ADE

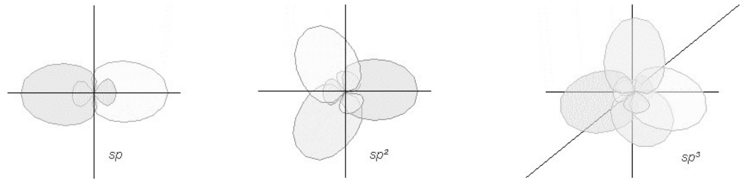
3D encounters

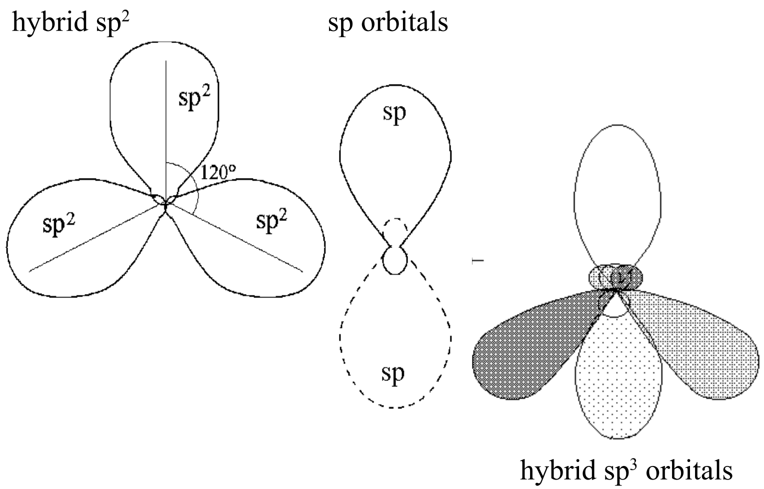
Orbitals hybridization

one *s* orbital can fuse with one *p* orbital to form 2 *sp* orbitals, placed at an angle of 180°

one *s* orbital can fuse with 2 *p* orbitals to form 3 sp^2 orbitals, placed at an angle of 120°

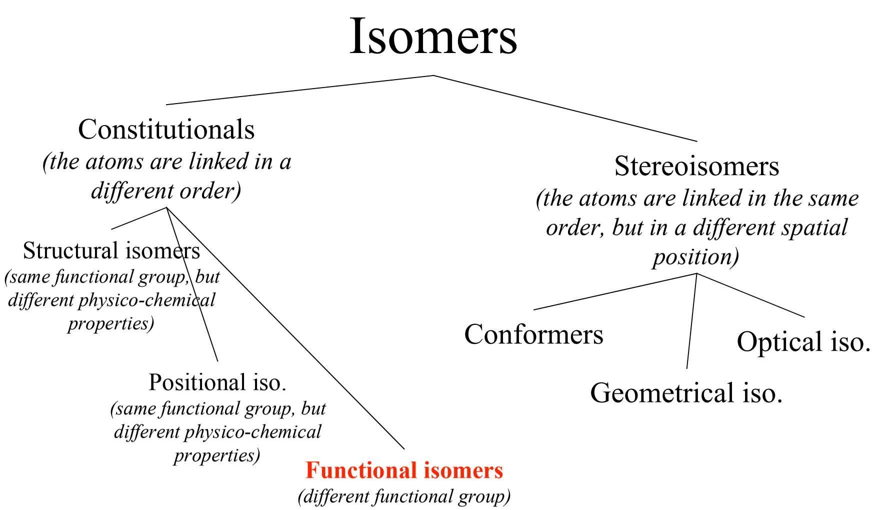
one *s* orbital can fuse with 3 *p* orbitals to form 4 sp^3 orbitals, each one placed at an angle of 109.5°, therefore forming a tetrahedron





Isomers

Chemical compounds with the same number of atoms, the same formula weight, but different structures

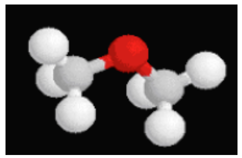


Functional isomers

Different chemical compounds, sharing the same atomic composition, but different functional groups, and **different structure**

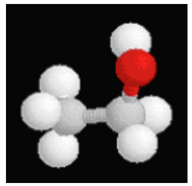
C_2H_6O

di-methyl-ether CH_3-O-CH_3

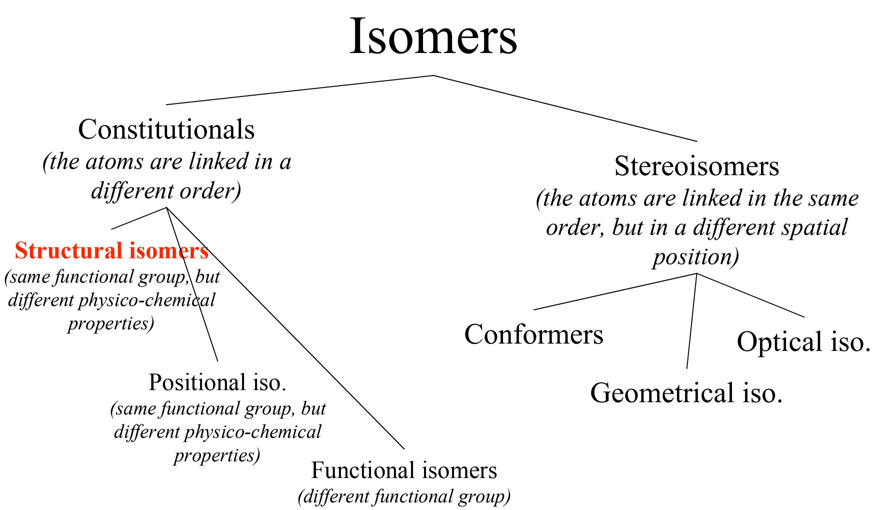


t_{eb}= -24°C
Insoluble in H_2O

ethanol CH_3CH_2OH



t_{eb}=78°C
soluble in H_2O



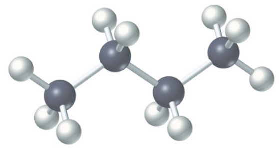
Structural isomers

Compounds with the same composition, the same funcitonal group, but different order of linkage between the atoms

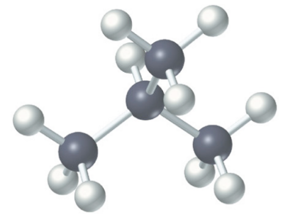
Ex.: butane & isobutane

C_4H_{10}

butane



isobutane (2-methyl-propane)



Structural isomers

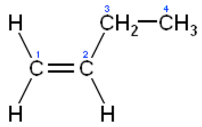
Compounds with the same composition, the same funcitonal group, but different order of linkage between the atoms

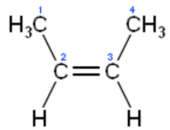
Ex.: positional isomers

C_4H_8

1-butene $CH_2CHCH_2CH_3$

2-butene $CH_3CHCHCH_3$





Isomers

- Constitutionals *(the atoms are linked in a different order)*
  - Structural isomers *(same functional group, but different physico-chemical properties)*
  - Positional iso. *(same functional group, but different physico-chemical properties)*
  - Functional isomers *(different functional group)*
- Stereoisomers *(the atoms are linked in the same order, but in a different spatial position)*
  - **Conformers**
  - Geometrical iso.
  - Optical iso.

Conformers

Conformers: the compound does not change, but the groups of atoms can freely rotate around the single covalent bond

→ Interconvertible molecular structures (rotamers)

Ex.: butane C_4H_{10}

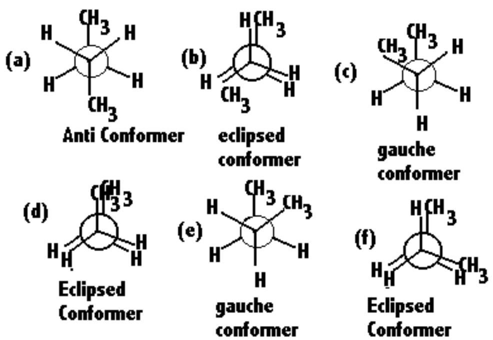


Fig 3- Conformers of Butane

Conformers

Conformers: the compound does not change, but the groups of atoms can freely rotate around the single covalent bond

→ Interconvertible molecular structures (rotamers)

Ex.: butane C_4H_{10}

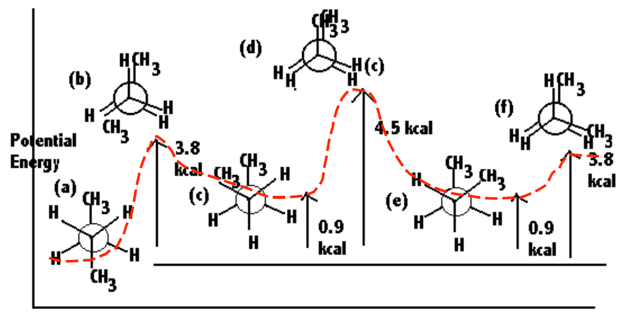


Fig 4- Energy States of Butane Conformers

Conformers

Cyclic conformers (rotamers): the compound does not change, but the groups of atoms can rotate around the single covalent bond to a smaller extent

Ex.: cyclohexane C_6H_{12}

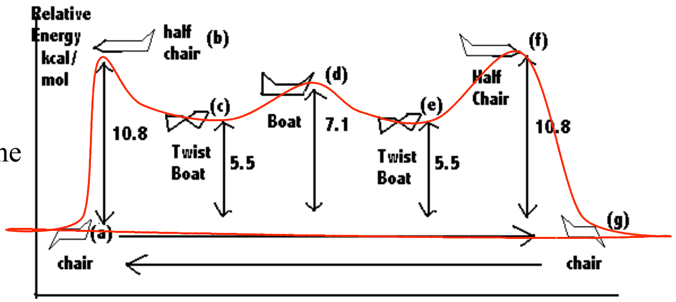


Fig 6- Conformers and Conformational Analysis of Cyclohexane

Cyclic conformers

The hydrogen atoms of cyclohexane are not entirely equivalent: those axials are perpendicular to the ring plane, those equatorial are parallel to the ring plane

When the ring flips form one char conformation to the other one, the axial hydrogens become equatorial and *vice versa*

Ex.: cyclohexane C_6H_{12}

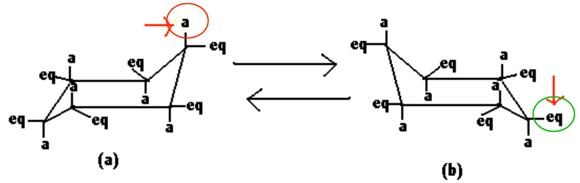


Fig 7- Ring Flip of Cyclohexane

Isomers

- Constitutionals *(the atoms are linked in a different order)*
  - Structural isomers *(same functional group, but different physico-chemical properties)*
  - Positional iso. *(same functional group, but different physico-chemical properties)*
  - Functional isomers *(different functional group)*
- Stereoisomers *(the atoms are linked in the same order, but in a different spatial position)*
  - Conformers
  - **Geometrical iso.**
  - Optical iso.

Geometric Stereoisomers

Whenever the rotation around a covalent bond is hampered, either because of a **double bond** or because of a cyclic compoud, two different isomers are formed: *cis* and *trans*, depending on the position of the groups

Ex.: 2-butene

C_4H_8

Cis 2-butene	*Trans* 2-butene
$CH_3CHCHCH_3$	$CH_3CHCHCH_3$

diastereoisomers

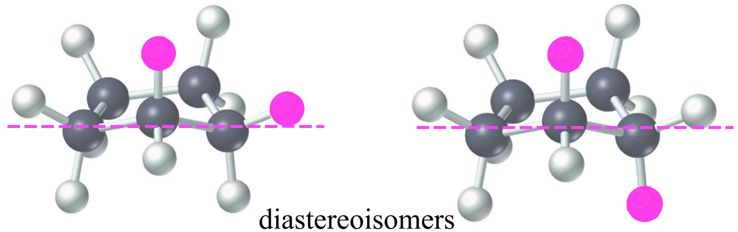
Geometric stereoisomers

Whenever the rotation around a covalent bond is impossible, either because of a double bond or because of a **cyclic compoud**, two different isomers are formed: *cis* and *trans*, depending on the position of the groups

Es.: 1,2-di-Cl-cyclopentane

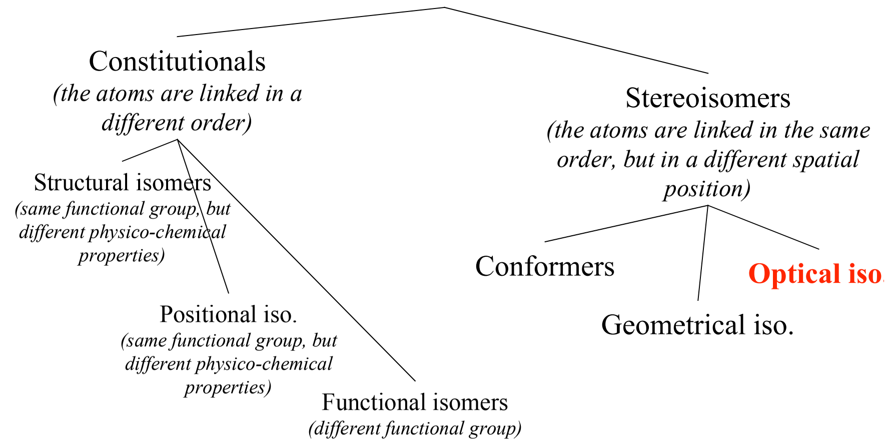
$C_5H_8Cl_2$

1,2-*cis*-di-Cl-cyclopentane — 1,2-*trans*-di-Cl-cyclopentane



diastereoisomers

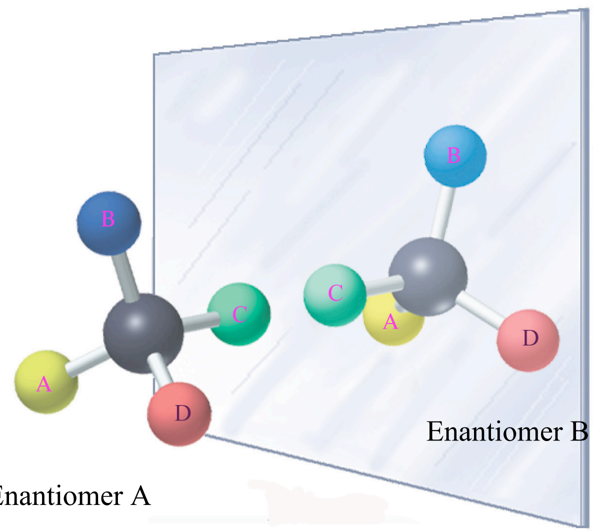
Isomers



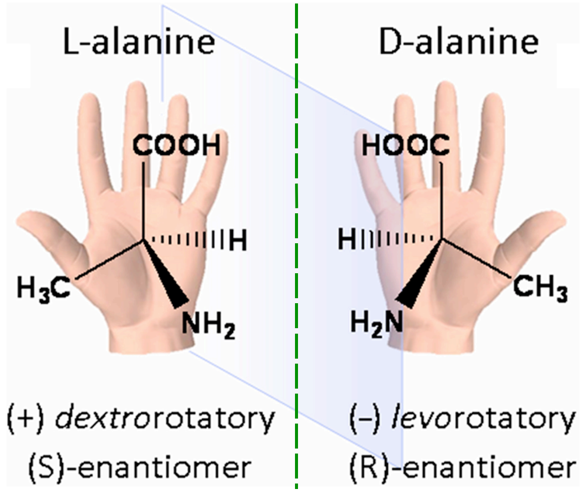
Optical Stereoisomers

- Compounds differing for the 3D assembly of the atoms
- Mandatory condition: one C with *sp3* hybridization, linking 4 different groups
- These compounds behave exactly equally, the only way of differentiating them is by placing in a polarimeter, since each of them will rotate the polarised light by the same angle but either clock-wise or anti-cw
- In case they are the exact mirror image of each other → enantiomers

Optical Stereoisomers

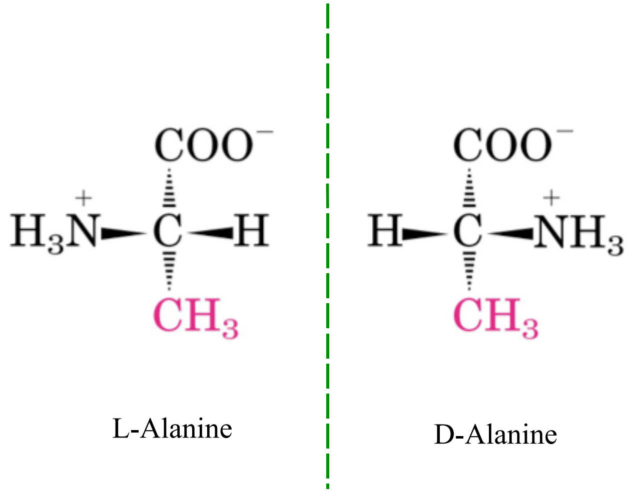


Optical stereoisomers



Enantiomers: perfect mirror image

Optical stereoisomers

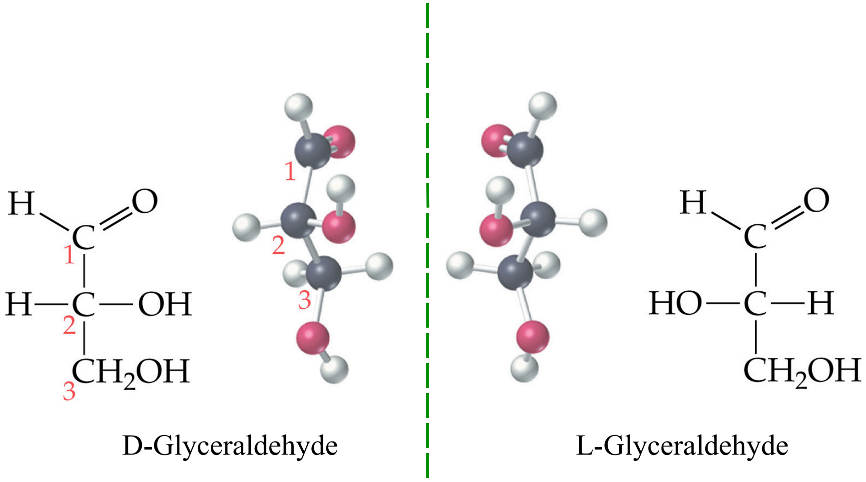


L-Alanine

D-Alanine

Enantiomers: perfect mirror image

Optical Stereoisomers



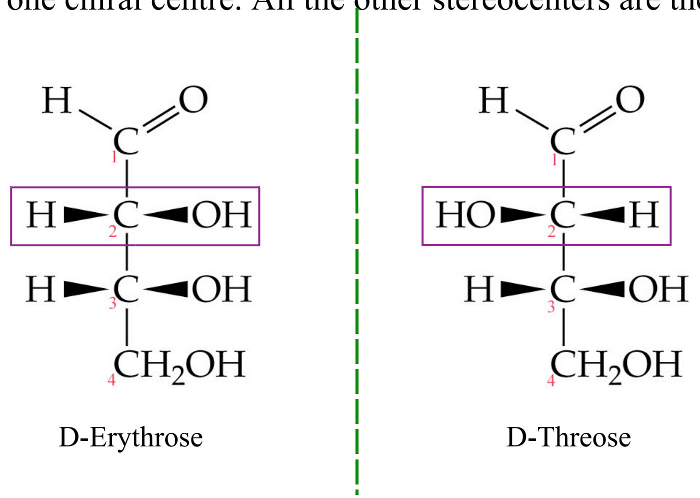
D-Glyceraldehyde

L-Glyceraldehyde

Enantiomers: perfect mirror image

Optical stereoisomers with more than one chiral centre

Epimers: stereoisomers that differ in the configuration of only one chiral centre. All the other stereocenters are the same

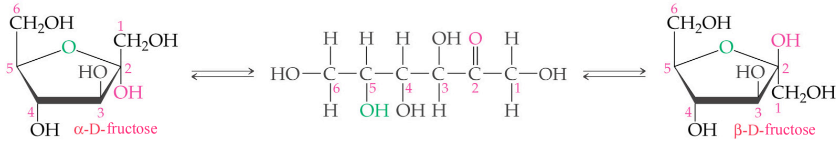


D-Erythrose

D-Threose

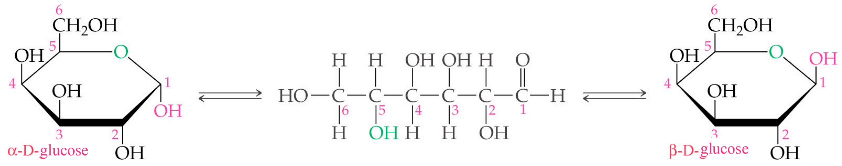
Optical stereoisomers with more chiral centers

Cyclic epimers are called ***Anomers***



α anomer (axial)

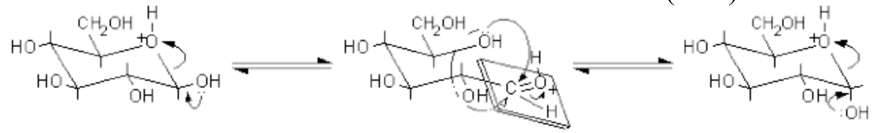
β anomer (equatorial)



Mutarotation of cyclic carbohydrates

Mutarotation is the change in optical rotation that occurs by epimerization of the new optical centre (C1 for aldehydes, C2 for ketons). Cyclic sugars show mutarotation when the α and β anomers interconvert in solution. The total optical rotation depends on that of each anomer and from their ratio in solution.

α-glucopyranose (36%)



β-glucopyranose (64%)

Free aldehyde: OH can attack the carbonyl from either side of the plane