Organic chemistry involves the study of the compounds formed by carbon. There are over five million known, so their investigation is greatly simplified by considering the behaviour of a few significant classes of molecules (chapter 21). The most important classes are covered in turn, starting with the simplest compounds: those that contain only carbon and hydrogen atoms (chapters 22 and 23).

The next pair of chapters introduce atoms that create significant polarity in the bonding within the organic compounds, which has very significant effects on the types of reaction the molecules undergo. Halogen atoms are present in the halogenoalkanes (chapter 24); oxygen atoms forming single bonds are present in the alcohols (chapter 25).

Oxygen atoms are also capable of forming double bonds, and so the consequences of such a bond are discussed in the next two chapters, on aldehydes and ketones (chapter 26) and carboxylic acids (chapter 27). The final important element in organic chemistry is nitrogen, and chapter 28 surveys some of the molecules that contain nitrogen atoms. Chapter 29 seeks to draw together some of the ideas presented earlier and includes a discussion of the efforts organic chemists make to synthesize chemicals of significant value, especially to medicine, such as ibuprofen.

Chapter 30 tries to provide an insight into the exceptionally important area of biochemistry, arguably the most significant application of chemistry. In particular, the illustrations provided should prove helpful.

The final two chapters in the book, while not falling specifically under the heading ‘organic chemistry’, revolve around the separation and identification of chemicals. Powerful and widely used techniques such as chromatography (chapter 31) and spectroscopy (chapter 32) were introduced in the 20th century and transformed our ability to identify the structure of molecules. Since 1950, advances have come most quickly in the area of biochemistry. In the second half of the 20th century, the detailed mechanism by which genetic information is passed from one generation to another via the replication, transcription, and translation of DNA was revealed. With little doubt, this is the most profound idea science has discovered during that period of time. At the heart of molecular biology is the double helix structure of the DNA molecule, shown here. You can read an account of this fascinating discovery in spreads 30.8–10.

There are still big questions to be answered. For example, it is unclear how (in full molecular detail) a single cell in the body differentiates to produce the appropriate limbs and organs. Maybe you will be the person who provides one of the vital links in this continuing quest.
Introduction to organic chemistry

Organic chemistry is the study of the compounds of carbon. Carbon compounds are far more numerous than those of other elements because carbon atoms are able to bond together to form a wide range of chains and rings. The subject is called organic chemistry because living organisms are composed mainly of carbon compounds. Organic chemistry is the chemistry of life. It also includes the chemistry of an enormous range of substances, including food, fuels, textiles, plastics, drugs, dyes, explosives, pesticides, and paint. Most of the world’s energy comes from burning carbon-based fuels, and the organic chemical industry is essential to most national economies. Major international crises have occurred over the supply and trade of carbon-containing substances such as crude oil, natural gas, coal, and their products. This chapter explores the basic principles of organic chemistry while giving you some feel for its scope. With over five million separate compounds, it would seem to be a vast subject. However, you will learn to group this huge array of organic compounds into separate families (called homologous series), each with its own distinct set of properties. This grouping together of compounds that react in a similar way makes studying them much simpler.

Organic chemistry and the carbon atom

The basic structure of any organic compound – be it plastic, protein, medicine, fuel, or fibre – consists of a skeleton of carbon atoms joined together in chains and rings. The ability of an element to form chains of atoms bonded together is called catenation. This spread gives examples of the types of carbon skeleton possible. Later spreads will discuss the actual shapes of organic molecules and the conventions used to name them.

Chains and rings of carbon atoms

Carbon is unique in that its atoms can bond together to make chains and rings of almost unlimited size and complexity. At the same time, bonds remain free to join with other atoms. Most of the diagrams below show only the carbon skeleton of some chains and rings; each line represents a bonding electron pair. Most of the diagrams do not show three-dimensional structure: they are projections onto the flat two-dimensional page. Carbon skeletons may also consist of branched chains or of two or more rings fused together.

Kinetic and thermodynamic stability

Another reason why carbon forms so many compounds is that its compounds are kinetically very stable. The activation energy required to break a carbon–carbon bond is high. At normal temperatures compounds with carbon–carbon bonds are very stable. Once the activation energy is overcome at high temperatures, carbon compounds combust readily in the presence of oxygen. The reactions are highly exothermic because carbon compounds are thermodynamically unstable relative to their combustion products. It is this combination of a high activation energy and exothermic combustion that makes many organic compounds very useful as fuels.

Summary

- Carbon compounds form the basis of living organisms. They form an enormous range of materials and fuels central to the function of any modern industrialized society.
- Catenation is the ability of an element to form chains with itself.
- Carbon catenates to form molecules of almost any size or shape.
21.2

ORGANIC MOLECULES

The properties of organic molecules frequently depend on their shape as well as on the atoms they contain. As a result, chemists have developed various ways of representing the three-dimensional shapes of molecules, especially organic molecules, on two-dimensional sheets of paper. This spread begins with a discussion of empirical and molecular formulae, with which you are already familiar. The shortcomings of these formulae lead to the development of two types of formulae that represent molecular shape. The spread ends by listing the 10 basic carbon skeletons on which many common organic compounds are based.

Writing molecular formulae

It is possible to represent organic molecules in a number of different ways. The molecular formulae (see chapter 9 ‘Reacting masses and volumes’) of a compound shows the actual numbers of each type of atom present. For example, the molecular formula of ethanol is C₂H₆O. A problem immediately arises because the molecular formula of the compound methoxymethane is also C₂H₆O. The molecular formula does not distinguish between these two compounds.

Condensed and displayed structural formulae

The structural formula provides more information because it specifies exactly which atoms are bonded together. The condensed (shortened) structural formulae of ethanol and methoxymethane are CH₃CH₂OH and CH₃OCH₃, respectively. (The CH₂CH₃ group is sometimes written as CH₃CH₂: this description is less clear and should be avoided.) Structural formulae can also be drawn to show the bonds between atoms or groups of atoms. Such a displayed structural formula (or graphic formula) projects the three-dimensional structure of a molecule onto a flat two-dimensional page. As a result, bond angles are distorted and appear generally to be 90° or 180°.

Drawing stereochemical formulae

The stereochemical formula represents bond angles more accurately. It shows each atom separately and all the bonds present; it also attempts to represent the shape of the molecule. It is agreed among chemists that:

- A bond in the plane of the paper is shown as a solid line.
- A bond going behind the paper is shown as a dashed line (or as a diminishing wedge or as a ‘striped’ wedge).
- A bond coming in front of the paper is shown as an enlarging wedge.

Applying these rules, the tetrahedral shape of methane appears as shown below, together with the stereochemical formulae of ethanol and methoxymethane. Stereochemical formulae are only rarely used (but see spreads 22.8 and 28.6).

Shorthand methods

The structural formulae of larger molecules containing rings and long chains of carbon atoms are tedious to draw out in full. A shorthand form of representation is often used, which makes the following assumptions:

- Each single line represents a single covalent bond between two carbon atoms; the symbols for the carbon atoms are not included.
- All other elements except for hydrogen are represented by their chemical symbols.

• The ends of all bonds are assumed to be occupied by hydrogen, unless otherwise indicated by a different chemical symbol.

The examples on the right show the skeletal formulae for cyclohexane C₆H₁₂ and hexane C₆H₁₄.

Saturated and unsaturated molecules

A molecule in which all the carbon atoms have four single covalent bonds is called a saturated molecule. A molecule containing one or more multiple bonds (i.e. double or triple covalent bonds) is said to be unsaturated.

Homologous series

The arrangement of carbon atoms may be thought of as the skeleton of an organic molecule. All the atoms of other elements are attached to that skeleton. The simplest skeleton is a single carbon atom; the next simplest consists of two carbon atoms bonded together. Then there can be chains of three, four, five, or more carbon atoms. A series of carbon compounds differing from each other only by the addition of more —CH₂— groups to increase the length of the carbon chain is called a homologous series. Compounds are named according to internationally agreed rules published by the International Union of Pure and Applied Chemistry (IUPAC) as explained in the next spread.

SUMMARY

- The empirical formula shows the simplest whole-number ratio of the numbers of each type of atom present in a molecule.
- The molecular formula shows the actual numbers of each type of atom present in a molecule.
- The structural formula shows exactly which atoms are bonded together. It may be condensed or displayed.
- The stereochemical formula represents the individual atoms in a molecule, the bonds between the atoms, and the angles between the bonds.
- A saturated molecule contains single covalent bonds only.
- An unsaturated molecule contains one or more multiple (double or triple) covalent bonds.
- The members of a homologous series differ from each other only in the length of the carbon chain.

PRACTICE

1. Copy the 10 carbon skeletons shown above. To each, add the bonds and hydrogen atoms necessary to produce the alkane homologous series from methane to decane.
2. Why are the compounds in question 1 referred to as being saturated?
3. Give the following for the compound propane C₃H₈:
   - a Molecular formula
   - b Condensed structural formula
   - c Displayed formula
4. Draw the structural formulae corresponding to each of the following skeletal formulae:
   - a
   - b
21.3

OBJECTIVES

• Naming alkanes
• Structural isomers
• Chain isomers

STRUCTURAL ISOMERISM

The first organic compounds which we shall study are the hydrocarbons, which consist of a carbon skeleton to which only hydrogen atoms are attached. The simplest skeletons take the form of a single chain or a branched chain. The name of an organic compound gives information about its structure, and understanding how to name hydrocarbons prepares you for the study of more complex organic molecules containing elements other than carbon and hydrogen.

Straight-chain and branched-chain hydrocarbons

An organic compound with a straight-chain or branched-chain carbon skeleton that does not contain a benzene ring, spread 23.1, is called an aliphatic compound. The simplest aliphatic compounds are the alkanes, which contain carbon–carbon single bonds only. To find the IUPAC name for an alkane, you must carry out the following steps:

1. Identify the longest unbroken carbon chain (called the main chain), count the number of carbon atoms in it, and name appropriately as methyl, ethyl, propyl, butyl, pentyl, etc. (see the previous spread).
2. Identify any shorter branches (called side chains) attached to this main chain as methyl (CH₃), ethyl (CH₃CH₂), propyl (CH₃CH₂CH₃), etc. groups, etc.
3. Number the carbon atoms at which the branches are attached by counting the carbon atoms of the main chain from the end that will give the lower number at the first point of difference.

For example, the first compound to the left is 3-methylpentane. The name consists of:
- a methyl because the compound only contains carbon–carbon single bonds and so is an alkane;
- pent- because there are five carbons in the main chain;
- methyl because the branch contains one carbon atom;
- 3- because the branch is attached at the third carbon atom, no matter from which end of the main chain you count.

The second compound to the left would be called 2-methylpentane counting from one end of the main chain or 4-methylpentane counting from the other end. The correct name is 2-methylpentane because it contains the lower number.

Worked example on naming an alkane

Question: Name the compound shown to the left.

Strategy: Follow the steps mentioned in the text above.

Answer:

Step 1 Count the carbon atoms in the longest unbroken chain and name it. The longest unbroken chain is five carbon atoms long and so the substance is a substituted pentane. The term substituted generally means that one or more hydrocarbon groups (e.g. methyl CH₃ —) or atoms other than hydrogen (e.g. Cl—) are attached to the main chain.

Step 2 Count the carbon atoms in each side chain and name them. The side chains all contain a single carbon atom and so they are all methyl groups. There are three methyl groups, so the substance is a trimethylpentane.

Step 3 Number the carbon atoms to which the side chains are attached, keeping the numbers as low as possible. Numbering from the left gives two methyl groups on carbon 2 and one on carbon 4, i.e. 2,2,4-... Numbering from the right gives one methyl group on carbon 2 and two on carbon 4, i.e. 2,4,4-... Numbering from the left gives the lower number at the first point of difference. So the IUPAC name is 2,2,4-trimethylpentane.

Structural isomerism

Alkanes with four or more carbon atoms can show different arrangements of the carbon atoms. For example, there are two structures (and two different substances) that have the molecular formula C₄H₁₀, namely butane and 2-methylpropane.

Molecules that share the same molecular formula but have different structural formulae are called structural isomers. There are three structures for the hydrocarbon C₅H₁₂, corresponding to the molecules pentane, 2-methylbutane, and 2,2-dimethylpropane.

Structural isomers with different arrangements of the carbon skeleton are often called chain isomers. Chain isomers may have different physical properties because the different shapes will alter the strength of the dispersion forces. For example, pentane boils at 36 °C, 2-methylbutane at 28 °C, and 2,2-dimethylpropane at 10 °C. Their chemical properties, however, are virtually the same because they are all alkanes.

Twisting the end of a molecule (by rotating a single carbon-carbon bond) does not create an isomer. For example, a bent chain is not an isomer of a straight chain, as shown in this example of pentane C₅H₁₂. Molecules are only isomeric if changing from one isomer to another involves breaking bonds and reassembling the molecule in a different way. Bond angles are represented as 90° in these structural formulae, which can be misleading. In reality, bond angles in alkanes are very close to the tetrahedral angle (109°28’).

SUMMARY

• The name of an organic compound is based on the number of atoms in the longest unbroken carbon chain.
• The carbon atoms in the main chain are numbered so that the positions of side chains are given the lower number at the first point of difference.
• Structural isomers have the same molecular formula but different molecular structures, i.e. the atoms are bonded together in different sequences.
• Chain isomers have different arrangements of their carbon skeletons.
• Chain isomers have similar chemical properties but different physical properties.

PRACTICE

1. Draw all the possible isomers of hexane C₆H₁₄ and give the name of each.
2. Draw structural formulae for the following alkanes:
   a. 2,2-Dimethylbutane
   b. 2-Methyl-4-ethylhexane
   c. Cyclohexane C₆H₁₂
3. A student gave the name of a hydrocarbon as 2-methyl-2-ethylbutane. Give the correct name.
4. a. Draw the structural formula of the most highly branched isomer of octane.
   b. Suggest why this isomer combusts more smoothly than the straight-chain isomer.
   c. Which of these two isomers has the higher boiling point? Give reasons why this isomer gives rise to the higher value.
21.4

OBJECTIVES

• Functional groups
• Positional isomers
• Functional group isomers

FUNCTIONAL GROUPS

The simplest organic molecules are the hydrocarbons, which consist of hydrogen atoms attached to a skeleton of carbon atoms. More complex substances result when hydrogen atoms are replaced by atoms of other elements. These atoms make up functional groups, which have significant effects on the properties of the compounds. We will not look at the properties of the various functional groups in this introductory chapter. At this stage you simply need to recognize the groups, name them, and name molecules that contain them.

Functional groups

Atoms other than carbon or hydrogen or groups of such atoms attached to the main carbon chain are called functional groups. As with hydrocarbons, the systematic IUPAC name of a substance that has a functional group allows you to determine its structural formula. For example, look at the structural formula of ethanol shown to the left. The first part of the name ethanol shows the length of the carbon chain (two carbon atoms in a saturated molecule CH3CH2—). The second part of the name —OH indicates the presence of the alcohol functional group —OH. There is a complete homologous series of alcohols (i.e. methanol, ethanol, propan-1-ol and propan-2-ol, butanol, etc.) that are based on the alkane homologous series. In each case, a hydrogen atom in an alkane molecule is replaced by a hydroxyl group —OH.

There are various different series of organic compounds, each with its own functional group. Examples include the ketones, aldehydes, carboxylic acids, ethers, and halogenoalkanes. The formulae and structures of these compounds are shown below. Note that, when writing a general formula for a homologous series containing a functional group, the symbol R (residue) may be used to denote an alkyl group such as CH3— or CH3CH2—.

\[
\begin{align*}
R & : \text{OH} \\
R & : \text{COH} \\
R & : \text{CHOH} \\
R & : \text{COOH} \\
R & : \text{OR} \\
R & : \text{X}
\end{align*}
\]

(a) Alcohols. (b) Ketones. (c) Aldehydes. (d) Carboxylic acids. (e) Ethers. (f) Halogenoalkanes.

Chemical and physical properties

Functional groups determine the chemical reactions that a molecule can undergo, so all members of a homologous series have very similar chemical properties. The length of the carbon chain does not affect chemical properties because the C—C and C—H bonds have large bond enthalpies and so do not react easily. The chain length mainly affects physical properties such as melting point and boiling point. As additional CH2— units are added, the molecules have larger dispersion forces, and so the melting and boiling points increase.

Naming molecules with different functional groups

The four compounds shown below have names including ‘butanol’ because the longest carbon chain consists of four carbon atoms (corresponding to the alkane butane). The other part of each name denotes the functional group present. The position of the functional group must be given in the name if there is any chance of ambiguity. For example, in (b), the hydroxyl group is attached to carbon atom 1 (butan-1-ol). It could also be attached to carbon atom 2 (butan-2-ol). These two substances both have the molecular formula C4H10O but different structures. Functional groups give rise to isomerism.

\[
\begin{align*}
\text{(a) butanol} & : \text{CH}_3\text{CH} = \text{CH}_2 \text{CH} \text{CH}_2 \text{OH} \\
\text{(b) butan-2-ol} & : \text{CH}_3\text{CH} = \text{CH}_2 \text{CH} \text{CH}_2 \text{OH} \\
\text{(c) butanoic acid} & : \text{CH}_3\text{CH} = \text{CH}_2 \text{CH} \text{COOH} \\
\text{(d) isobutanol} & : \text{CH}_3\text{C} = \text{CH} \text{CH} \text{CH}_2 \text{OH}
\end{align*}
\]

Isomers

Structural isomers can arise from placing a functional group in a different position on the chain. For example, CH3COH is the molecular formula for both propan-1-ol and propan-2-ol, but the functional group —OH occurs at position 1 or 2, giving different structural formulae.

These structural isomers are sometimes called positional isomers. The physical properties of positional isomers may vary slightly; for example, propan-1-ol boils at 97 °C whereas propan-2-ol boils at 82 °C. Their chemical properties may also vary because of the different position of the functional group on the carbon skeleton.

Structural isomers may also have different functional groups. The molecular formula C4H10O may correspond to propan-2-CH3CH2CHO (an aldehyde) or to propanone CH3COCH3 (a ketone) – see illustrations to the right. These structural isomers are sometimes called functional group isomers. Functional group isomers not only have different physical properties but they also have different chemical properties because the functional group is different.

Methoxymethane CH3CH2OH (see spread 21.2) is an ether; it is a functional group isomer of ethanol CH3CH2OH. Hydrogen bonding between ethanol molecules results in a much higher boiling point for ethanol (78 °C) than for methoxymethane (~25 °C). Ethanol reduces aqueous dichromate(VI) ions, turning the solution from orange to green. Methoxymethane does not react with aqueous dichromate(VI) ions.

Hydrocarbons revisited

The simplest hydrocarbons are saturated and are the homologous series called the alkanes. If a double bond is present, then the result is the homologous series of alkenes. The first few members of this series are shown to the right. The double bond in alkenes is called a functional group because it gives the series its distinctive chemical properties.

SUMMARY

• A functional group is an atom other than carbon or hydrogen (e.g. —Cl), a group of atoms (e.g. —OH), or a carbon–carbon double bond.
• The length of the carbon chain has little effect on the properties of a homologous series containing a functional group.
• Structural isomers of compounds that have functional groups may be positional isomers or functional group isomers.

PRACTICE

1. Draw the structural formulae of all possible isomers corresponding to each of the following molecular formulae:
   a) C4H8     c) C4H9Cl
   b) C4H10    d) C3H6O.
The reactions of organic compounds fall into a small range of distinct types. Apart from combustion, in which the molecular structure is completely destroyed, reactions tend to involve only part of the molecule, usually the functional groups. These act as reactive sites, reacting with other chemicals. You will meet the specific reactions of functional groups in the following chapters. The aim of the last two spreads in this chapter is to introduce the types of reaction undergone by organic molecules.

The site of attack

Alkanes are very unreactive. The carbon–carbon and carbon–hydrogen bonds do not break easily because they have high average bond enthalpies (C–C, 348 kJ mol\(^{-1}\); C–H, 413 kJ mol\(^{-1}\)). The elements have similar electronegativities (C, 2.5; H, 2.2) and so the bonds have little polarity.

Molecules with functional groups are generally more reactive. For example, the halogenoalkane bromoethane reacts to form ethanol when heated with aqueous base:

\[
\text{CH}_3\text{CH}_2\text{Br} (aq) + \text{OH}^-(aq) \rightarrow \text{CH}_3\text{CH}_2\text{OH} (aq) + \text{Br}^-(aq)
\]

Comparing bromoalkanes with alkanes, we can see that:
1. The C–Br bond is weaker than the C–C and C–H bonds (average C–Br bond enthalpy 276 kJ mol\(^{-1}\)).
2. The electronegativity of bromine is 3.0, so the C–Br bond is polarized

Reactive sites

Functional groups in molecules contain reactive sites that are attacked by incoming species. A reactive site is a region of higher or lower electron density.

Electron-deficient sites include:
- atoms with a partial +\(\delta\) charge because they are bonded to a more electronegative atom;
- positive ions.

Electron-rich sites include:
- atoms with a partial −\(\delta\) charge because they are bonded to a less electronegative atom;
- negative ions;
- double bonds between carbon atoms;
- lone pairs.

The attacking species

Two important classes of reagent are used in organic reactions: these classes are called nucleophiles and electrophiles.

- **Nucleophiles** are species that are electron-pair donors. Nucleophiles include negatively charged ions such as $\text{CN}^-$, $\text{OH}^-$, or $\text{Cl}^-$, as well as molecules bearing lone pairs of electrons like $\text{H}_2\text{O}$ or $\text{NH}_3$. Nucleophiles attack the partially positively charged (\(\delta^+\)) atoms of polar covalent bonds. They also often attack the regions of high electron density in the double bond in alkynes and other double-bonded structures. Electrophiles accept electron pairs to form new bonds.

- **Electrophiles** are species that are electron-pair acceptors. Electrophiles are typically positive ions like $\text{H}^+$ or $\text{NO}_2^+$. Electrophiles attack the partially negatively charged (\(\delta^-\)) atoms of polar covalent bonds.