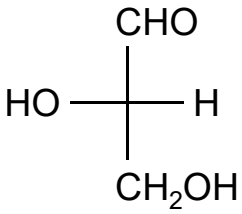


(R)-glyceraldehyde

(+)-glyceraldehyde

D-glyceraldehyde



(S)-glyceraldehyde

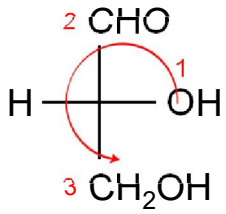
(-)-glyceraldehyde

L-glyceraldehyde

Enantiomers – Relative configuration

(*D*) or (*L*) nomenclature

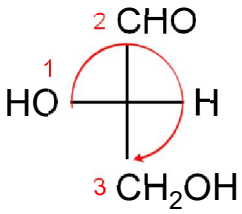
Lowest priority (usually H) comes forward, so assignment rules are backwards!
Clockwise 1-2-3 is (*S*) and counterclockwise 1-2-3 is (*R*).



(R)-glyceraldehyde

(+)-glyceraldehyde

D-glyceraldehyde



(S)-glyceraldehyde

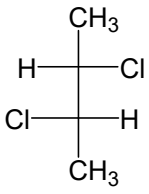
(-)-glyceraldehyde

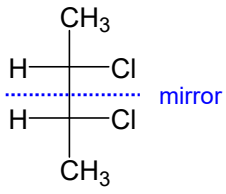
L-glyceraldehyde

Enantiomers – Relative configuration

(*D*) or (*L*) nomenclature

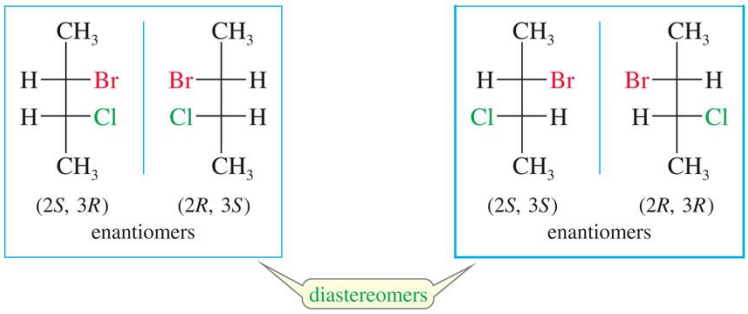
Fisher projections are easy to draw and make it easier to find enantiomers and internal mirror planes when the molecule has 2 or more chiral centers.





Diastereoisomers

- Molecules with two or more chiral carbons.
- Stereoisomers that are not mirror images.

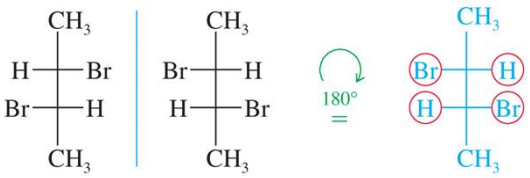


Number of different diastereoisomers: 2^n

where n is the number of stereocenters

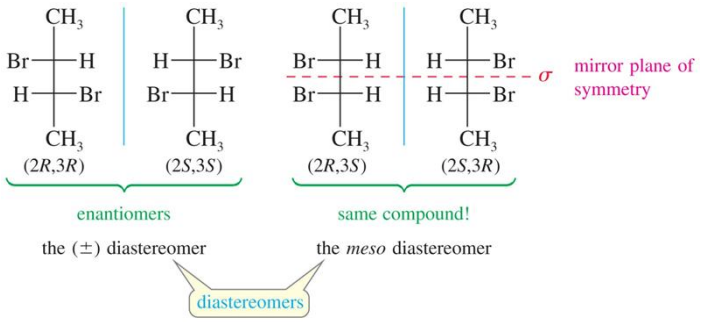
Diastereoisomers - *meso* compounds

(2*S*,3*S*)-2,3-dibromobutane



- Meso compounds have a plane of symmetry.
- If one image was rotated by 180°, then it could be superimposed on the other image.
- Meso compounds are achiral even though they have chiral centers.

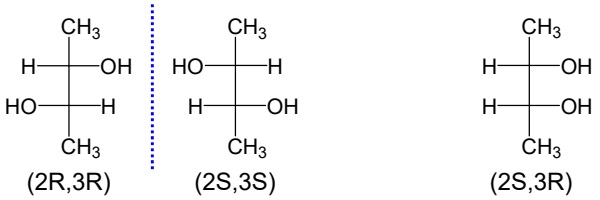
Diastereoisomers - *meso* compounds



The **2^n rule** will not apply to compounds that may have a plane of symmetry. 2,3-dibromobutane has only 3 stereoisomers: (±) *diastereomer* and the *meso diastereomer.*

Diastereoisomers - Properties

- Diastereomers have different physical properties, so they can be easily separated.



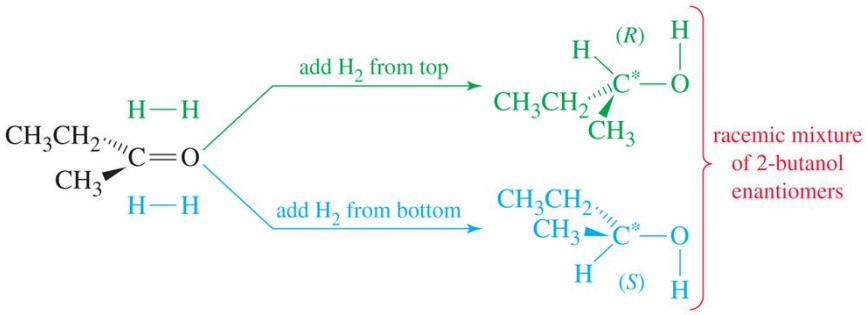
b.p. = 180 °C

b.p. = 184 °C

- Enantiomers differ only in reaction with other chiral molecules and the direction in which polarized light is rotated.
- Enantiomers are difficult to separate.
- Convert enantiomers into diastereomers to be able to separate them.

Racemic products

If optically inactive reagents combine to form a chiral molecule, a racemic mixture is formed.



Resolution of enantiomers

Chemical method

(*R*)- and (*S*)-2-butanol

plus

(*R*,*R*)-tartaric acid

$\xrightarrow{H^+}$

(*R*)-2-butyl (*R*,*R*)-tartrate + (*S*)-2-butyl (*R*,*R*)-tartrate

diastereomers, *not* mirror images

React the racemic mixture with a pure chiral compound, such as tartaric acid, to form diastereomers, then separate them.

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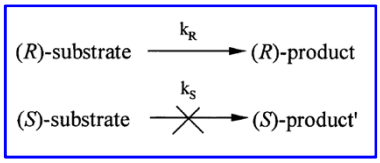
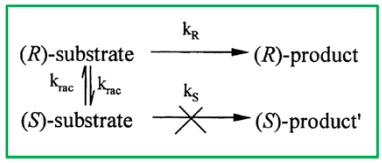
Resolution of enantiomers

Enzymatic method

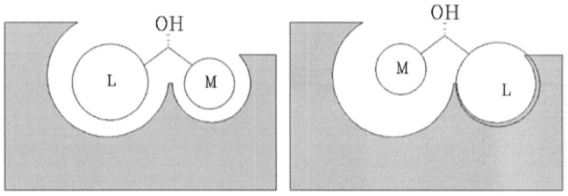
Enzymes can react one enantiomer faster than the other.



Maximum yield = 50%



Maximum yield = 100%



The active site of an enzyme hosts perfectly one enantiomer but not the other one.

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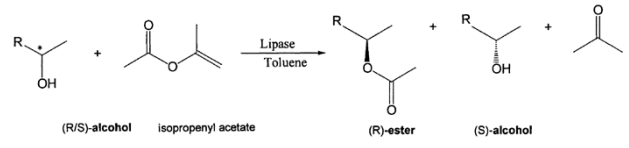
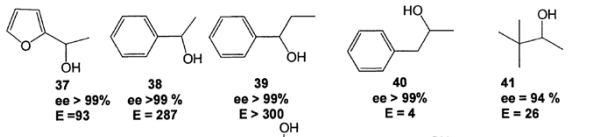
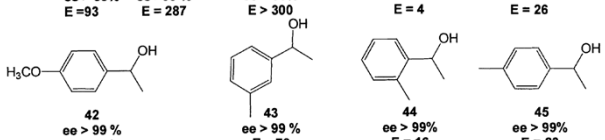
Resolution of enantiomers

Enzymatic method

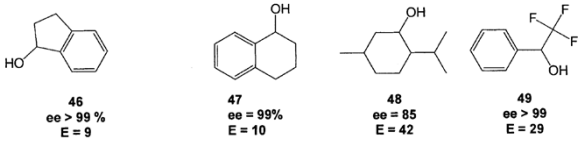




37 ee > 99% E =93 | 38 ee >99 % E = 287 | 39 ee > 99% E > 300 | 40 ee > 99% E = 4 | 41 ee = 94 % E = 26



42 ee > 99 % E = 141 | 43 ee > 99 % E = 78 | 44 ee > 99% E = 16 | 45 ee > 99% E = 23



46 ee > 99 % E = 9 | 47 ee = 99% E = 10 | 48 ee = 85 E = 42 | 49 ee > 99 E = 29

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