

An introduction to AS Level organic chemistry

A-Level Chemistry 9701 · Topic 13 revision notes

Everything from the 6 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

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|---|---|
| 1. <u>Organic formulae and functional groups</u> | 4. <u>Shapes of organic molecules, sigma and pi bonds</u> |
| 2. <u>Naming organic compounds</u> | 5. <u>Structural isomerism</u> |
| 3. <u>Types of organic reaction and mechanism</u> | 6. <u>Cis-trans and optical isomerism</u> |

1 Organic formulae and functional groups

Syllabus 13.1

A **molecular formula** gives the actual number of each atom ($C_4H_{10}O$); a **structural formula** shows the arrangement unambiguously ($CH_3CH_2CH_2CH_2OH$); a **displayed formula** shows every bond; a **skeletal formula** shows only the carbon skeleton and functional groups, with carbon atoms at corners and line ends and hydrogens on carbon left out. A **homologous series** shares a general formula and functional group, with each member differing by CH_2 . The **functional group** is the atom or group responsible for the characteristic reactions.

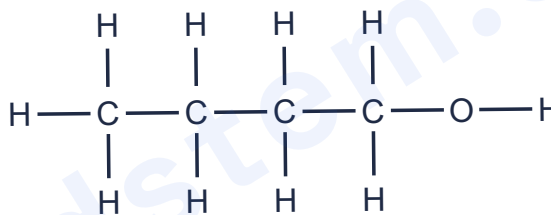
molecular



structural



displayed



skeletal



each corner or
line end is a C

four ways to draw butan-1-ol

Fig. 1: molecular, structural, displayed and skeletal formulae of butan-1-ol

Every carbon makes four bonds.

- ✓ **Skeletal:** corners and ends are C; H on C omitted.
- ✓ **Structural:** must be unambiguous.
- ✓ **Homologous series:** same general formula, differ by CH_2 .
- ✓ **Functional group** decides the reactions.

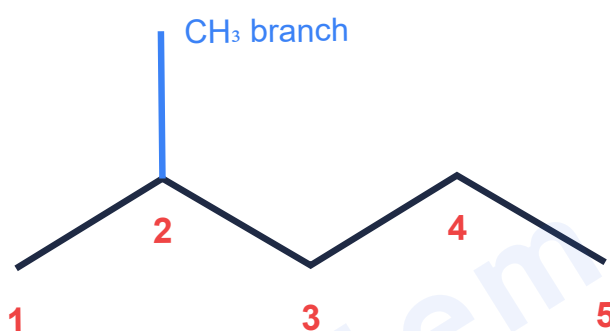
Watch out!

In a skeletal formula hydrogens on carbon are not drawn, but they are still there: work out how many each carbon needs to make four bonds. Hydrogens on O or N are shown ($-OH$, $-NH_2$). A structural formula must be unambiguous: C_3H_7OH is not acceptable because it could be propan-1-ol or propan-2-ol.

2 Naming organic compounds

Syllabus 13.1

Find the **longest carbon chain** containing the functional group; its length gives the stem (meth-, eth-, prop-, but-, pent-, hex-). The functional group gives the **suffix** (-ane, -ene, -ol, -al, -one, -oic acid, -nitrile, -amine) or a **prefix** (chloro-, bromo-, methyl-). Number the chain from the end that gives the **lowest locants**, list prefixes **alphabetically**, and use di-, tri- for repeats.



2-methylpentane

longest chain = 5 C (pent-); number from the end nearer the branch

Fig. 1: naming a branched alkane

Longest chain, lowest numbers, alphabetical prefixes.

- ✓ **Stem** from the longest chain including the functional group.
- ✓ **Suffix** from the main group; halogens and alkyl groups are prefixes.
- ✓ **Lowest locants**; di/tri for repeats.
- ✓ **Esters**: alkyl + -oate.

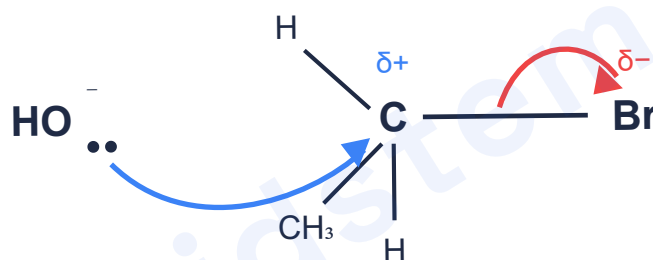
Watch out!

Always find the **longest** chain, which may bend round a corner in a drawn structure; a "branch" at the end of a chain is just part of the chain. Number from the end that gives the lowest locants, and in nitriles, acids and aldehydes the functional-group carbon is C1 and is included in the stem count.

3 Types of organic reaction and mechanism

Syllabus 13.2

In **homolytic fission** a covalent bond breaks with one electron going to each atom, giving two **free radicals** (species with an unpaired electron). In **heterolytic fission** both electrons go to one atom, giving ions. A **nucleophile** is an **electron-pair donor** that attacks a $\delta+$ carbon (OH^- , CN^- , NH_3 , H_2O); an **electrophile** is an **electron-pair acceptor** attracted to regions of high electron density such as a $\text{C}=\text{C}$ (H^+ , $\text{Br}^{\delta+}$, NO_2^+). A **curly arrow** shows the movement of a pair of electrons, starting from a lone pair or bond.



arrows start at a lone pair or a bond and end where the pair goes
 OH^- is the nucleophile; the $\text{C}-\text{Br}$ bond breaks heterolytically

Fig. 1: curly arrows for hydroxide attacking bromoethane

Arrows move pairs of electrons.

- ✓ **Homolytic** $\rightarrow$ radicals; **heterolytic** $\rightarrow$ ions.
- ✓ **Nucleophile** donates a pair; **electrophile** accepts one.
- ✓ **Arrow** starts at a lone pair or bond.
- ✓ **Type** (what happens) + **attacker** = mechanism name.

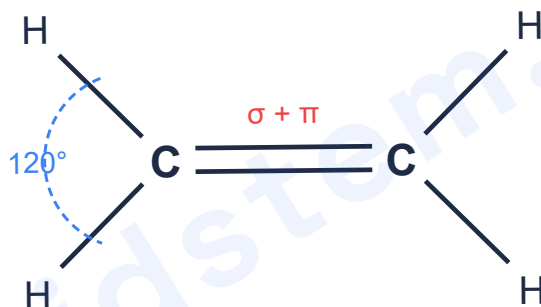
Watch out!

A nucleophile **donates** an electron pair; an electrophile **accepts** one. Curly arrows start from a **lone pair or a bond**, never from an atom symbol or a charge sign. Homolytic fission gives radicals, not ions.

4 Shapes of organic molecules, sigma and pi bonds

Syllabus 13.3

A carbon bonded to **four** atoms (single bonds only) is **sp^3** , tetrahedral, 109.5° . A carbon in a double bond is bonded to **three** atoms: **sp^2** , trigonal planar, 120° . A carbon in a triple bond (or with two double bonds) is bonded to **two**: **sp** , linear, 180° . Every single bond is a σ bond; a double bond is $\sigma + \pi$. The π bond forms by sideways overlap of p orbitals above and below the plane, so ethene is **planar** and there is **no rotation** about $C=C$, which is why cis-trans isomers exist.



each C is sp^2 : trigonal planar; all six atoms lie in one plane
5 σ bonds and 1 π bond; no rotation about $C=C$

Fig. 1: ethene is planar, with 120° bond angles

Atoms bonded to carbon decide its shape.

- ✓ **4** $\rightarrow sp^3$, 109.5° ; **3** $\rightarrow sp^2$, 120° ; **2** $\rightarrow sp$, 180° .
- ✓ **Every bond** has one σ .
- ✓ **Double** +1 π ; **triple** +2 π .
- ✓ **π bond**: planar, no rotation.

Watch out!

Count the $C-H$ bonds; they are σ bonds too. A double bond is **one** σ and **one** π , not two π . In propene only the two $C=C$ carbons are planar; the CH_3 carbon is tetrahedral.

5 Structural isomerism

Syllabus 13.4

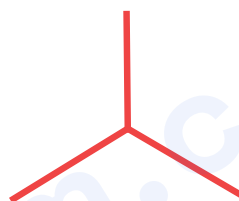
Structural isomers have the **same molecular formula** but a **different structural formula**. **Chain** isomers differ in the carbon skeleton (butane and methylpropane).

Positional isomers have the same functional group in a different position (propan-1-ol and propan-2-ol). **Functional group** isomers belong to different homologous series (propanal and propanone; ethanoic acid and methyl methanoate). Branching lowers boiling point because branched molecules have less surface contact.



butane

b.p. $-1\text{ }^{\circ}\text{C}$



methylpropane

b.p. $-12\text{ }^{\circ}\text{C}$

both C_4H_{10} : chain isomers
same molecular formula, different structural formula

Fig. 1: the two chain isomers of C_4H_{10}

Same formula, different connections.

- ✓ **Chain:** different carbon skeleton.
- ✓ **Positional:** same group, different position.
- ✓ **Functional group:** different homologous series.
- ✓ **Name each** structure to avoid duplicates.

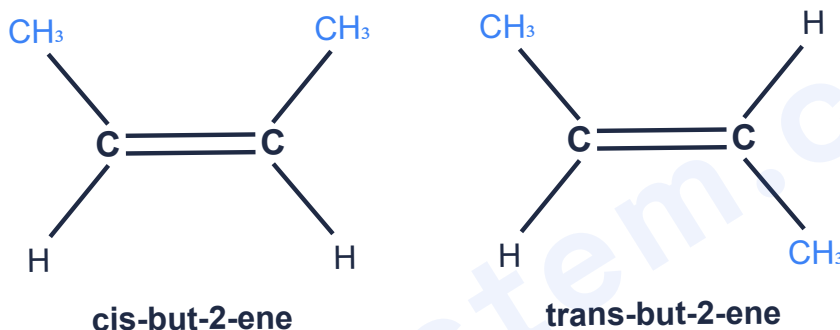
Watch out!

Drawing the same molecule twice is the commonest error: a chain drawn bent, or numbered from the other end, is not a new isomer. Name each structure; if two names are identical, the structures are the same. 3-bromobutane is not a new isomer; it is 2-bromobutane.

6 Cis-trans and optical isomerism

Syllabus 13.4

Stereoisomers have the same structural formula but a different arrangement of atoms in space. **Cis-trans isomerism** arises because rotation about a $C=C$ bond is restricted; it needs **two different groups on each carbon** of the double bond. **Optical isomerism** arises when a carbon atom carries **four different groups** (a **chiral centre**); the two forms, **enantiomers**, are non-superimposable mirror images that rotate plane-polarised light equally in opposite directions. A 50 : 50 mixture is a **racemic mixture** and has no overall effect on the light.



butan-2-ol: * marks a chiral centre (H, OH, CH_3 , C_2H_5)

restricted rotation gives cis/trans; four different groups give optical isomers

Fig. 1: cis and trans but-2-ene, and the chiral centre in butan-2-ol

Rigid $C=C$ or four different groups.

- ✓ **Cis-trans:** $C=C$ with two different groups on each carbon.
- ✓ **Chiral centre:** C with four different groups.
- ✓ **Enantiomers:** non-superimposable mirror images.
- ✓ **Racemic:** 50 : 50, optically inactive.

Watch out!

Cis-trans isomerism needs **two different groups on each carbon** of the $C=C$, so but-1-ene does not show it. A chiral centre needs **four different groups**; a carbon with two identical groups, such as the central carbon in propan-2-ol, is not chiral.