

University of Sydney
Chemistry 1B (CHEM1102)

Organic Chemistry Lecture Notes

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Topic 1 – Introduction to Organic chemistry, representation of structures, functional groups, nomenclature, isomers

Introduction

Definition of Organic Chemistry

- Organic chemistry deals with compounds in which carbon is the principal element
- Organic substances arise in all sorts of places - plants, animals, food, medicines, industry, research laboratories
- Every living organism is made of organic chemicals
- 14 million organic substances - number increases by 10,000 per week!!

The Unique Nature of Carbon – Bonding in Organic Carbon

- Catenation - Carbon atoms can bond together to form
 - Stable extended chains of atoms
 - Rings
 - Multiple bonds
- Carbon has atomic number = 6
 - Electronic configuration: $1s^2 2s^2 2p^2$
 - Valence of 4 – four bonds to completely fill outer electron shell of carbon
- Carbon forms bonds to
 - Itself – single, double, triple
 - Metals – Na, K, Fe, Cu, Mg ...
 - Heteroatoms – N, P, O, S, X

- C-C and C-H bonds are strong

C-C	348 kJ mol ⁻¹
C-H	412
Si-Si	176
N-N	163
O-O	146
I-I	152

- C-C and C-H bonds are non-polar
- A combination of the strength and non-polar nature make C-C and C-H bonds unreactive

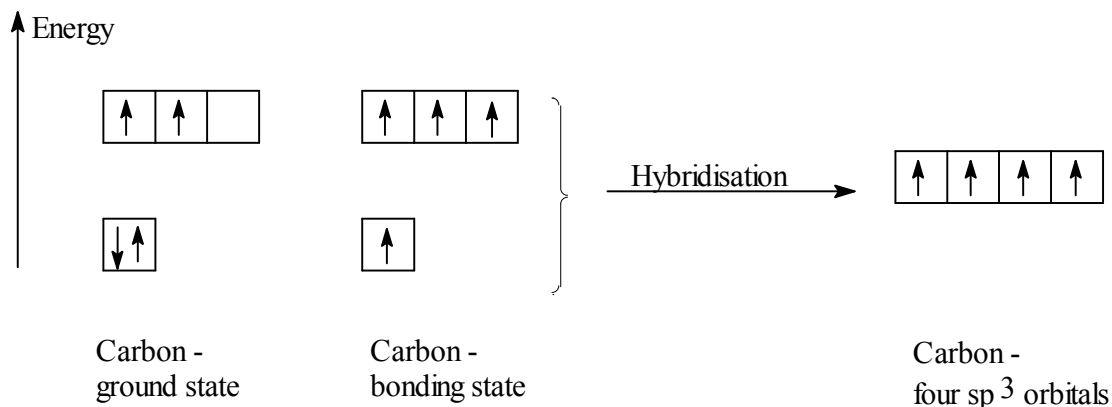
There are four experimentally observed bonding arrangements for carbon:

Type of bonds	Hybridisation	Geometry	Examples
4 single bonds	sp^3	Tetrahedral	CH_4 , CH_3CH_3
2 single, 1 double bond	sp^2	Trigonal planar	$\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{O}$
1 single, 1 triple bond 2 double bonds	sp	Linear	$\text{H}-\text{C}\equiv\text{C}-\text{H}$ $\text{CH}_2=\text{C}=\text{O}$

Hybridisation

Hybridisation is a convenient way of describing the sigma-bonding orbitals and lone pair orbitals (if present) of an atom.

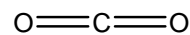
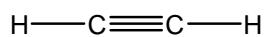
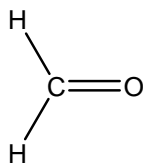
In alkanes, hybridisation gives four identical sp^3 orbitals, which form a tetrahedral shape to minimise repulsion between the orbitals.



In alkenes, each pi-bond results from the combination of a p -orbital on adjacent carbon atoms and consequently the orbitals available for sigma bonding result from an s -orbital and the remaining p -orbitals.

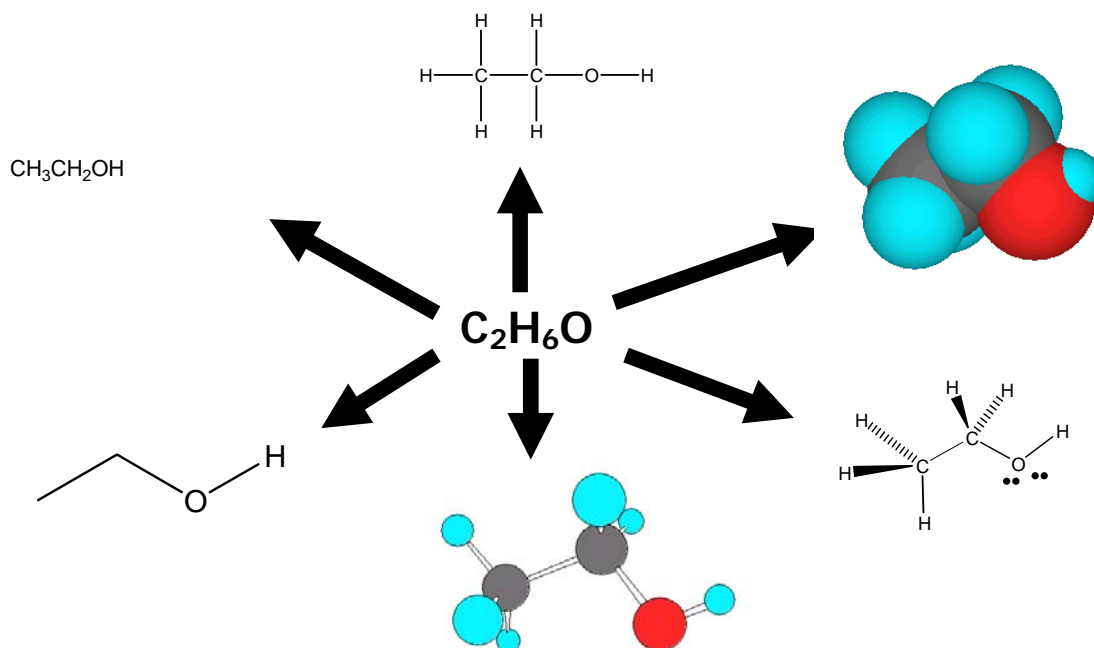
Question: Work out the hybridization of carbon in the following molecules. Note: A quick way of determining the hybridisation of an atom is to count the σ bonds *and* lone pairs around that atom and assign one hybrid orbital to each.

2 electron pairs $\Rightarrow sp$, 3 electron pairs $\Rightarrow sp^2$, 4 electron pairs $\Rightarrow sp^3$



Representation of Organic Molecules

Organic compounds may be represented in several ways as illustrated in the examples below.



Concept

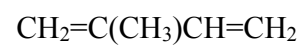
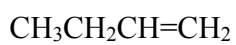
- Catenation – chains and rings of carbon atoms
- Bonding – single, double, triple bonds possible
- Geometry – depends on hybridisation of carbon atom
- Valence – 4 for carbon (3 – N, 2 – O, 1 – H, Cl, Br, I)
- Reactivity – often associated with heteroatoms (atoms other than C or H)

In the stick representation:

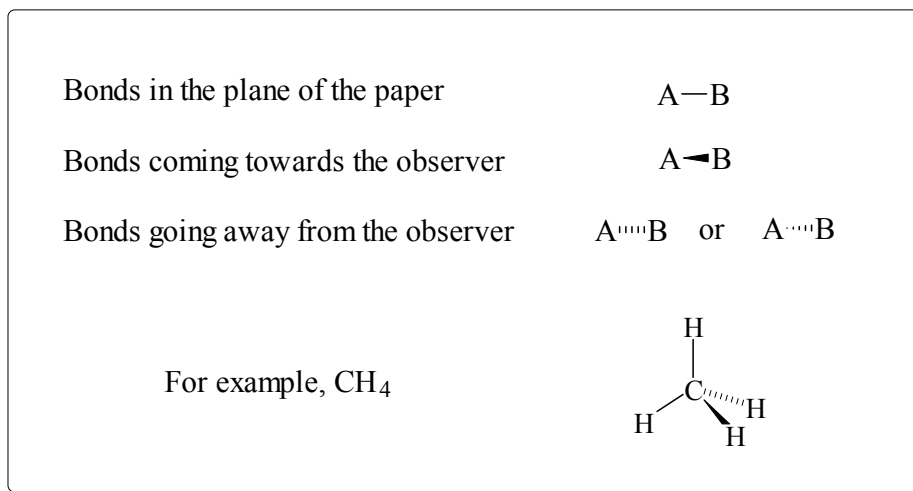
- C is basis of structure
- Carbon atoms are not usually shown but assumed to be at the intersection of 2 or more bonds and at the end of each line
- 1, 2 or 3 lines to represent single, double and triple bonds
- Indicate bond angles ($\sim 120^\circ$ or 180°)
- Omit all C-H bonds, hydrogen count assumed
- Specify all heteroatoms (O, N, F, Cl, B, I, S etc) and H – heteroatom bond
- When drawing neutral organic molecules:
 - C always has a valence of 4
 - N always has a valence of 3
 - O always has a valence of 2
 - X (halogen) always has a valence of 1

Condensed Structural Formula	Structural Formula	Stick representation
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ or $\text{CH}_3\text{CH}_2\text{COOH}$		
$\text{CH}_3\text{CHClCH}=\text{CH}_2$ or $\text{CH}_3\text{CHClCHCH}_2$		
$\text{CH}_3\text{COCH}_2\text{CH}_3$		
$\text{CH}_3\text{OCH}_2\text{CH}_3$		

Questions: Give the stick representation of the following molecules:



Where it is important to represent the three-dimensional shape of a molecule, the following convention is adopted:



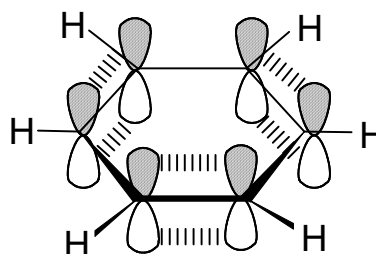
Structure of benzene

Benzene is also about 140 kJ mol⁻¹ more stable than predicted for 1,3,5-cyclohexatriene.

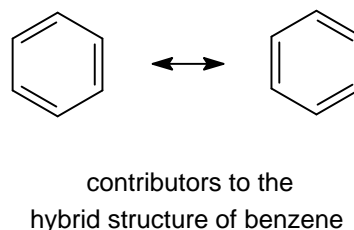
	Bond length	Bond strength
C-C	154 pm	356 kJ mol ⁻¹
C=C	133 pm	636 kJ mol ⁻¹
benzene	139 pm	518 kJ mol ⁻¹

There are two models of bonding in benzene

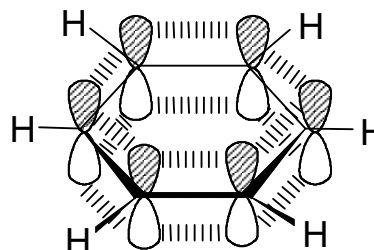
1. In the valence bond model each of the carbon atoms in benzene is sp^2 hybridised and forms σ -bonds to two neighbouring carbon atoms and a σ -bond to one hydrogen. Each carbon atom has a p -orbital which can participate in π -bonding.



If the bonds were normal C=C bonds, the bonding in benzene could be drawn in either of two identical ways. The **valence bond theory** says that the bonding in benzene is best described as an average or "resonance hybrid" of the bonding arrangements which can be drawn.

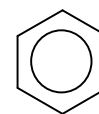


2. The bonding in benzene can also be described in terms of **molecular orbital theory**. Here the p -orbitals of the six sp^2 -hybridised carbon atoms overlap with each other to form a single continuous π -bond. The six electrons in this bond effectively form a toroidal electron cloud which lies above and below the plane of the carbon atoms.



Irrespective of which theory is used to describe the bonding, benzene is a perfect hexagon where all the bond angles are 120° and where all six C-C bonds are identical.

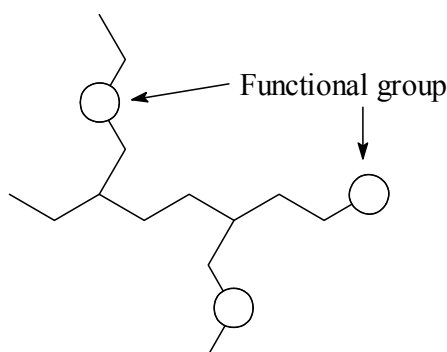
When drawing a benzene molecule, some books draw a circle in the centre of the hexagon of carbon atoms. This implies 'delocalisation' of the 6 π -electrons around the aromatic ring and indicates the real symmetry of the benzene molecule.



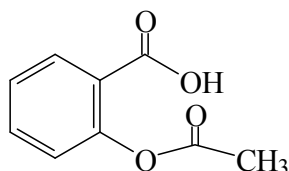
Functional Groups

Organic compounds are classified by *Functional Groups*, which are responsible for chemical behaviour. Functional groups are involved in naming organic compounds.

- C=C, C≡C and the polar bonds from carbon to heteroatoms are more reactive than C-C or C-H bonds and hence where the chemistry takes place. This part of the molecule is called the *Functional Group*.
- An organic compound can be viewed as a backbone (skeleton) of carbon-carbon single bonds with other groups of atoms, functional groups, attached at various points.

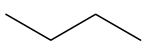
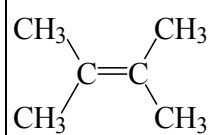
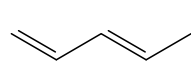
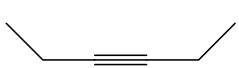
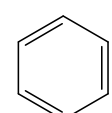
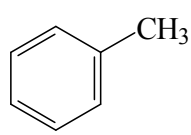
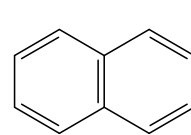
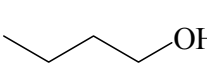
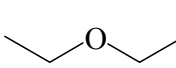
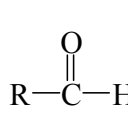
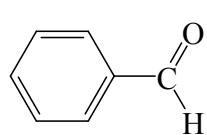
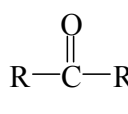
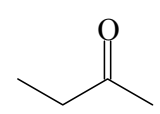
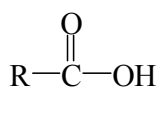
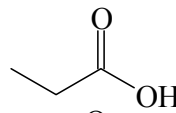
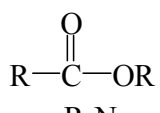
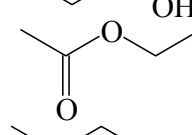
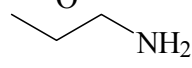
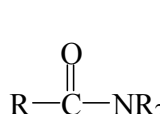
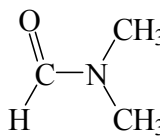
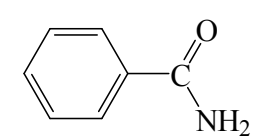
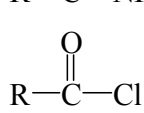
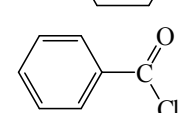
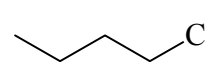


- The combination of the ability to form a vast range of unreactive carbon frameworks to which can be added special reactive sites gives the diversity of organic chemistry.
- Functional groups confer the characteristic chemical and physical properties of the compounds that contain them.
- Functional groups undergo the same chemical reactions irrespective of the type of molecule that contains them.
- A molecule containing several functional groups displays reactions that represents the sum of the reactions of each functional group.

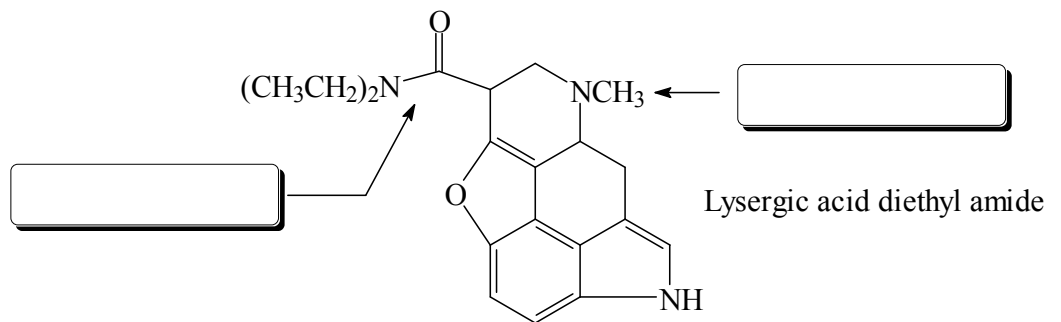
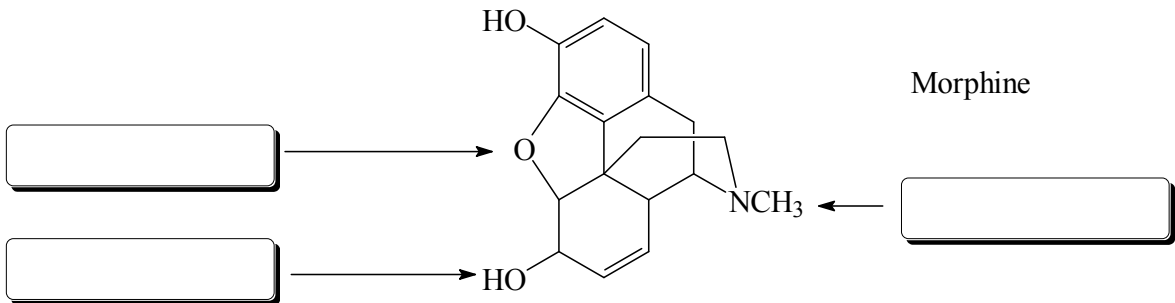
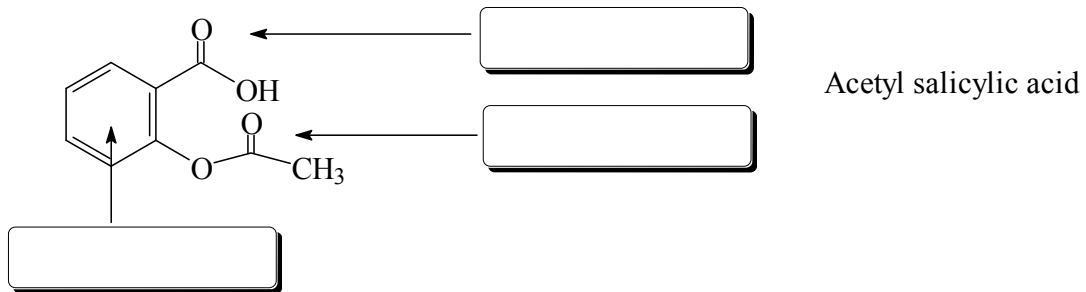
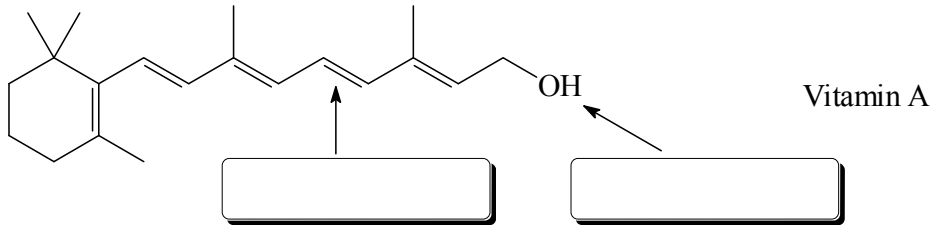


Acetylsalicylic acid (aspirin)
shows the properties of
- a carboxylic acid
- an ester
- an aromatic compound

Note: **R** is the general abbreviation for the “rest of the molecule”.

	Class	General formula	Examples
C & H	alkane	RCH_3	CH_4 $CH_3CH_2CH_2CH_3$ 
	alkene	$R_2C=CR_2$	 
	alkyne	$RC\equiv CR$	$CH_3C\equiv CH$ 
	aromatic compound		 
C, H, O -O-	alcohol	$R-OH$	CH_3CH_2OH 
	ether	$R-O-R$	$CH_3CH_2OCH_3$ 
C, H, O =O	aldehyde		$CH_3-C(=O)H$ 
	ketone		$CH_3C(=O)CH_3$ 
	carboxylic acid		CH_3COOH 
	ester		CH_3COCH_3 
C, H, N	amine	R_3N	$(CH_3)_3N$ 
C, H, N, O	amide		 
C, H, Cl, O	acid chloride		CH_3COCl 
C, H, X	Alkyl halide	$R-X$ (X = Cl, Br, I)	CH_3CH_2Br 

Question: Name the functional groups in the following molecules:



Nomenclature

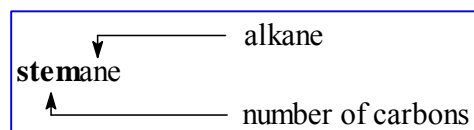
The name of an organic molecule consists of several parts:



The *stem* indicates the number of carbon atoms in the longest chain containing the functional group. The ending indicates the nature of the functional group present. Substituents are indicated by prefixes and a number is used to locate any substituent or functional group unambiguously in a molecule.

Rules:

- Find and name the longest carbon chain → stem
- Identify substituents
- Number longest carbon chain to give lowest numbering for substituents
- Allocate a number to **every** substituent
- List substituents in alphabetical order
- Identical side chains are indicated by using prefixes: di (2), tri (3), tetra (4) etc



Methane	CH ₄
Ethane	CH ₃ CH ₃
Propane	CH ₃ CH ₂ CH ₃
Butane	CH ₃ CH ₂ CH ₂ CH ₃
Pentane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃
Hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Heptane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Octane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Nonane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Decane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃

Alkane		Alkyl group substituent	
propane	CH ₃ CH ₂ CH ₃	propyl	CH ₃ CH ₂ CH ₂ -
butane	CH ₃ CH ₂ CH ₂ CH ₃	butyl	CH ₃ CH ₂ CH ₂ CH ₂ -

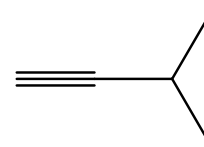
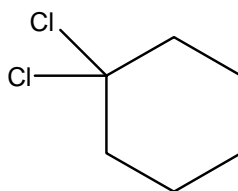
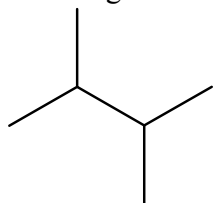
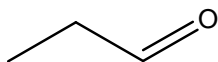
Give the stick structures of the following molecules:

2,2-dimethylpentane

1,4-butandiol

3-pentanone

Give the name of the following molecules:



Summary

You should now be able to

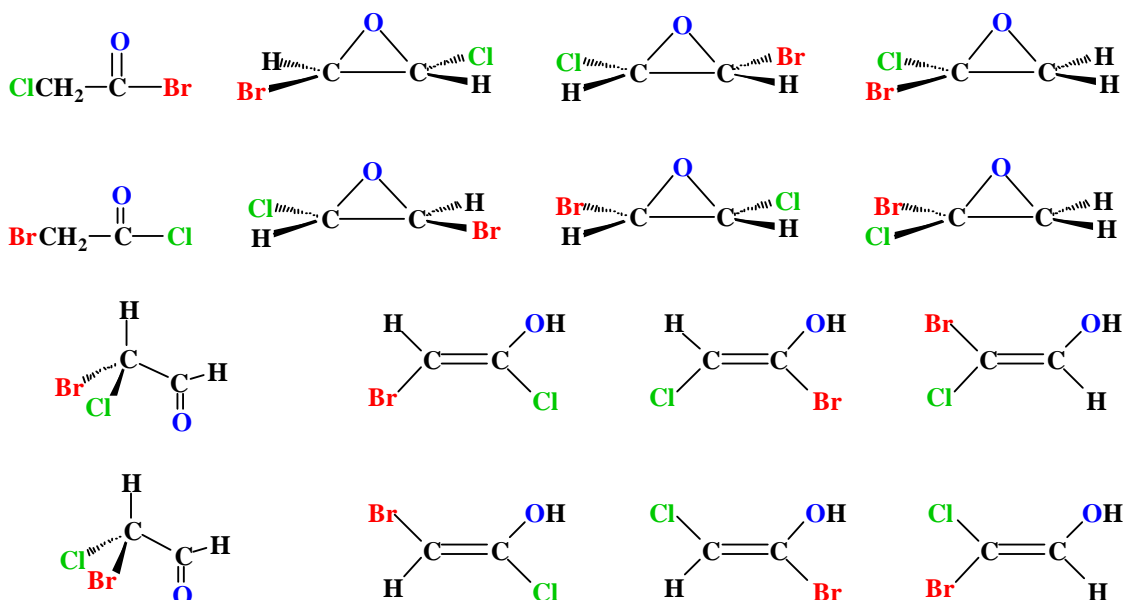
- Understand the basis of drawing organic structures
- Convert between a condensed molecular formula and a skeletal or line structure
- Determine the formula of a molecule from its skeletal representation

Isomerism

The problem of isomers...

- How many different compounds are there with the formula C_2H_2BrClO ?
(Excluding those with charged atoms and O-Cl or O-Br bonds)
- How do we tell them apart?
- How do we name them?
- How are they different?
- Do they have different properties?

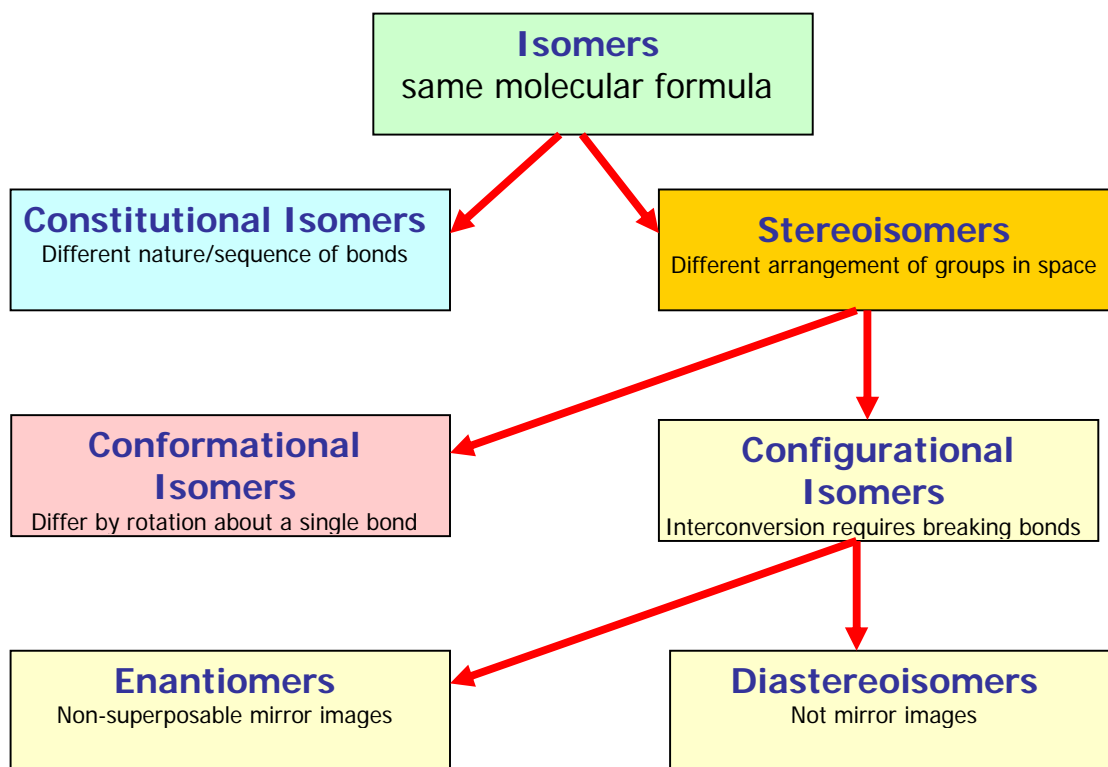
There are 16 different possible compounds



Isomers are

- Compounds that have the same molecular formula but different structures
- Very important in chemistry but especially important in the chemical reactions that take place in living organisms - the shape is as important as the functional groups present!
- Classified according to type

Classification of isomers



Constitutional isomers

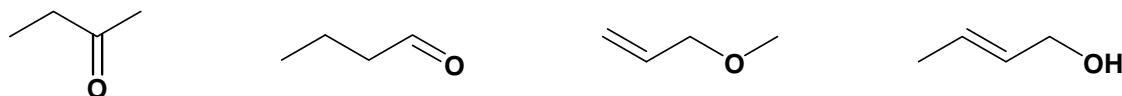
Isomers differ in the nature and/or sequence of bonding

- Within a homologous sequence of alkanes, the number of constitutional isomers increases rapidly

n	C_nH_{2n+2}	No. of Constitutional isomers	Constitutional formula
1	CH ₄	1	CH ₄
2	C ₂ H ₆	1	CH ₃ CH ₃
3	C ₃ H ₈	1	CH ₃ CH ₂ CH ₃
4	C ₄ H ₁₀	2	CH ₃ CH ₂ CH ₂ CH ₃ AND $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_3 \end{array}$
5	C ₅ H ₁₂	3	
6	C ₆ H ₁₄	5	
:	:	:	
10	C ₁₀ H ₂₂	75	
20	C ₂₀ H ₄₂	366 319	

Question: Draw and name the constitutional isomers of C₆H₁₄

- The physical and chemical properties of constitutional isomers may be very different, particularly when different functional groups are present
- For example the molecule with formula C_4H_8O may be a ketone, aldehyde, alkene/ether or alkene/alcohol



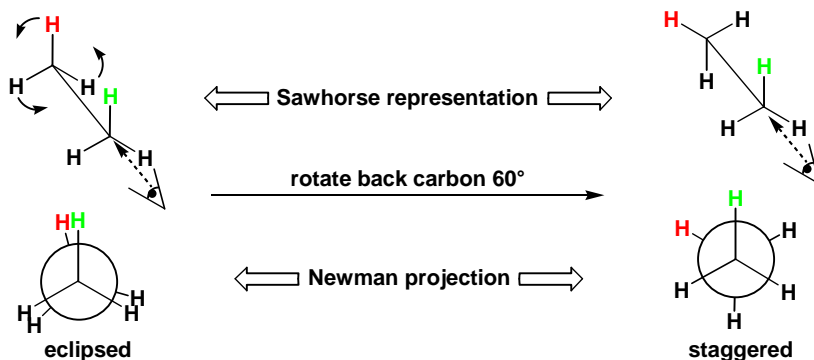
Stereoisomers

Stereoisomers have the same nature and/or sequence of bonding but differ in the arrangement of groups in space

- There are two groups of stereoisomers
 - **Conformational isomers or conformers** differ by rotation about a single bond and can not normally be separated from each other at room temperature
 - **Configurational isomers** may be interconverted only by breaking and remaking bonds. This process normally requires considerable energy and does not happen at room temperature

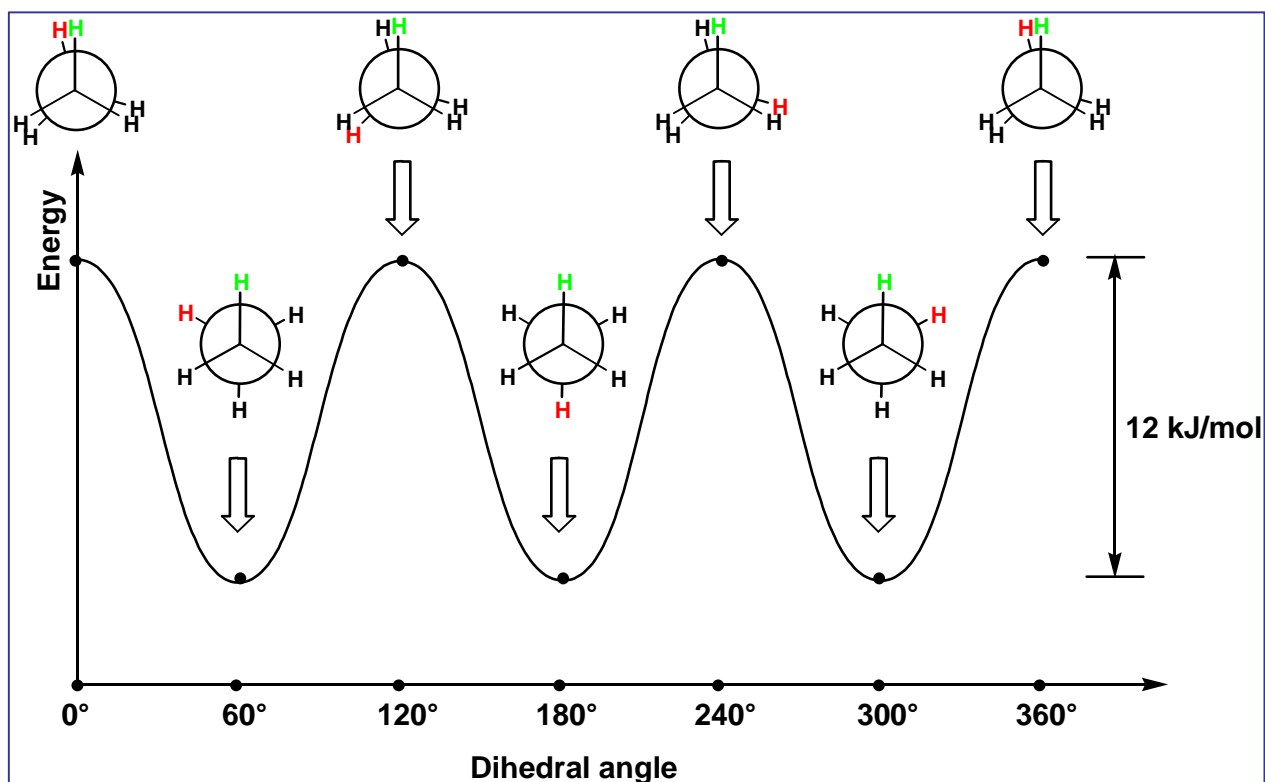
Conformational isomers

Use ethane as an example (CH_3CH_3)



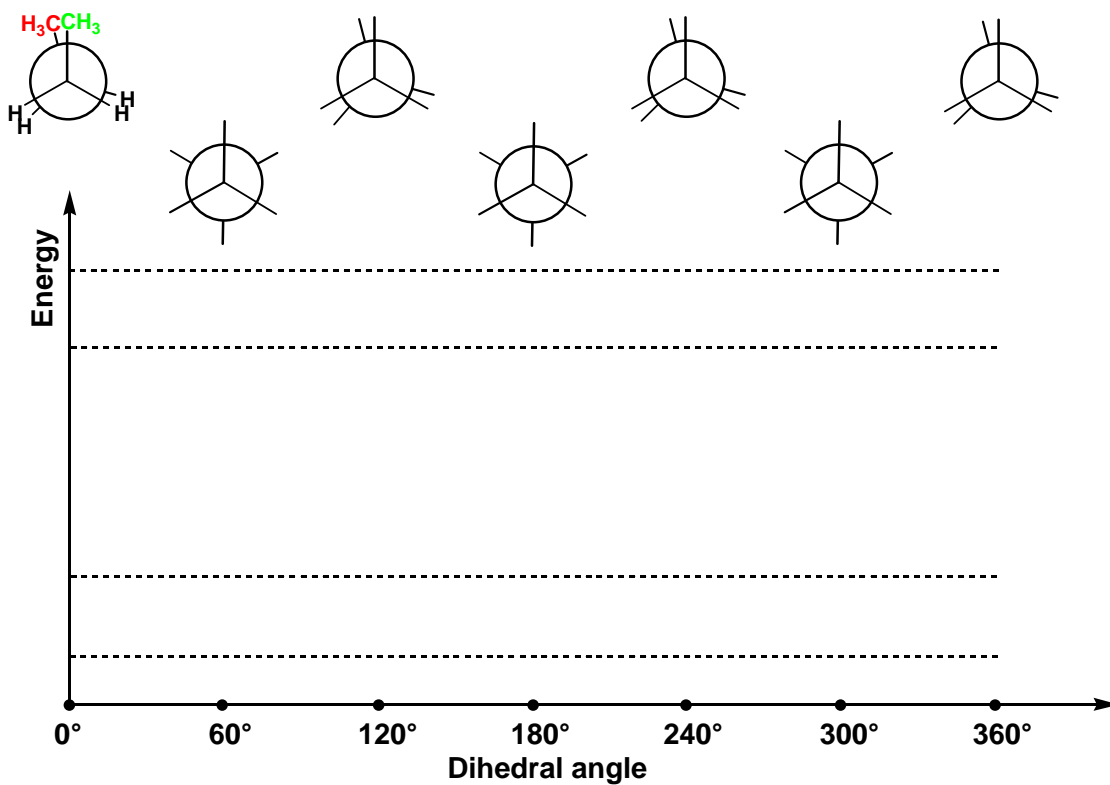
Conformers differ in energy

- In 'straight chain' alkanes rotation about a C-C single bond occurs rapidly at room temperature
- The difference in energy between conformers arises from *steric* interaction



Question: Draw the energy profile of the butane molecules as the C2-C3 bond rotates through 360°.

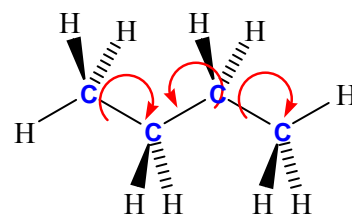
- Start by drawing the appropriate Newman projections to help decide the relative energies of different conformers.
- The back carbon rotates and the front one stays stationary.



Cyclic alkanes

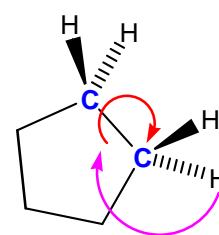
Straight chain alkanes

- Rotation around each C-C bond readily occurs
- Conformational isomers result



Cyclic alkanes

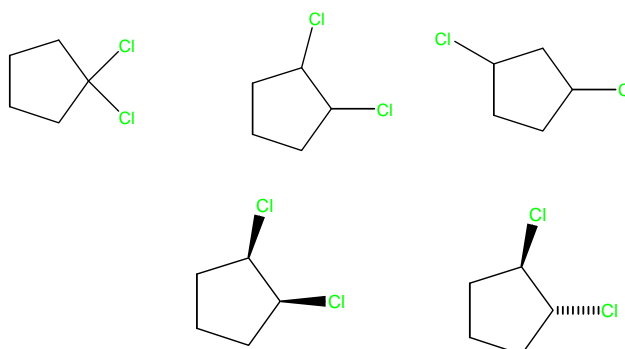
- Rotation is restricted within a ring of carbon atoms
- This is because rotation would require the atoms attached to carbon to pass through the centre of the ring – this has a high energy barrier



Disubstituted cycloalkanes

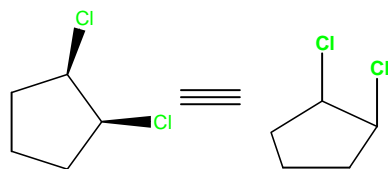
A number of isomers are possible

- Constitutional:
eg 1,1-dichlorocyclopentane,
1,2-dichlorocyclopentane and
1,3-dichlorocyclopentane
- Configurational: eg two forms of 1,2-dichlorocyclopentane

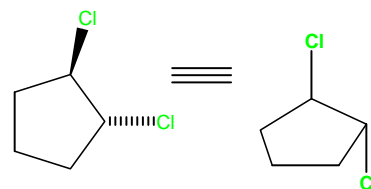


Nomenclature: *cis* and *trans*

- These structures are diastereoisomers or diastereomers
- They have different physical and chemical properties
- The terms *cis* and *trans* are used to distinguish them

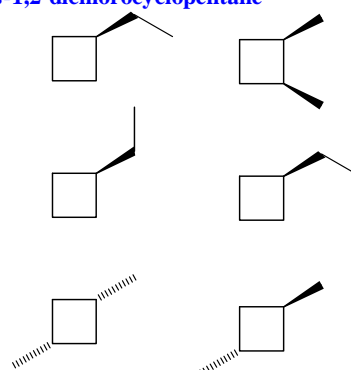


cis-1,2-dichlorocyclopentane



trans-1,2-dichlorocyclopentane

Question: Identify the type of isomer represented by the pairs:



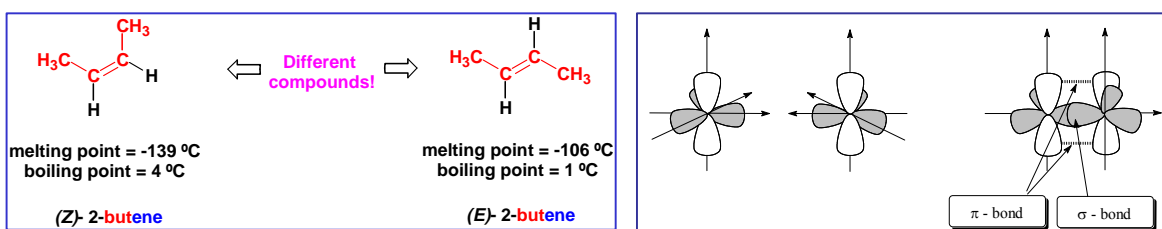
Isomers resulting from structural rigidity

- Rotation around the C-C bond within a cycloalkane ring is restricted compared to that of a hydrocarbon chain
- Consequently disubstituted cycloalkanes occur as diastereoisomers as well as constitutional isomers
- A pi-electron overlap requires a fixed geometry around the bonded carbon atoms

Alkene 'diastereoisomers'

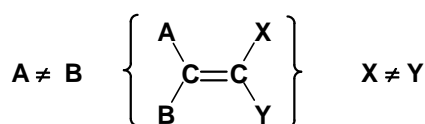
A double bond is constructed of a σ - and π -bond

- Pi-bonds result from p-orbital overlap and are directional
- Electron density concentrated above and below plane
- Rotation around the C-C axis would require breaking the pi-bond ($\sim 128 \text{ kJ mol}^{-1}$) and does not occur at room temperature

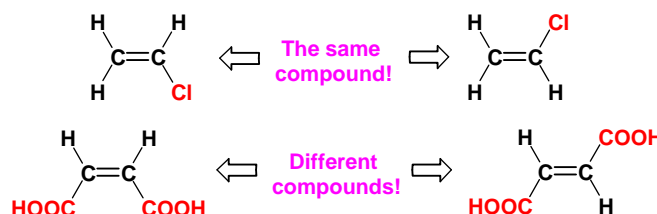


Both ends of the C=C bond must have two different groups

- If these conditions are met, TWO diastereoisomers result



But A and B *can* be the same as X and Y



Nomenclature – Z and E

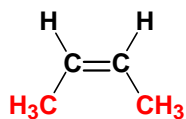
The rules

- Z/E determined by assigning a priority to each of the pairs of groups on each carbon of the double bond
- The higher the atomic number of the atom attached, the higher the priority
- If identical atoms are attached to each carbon of C=C, work outwards along the chain until the first point of difference is reached
- If groups of high priority are on the same side of the double bond the alkene is denoted (Z)
- If groups of high priority are on the opposite side of the double bond the alkene is denoted (E)

Example

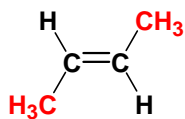
Higher priority groups on the **same side** of double bond \Rightarrow alkene is denoted **(Z)**

Higher priority groups on **opposite sides** of double bond \Rightarrow alkene is denoted **(E)**



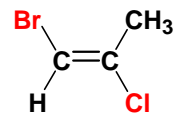
(Z)-2-butene

higher priority groups on **same side**



(E)-2-butene

higher priority groups on **opposite sides**



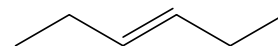
(E)-1-bromo-2-chloropropene

higher priority groups on **opposite sides**

Question: name these molecules



A.....

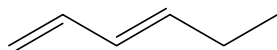


B.....

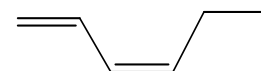
What is the isomeric relationship between the pairs:

A and B.....

C and D.....



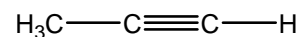
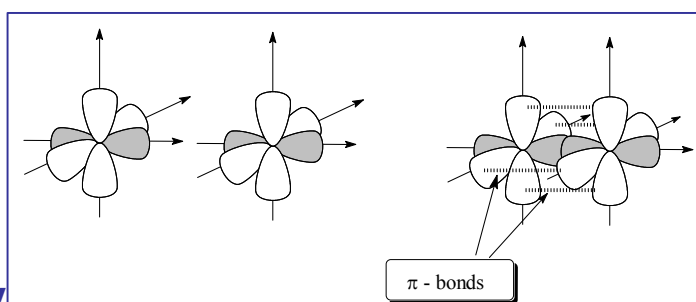
C.....



D.....

Note: No diastereoisomers of alkynes

- Two pi bonds and two sigma bonds associated with each carbon of the triple bond
- Geometry of both carbon atoms is linear
- There is only one way to attach two substituents in a straight line



Summary

You should now be able to

- Understand the difference between constitutional isomers and stereoisomers
- Recognise constitutional, conformational and diastereomeric (*cis/trans* and *Z/E*) isomers
- Name isomeric structures correctly