Isomerism

- **Isomers** are molecules with the same molecular formula but different chemical structures.
  - That is, isomers contain the same number of atoms of each element, but have different arrangements of their atoms in space
- There are two main forms of isomerism:
  - Structural isomerism
  - Stereoisomerism
- Isomers do not necessarily share similar properties, unless they also have the same functional groups.
- There are many different classes of isomers, like positional isomers, *cis-trans* isomers and enantiomers, etc.

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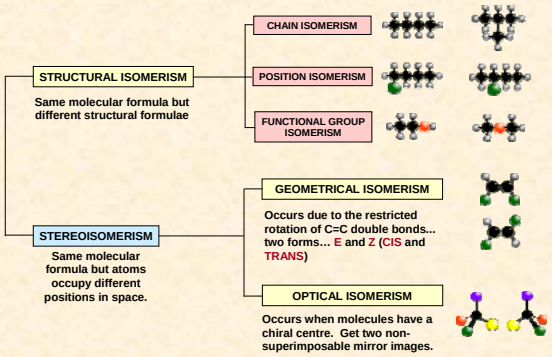
TYPES OF ISOMERISM



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STRUCTURAL ISOMERISM - INTRODUCTION

COMPOUNDS HAVE THE SAME MOLECULAR FORMULA
BUT DIFFERENT STRUCTURAL FORMULA

Chain
different arrangements of the carbon skeleton
similar chemical properties
slightly different physical properties
more branching = lower boiling point

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Positional
same carbon skeleton
same functional group
functional group is in a different position
similar chemical properties - slightly different physical properties

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Positional
same carbon skeleton
same functional group
functional group is in a different position
similar chemical properties - slightly different physical properties

Functional Group
different functional group
different chemical properties
different physical properties

- Sometimes more than one type of isomerism occurs in the same molecule.
- The more carbon atoms there are, the greater the number of possible isomers

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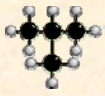
STRUCTURAL ISOMERISM - CHAIN

caused by different arrangements of the carbon skeleton
similar chemical properties
slightly different physical properties
more branching = lower boiling point

There are two structural isomers of C_4H_{10}. One is a straight chain molecule where all the carbon atoms are in a single row. The other is a branched molecule where three carbon atoms are in a row and one carbon atom sticks out of the main chain.

BUTANE
straight chain

2-METHYLPROPANE
branched



C_4H_{10}

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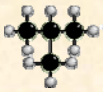
STRUCTURAL ISOMERISM - CHAIN

DIFFERENCES BETWEEN CHAIN ISOMERS

Chemical	Isomers show similar chemical properties because the same functional group is present.
Physical	Properties such as density and boiling point show trends according to the of the degree of branching
Boiling Point	"straight" chain isomers have higher values than branched ones the greater the degree of branching the lower the boiling point branching decreases the effectiveness of intermolecular forces less energy has to be put in to separate the molecules

- 0.5°C
straight chain

- 11.7°C
branched



greater branching
= lower boiling point

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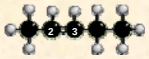
STRUCTURAL ISOMERISM - POSITIONAL

molecule has the same carbon skeleton
molecule has the same same functional group... BUT
the functional group is in a different position
have similar chemical properties / different physical properties

Example 1 POSITION OF A DOUBLE BOND IN ALKENES

PENT-1-ENE
double bond between carbons 1 and 2



PENT-2-ENE
double bond between carbons 2 and 3

There are no other isomers with five C's in the longest chain but there are three other structural isomers with a chain of four carbons plus one in a branch.

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STRUCTURAL ISOMERISM - POSITIONAL

molecule has the same carbon skeleton
molecule has the same same functional group... BUT
the functional group is in a different position
have similar chemical properties / different physical properties

Example 2 POSITION OF A HALOGEN IN A HALOALKANE

1-CHLOROBUTANE
halogen on carbon 1

2-CHLOROBUTANE
halogen on carbon 2

BUT

is NOT
3-CHLOROBUTANE

Moving the chlorine along the chain makes new isomers; the position is measured from the end nearest the functional group... the third example is 2- NOT 3-chlorobutane.

There are 2 more structural isomers of C_4H_9Cl but they have a longest chain of 3

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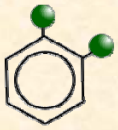
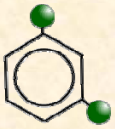
STRUCTURAL ISOMERISM - POSITIONAL

molecule has the same carbon skeleton
molecule has the same same functional group... BUT
the functional group is in a different position
have similar chemical properties / different physical properties

Example 3 RELATIVE POSITIONS ON A BENZENE RING



1,2-DICHLOROBENZENE
ortho dichlorobenzene



1,3-DICHLOROBENZENE
meta dichlorobenzene

1,4-DICHLOROBENZENE
para dichlorobenzene

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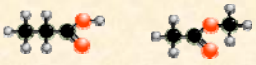
STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

molecules have same molecular formula
molecules have different functional groups
molecules have different chemical properties
molecules have different physical properties

ALCOHOLS and ETHERS

ALDEHYDES and KETONES

ACIDS and ESTERS



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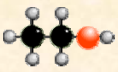
STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

ALCOHOLS and ETHERS



	ETHANOL	METHOXYMETHANE
Name		
Classification	ALCOHOL	ETHER
Functional Group	R-OH	R-O-R
Physical properties	polar O-H bond gives rise to hydrogen bonding. get higher boiling point and solubility in water	No hydrogen bonding low boiling point insoluble in water
Chemical properties	Lewis base Wide range of reactions	Inert

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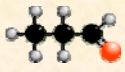
STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

ALDEHYDES and KETONES




Name	PROPANAL	PROPANONE
Classification	ALDEHYDE	KETONE
Functional Group	R-CHO	R-CO-R
Physical properties	polar C=O bond gives dipole-dipole interaction	polar C=O bond gives dipole-dipole interaction
Chemical properties	easily oxidised to acids of same number of carbons reduced to 1° alcohols	undergo oxidation under extreme conditions only reduced to 2° alcohols

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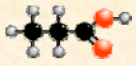
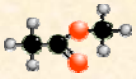
STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

CARBOXYLIC ACIDS and ESTERS

Name	PROPANOIC ACID	METHYL ETHANOATE
Classification	CARBOXYLIC ACID	ESTER
Functional Group	R-COOH	R-COOR
Physical properties	O-H bond gives rise to hydrogen bonding. get higher boiling point and solubility in water	No hydrogen bonding insoluble in water
Chemical properties	acidic react with alcohols	fairly unreactive hydrolysed to acids

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STEREOISOMERISM

Molecules have the **SAME MOLECULAR FORMULA** but the atoms are joined to each other in a **DIFFERENT SPACIAL ARRANGEMENT** - they occupy a different position in 3-dimensional space.

There are two types...

- GEOMETRICAL ISOMERISM
- OPTICAL ISOMERISM

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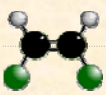
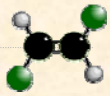
GEOMETRICAL ISOMERISM IN ALKENES

Introduction

- an example of stereoisomerism
- found in some, but not all, alkenes
- occurs due to the **RESTRICTED ROTATION** OF C=C bonds
- get two forms...

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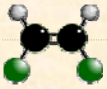
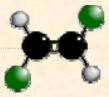

CIS (Z)
Groups/atoms are on the **SAME SIDE** of the double bond

TRANS (E)
Groups/atoms are on **OPPOSITE SIDES** across the double bond

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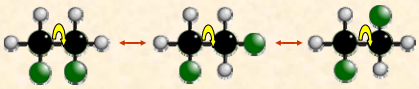
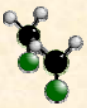
GEOMETRICAL ISOMERISM

RESTRICTED ROTATION OF C=C BONDS

Single covalent bonds can easily rotate. What appears to be a different structure is not. It looks like it but, due to the way structures are written out, they are the same.



ALL THESE STRUCTURES ARE THE SAME BECAUSE C-C BONDS HAVE 'FREE' ROTATION



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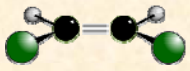
GEOMETRICAL ISOMERISM

RESTRICTED ROTATION OF C=C BONDS

C=C bonds have restricted rotation so the groups on either end of the bond are 'frozen' in one position; it isn't easy to flip between the two.



This produces two possibilities. The two structures cannot interchange easily so the atoms in the two molecules occupy different positions in space.

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GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

CIS / TRANS Should only be used when there are two H's and two non-hydrogen groups attached to each carbon.

cis non-hydrogen groups / atoms on the SAME side of C=C bond

trans non-hydrogen groups / atoms on OPPOSITE sides of C=C bond

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trans non-hydrogen groups / atoms on OPPOSITE sides of C=C bond

cis trans *cis* trans

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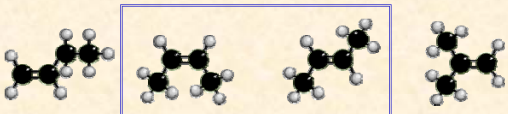
GEOMETRICAL ISOMERISM

Isomerism in butene

There are 3 structural isomers of C_4H_8 that are alkenes*. Of these ONLY ONE exhibits geometrical isomerism.



but-1-ene | *cis* but-2-ene (Z) but-2-ene | *trans* but-2-ene (E) but-2-ene | 2-methylpropene

* YOU CAN GET ALKANES WITH FORMULA C_4H_8 IF THE CARBON ATOMS ARE IN A RING

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GEOMETRICAL ISOMERISM

How to tell if it exists

Two different atoms/groups attached	Two different atoms/groups attached	✓	GEOMETRICAL ISOMERISM
Two similar atoms/groups attached	Two similar atoms/groups attached	✗	Once you get two similar atoms/groups attached to one end of a C=C, you cannot have geometrical isomerism
Two similar atoms/groups attached	Two different atoms/groups attached	✗	
Two different atoms/groups attached	Two different atoms/groups attached	✓	GEOMETRICAL ISOMERISM

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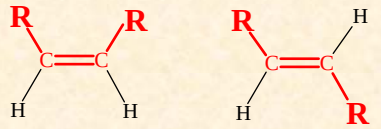
CIS / TRANS ISOMERS

Because there is no rotation about a carbon-carbon bond, isomers are possible.



cis substituents on the same side of main chain

trans substituents on opposite sides of main chain

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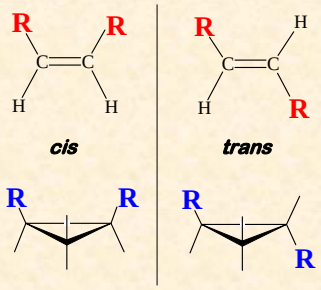
COMPARE *cis / trans* ISOMERS IN RING COMPOUNDS



cis ***trans***

In alkenes *cis / trans* isomers used to be called geometric isomers, a term generally not used for cyclic systems (rings). You may find the term geometric isomers used in older books or papers.

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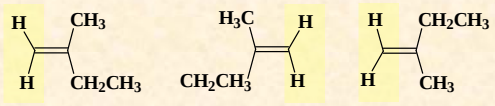
TWO IDENTICAL SUBSTITUENTS

If an alkene has two identical substituents on one of the double bond carbons, ***cis / trans*** (or E / Z) isomers are not possible.



all of these compounds are identical
no ***cis / trans*** isomers

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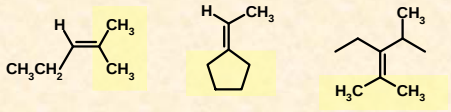
SOME OTHER COMPOUNDS WITH NO *CIS / TRANS*



no ***cis / trans*** isomers

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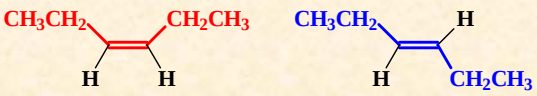
NAMING cis / trans ISOMERS OF ALKENES

main chain stays on same side of double bond = *cis*

main chain crosses to other side of double bond = *trans*



cis-3-hexene ***trans***-3-hexene

notice that these prefixes are in italics

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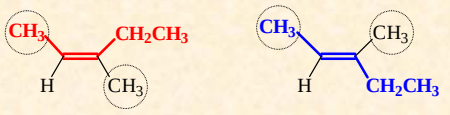
Be Careful !!!

The main chain determines cis / trans in the IUPAC name



cis-3-methyl-2-pentene

This compound is ***cis*** but the two methyl groups are ***....trans*** to each other.

trans-3-methyl-2-pentene

This compound is ***trans*** but the two methyl groups are ***....cis*** to each other.

but the terms *cis* and *trans* are also used to designate the relative position of two groups

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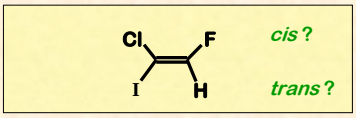
E/Z SYSTEM OF NOMENCLATURE

To avoid the confusion between what the main chain is doing and the relationship of two similar groups ..... the IUPAC invented the E/Z system.



This system also allows alkenes like the one above to be classified .....
an impossibility with cis / trans.

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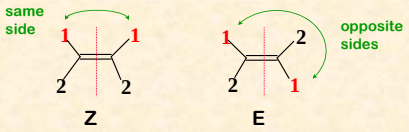
E / Z NOMENCLATURE

In this system the two groups attached to each carbon are assigned a priority (1 or 2).

If priority 1 groups are both on same side of double bond:

Z isomer = zusammen = *together (in German)*



If priority 1 groups on opposite sides of double bond:

E isomer = entgegen = *opposite (in German)*

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GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

E / Z

Z *(zusammen)* — higher priority groups / atoms on the SAME side of C=C bond

E *(entgegen)* — higher priority groups / atoms on OPPOSITE sides of C=C bond

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E *(entgegen)* — higher priority groups / atoms on OPPOSITE sides of C=C bond

To determine priority, the Cahn, Ingold and Prelog convention is used.

eg $C_2H_5 > CH_3 > H$ and $I > Br > Cl > F > C > H$

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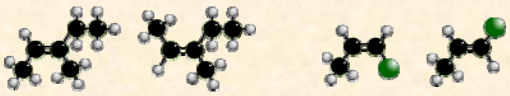

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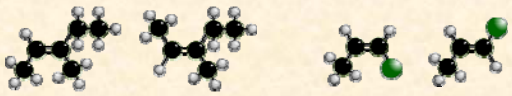

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Cahn–Ingold–Prelog priority rules

- The **Cahn–Ingold–Prelog priority rules**, **CIP system** or **CIP conventions** (after Robert Sidney Cahn, Christopher Kelk Ingold and Vladimir Prelog) are a set of rules used in organic chemistry to name the stereoisomers of a molecule.
- A molecule may contain any number of stereocenters and any number of double bonds, and each gives rise to two possible configurations.
- The purpose of the CIP system is to assign an R or S descriptor to each stereocenter and an E or Z descriptor to each double bond so that the configuration of the entire molecule can be specified uniquely by including the descriptors in its systematic name.

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Cahn–Ingold–Prelog priority rules

Steps for naming

- The steps for naming molecules using the CIP system are often presented as:
- Identification of stereocenters and double bonds
- Assignment of priorities to the groups attached to each stereocenter or double-bonded atom
- Assignment of R/S and E/Z descriptors

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Cahn–Ingold–Prelog priority rules

Assignment of priorities

- Compare the atomic number (Z) of the atoms directly attached to the stereocenter; the group having the atom of higher atomic number receives higher priority.
- If there is a tie, we must consider the atoms at distance 2 from the stereocenter—as a list is made for each group of the atoms bonded to the one directly attached to the stereocenter.
- Each list is arranged in order of decreasing atomic number. Then the lists are compared atom by atom; at the earliest difference, the group containing the atom of higher atomic number receives higher priority.

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Cahn–Ingold–Prelog priority rules

Assignment of priorities

- If there is still a tie, each atom in each of the two lists is replaced with a sub-list of the other atoms bonded to it (at distance 3 from the stereocenter), the sub-lists are arranged in decreasing order of atomic number, and the entire structure is again compared atom by atom.
- This process is repeated, each time with atoms one bond farther from the stereocenter, until the tie is broken.

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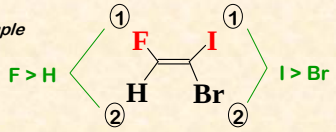
ASSIGNING PRIORITIES

1. Look at the atoms attached to each carbon of the double bond.
2. The atom of higher atomic number has higher (1) priority.

example



Since the 1's are on the same side, this compound is Z

(Z)-1-bromo-2-fluoro-1-iodoethene

notice use of parentheses

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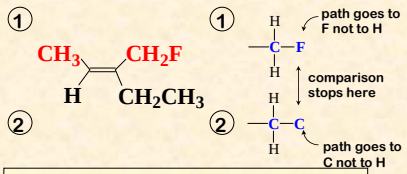
3. If you can't decide using the first atoms attached, go out to the next atoms attached. If there are non-equivalent paths, always follow the path with atoms of higher atomic number.

Once you find a difference, you can stop.



This molecule has Z configuration.

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Cahn - Ingold - Prelog Sequence Rules

- If a group contains multiple bonds, the doubly or triply bonded atoms are counted as two or three of those atoms, respectively.

- Thus the carbonyl group is considered to have two carbon - oxygen bonds, one actual and one theoretical.

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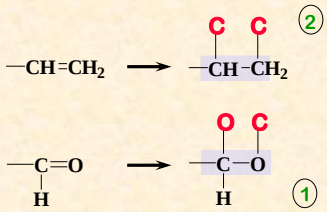
4. The atoms in double bonds are "replicated" at either end of the double bond.



Then, when comparing groups, follow the path of highest priority as before.

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Cahn - Ingold - Prelog Sequence Rules

- A cyano group is considered to have three carbon - nitrogen bonds, one actual and two theoretical. For comparison purposes, an actual bond ranks higher than a theoretical bond of the same type.

- For example, when ranking the cyano group against the displayed group takes priority, due to its three actual carbon - nitrogen bonds.

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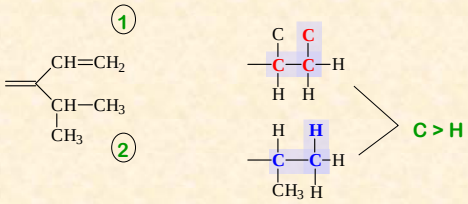
EXAMPLE USING REPLICATION



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MORE THAN ONE DOUBLE BOND

DIENES AND POLYENES

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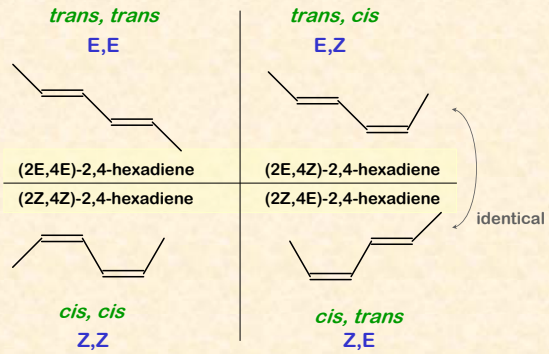
DIENES AND POLYENES
Hexadiene



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