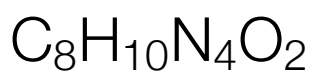
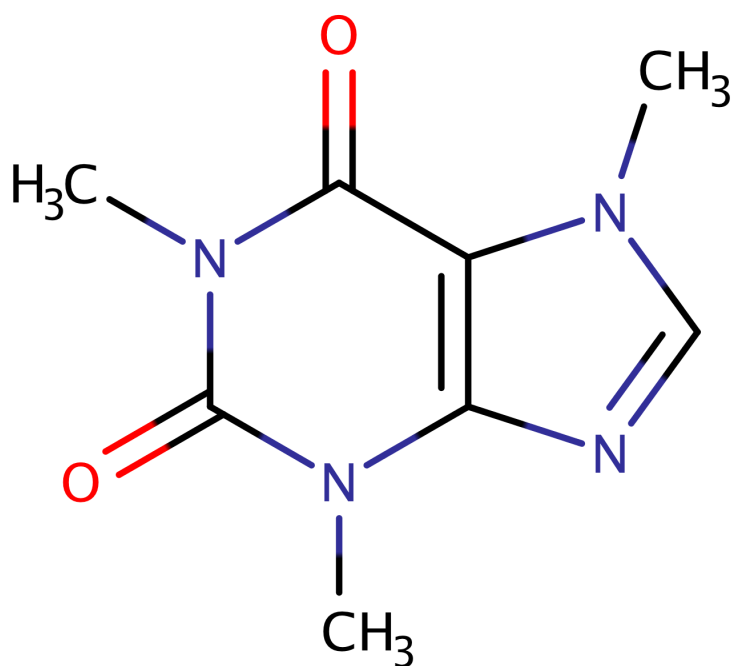


# Organic Chemistry



1,3,7-trimethylpurine-2,6-dione

*or*

Caffeine

Chapters 8 to 12

# 1 Functional Groups

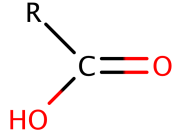
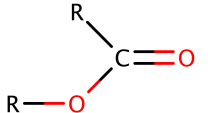
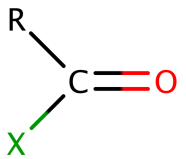
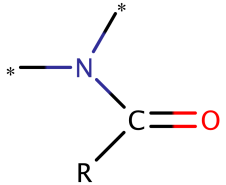
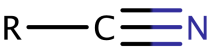
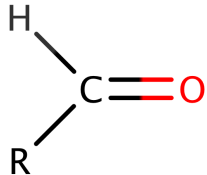
## 1.1 Overview

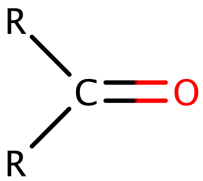
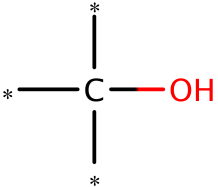
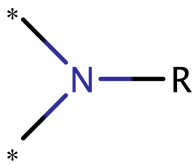
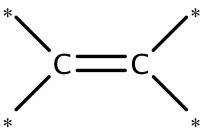
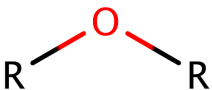
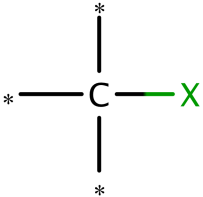
Functional groups are the main determinant of the chemical properties of a molecule. Molecules with the same functional group are of the same *family* and similar *chemical properties*.

Functional groups can be any size — the ketone functional group is just an oxygen double-bonded to a carbon atom in any position, while the carboxylic acid functional group has a more complex structure.

## 1.2 Basic Functional Groups

Note that this table is ordered based on the *priority* of the functional group, in terms of where it appears in an IUPAC-named chemical compound.

Name	Prefix Form	Suffix Form	Structure
Carboxylic Acid	carboxy-*	*-oic acid	
Ester	-	*-oate	
Acyl Halide	halocarbonyl-*	*-oyl halide	
Amide	carbamoyl-*	*-amide	
Nitrile	cyano-*	*-nitrile	
Aldehyde	formyl-*	*-al	

Ketone	oxo-*	*-one	
Alcohol	hydroxy-*	*-ol	
Amine	amino-*	*-amine	
Alkene	alkenyl-*	*-ene	
Ether	alkoxy-*	-	
Alkyl Halide	halogen-*	-	

## 2 Isomers

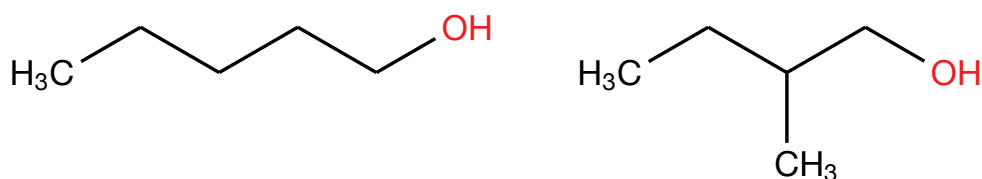
### 2.1 Overview

Isomers are molecules that share the same structural formula, yet exist in different forms. The two main forms of isomerism are structural isomerism and stereoisomerism. In both cases, the molecular formula of the compounds is the same, while the chemical and physical properties may differ greatly.

### 2.2 Structural Isomerism

#### 2.2.1 Chain Isomerism

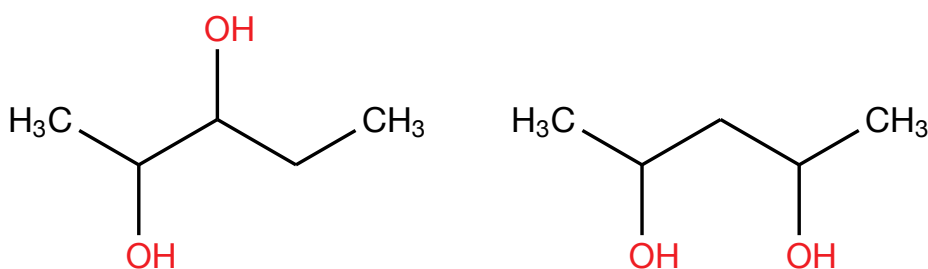
In chain isomerism, molecules have the same functional groups, except they are placed in different positions along the carbon chain. Chain isomers typically have similar chemical properties, but different physical properties (since the shape of the carbon chain can determine the strength of intermolecular interactions).



Pentanol and 3-methylbutan-1-ol are chain isomers.

#### 2.2.2 Positional Isomerism

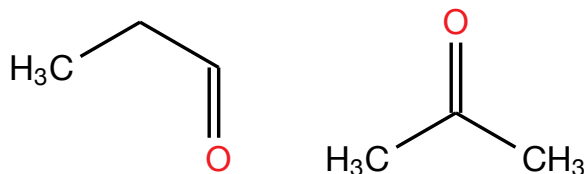
Positional isomers have the same arrangement of carbon chains, and the same functional groups. However, said functional groups are placed at different positions.



Butan-2,3-diol and butan-2,4-diol are positional isomers.

### 2.2.3 Functional Group Isomerism

This is somewhat a misnomer, since it is exactly the opposite of what it seems to intuit. Functional group isomers share only their molecular formulas; the carbon chain, the functional groups, etc. are all different.



Propanal and acetone are functional group isomers.

## 2.3 Stereoisomerism

### 2.3.1 Overview

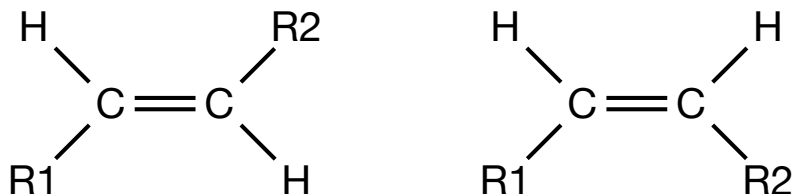
Stereoisomers of molecules have the same structure and functional groups, but those groups are arranged in a spatially differing way. The main forms of stereoisomerism are cis/trans (or E/Z) isomerism, and optical isomerism.

Note that for certain cis/trans (E/Z) isomers, the trans (or E) variant can 'pack' better, resulting in a higher melting point. This doesn't affect the boiling point, since the molecules are too far apart in the gaseous phase for this to matter.

Additionally, the presence of *intramolecular* (within the same molecule) hydrogen bonds can also be a factor, since it reduces the strength of *intermolecular* hydrogen bonds. Other than these, the chemical and physical properties of stereoisomers are mostly the same.

### 2.3.2 Cis/Trans Isomerism

Only alkenes can exhibit stereoisomerism, due to the C=C bond that restricts rotation along its axis. This is because of the  $\pi$ -bonds that only bond at 180° intervals. At these positions, it forms the cis and trans isomers.

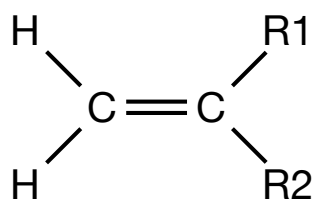


The molecule on the left is the *trans* isomer, while the one on the right is the *cis* isomer. *trans* is from Latin, meaning *other side*, while *cis* obviously means *same side*. In the former, the larger groups are on opposite sides of the alkene double bond, while in the latter, the larger groups are on the same side. Note that these *groups* do not necessarily have to be functional groups — they can be as large or as simple as one wishes.

When naming cis/trans isomers, the qualifier *cis* or *trans* is placed before the stem name, like so:

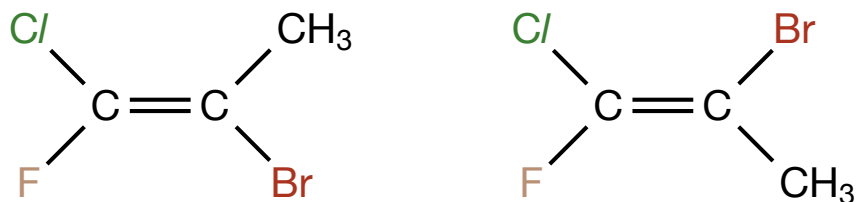
- cis-but-2-ene
- trans-but-2-ene

Note that cis/trans isomerism is not applicable to molecules where identical groups are attached to the any one carbon atom, since there is a line of symmetry going along the plane of the double bond.



### 2.3.3 E/Z Isomerism

E/Z is thought of as the more comprehensive, general form of cis/trans. Consider the alkene below, with two variants due to the lack of a plane of symmetry:



It has 4 distinct substituents, and thus a cis/trans designation cannot be used. Behold, E/Z isomerism. At its core it is simply another method of handling alkene isomers that works for more general forms of molecules.

It follows a scheme of priorities (Cahn-Ingold-Prelog, or CIP), which are determined as such:

- i. The group with the largest atomic mass *directly attached* to the alkene's carbon has the highest priority.
- ii. In the event of a tie, look at the atoms directly attached to *that* offending atom. Use the previous rule, favouring higher priority atoms, to tiebreak. Double bonds are counted twice.
- iii. Recursively evaluate the previous rule with attached atoms, to continue the tiebreaking process.

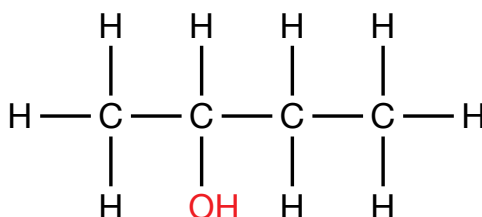
The above scheme should be used to find the two highest-priority groups attached to the alkene, after which, if the two groups are attached on the same side of the alkene, then the molecule is the *Z* isomer, and it is known as the *E* isomer if the reverse is true.

E and Z come from the German *entgegen* and *zusammen*, *opposite* and *together* respectively.

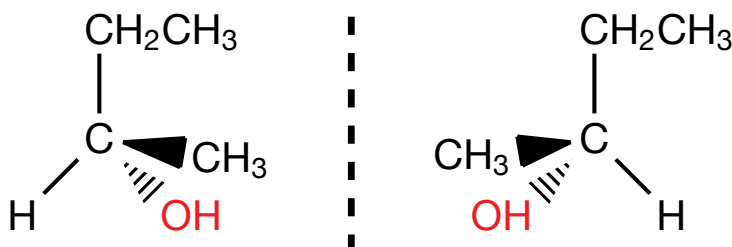
### 2.3.4 Optical Isomerism

Due to the 3-dimensional tetrahedral nature of a carbon atom, if there are 4 *distinct* substituents, two non-superimposable mirror images can exist, resulting from a lack of any plane of symmetry. Such carbons are called *chiral carbons*, and are the *chiral centres* of the molecule. A molecule can have multiple chiral centres.

Consider butan-2-ol below. Carbon 2, with the OH group, has 4 different groups attached to it. As such, it is a chiral carbon.



Indeed, it can take the form of 2 non-superimposable mirror images, that are differentiated by the adjacency of 2 of the 4 groups bonded to the chiral carbon. As can be seen, these two mirror images cannot be rearranged into the other, and are distinct — these are called *enantiomers*.



The solid wedge indicates a bond coming out of the plane of the paper, while the dashed wedge indicates a bond going into the plane.

Optical isomers have identical physical properties, except for their treatment of plane-polarised light (this is where the light wave is only oscillating along one plane). One of the isomers will rotate this light clockwise, while the other will rotate it counterclockwise. The magnitude of both rotations are the same.

If equal amounts of each enantiomer are present in a solution, it is called a *racemic mixture*, and the net rotation of plane polarised light will be 0, for obvious reasons.

Enantiomers usually have identical chemical properties, except for certain interactions that require a certain spatial orientation to work, such as proteins, that can only work with one of the optical isomers.



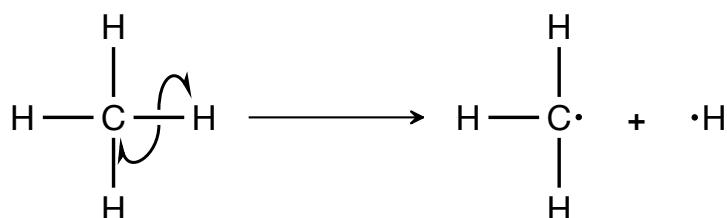
## 3 Reaction Mechanisms

### 3.1 Bond Breaking

#### 3.1.1 Homolytic Fission

Homolytic fission involves the splitting of a single bond, with an equal (*homo*) distribution of the two electrons of the aforementioned bond. This results in the formation of radicals, since now both atoms from the bond will have unpaired electrons.

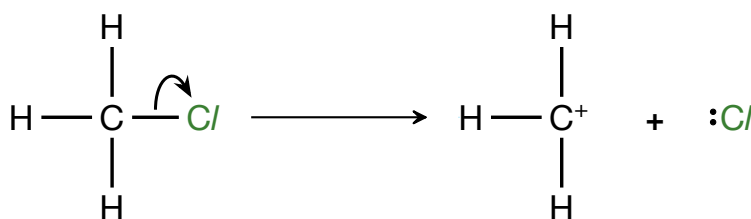
The movement of these single electrons is represented with single-hooked arrows. The arrow starts from the bond line, and points towards the target atom receiving the electron.



The homolytic fission of  $\text{CH}_4$ , forming  $\text{CH}_3$  and  $\text{H}$  radicals.

#### 3.1.2 Heterolytic Fission

As the name implies, heterolytic fission is the opposite; it distributes both electrons of the bond to a single atom, which usually results in the formation of ions. The transfer here is represented using a full (double-hooked) arrow.



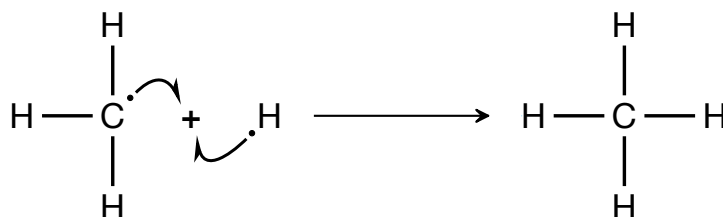
The heterolytic fission of  $\text{CH}_3\text{Cl}$ , resulting in  $\text{CH}_3^+$  and  $\text{Cl}^-$  ions

## 3.2 Bond Forming

### 3.2.1 Single Electrons

Bond forming is essentially the reverse of bond breaking, and hence the same notations apply — single-hooked arrow for the movement of single electrons, and double-hooked arrows for the movement of an electron pair.

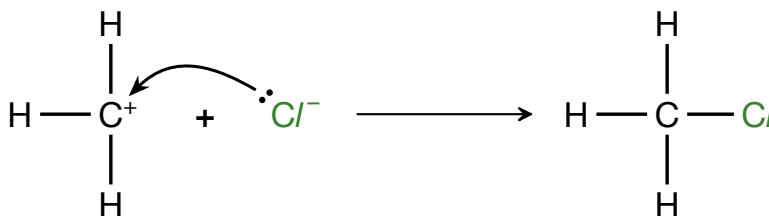
In this case, two single electrons from each atom contribute to the new bond.



The formation of a bond between  $\text{CH}_3$  and  $\text{H}$  radicals to form  $\text{CH}_4$ .

### 3.2.2 Electron Pairs

Electron pairs usually come from negatively charged radicals or lone pairs, although this is not a rule. Both electrons come from a single source to form a bond, but this is *not* a dative bond — it is simply a normal bond.



The formation of a bond between  $\text{CH}_3$  and  $\text{Cl}^-$  radicals, to form  $\text{CH}_3\text{Cl}$ .