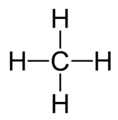
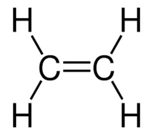
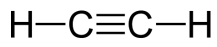
Chapter 22: Introducing Hydrocarbons - The Alkanes

This chapter introduces you to organic chemistry – the study of (most!) carbon compounds.

A reminder: Carbon is in Group 4 of the periodic table and can therefore form four bonds (has a valency of 4).

These can be:
- (a) 4 single bonds
- (b) 1 double and 2 single bonds
- (c) 1 triple and 1 single bond

IUPAC – the International Union of Pure and Applied Chemistry – **has created a universal system for categorising and naming organic compounds.**

Organic compounds are organised into different 'families', called **homologous series.** These homologous series contain members with **similar structures** and **similar chemical properties.**

A homologous series is a family of organic compounds with the same functional group, same general formula, similar chemical properties and with successive members differing from each other by a CH_2 unit.

The functional group is a group of atoms which determines the characteristic reactions of a particular compound.

Hydrocarbons

A hydrocarbon is a compound made of hydrogen and carbon only.

For example, CH_4 (methane), C_2H_4 (ethene), and C_6H_6 (benzene) are all hydrocarbons.

Sources of hydrocarbons

The main sources of hydrocarbons are:

1. Fossil fuels

Fossil fuels are fuels formed millions of years ago from the remains of dead plants and animals. They are non-renewable fuels, e.g. coal, oil and natural gas. Crude oil (unrefined oil) is a mixture of substances, many of which are hydrocarbons. We can separate these hydrocarbons in oil refineries and use them to produce a wide range of products such as plastics, tar for our roads and fuel for cars, trucks, ships and airplanes. Natural gas, composed primarily of methane (CH_4), is used in factories, as well as in the home for heating and cooking.

2. Living matter (biomass)

Biomass refers to any organic material derived from living or recently living plants and animals. Examples of biomass include trees, crops (e.g. sugarcane), grasses, algae and animal waste.

Processes which convert biomass into hydrocarbons include:

a) Anaerobic digestion: Microorganisms break down biomass, producing methane that can be captured and used as a fuel.

b) Pyrolysis: Biomass is heated causing it to break down into various products, including bio-oil and syngas. Syngas is a mixture of carbon monoxide and hydrogen, which can be used in the Fischer-Tropsch process (see 3. synthesis). The bio-oil can be further refined to produce hydrocarbons.

Biomass is considered a more sustainable option than fossil fuels since it is a renewable source of energy.

3. Synthesis

Hydrocarbons can also be synthesised. This process involves creating hydrocarbon molecules from other molecules containing carbon and hydrogen (sometimes from other hydrocarbons).

a) The Fischer-Tropsch process

The Fischer-Tropsch process is a two-step method to produce hydrocarbons:

1. Producing carbon monoxide and hydrogen (syngas) from coal, natural gas or biomass, and

2. Combining the carbon monoxide and hydrogen to form liquid hydrocarbons.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

e.g. if n = 10 $\quad 10CO + 21H_2 \rightarrow C_{10}H_{22} + 10H_2O$

carbon monoxide + hydrogen → decane + water

b) CCU: Carbon Capture and Utilisation

Carbon dioxide (CO_2) captured from factories and power plants can be combined with hydrogen to produce hydrocarbons. This process produces useful fuels in a more sustainable way (if the hydrogen is 'green').

Aliphatic vs. Aromatic hydrocarbons

Aliphatic hydrocarbons are organic compounds consisting of carbons joined in straight chains, branched chains or non-aromatic rings.

Aromatic hydrocarbons are compounds that contain a benzene ring in their molecules.

The Alkanes

The alkanes are a homologous series (organic family) of **saturated hydrocarbons.**

A saturated compound contains only single bonds between the atoms in the molecule.

Naming alkanes

1 C = meth	+ ane	= **methane**
2 C = eth	+ ane	= **ethane**
3 C = prop	+ ane	= **propane**
4 C = but	+ ane	= **butane**
5 C = pent	+ ane	= **pentane**
6 C = hex	+ ane	= **hexane**

General formula: $\mathbf{C_nH_{2n+2}}$, where n is a positive whole number.

Substituents

Alkanes can have substituents. **A substituent is an atom or group of atoms that replaces an atom.** In alkanes, substituents always replace a hydrogen atom.

Alkyl groups

Alkyl groups are substituents derived from an alkane molecule that have had a hydrogen atom removed. They are named by replacing the 'ane' of the alkane with 'yl'.

CH_4 = Methane	→	CH_3 = methyl
C_2H_6 = ethane	→	C_2H_5 = ethyl
C_3H_8 = propane	→	C_3H_7 = prop yl

Halogens

F – fluoro   Cl – chloro   Br – bromo   I – iodo

If an alkane has a halogen substituent, it is no longer an alkane since it is no longer a hydrocarbon. Instead, we call these **haloalkanes** as they are alkanes containing elements from Group 17, the halogens. More specifically we call them bromoalkanes, chloroalkanes, fluoroalkanes etc.

Naming alkanes with substituents

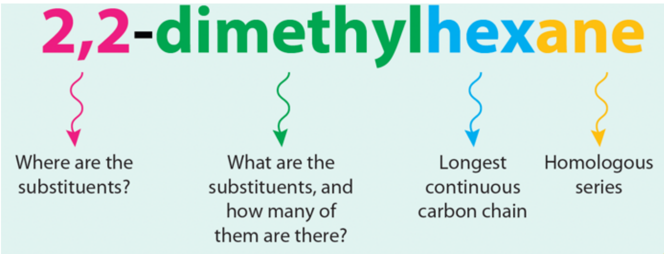
First we name the longest carbon chain (the parent chain) of the molecule, e.g. hexane. Then, using prefixes, suffixes and numbers, we will indicate the name and location of any substituents.

- The parent chain = longest continuous carbon chain present.
- The suffix indicates the homologous series (e.g. 'ane' indicates an alkane).
- The prefixes indicate any substituents on the parent chain, e.g. methyl, ethyl, chloro etc.
- Numbers are used to indicate the location of these substituents, e.g. 2-methyl.
- If two different substituents are present they are listed alphabetically, e.g. ethyl would be listed before methyl.
- If there are two of the same type of substituent present then 'di' is placed in front of the prefix to indicate there are two – e.g. dimethyl indicates two methyl groups.

Similarly, tri is used to indicate there are three – trimethyl tells us there are three methyl groups present. ‘Di’ and ‘tri’ do not count when alphabetising substituents (e.g. ethyl would go before dimethyl).

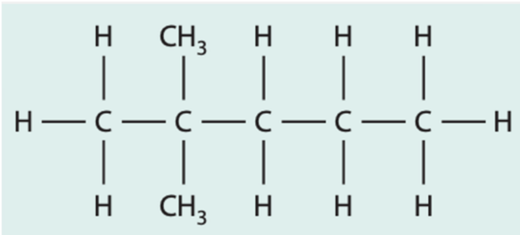
- The number of locants (numbers in the name must equal the number of substituents *(i.e. if there are two substituents there must be two numbers).*

- Hyphens are used to separate numbers from letters and commas are used to separate numbers.



Example 1

Give the IUPAC name for the compound shown below.

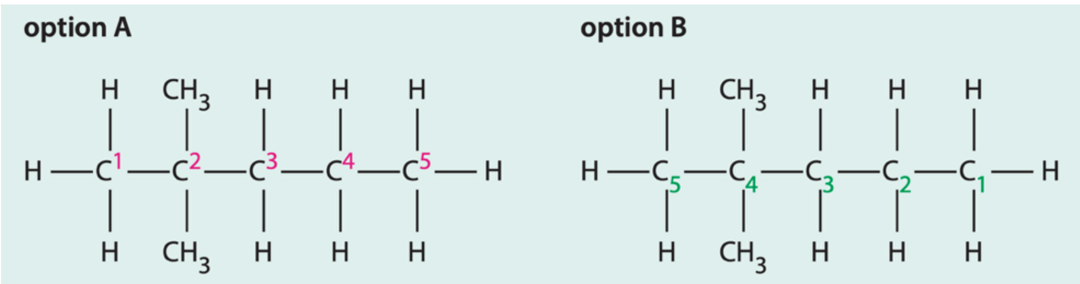


Step 1: Count the longest continuous chain of carbon atoms, i.e. the parent hydrocarbon.

The longest chain is five carbon atoms = pent. This molecule is a saturated hydrocarbon = ‘ane’. The parent alkane is **pentane.**

Step 2: Number the carbon atoms in the parent hydrocarbon starting from the end that gives the substituents the lowest possible numbers.

This is achieved by starting at the end nearest the first branch point.



Option A gives the methyl groups a number of 2, while option B gives the methyl groups a number of 4. We will choose option A, as we want our substituents to have the lowest possible number.

Step 3: Use prefixes and numbers to indicate the type and position of any substituents present.

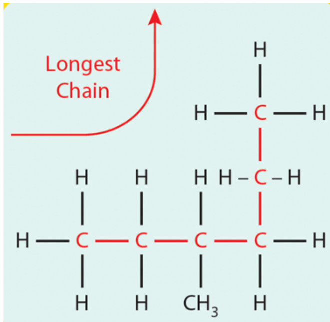
There are two CH_3 groups, i.e. there are two methyl groups. Since there are two, we place 'di' before the methyl: dimethyl.

They are both located on carbon 2 so we write 2,2-dimethyl.

Step 4: Write out the name as a single word

Use hyphens (-) to separate the prefixes (methyl, ethyl, etc,) and use commas to separate the numbers. If two or more substituents are present, list them alphabetically.

This compound is 2,2-dimethylpentane (molecular formula C_7H_{16}).



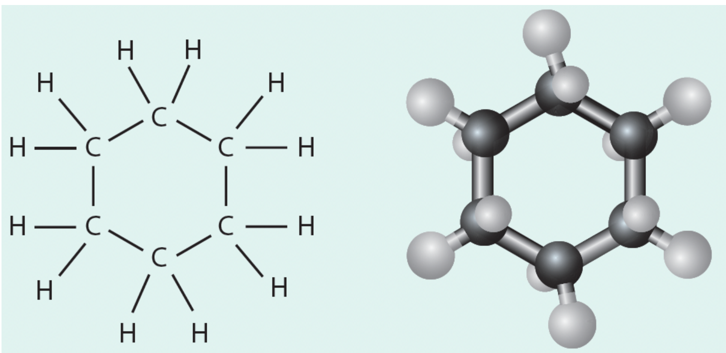
A note on finding the parent alkane: Be careful – the longest chain may be one that includes 'turning corners'.

Also note that, if there are two chains of equal length (and both are the longest continuous chains of carbon in the molecule), then choose the one with the most branching as the parent hydrocarbon.

Note: Having a bromine or chlorine on carbon 1 is possible. However, there cannot be an alkyl group, e.g. a methyl or an ethyl, on the first or last carbon of a molecule. This is because it would simply be an extension of the chain. For instance, 1-methylethane does not exist – it is propane!

Cyclohexane

Cyclohexane (C_6H_{12}) is a common non-polar organic solvent. It is a cyclic alkane. It has six carbons ('hex') but rather than being a straight-chain alkane, it is arranged in a cyclic structure.



Drawing alkanes

Example 1

Draw 2,5-dimethylhexane.

Step 1: Pick out the parent hydrocarbon (the longest continuous carbon chain – it is always at the end of the name) and draw its carbons.

Hex = 6 carbons   ane = alkane (saturated hydrocarbon)

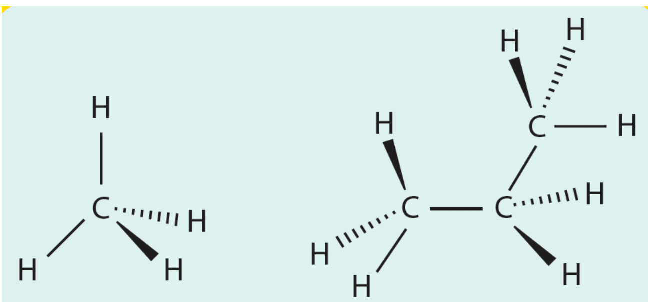
Step 2: Add the substituents to the correct carbons.

It doesn't matter which way you choose to number your carbons (left to right or right to left) but you must pick one way and stick to it. It also does not matter if your substituents are added 'above' or 'below' the carbon chain, as **single bonds have 360° rotation**.

Step 3: Fill in the remaining bonds and hydrogen atoms, remembering that carbon must always have four bonds and hydrogens must always have one.

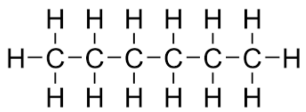
Drawing alkanes

For ease, we usually draw alkanes as 2-D, although it is important to understand that they are, of course, 3-D. We can show this by using dashed and wedged lines. All carbon atoms in the alkanes are in tetrahedral geometry.



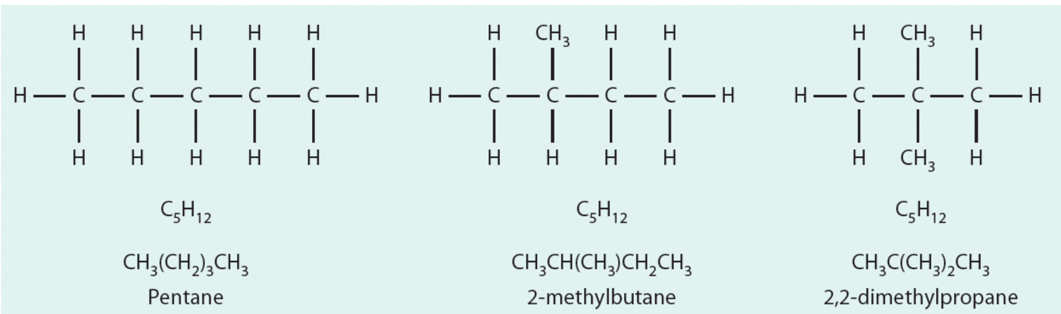
Alkanes can be modelled using molymod kits, computer simulations and diagrams.

Building and visualising 3D models of alkanes can also help us understand their molecular, expanded structural and condensed structural formula.

	Example	Advantage	Disadvantage
Molecular formula	C_6H_{14}	Quickly shows the number of each type of atom in a molecule.	Doesn't indicate anything about how the atoms are arranged, i.e. does not indicate anything about the 3D structure of the molecule. The compound usually cannot be identified form the molecular formula alone.
Expanded molecular structure (structural formula)		The compound can be immediately identified. Shows all of the bonds present in the molecule and how they connect all atoms.	Takes the longest to draw.
Condensed structural formula	$CH_3CH_2CH_2CH_2CH_2CH_3$ $CH_3(CH_2)_4CH_3$	The compound can be identified. The single line makes it faster to write than the expanded structural formula.	It shows the order of the atoms in a molecule, but the 3D structure of the molecule isn't very visually clear.

Structural isomers

Structural isomers are compounds with the same molecular formula but different structural formulas.



2-methylpropane and butane are structural isomers. Can you draw them?

Properties of Alkanes

Identifying features	Saturated hydrocarbon
Carbon-carbon bonds	Single (sigma)
Intramolecular bonds	Pure (non-polar) covalent bonds
Type of molecule	Non-polar
Intermolecular forces	London dispersion forces
Melting and boiling points	Relatively low Increases as the size of the molecules increases
State of matter at room temperature	$C_1 – C_4$ are gases $C_5 – C_{16}$ are liquids C_{17} onwards are solids
Combustion	Alkanes are fuels and burn in excess oxygen to produce carbon dioxide and water vapour Hydrocarbon + oxygen → carbon dioxide + water vapour
Solubility in water	Insoluble Like dissolves like
Solubility in non-polar substances	Soluble Like dissolves like
Reactivity	Relatively unreactive

Comparing properties of straight chain alkanes of different carbon numbers

- Larger alkanes have more electrons, and can therefore form stronger temporary dipoles, resulting in stronger London dispersion forces.
- More energy is needed to overcome these stronger London dispersion forces, which results in a higher boiling point.
- As a result, at room temperature, for alkanes, $C_1 – C_4$ are gases, $C_5 – C_{16}$ are liquids and C_{17} onwards are solids.

Comparing properties of alkanes of the same carbon number

Straight-chain vs. Branched

- Straight chain alkanes generally have higher boiling points than their corresponding branched isomers.
- This difference arises because straight-chain alkanes can pack more tightly together than branched-chain alkanes.
- Since the molecules are closer together, the London dispersion forces between them are stronger; more energy is required to separate the molecules, resulting in a higher boiling point.

Straight vs. Cyclic

- Cycloalkanes typically have higher boiling points because cyclic molecules can pack closer together than their corresponding straight chain molecules.
- Since the molecules are closer together, they experience stronger intermolecular forces. Stronger intermolecular forces require more energy to overcome and this leads to a higher boiling point.

Reactivity of Alkanes

Alkanes are **relatively unreactive** and therefore do not easily undergo many reactions. This is for two reasons:

1. Low polarity

Alkanes, since they contain only non-polar bonds, have very low polarity. Electrons in both the C-C and C-H bonds are shared nearly equally between atoms. No part of the molecule is significantly positive or negative. Therefore there are no electron-deficient or electron-rich areas to attract other molecules.

2. Sigma bonding

All bonds in alkane molecules are **single** bonds and therefore are also **sigma** (σ) bonds. Sigma bonds form when two atomic orbitals overlap head-on and are **stronger and more stable** than other bond types, e.g. pi bonds, due to a greater overlap of atomic orbitals. As a result, it requires a lot of energy to break them, i.e. a lot of energy is needed for an alkane to react.

Aromatic hydrocarbons

Aromatic compounds are compounds that contain a benzene ring structure in their molecules.

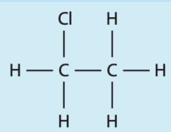
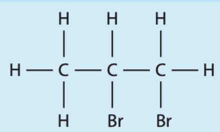
Properties of aromatic compounds

Identifying features	Contain a benzene ring
Carbon-carbon bonds	The C-C bonds are of intermediate length
Intramolecular bonds	Pure (non-polar) covalent bonds
Type of molecule	Non-polar
Intermolecular forces	London dispersion forces
Melting and boiling points	Relatively low (higher than corresponding alkanes, but lower than many other homologous series we shall soon encounter)
Solubility in water	Insoluble
Solubility in non-polar substances	Soluble

Methylbenzene is used as a solvent in household cleaning products. Benzene is not, since it is a carcinogenic (has the potential to cause cancer).

Haloalkanes

Haloalkanes are alkanes with a hydrogen atom replaced by a halogen (Group 17 element). You have already learnt how to name and draw haloalkanes.

	Chloroethane	1,2-dibromopropane
Molecular formula	C_2H_5Cl	$C_3H_6Br_2$
Expanded molecular structure		
Condensed structural formula	CH_2ClCH_3	$CH_3CHBrCH_2Br$

Properties of haloalkanes

Identifying features	One or more hydrogen atoms of an alkane have been replaced by a halogen (Group 17 element, e.g. F, Cl, Br)
Carbon-carbon bonds	Single (sigma)
Intramolecular bonds	Pure or non-polar covalent bonds *(electronegativity difference of 0.35)* Polar covalent bond (between C and halogen)
Type of molecule	Polar (unless halogens arranged in such a way that the shape is symmetrical, e.g. CCl_4 is non-polar
Intermolecular forces	Dipole-dipole London dispersion forces
Melting and boiling points	Higher than the corresponding alkanes due to the presence of dipole-dipole forces (and larger M_r). Increases as the size of the molecules increases
Solubility in water	Usually insoluble in water (small very halogenated alkanes may be slightly soluble in water)
Solubility in non-polar substances	Usually soluble Solubility increases as carbon chain length increases

Haloalkanes are widely used commercially: in fire extinguishers, as refrigerants, propellants, in solvents and in pharmaceuticals. The solvents used in dry cleaning clothes contain haloalkanes.

Uses of hydrocarbons

Hydrocarbons are widely used as fuels.

A fuel is a substance that releases energy when burnt in oxygen.

1. Energy production: Coal, oil and natural gas are all burnt in power plants to produce electricity.

2. Transportation: Hydrocarbons from crude oil are used to make gasoline, diesel, fuel oil and kerosene.

3. Domestic use, e.g. natural gas, used for heating and cooking, is primarily methane (the smallest hydrocarbon, CH_4).

4. Chemical production: Hydrocarbons are used to produce plastics (e.g. poly(ethene)) and synthetic fabrics (e.g. polyester).