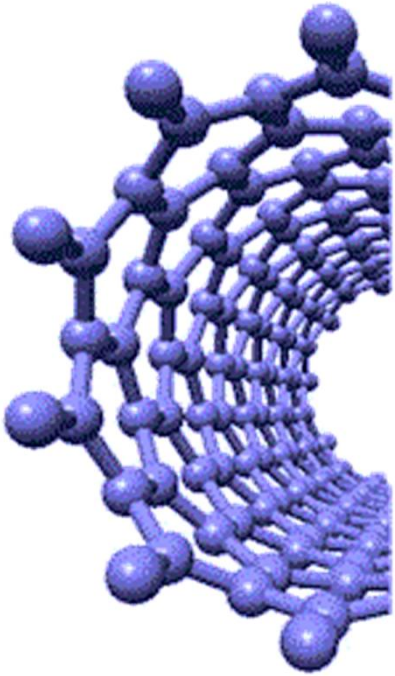
esf european social fund in the czech republic
EUROPEAN UNION
MINISTRY OF EDUCATION, YOUTH AND SPORTS
OP Education for Competitiveness
INVESTMENTS IN EDUCATION DEVELOPMENT

Innovation and Development of Study Field Nanomaterials at the Technical University of Liberec

nano.tul.cz



These materials have been developed within the ESF project: Innovation and development of study field Nanomaterials at the Technical University of Liberec

TECHNICAL UNIVERSITY OF LIBEREC
www.tul.cz

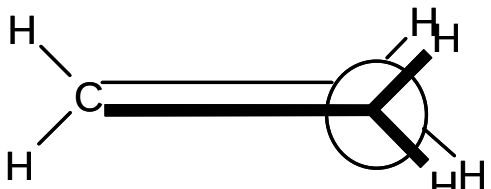
Organic Chemistry I – Chapter 3

- **Alkanes – acyclic, cyclic, bicyclic**

- **reactivity**
  - free-radical substitutions
  - halogenation
  - chemoselectivity and regioselectivity

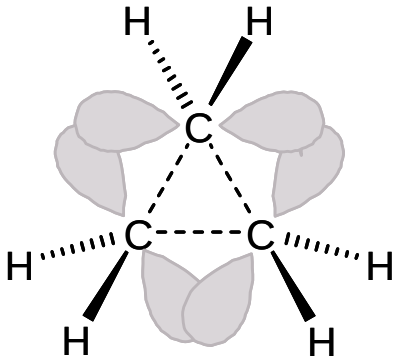
- **optical activity - chirality**

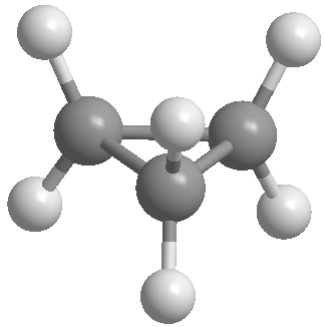
Conformation of cyclopropane and cyclobutane

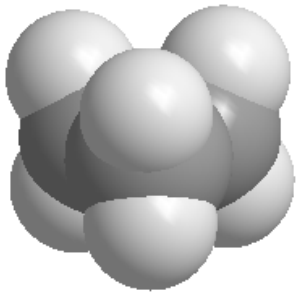


Newman projection of cyclopropane

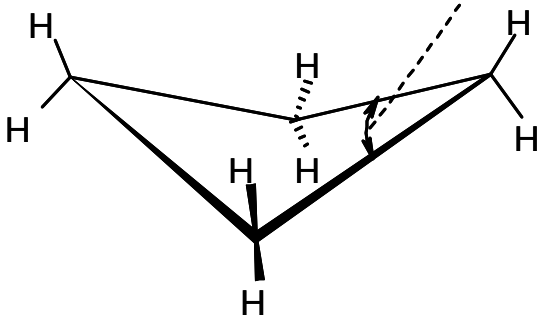
Newmanova projekce cyklopropanu

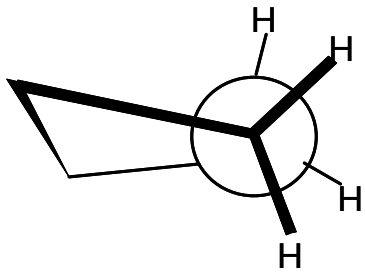


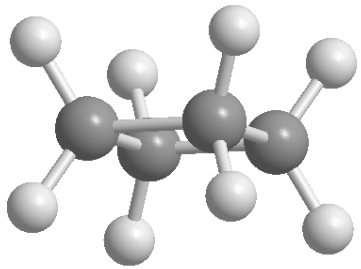




Bond angle 88°



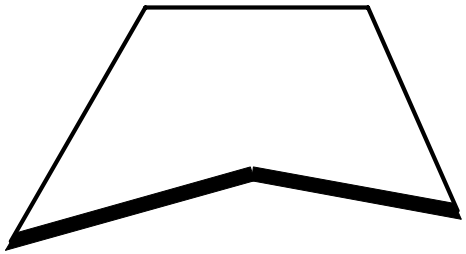




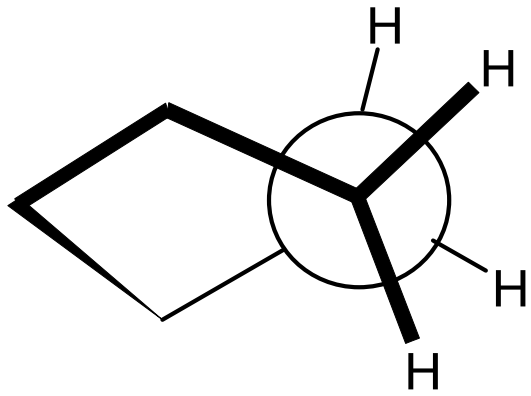
Newman projection of cyclobutane

Newmanova projekce jedné vazby

Conformation of cyclopropane and cyclobutane

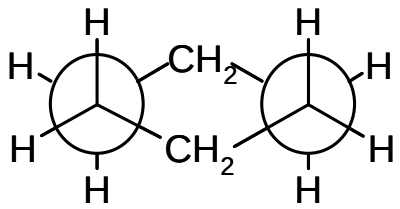


envelope conformation



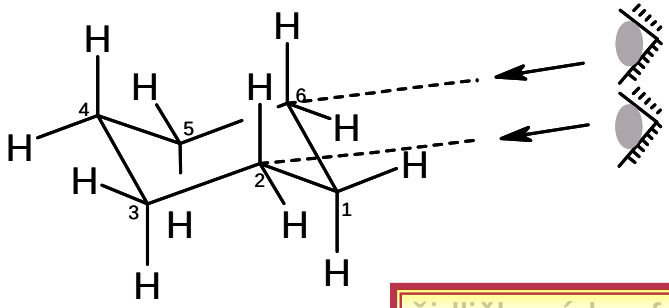
Newman projection of ring bond

Conformation of cyclohexane I
axial and equatorial bonds



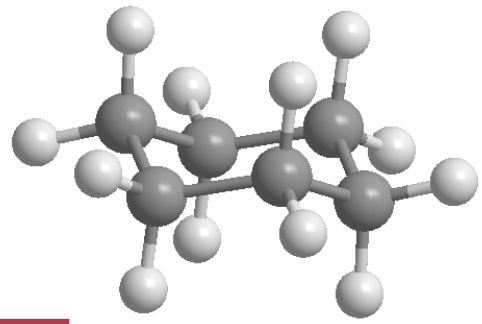
Newmanova projekce

Newman projection of ring C-C bonds

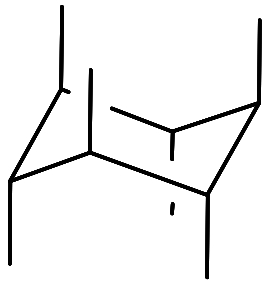


židličková konformace

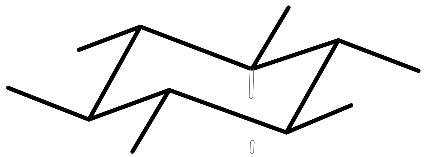
Chair conformation



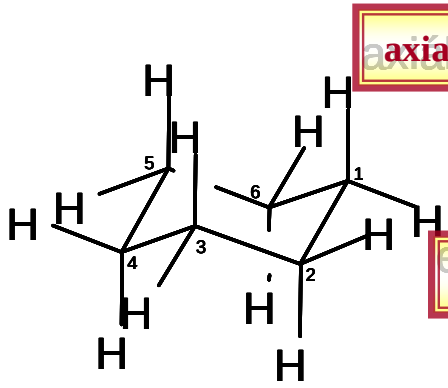
Conformation of cyclohexane II

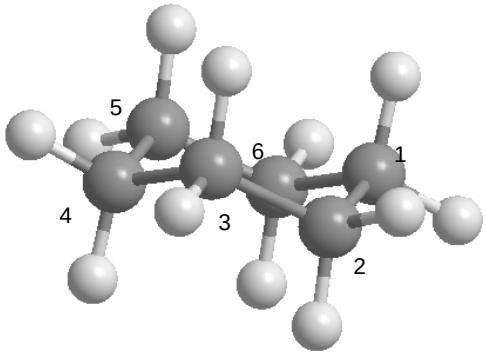


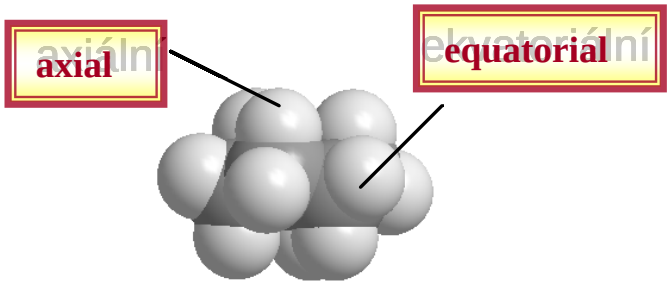
axial



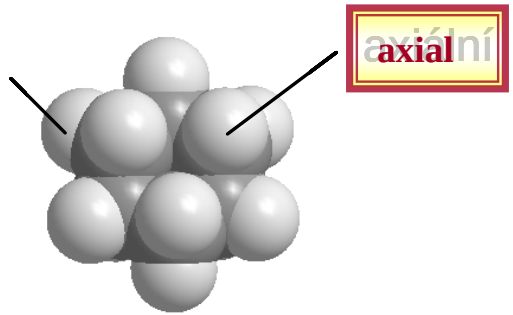
equatorial





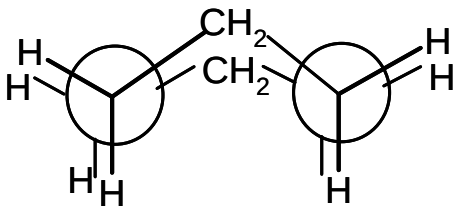


Side-view



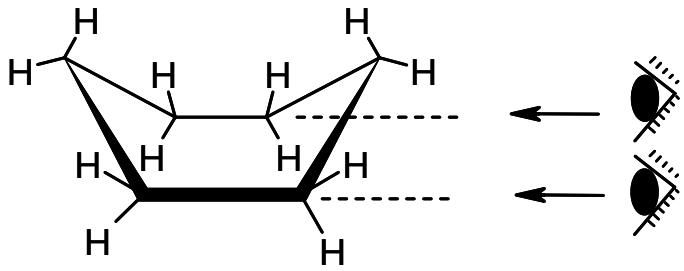
From the above

Conformation of cyclohexane II



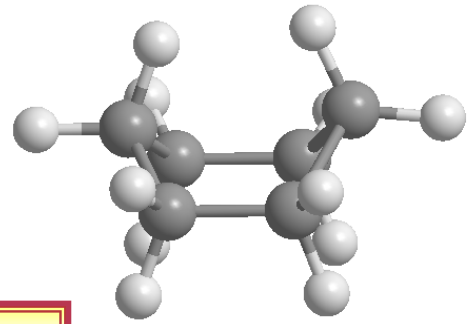
Newmanova projekce

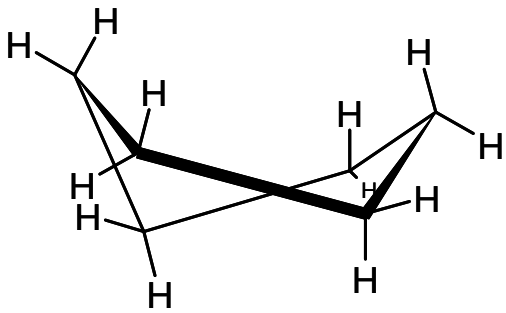
Newman projection



vaničková konformace

boat conformation

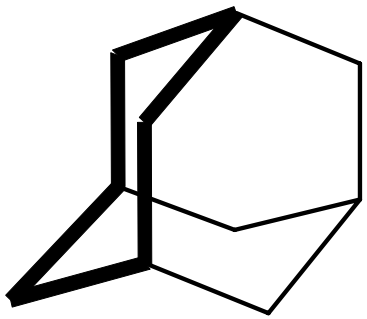




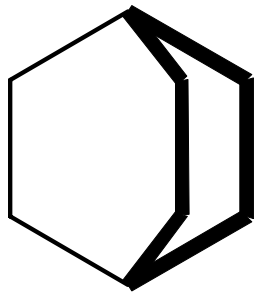
zkřížená vanička (twistová)

Twist-boat conformation

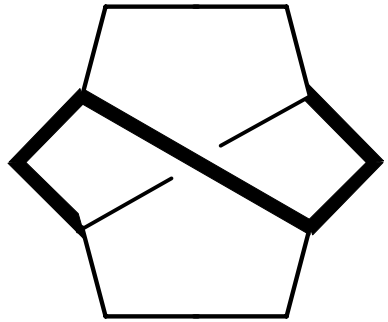
Conformation of cyclohexane III
- polycyclic structures



adamantane

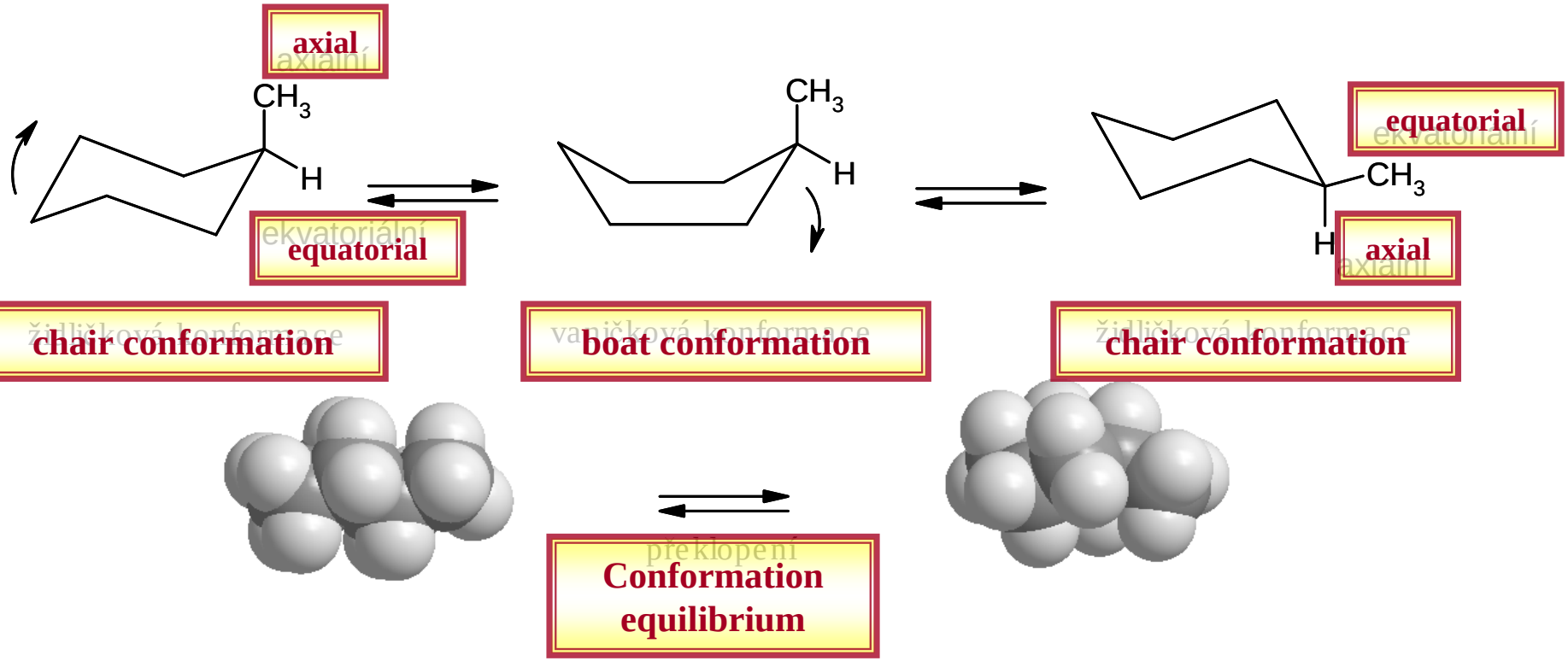


bicyclo[2.2.2]octane

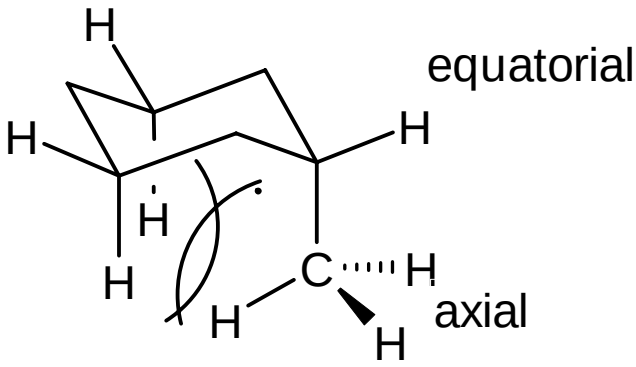


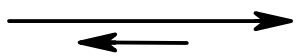
twistane

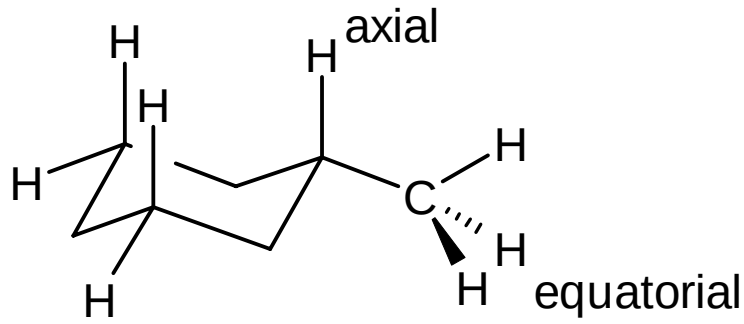
Conformation of cyclohexane IV
- dynamic equilibrium



Conformation of cyclohexane IV
- dynamic equilibrium



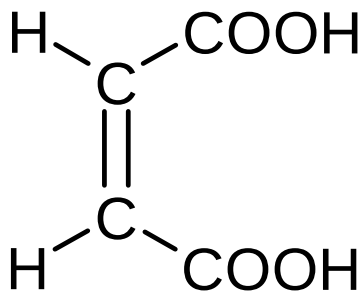




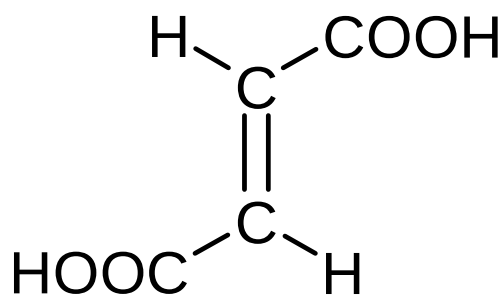
1,3-diaxial interaction

thermodynamically more stable

Positional isomers - diastereoisomers

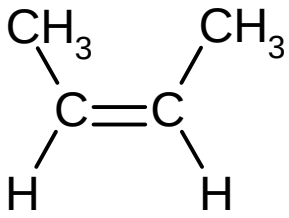


maleic acid
cis-but-2-enoic acid
(*Z*)-but-2-enoic acid
m.p. 137-140 °C

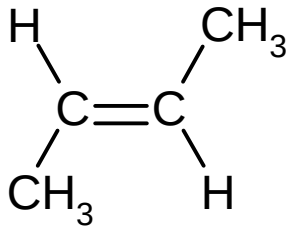


fumaric acid
trans-but-2-enoic acid
(*E*)-but-2-enoic acid
m,p, 298-300 °C

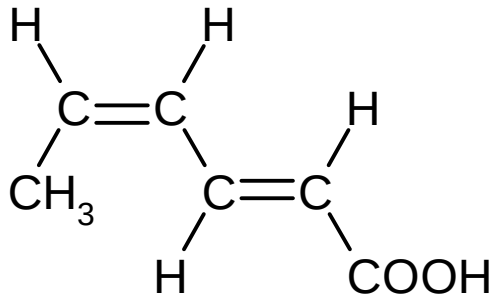
Positional isomers - diastereoisomers



cis-but-2-ene
(Z)-but-2-ene

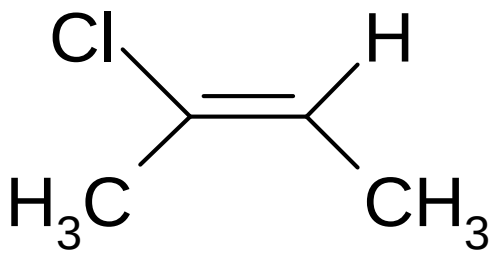


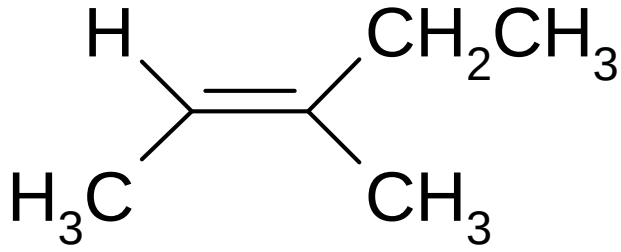
trans-but-2-ene
(E)-but-2-ene



2-*trans*,4-*cis*-hexa-2,4-dienoic acid
(2*E*, 4*Z*)-hexa-2,4-dienoic acid

Positional isomers - diastereoisomers



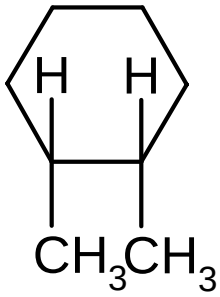


E or Z ???

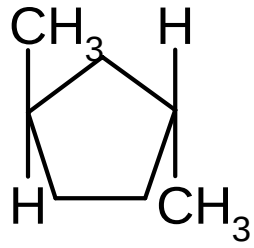
Priority determinationion

- atomic number
- „tree“ system

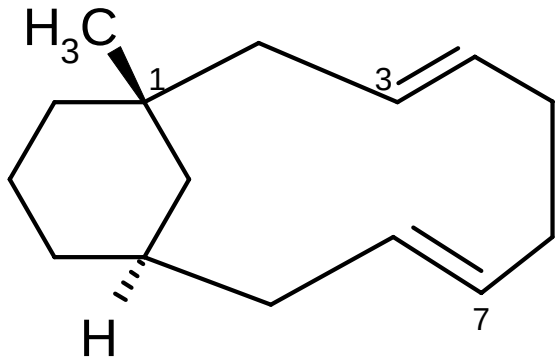
Positional isomers – diastereoisomers – cyclic compounds



cis-1,2-dimethylcyclohexane

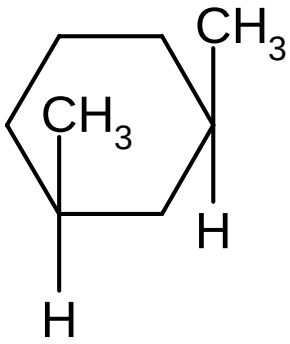


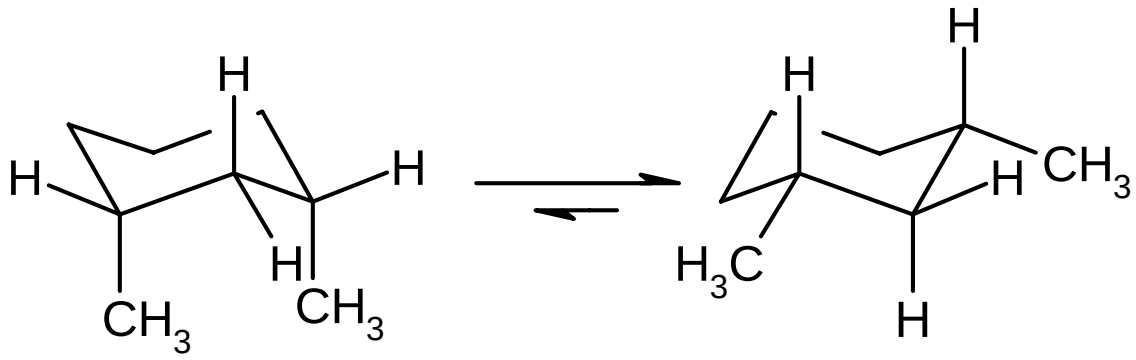
trans-1,3-dimethylcyclopentane



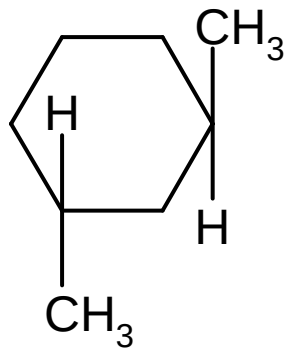
1-methyl-*trans*-bicyclo[8.3.1]tetradeca-3-*trans*,7-*trans*-diene

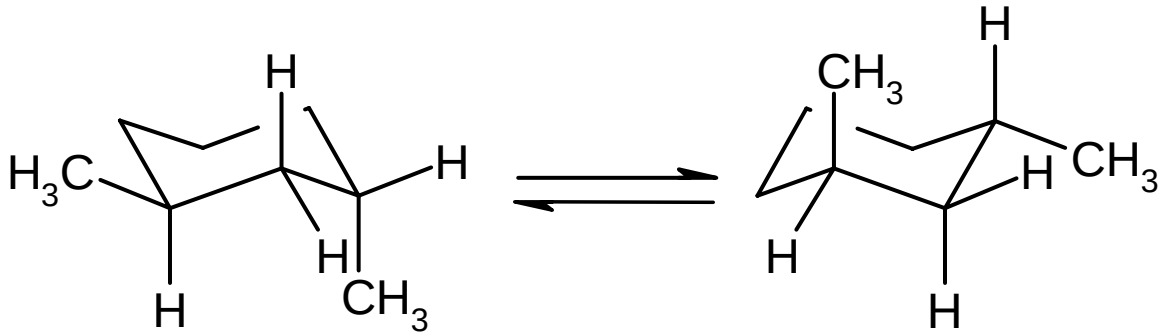
Positional isomers – diastereoisomers – cyclic compounds





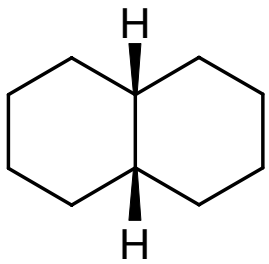
cis-1,3-dimethylcyclohexane



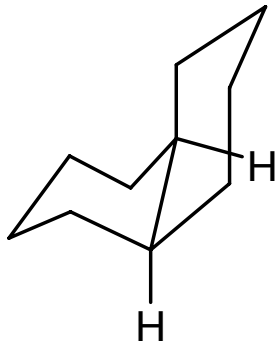


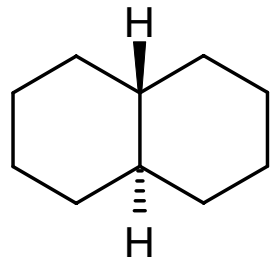
trans-1,3-dimethylcyclohexane

Positional isomers – diastereoisomers – cyclic compounds

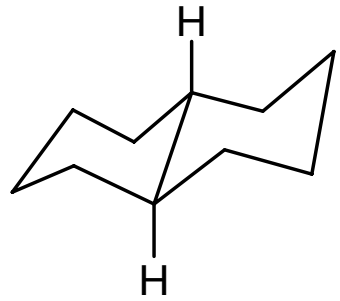


cis-decaline



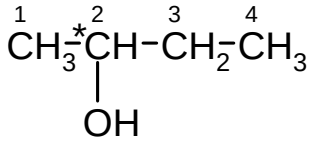


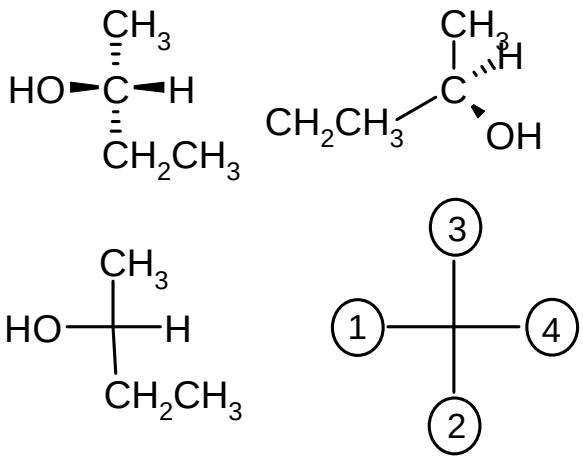
trans-decaline

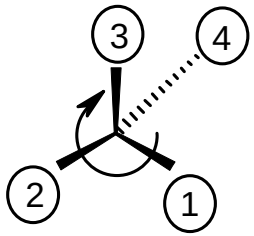


Organic Chemistry – molecular (carbon) scaffold

Optical isomers – chirality – Fischer projection

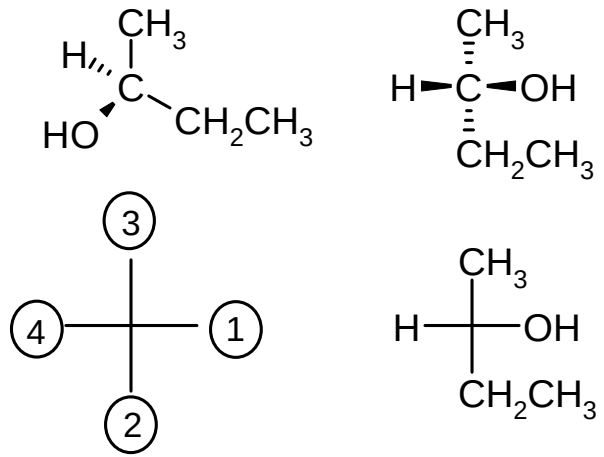


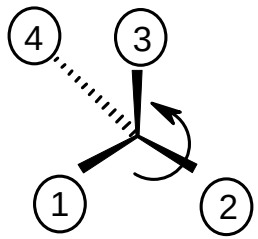




(*R*)-butane-2-ol

$[\alpha]_D^{27}$ = -13,5

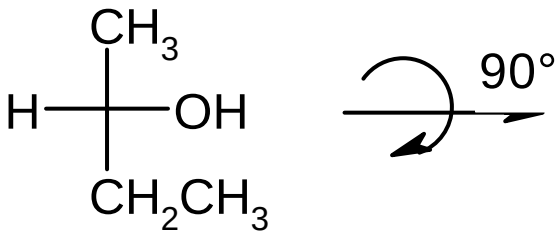




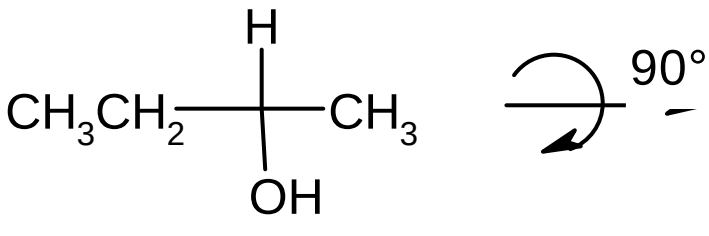
(*S*)-butane-2-ol

$[\alpha]_D^{27}$ = +13,5

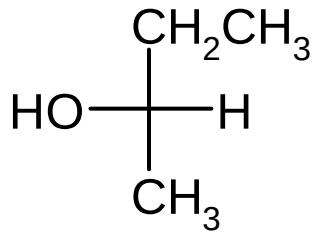
Optical isomers – chirality
Fischer projection – Fischer formulae



(*S*)-butane-2-ol

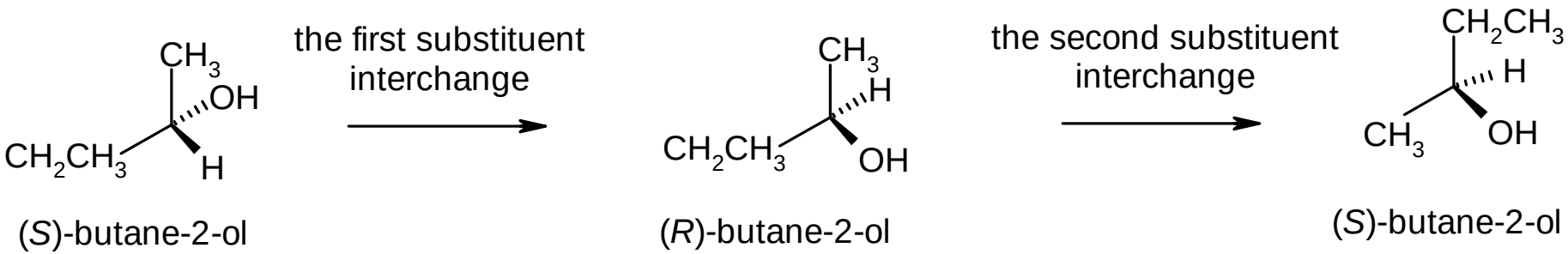


(*R*)-butane-2-ol



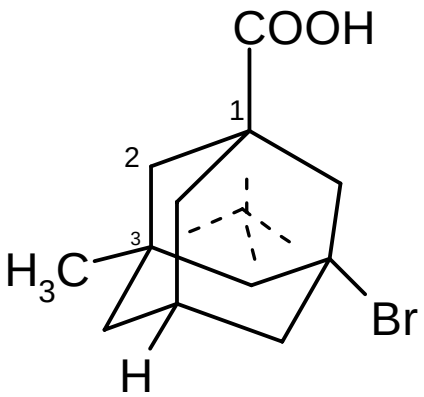
(*S*)-butane-2-ol

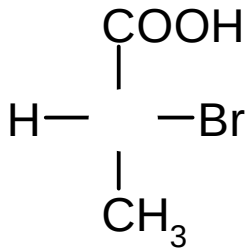
Optical isomers – chirality
substtituent interchange three-dimensional structure

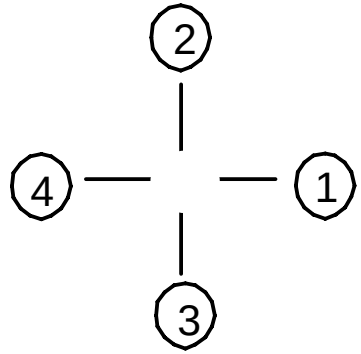


(*S*)-butane-2-ol (*R*)-butane-2-ol (*S*)-butane-2-ol

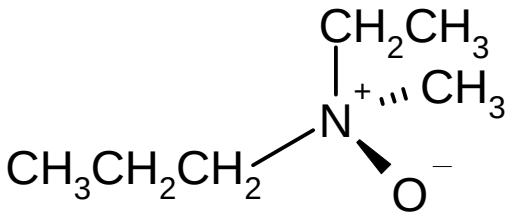
Optical isomers – chirality - other than on carbon

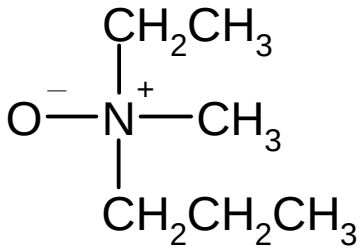


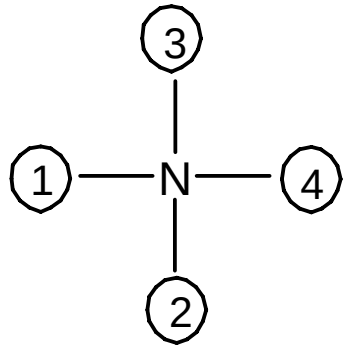




(*R*)-5-bromo-3-methyladamantane-1-carboxylic acid

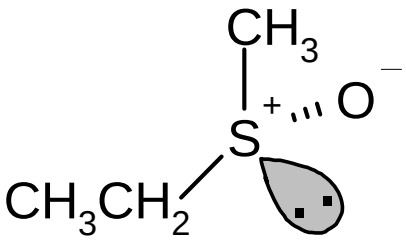


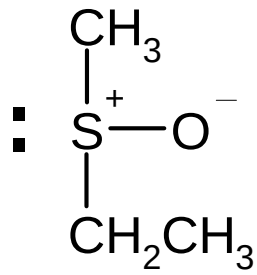


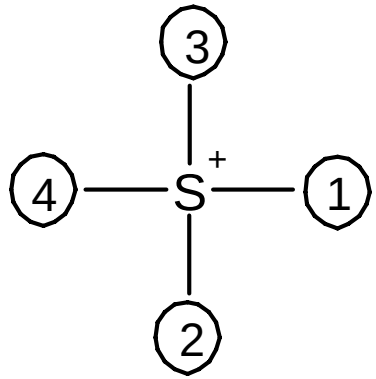


(*R*)-ethyl(methyl)propylamine-*N*-oxide

Optical isomers – chirality - other than on carbon







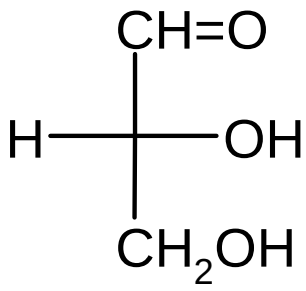
(*S*)-ethyl(methyl)sulfoxide

Organic Chemistry – molecular (carbon) scaffold

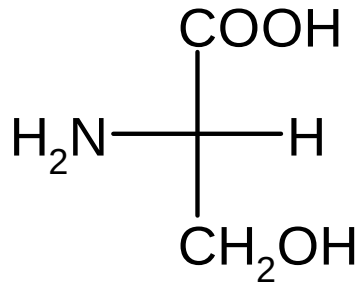
Optical isomers of natural compounds

D - and L- compounds, traditional and useful

ATTENTION !!! d-(+) and l-(-)

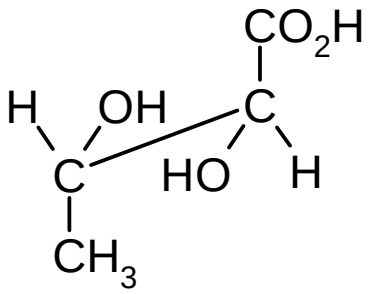


D-glyceraldehyde
(*R*)- 2,3-dihydroxypropanal



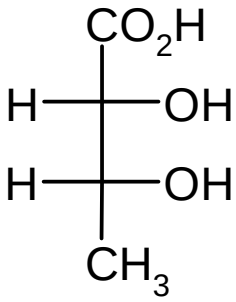
L-serine
(*S*)- 2-amino-3-hydroxypropanoic acid

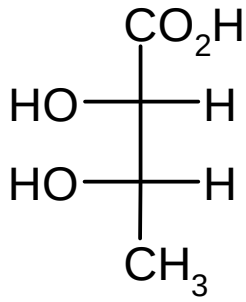
Definition of enantiomers, racemates and diastereoisomers



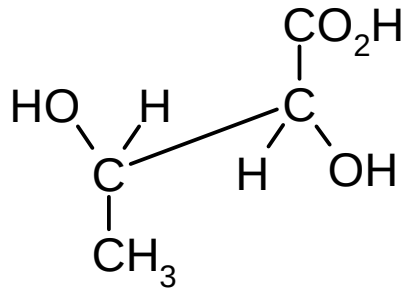
(2*R*,3*R*)-

I



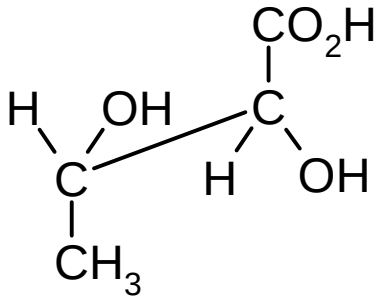


-2,3-dihydroxybutanoic acid



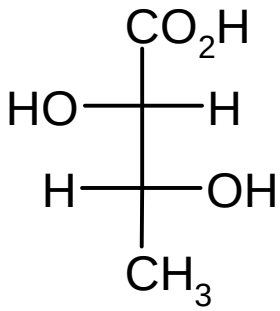
(2*S*,3*S*)-

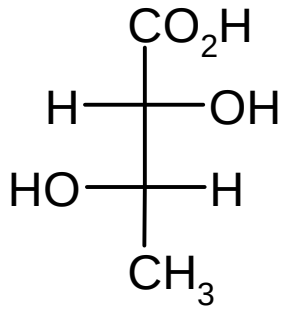
II



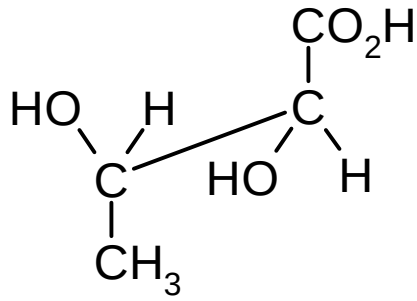
(2*S*,3*R*)-

III





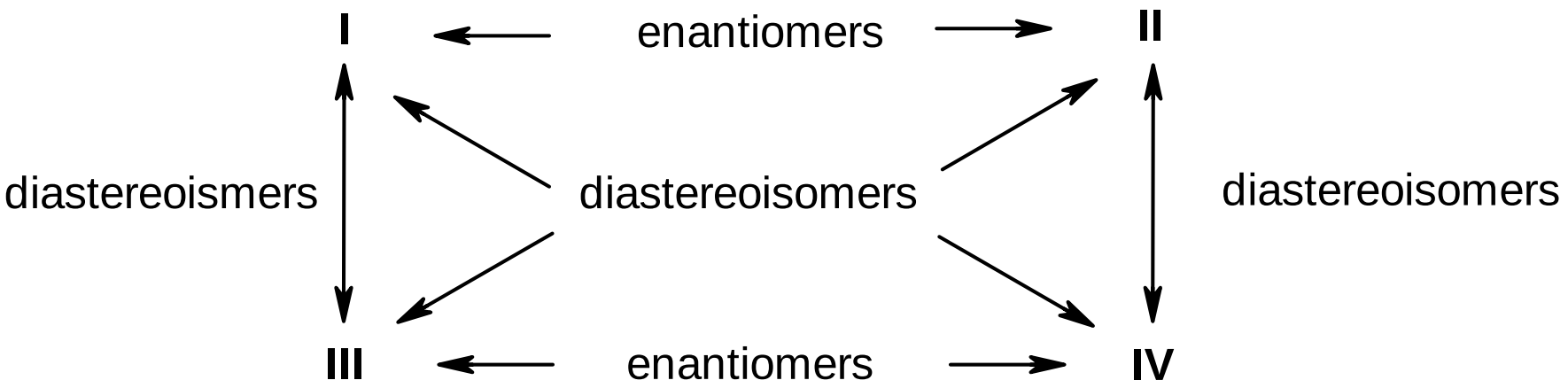
-2,3-dihydroxybutanoic acid



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

IV

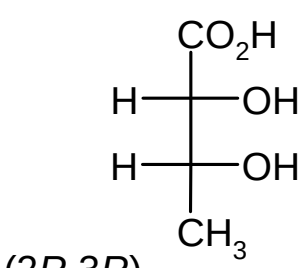
Definition of enantiomers, racemates and diastereoisomers



Racemate - 1 : 1 mixture of both enantiomers

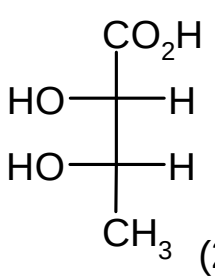
!!! Different physical properties – e.g. melting point !!!

Diastereoisomers *threo* - and *erythro* -



(2*R*,3*R*)-

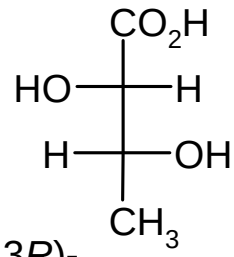
I



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

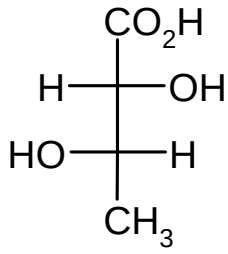
II

erythro-2,3-dihydroxybutanoic acid
(2*R**,*3R**)-2,3-dihydroxybutanoic acid



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

III

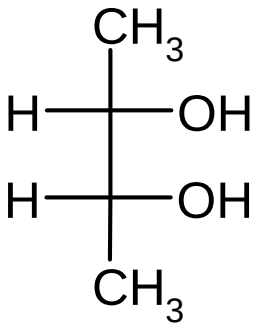


(2*R*,3*S*)-

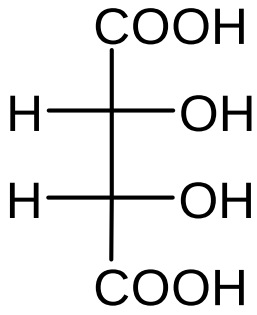
IV

threo-2,3-dihydroxybutanoic acid
(2*R**,3*S**)-2,3-dihydroxybutanoic acid

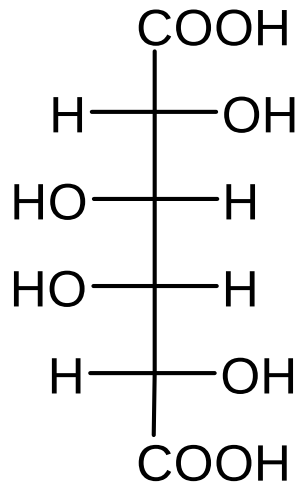
Diastereoisomers *meso* - case
achiral compounds with „asymmetric carbon“



meso-butane-2,3-diol



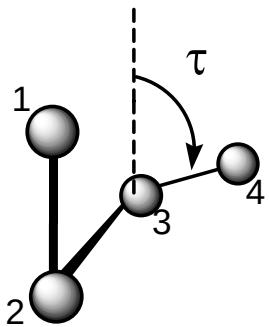
meso-tartaric acid



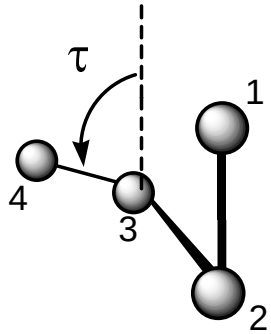
galactaric acid

Organic Chemistry – molecular (carbon) scaffold

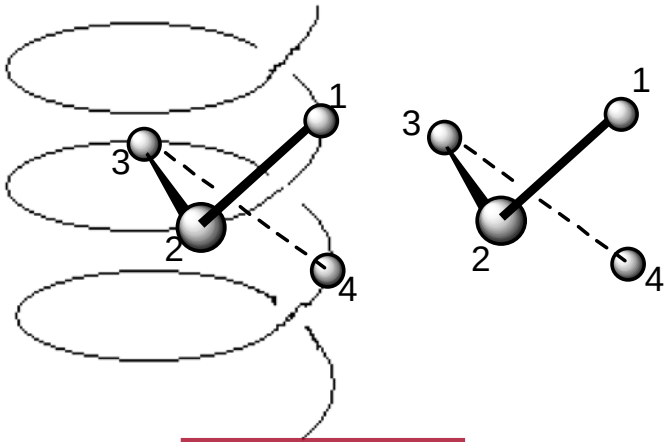
Helicity chiral compounds without „asymmetric carbon“



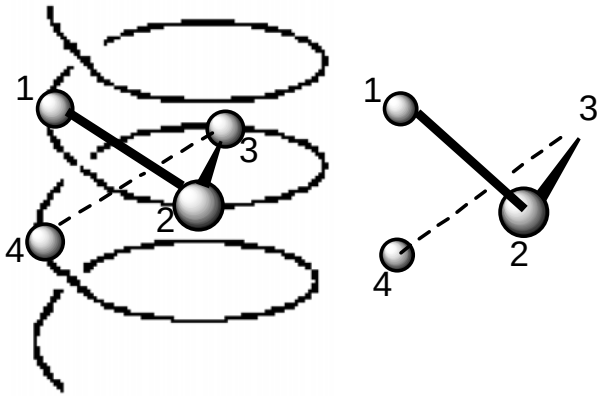
(+) or P



(=) or M



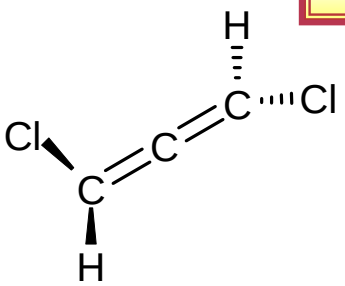
(+) or P

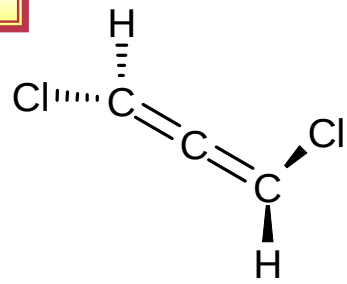


(=) or M

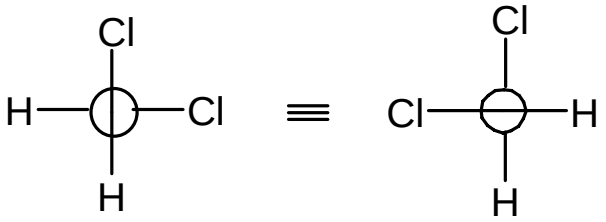
Organic Chemistry – molecular (carbon) scaffold

Helicity - allenes

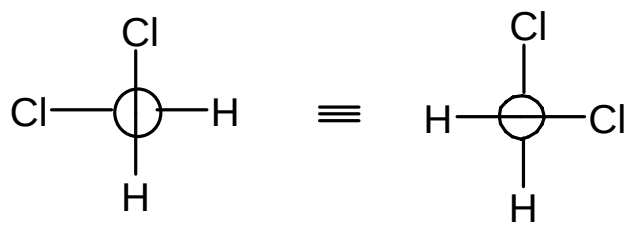


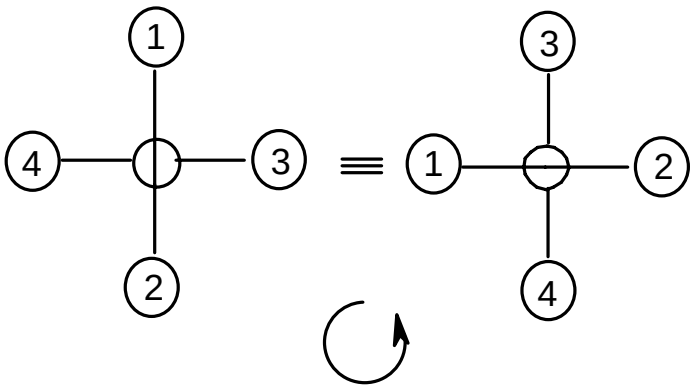


front view rear view

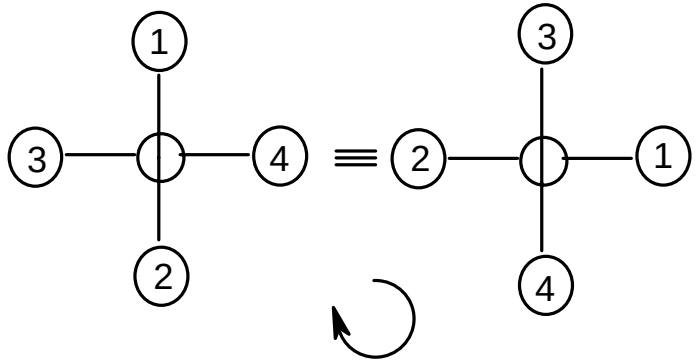


front view rear view





(a*S*)-1,3-dichloropropanediene



(a*R*)-1,3-dichloropropanediene

Chirality – specific rotation

$$[\alpha]_D^{20} = \alpha / l.c$$

α …… rotation measured in °
l …….. length od cuvette in dm
c ……. concentration in g/100 ml of solution

Solvent and temperature (20°C) should be given.

Optical isomers - identical absolute rotation value $+_x$ -
Diastereoisomers – no relationship in terms of numbers