2.2 Stereochemistry

Stereoisomerism

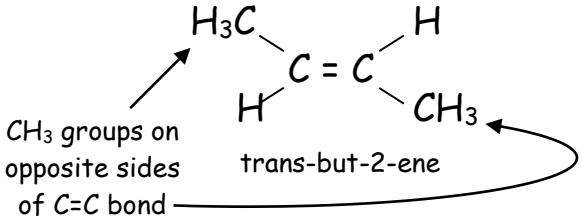
Isomers are defined as

- Compounds with the same molecular formula but different structural formula
    - stereoisomers have different spatial arrangement of atoms which makes superimposing of molecules on top of each other impossible.

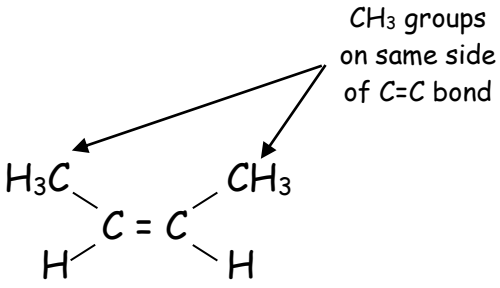
Geometric Isomerism

- Geometric isomerism occurs because of the lack of free rotation inside molecules
    - usually found in molecules containing C=C double bonds
    - π–bonds in alkenes prevent rotation

- but-2-ene has two structures



trans-but-2-ene



cis-but-2-ene

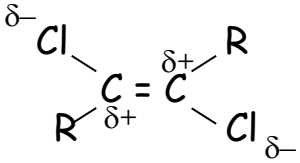
- in *trans*- isomers: groups are located on opposite side of the double bond
- in *cis*- isomers: groups are located on the same side of the double bond

Properties of Geometric Isomers

Isomer	Melting Point (°C)	Boiling Point (°C)
cis-but-2-ene	-139	+4
trans-but-2-ene	-106	+1
cis-1,2-dichloroethene	-80	+60
trans-1,2-dichloroethene	-50	+48

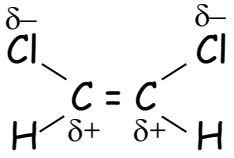
- trans-isomers have higher melting points than cis-isomers
  - trans-isomers pack more closely together in solid state
  - London Dispersion Forces forces higher due to close packing
  - Increased melting point for trans-isomers

- cis-isomers of polar molecules have higher boiling points than trans-isomers
  - shape of trans-isomer of 1,2-dichloroethene cancels out polarity
    - trans-isomer has a lower boiling point



trans-1,2-dichloroethene

  - shape of cis-isomer of 1,2-dichloroethene is more polar due to shape
    - cis-isomer has a higher boiling point

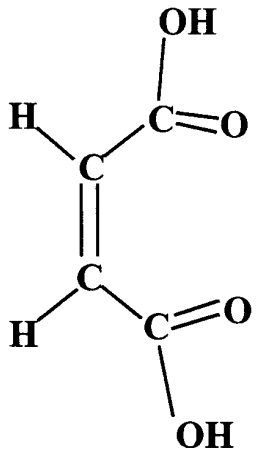


cis-1,2-dichloroethene

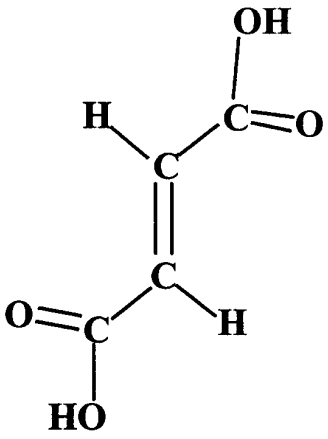
- some geometric isomers show different physical and chemical properties

e.g. but-2-enedioic acid

Name	Melting Point (°C)	Density (g cm^{-3})
cis-but-2-enedioic acid	139	1.59
trans-but-2-enedioic acid	300	1.64



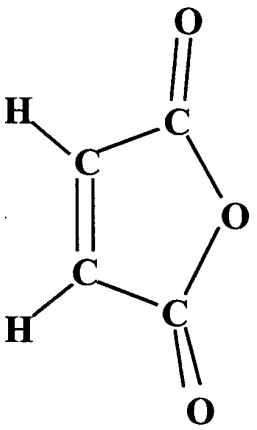
cis-but-2-enedioic acid



trans-but-2-enedioic acid

dehydration

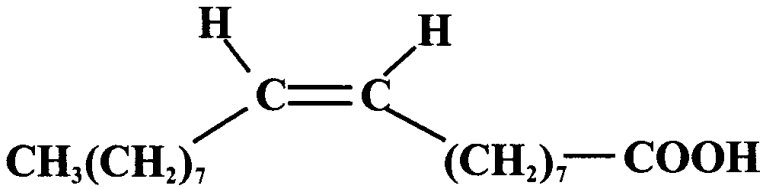
No dehydration



but-2-enedioic anhydride

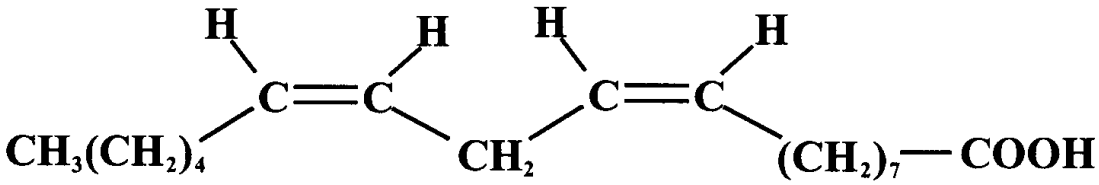
Fatty Acids

- cis- arrangement fatty acids do not pack together as closely as trans-arrangement fatty acids



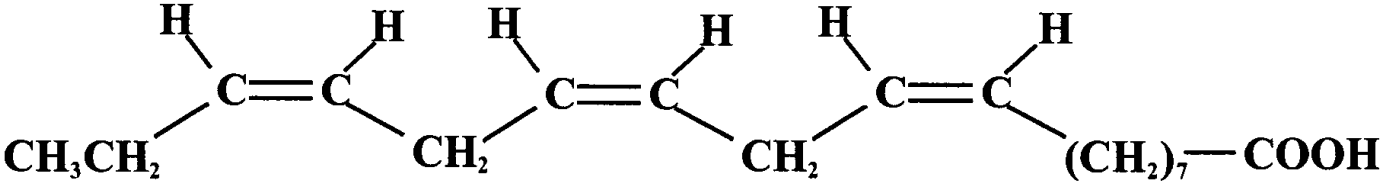
Oleic Acid

Octadec-cis-9-enoic acid



Linoleic Acid

Octadec-cis-9,cis-12-dienoic acid



linolenic Acid

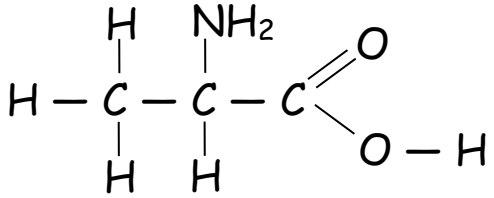
Octadec-cis-9,cis-12,cis-15-trienoic acid

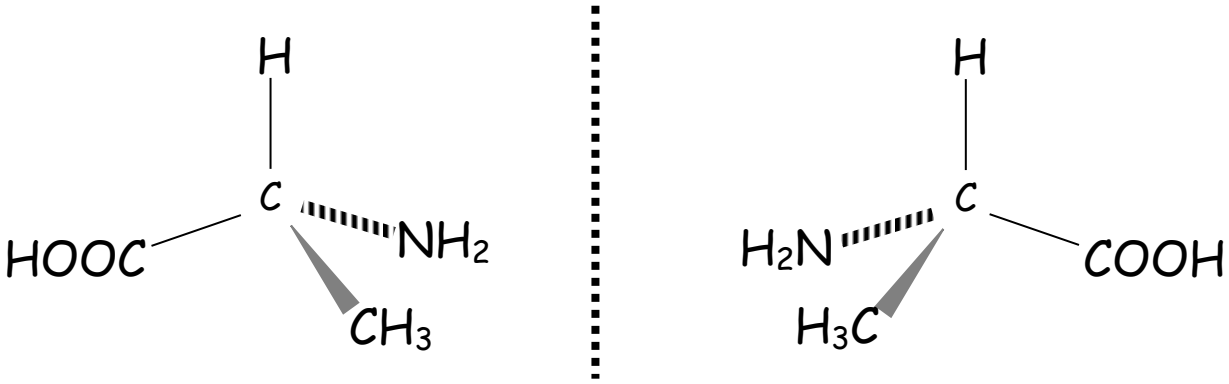
  - trans-arrangement fatty acids behave the same way as saturated fatty acids in the build up of heart disease

Optical Isomerism

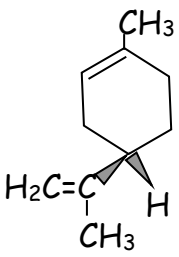
Optical isomerism occurs in compounds where four different groups are attached to a central tetrahedral carbon

e.g. 2-aminopropanoic acid

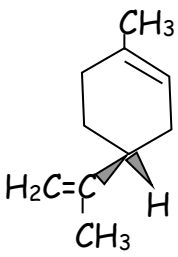




- images are mirror-images of each other
  - they are asymmetric (no centre of symmetry)
  - they cannot be superimposed on top of each other
  - known as enantiomers (enantio = Greek for opposite)
- central carbon is described as chiral
- optical isomers have identical chemical reactions
  - sometimes optical isomers can give different properties in chiral environments, usually in biological systems.
- Biological receptors can tell the difference between optical isomers



(-) limonene
Smells of Oranges



(+) limonene
Smells of Lemons

- In biological systems, only one optical isomer is generally present.

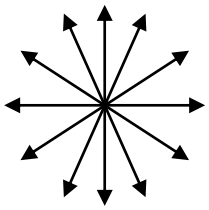
Plane Polarised Light

Optical isomers have identical physical properties except they have an opposite effect on plane polarised light

- Optical isomers are described as optically active

Light is electromagnetic radiation and a wave.

- Wave motion direction in *normal* light varies around 360° axis



- Plane polarised light, the wave motion only moves in one direction

- Optically active isomers rotate the plane of polarised light
  - Optical isomers which rotate the plane of polarised light to the <u>right</u> are given the sign (+)
  - Optical isomers which rotate the plane of polarised light to the <u>left</u> are given the sign (–)

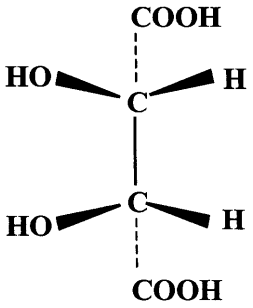
- A mixture of both optical isomers (i.e. both + and – forms) is optically inactive
  - called a **racemic** mixture

Questions

1.
   a) Draw structures for all possible isomers (structural and geometric) with molecular formula, C_4H_8.
   b) If that was too easy, try to draw structures for the 12 isomers with formula C_5H_{10}.

2. Draw the full structural formula for the first alkane to show optical isomerism and name the compound.

3. Would you expect the isomer of tartaric acid shown here to be optically active? Explain your answer.



4. Thalidomide is a notorious drug. In the 1960s it was prescribed to pregnant women to treat morning sickness. There are two optical isomers. One of the isomers provided an effective treatment for the morning sickness but unfortunately the other caused serious malformation of the foetus.

   Explain why thalidomide exhibits optical isomerism.