10.1 Fundamentals of Organic Chemistry

Mark Schemes

Course	DP IB Chemistry
Section	10. Organic Chemistry
Topic	10.1 Fundamentals of Organic Chemistry
Difficulty	Medium

Exam Papers Practice

To be used by all students preparing for DP IB Chemistry SL
Students of other boards may also find this useful

1a

A *homologous series* has the following features:

Any **three** from:

- Members have the same functional group; [1]
- Members have the same general formula; [1]
- Successive members differ by CH_2; [1]
- Members have similar chemical properties; [1]
- There is a gradual change in the physical properties; [1]

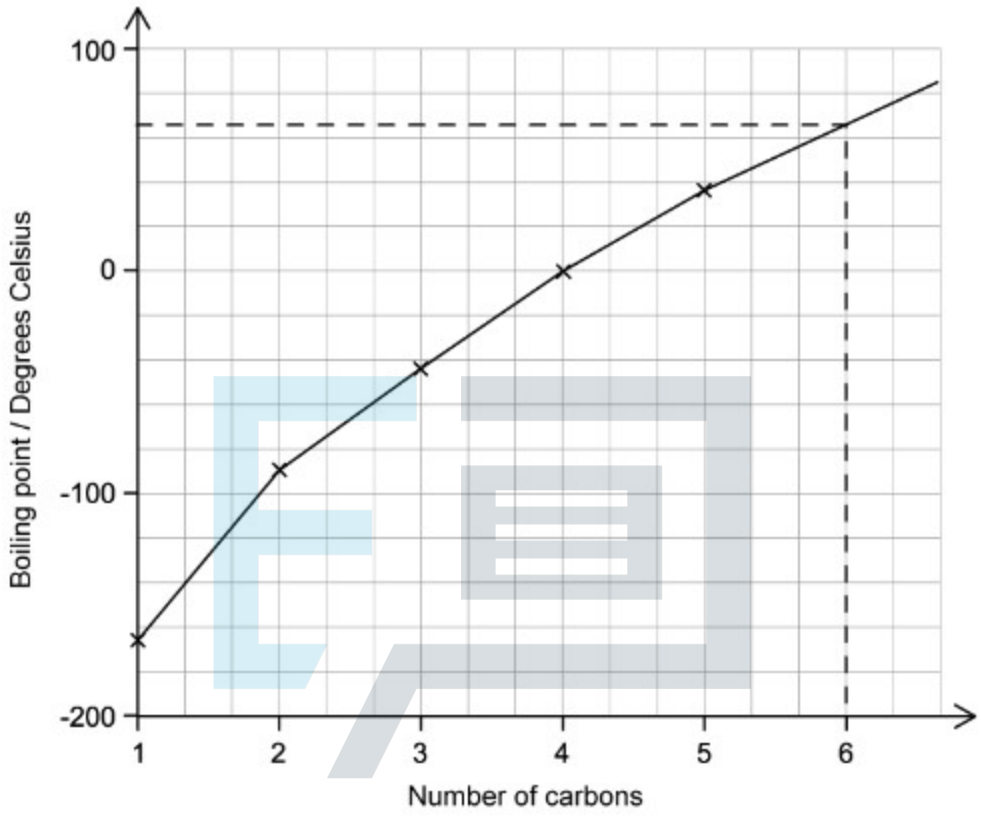
[Total: 3 marks]

- A functional group can be thought of as the 'reactive' part of the molecule, although in the case of alkanes we can't really say that they have a reactive part
- The word *similar* is important here and cannot be substituted by 'the same'
- That is because as the chain length increases it can subtly affect the chemical reactivity of the molecules, so the reactions of the group members are not identical
- Increasing the chain length adds more electrons (and atoms) to the molecule so the distribution of electron density changes and so does the overall polarity of the molecule, affecting the chemical reactivity
- The physical properties that change would be things like melting point, boiling point, and density

Exam Papers Practice

1b

The graph of boiling point of the alkanes:



Exam Papers Practice

- Quality of point plotting; [1]
- Accurate trend line; [1]
- Estimated boiling point in the range: 60–70 °C; [1]
- Vertical tie line shown starting from 6 carbons and intercepting the trend line **AND** horizontal tie line from the trend line to the y axis; [1]

[Total: 4 marks]

- When you are asked to plot a graph make sure you use a **sharp pencil** and a **ruler** to help you with the straight lines
- The quality of point plotting is how close you are to the actual point
  - A small tolerance will be allowed, so this is why using a sharp pencil and ruler helps you get it spot on
- Mark tiny crosses for the points and show one thin trend line
- If you draw the points and line too thickly you may lose accuracy on your graph and not be able to read values precisely enough
- It helps the examiner if you draw *dotted* tie lines when estimating values from a graph
  - Marks are often awarded if you have read *your own* graph correctly

1c

The general formula of an alkyne is:

- C_nH_{2n-2}; [1]
  (Allow if another symbol other than *n* has been used in the general formula)

The fifth member of the alkyne family is

- Hexyne **AND** C_6H_{10}; [1]
  (Allow if the position of the triple bond is given in the name, e.g., hex-1-yne, hex-2-yne or hex-3-yne)

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[Total: 2 marks]

- Be careful with alkenes and alkynes when working out the family members as there is no molecule with n=1, so the fifth member of the series has six carbons
- The minimum number of carbons here is n=2 as it takes two carbons to make a double or triple bond
- You need to know the general formulae of:
  - Alkanes, alkenes, alkynes, ketones, alcohols, aldehydes, and carboxylic acids

1d

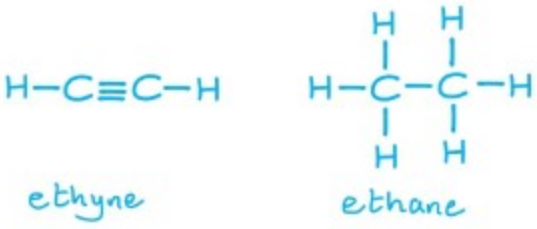
The boiling point of ethyne:

- Would be expected to be lower than ethane; [1]
- Ethyne has fewer (atoms and) electrons than ethane **AND** the intermolecular forces / Van der Waals forces / London dispersion forces would be weaker (so the boiling point should be lower); [1]
  (The type of attractive forces must be mentioned to score the mark)

[Total: 2 marks]

- Sometimes predictions in chemistry are not always straightforward, as more than one factor can be involved. In fact ethyne actually has a higher boiling point than ethane
- Ethyne is a small linear molecule, so although it has fewer electrons than ethane, the molecules can pack together more closely than ethane increasing the strength of the intermolecular forces

Exam Papers Practice



- These differences in structure explain why linear and branched isomers of the same molecule have slightly different boiling points
  - The linear isomer will have the higher boiling point because the molecules can pack more closely together, meaning there are more surface area points of contact
- Atoms or branches that stick out prevent molecules from a close approach so branched isomers generally have a slightly lower boiling point than linear ones

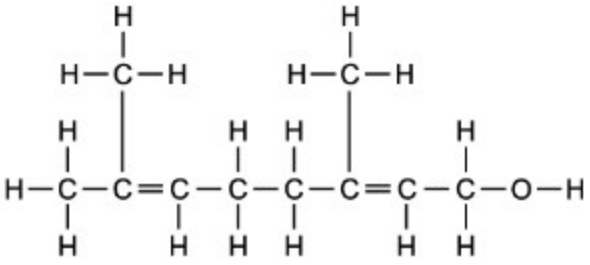
2a

i) The two functional groups found in geraniol are:

- Hydroxyl **AND** alkenyl; [1]

ii) The molecular formula of geraniol is $C_{10}H_{18}O$; [1]

iii) Displayed formula correctly drawn; [1]



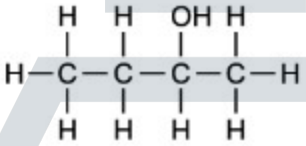
Exam Papers Practice

[Total: 3 marks]

- Alcohol and alkene are **not** acceptable answers for part (i) because these are the names of organic families and **not** the names of the functional groups
- **Be careful** in skeletal diagrams to count the hydrogens on the double bonds as well as on the methyl side groups
- The displayed formula must show all the atoms and bonds in a molecule
- You are not expected to show true bond angles in a displayed formula – in fact, it can be more confusing if you do so in a large complex molecule

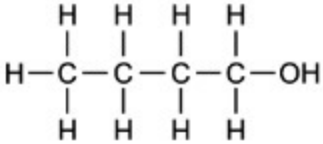
2b

i) The displayed structure of butan-2-ol is:



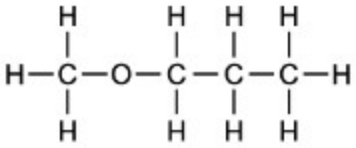
- Correctly drawn structure showing all the bonds; [1]

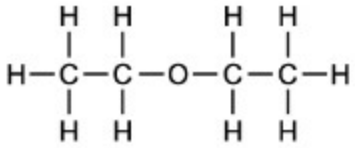
ii) A positional isomer of butan-2-ol is:



- Correct drawing of butan-1-ol; [1]

A functional group isomer of butan-2-ol is:

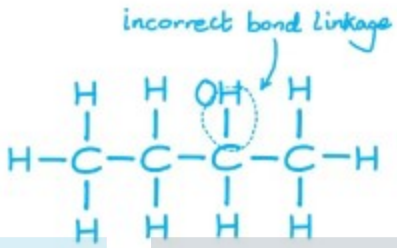




- Either correct drawing of an ether; [1]

[Total: 3 marks]

- To draw a displayed structure, you need to interpret the IUPAC naming rules correctly
- Be careful to join the correct bonds - students frequently lose marks by joining carbon to the H on a hydroxyl group as the following drawing shows:



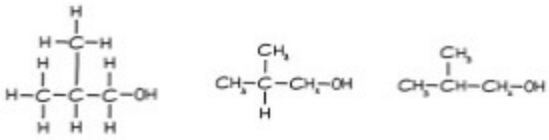
- **Positional isomers** retain the same carbon chain, but the functional group is moved along the chain
- **Functional group isomers** show a rearrangement of the atoms to produce a new functional group
  - Alcohols are functional group isomers of ethers

Exam Papers Practice

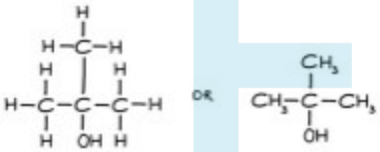
2c

The branched-chain isomers of butan-2-ol are:

(Any of the following representations shown)



- Correct drawing
  AND
  2-methylpropan-1-ol; [1]



- Correct drawing
  AND
  2-methylpropan-2-ol; [1]

[Total: 2 marks]

Exam Papers Practice

- A branched-chain isomer has the same molecular formula and retains the same functional group (if one is present)
- When drawing branched-chain isomers start by reducing the original chain length by one carbon and relocate the carbon in as many positions along the chain as you can
- Be careful that you don't mistake an 'up' or 'down' position as different isomers
  - Sometimes a group could be 'sticking up' off the end carbon, which would mean that it is still part of the main chain
- The true test for an isomer is to try and name it - an isomer will have a different name to the original molecule

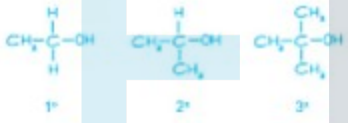
2d

The class of alcohols which butan-2-ol belongs to:

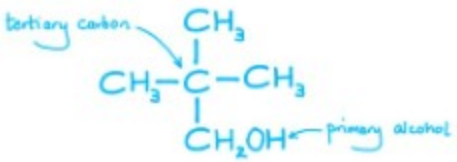
- Secondary
  AND
  The carbon attached to the functional group is joined to two other carbon atoms; [1]

[Total: 1 mark]

- The three classes of alcohols are primary, secondary, and tertiary
- The classification depends on the number of carbon atoms joined to the functional group carbon



  - Primary: functional group carbon is bonded to one other carbon (or hydrogen)
  - Secondary: functional group carbon is bonded to two other carbons
  - Tertiary: functional group carbon is bonded to three other carbons
- Be careful not to confuse a tertiary carbon with a tertiary alcohol:



Exam Papers Practice

3a

The names of the compounds are:

compound	name
$CH_3CH_2CH_2CH(OH)CH_3$	pentan-2-ol
$CH_3CH_2COCH_3$	butanone
$CH_3CH_2CH_2OH$	propan-1-ol
$CH_3CH_2CH_2CHO$	butanal

- Four correct names; [2]
  OR
  Three or two correct names scores; [1]

[Total: 2 marks]

- The numbers are essential when positional isomers are possible
- You can also place the number in front of the name of the alcohols
  - E.g., 2-pentanol and 1-propanol
- It is not necessary to write a number for butanone or butanal as there is no other place for the functional group to be in the molecule

Exam Papers Practice

3b

The structural isomers are:

- Butanone and butanal; [1]
- They show functional group isomerism; [1]

[Total: 2 marks]

- There are three types of structural isomers you should know: branched-chain, positional and functional group
- It is a good idea to have some examples of these up your sleeve in case you have to drawn them in an answer
  - Branched: butane and methylpropane: $CH_3CH_2CH_2CH_3$ and $CH_3CH(CH_3)CH_3$
  - Positional: 1-chloropropane and 2-chloropropane: $CH_3CH_2CH_2Cl$ and $CH_3CHClCH_3$
  - Functional group: ethanol and methoxymethane: CH_3CH_2OH and CH_3OCH_3

3c

i) The empirical formula of propofol is:

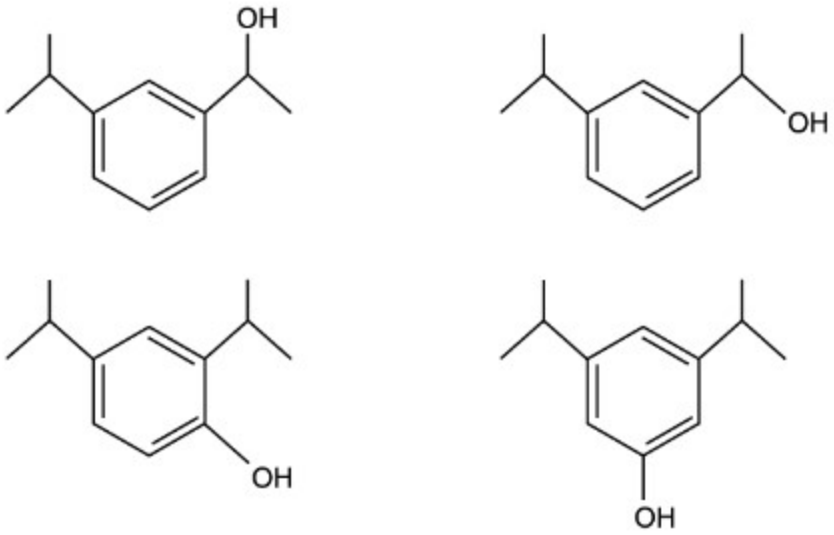
- $C_{12}H_{18}O$; [1]

ii) The number of positional isomers or propofol:

- 4; [1]

(Shown below for reference – not needed for the mark)

Exam Papers Practice



iii) Two functional groups in propofol are:

- Phenol **AND** phenyl; [1]

  (Allow hydroxyl for phenol)

[Total: 3 marks]

- The empirical formula is the simplest possible whole number ratio of atoms of each element in a compound
- In this case, the molecular and empirical formula are the same since $C_{12}H_{18}O$ cannot be further simplified
- Phenyl is the name of the functional group and benzene is the specific molecule, C_6H_6.

Exam Papers Practice

3d

i) The general formula for a carboxylic acid is:

- $C_nH_{2n+1}COOH$; [1]

ii) The systematic name for valeric acid is:

- Pentanoic acid; [1]

iii) The condensed structural formula for valeric acid is:

- $CH_3CH_2CH_2CH_2COOH$; [1]

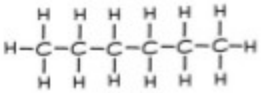
[Total: 3 marks]

- You need to know the general formulae of:
  - Alkanes, alkenes, alkynes, ketones, alcohols, aldehydes, and carboxylic acids
- The systematic name for carboxylic acids follows the generic rule: alkanoic + acid so we have the homologous series:
  - Methanoic acid, ethanoic acid, propanoic acid, butanoic acid, pentanoic acid and hexanoic acid
- There are no positional isomers for carboxylic acids because the functional group will always be on the first carbon in the chain

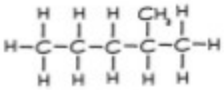
Exam Papers Practice

4a

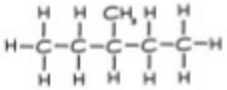
The five isomers of C_6H_{14} are:



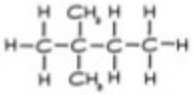
hexane



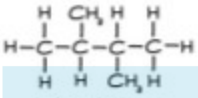
2-methylpentane



3-methylpentane



2,2-dimethylbutane



2,3-dimethylbutane

- All five isomers correctly drawn **AND** named: [5]

[Total: 5 marks]

- Since the question doesn't specify it, you can draw displayed or a mixture of displayed and condensed formulae
- When drawing isomers of hydrocarbons start by reducing the original chain length by one carbon and relocate the carbon in as many positions along the chain as you can
- Repeat this with two carbons, and so on
- Make sure that you join the C-C bonds in the branches and not C-H by mistake

Exam Papers Practice

4b

i) The IUPAC name of the molecule is:

- Methyl propanoate; [1]

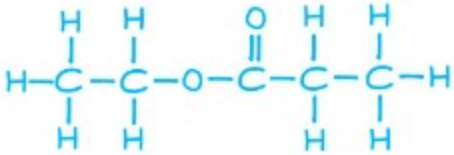
ii) A functional group isomer of the molecule is:

- Correct drawing
  AND
  Butanoic acid or 2-methylpropanoic acid; [1]

  (Allow condensed structures as long as the carbons are separated
  Name given must match the structure given)

[Total: 2 marks]

- You should have experience of either using model kits or suitable computer-generated molecular graphics programmes to construct three-dimensional models of a wide range of organic molecules, which will make you familiar with the types of three-dimensional drawings sometimes used in exam questions
- A suitable freeware programme to practice with is ACD Chemsketch
- Naming esters follows this protocol: alkyl + alkanoate
- Be careful that you get the correct carbon chain length in each part of the ester, no matter which way round you draw the ester
  - For example, $CH_3CH_2COOCH_2CH_3$ is ethyl propanoate and not propyl ethanoate, no matter which way round you draw it

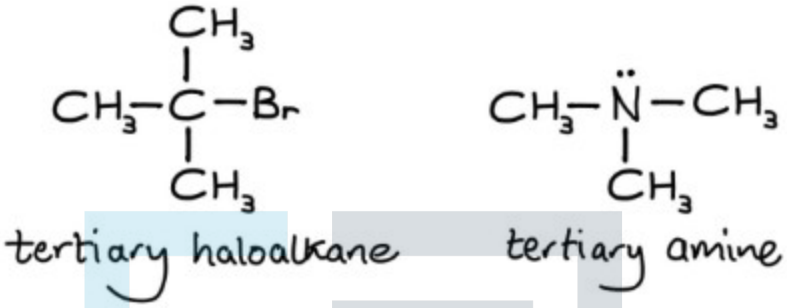


  - Ethyl propanoate can also be written as $CH_3CH_2OOCCH_2CH_3$
  - To avoid ambiguity, some people use brackets on the side oxygen to signify it is not part of the chain: $CH_3CH_2CO(O)CH_2CH_3$

4c

The difference between a tertiary haloalkane and a tertiary amine:

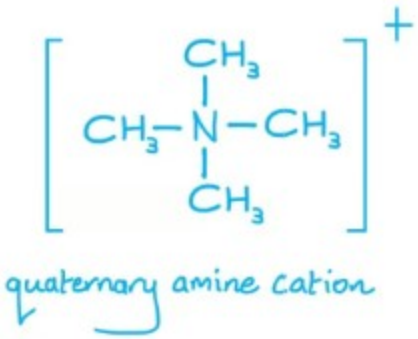
- A tertiary haloalkane has three other carbon atoms attached to the functional group carbon / carbon joined to the halogen
  AND
  A tertiary amine has three carbons attached to the nitrogen atom; [1]



- Correctly drawn diagrams including the lone pair on the nitrogen atom; [1]

[Total: 2 marks]

- Although the terminology is the same, the classification of amines is different to the classification of alcohols and haloalkanes
- In amines you have to count the number of carbons attached to the nitrogen atom
- Unlike alcohols and haloalkanes, it is possible to have a quaternary amine which makes use of the lone pair on the nitrogen to form an additional bond:

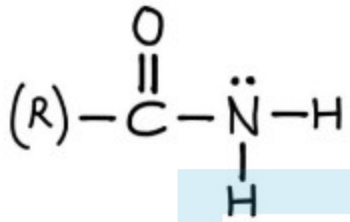


Exam Papers Practice

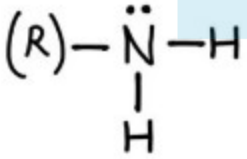
- This is directly analogous to the ammonium ion, NH_4^+, but you don't need to know about the classification of quaternary ammonium ions for the exam

4d

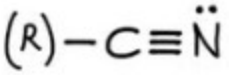
The Lewis structure of a carboxamide, nitrile, and an amine are:



- Correct structure of the carboxamide drawn; [1]
  Allow if 'R' groups drawn instead of H atoms



- Correct structure of the amine drawn; [1]
  Allow if 'R' groups drawn instead of H atoms



- Correct structure of the nitrile drawn; [1]

[Total: 3 marks]

- You must be able to draw all of the key functional groups
- Don't forget to draw all bonds and lone pairs

Exam Papers Practice

5a

The physical evidence for the structure of benzene is:

Any **two** from:

- The C-C bonds / bonds between the carbons in the ring are all the same length
  OR
  The C-C bonds / bonds between the carbons are an intermediate length between the length of a double and a single bond; [1]
- The C-C-C bond angles are all the same; [1]
- All the bonds have the same strength
  OR
  The C-C bond energy is equal; [1]
- The molecule is planar / flat; [1]

[Total: 2 marks]

- If the bonds were different lengths or the bonds had different angles, then the shape could not be a regular hexagon
- The bond length in benzene is 0.139 nm which is between the value of a single bond (0.154nm) and a double bond (0.134 nm)
- This is why chemists sometimes talk about benzene having a 'bond order' of 1.5; that is between 1 and 2, representing a single and double

Exam Papers Practice

5b

i) The meaning of the terms *saturated* and *unsaturated*:

- Saturated means the molecule only contains single (C-C) bonds
  AND
  Unsaturated means there is at least one double or triple (C-C) bond (present in the molecule); [1]

ii) The difference in reactivity with bromine for benzene and cyclohexene:

- The π / pi /double bonds in benzene are delocalized;
  OR
  The π / pi / double bonds in benzene are stronger than the double bond in cyclohexene;
  OR
  The π / pi / double bonds in benzene are more stable than the double bond in cyclohexene; [1]

- $C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$; [1]

[Total: 3 marks]

- Sometimes when writing equations with aromatic compounds or cyclic structures, it is easier to write an equation for the reactions showing the displayed formula
  - This would be allowed instead of using the molecular formulae in the equation

Exam Papers Practice

5c

i) The enthalpy of hydrogenation of 1,3,5–cyclohexatriene is:

- $\Delta H = -120 \times 3 = \underline{-360}$ kJmol^{-1}; [1]

ii) The difference between the enthalpy of hydrogenation of 1,3,5–cyclohexatriene and of benzene and the reason for it is:

- Benzene has a lower enthalpy of hydrogenation than 1,3,5–cyclohexatriene;
  OR
  Benzene is more (energetically) stable (by 152 kJ) than 1,3,5–cyclohexatriene; [1]
- The bonds are stronger / more stable in benzene than 1,3,5–cyclohexatriene;
  OR
  Benzene has delocalized π bonds / a delocalised π system whereas 1,3,5–cyclohexatriene has 3 double bonds; [1]

[Total: 3 marks]

Exam Papers Practice

- Hydrogenation is a reaction with hydrogen gas, and specifically here it is the addition of hydrogen across the C=C double bonds
- Cyclohexene has one double bond and 1,3,5–cyclohexatriene has three double bonds, so the theoretical enthalpy change for hydrogenation should be three times the value for cyclohexene, since there is no other difference between the molecules
- 1,3,5–cyclohextriene is the Kekulé structure for benzene, a model which proposed alternating double and single bonds:

- The Kekulé structure predicts a higher enthalpy of hydrogenation than is measured with benzene, so this provides evidence that benzene is more stable than expected
- This difference in stability, approximately 152 kJ, is known as the stabilization energy or resonance energy
- Delocalization reduces the repulsion between electrons and gives benzene a more stable structure – this is why we draw it with a circle in the centre, to represent three delocalised double bonds, a delocalised pi system

5d

Two aromatic isomers which contain an ester group are:

Exam Papers Practice

- Each isomer correctly drawn; [1]

[Total: 2 marks]

- Since the question does not specify which type of formula, you could also draw the condensed structural formulas to score the marks
- Respectively, they would be $C_6H_5COOCH_3$, $CH_3COOC_6H_5$ and $HCOOCH_2C_6H_5$