Nitrogen Compounds: Amino Acids, Amides/Polyamides & Chirality

A Level only

Model Answers 1

Level	A Level
Subject	Chemistry
Exam Board	OCR
Module	Organic Chemistry & Analysis
Topic	Nitrogen Compounds: Amino Acids, Amides/Polyamides & Chirality
Paper	A Level only
Booklet	Model Answers 1

Time allowed: **68 minutes**

Score: **/50**

Percentage: **/100**

Grade Boundaries:

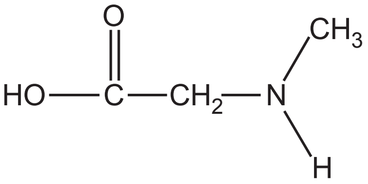
A*	A	B	C	D	E
>85%	73%	60%	47%	34%	21%

Question 1

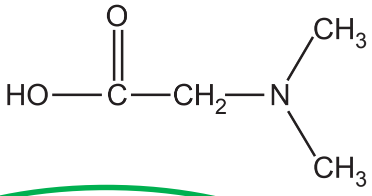
Which compound is a secondary amide?

[1]

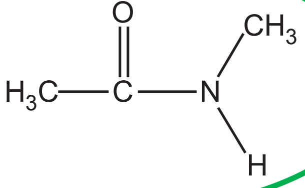
A



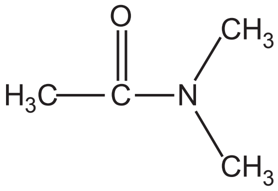
B



[✓ **C**]



D



- A secondary amide is an amide in which the nitrogen atom is bonded to **two carbon** atoms: the carbonyl group carbon plus one other carbon.
- This arrangement is present in option C only.
- A and B are incorrect as there is a hydroxyl group present on the molecules.
- D is incorrect as the N atom is bonded to three carbon atoms, hence it is a tertiary amide.

Question 2

How many straight-chain structural isomers of $C_7H_{15}Cl$ contain a chiral carbon atom?

A. 1

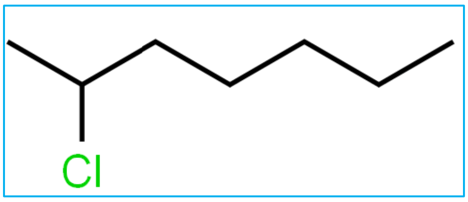
[✓ B. 2]

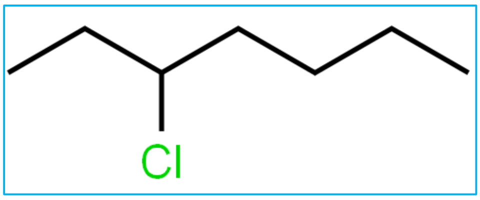
C. 3

D. 4

[1]

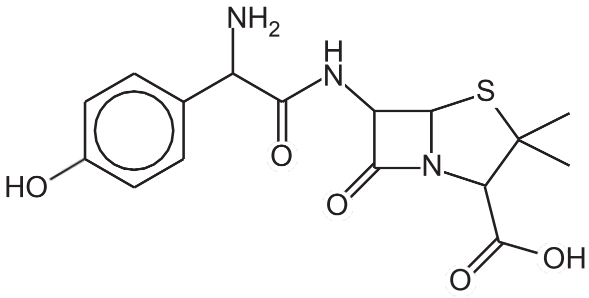
- The question states that the isomers are straight chain, so there is no branching or rings.
- Two structural isomers can be achieved by drawing out the chain and placing the chlorine on carbon number 2 or number 3 as shown below.
- A, C and D are thus incorrect.





Question 3

What is the number of chiral centres in the molecule below? **[1]**



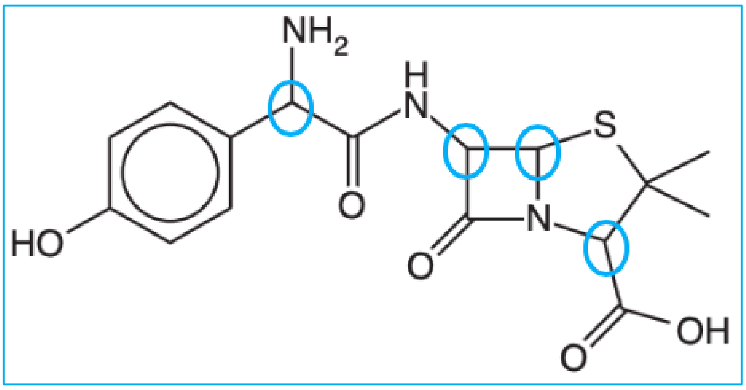
A. 2

B. 3

[✓ C. 4]

D. 5

- A chiral centre is a carbon atom bonded to four different groups.
- Starting on the left-hand side identify the groups attached to each carbon atom and identify those carbon atoms that are chiral.
- There are 4 chiral carbons which are identified on the diagram of the molecule below.
- A, B and D are thus incorrect.



Question 4

Which reagents could be used to prepare $CH_3CH_2CONHCH_3$?

[✓ A. $CH_3CH_2COCl + CH_3NH_2$]

B. $CH_3CH_2CONH_2 + CH_3Br$

C. $CH_3CH_2COONa + CH_3NH_2$

D. $CH_3CH_2COCH_3 + NH_3$

[1]

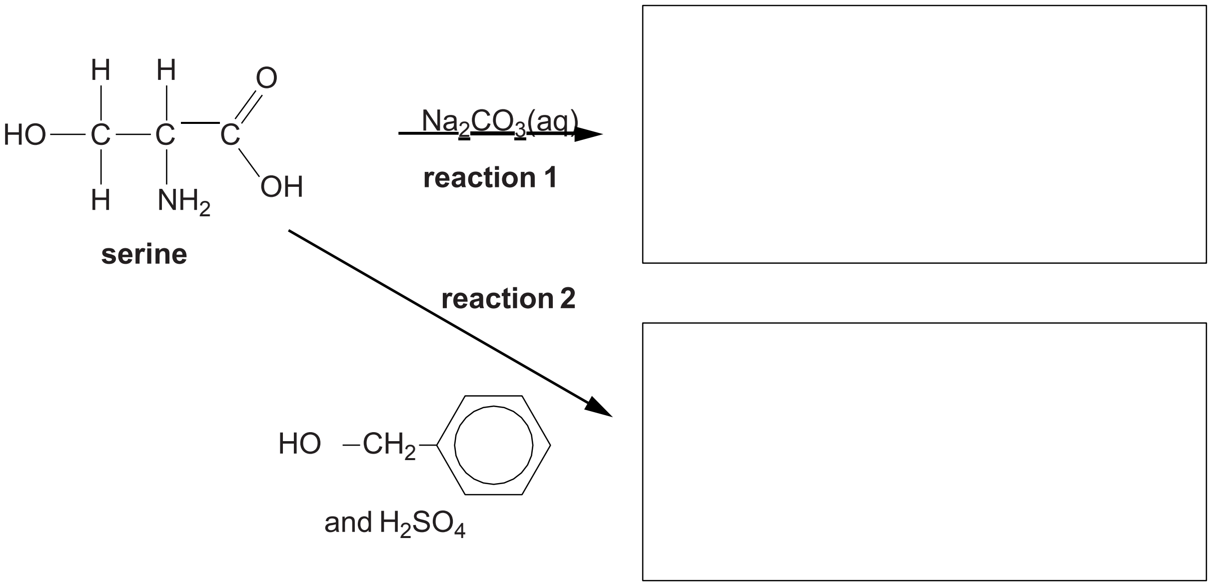
- **Acyl chlorides** react with **amines** to produce the product molecule which is an **amide**.
- The amine acts as the nucleophile through lone pair donation from the nitrogen atom to the electron deficient species.
- B, C and D are incorrect as none of these reactions produce amides.

Question 5

Many α-amino acids have several functional groups.

(a) Serine, shown below, is a naturally occurring α-amino acid.

(i) In the boxes below, draw the structure of the organic compounds formed by each reaction.

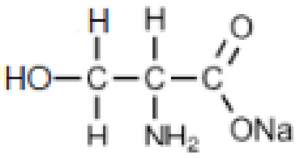


[3]

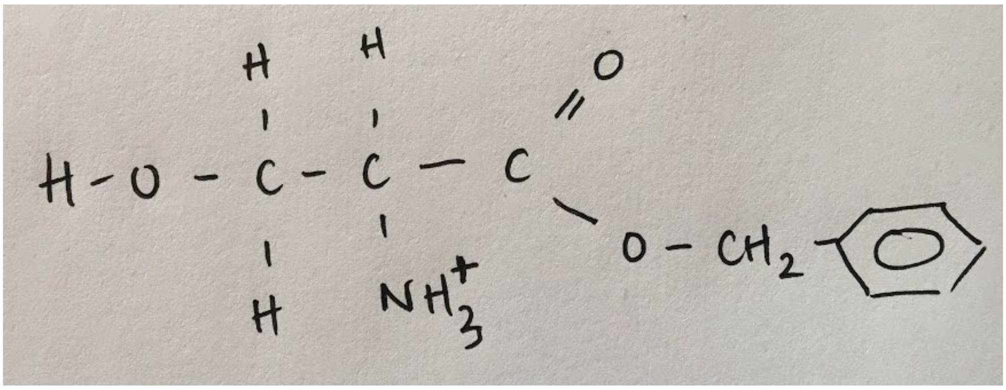
Acid + carbonate → salt + water + carbon dioxide

$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

With the addition of Na_2CO_3, the **COOH terminus of serine would act as the acid** and **donate its proton (reaction equation above)** and the **COO^- would attract the Na^+** to form the salt:



The **COOH** group in **serine** reacts with the -**OH** group in the **benzene** compound to form an ester:



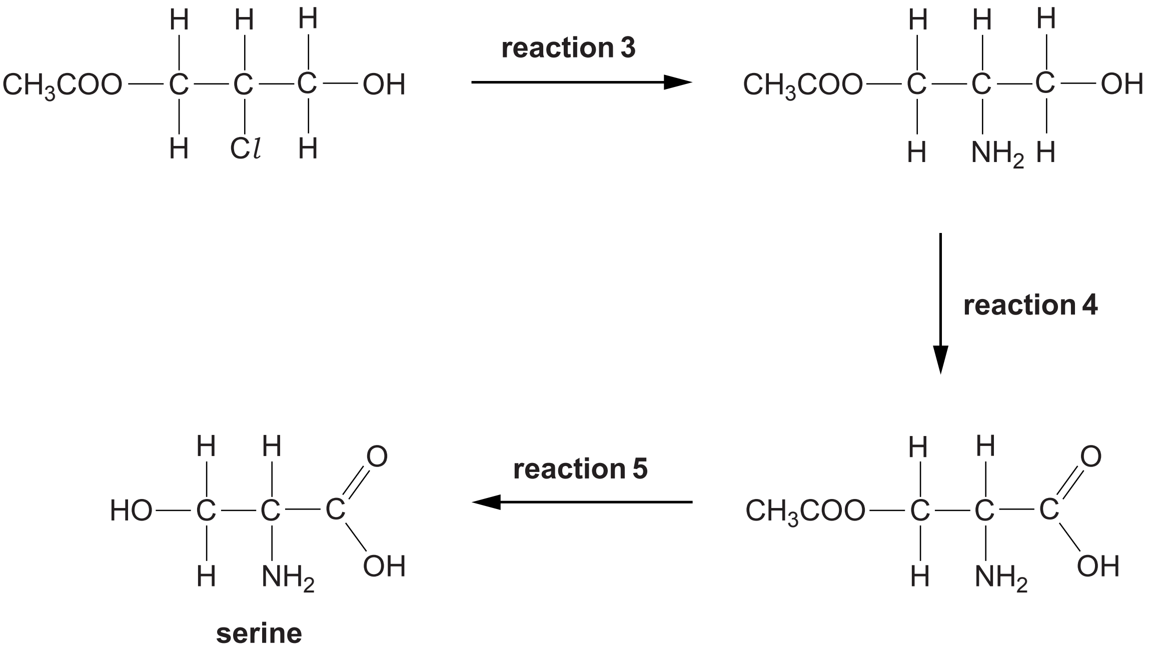
Due to high concentrations of H^+ (from the sulphuric acid catalyst used), **the NH_2 group** is protonated to NH_3^+ in the final product.

(ii) Suggest a use for the organic compound formed by **reaction 2**. [1]

Esters are usually used to **make perfumes, fragrance and flavouring**

(iii) Serine is commonly used in organic synthesis.

One possible method of synthesising serine is shown below.



Complete the following:

Reagent and conditions used for **reaction 3**.

Type of reaction for:

reaction 4

reaction 5 [3]

Reaction 3 requires **hot ethanolic ammonia** to substitute the Cl atom to NH_2

Reaction 4 is the **oxidation** of a primary alcohol to a carboxylic acid group

Reaction 5 is the **hydrolysis** of an ester group into an alcohol

(b) Compound **E**, C_4H_7NO, is one of two optical isomers. It can be oxidised by Tollens' reagent to an α-amino acid, **F**.

The α-amino acid **F** forms two different polymers, **G** and **H**.
Polymer **G** has the empirical formula $C_4H_7NO_2$.
Polymer **H** has the empirical formula C_4H_5NO.

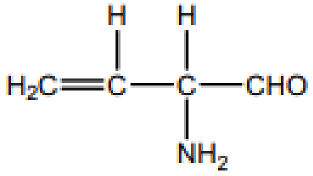
- Suggest structures for compound **E** and compound **F**.
- Draw repeat units of polymer **G** and polymer **H**.
- Describe how **F** forms **G** and **H**. [6]

Since compound E can be oxidised by Tollens' reagent, it has an **aldehyde** group.

Once oxidised to a carboxylic acid by Tollens' reagent, it is an amino acid (F), therefore there must be an NH_2 group present in E.

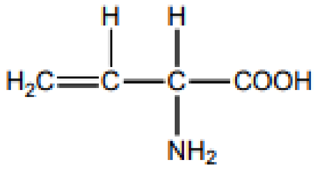
It is also an optical isomer, therefore there must be a chiral centre, with one C atom attached to 4 different groups.

Polymers can be formed via addition and condensation reactions. As the amino acid F can form two different polymers, it is likely to be able to undergo both types of polymerisation reaction. Therefore E, it must also have a C=C bond for addition polymerisation:



$H_2C{=}CH{-}CH(NH_2){-}CHO$

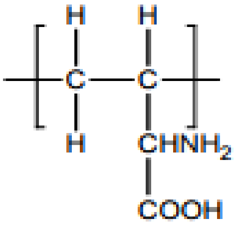
Compound F upon oxidation by the Tollens' reagent converts the aldehyde to carboxylic acid group to form amino acid F:

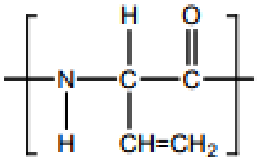


$H_2C{=}CH{-}CH(NH_2){-}COOH$

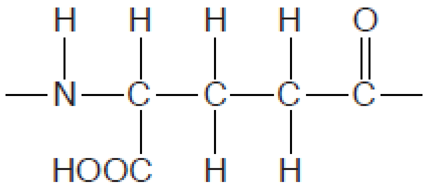
Difference between compound **G and H based on their empirical formula**, is that H is missing 2 H and 1 O atoms and has therefore lost a water molecule during polymerisation.

Therefore, **polymer G (left) is an addition polymer** while **compound H (right) is a condensation polymer** with their respective structures,





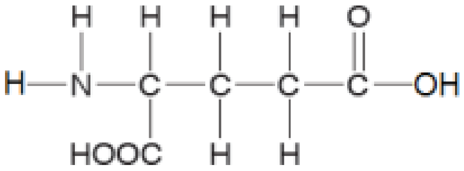
(c) Poly(glutamic acid) is a polymer of the amino acid, glutamic acid.



repeat unit of poly(glutamic acid)

(i) Draw the structure of glutamic acid. [1]

Completing the NH_2 and COOH terminus for a monomer of glutamic acid,

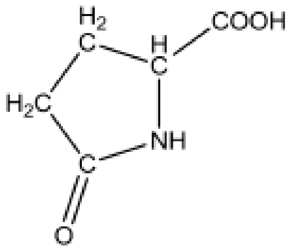


(ii) A student tried to prepare poly(glutamic acid) from glutamic acid. No polymer was found in the product mixture.

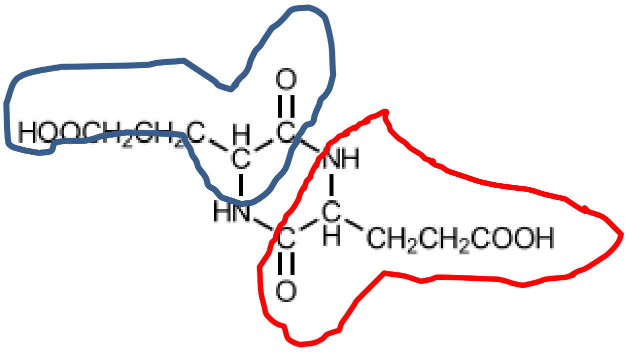
The student isolated the two major compounds in the mixture. The mass spectra of these two compounds showed molecular ion (M^+) peaks at $m/z = 129$ and $m/z = 258$.

Suggest structures for these two compounds. [2]

One molecule of glutamic acid can form a cyclic compound with itself during which, the COOH group and NH_2 group form an amide link and **water is lost.** The Mr of glutamic acid is 147, therefore the Mr of the cyclic compound made is 147 - Mr of water (18) = 129



Two molecules of glutamic acid can combine together to form a cyclic compound, losing 2 water molecules in the process. Two amide links are formed between the two NH_2 groups and the two COOH groups on the two molecules. Therefore, the mass of this molecule will be twice the mass of the cyclic compound formed from only one molecule (129 x 2 = 258).



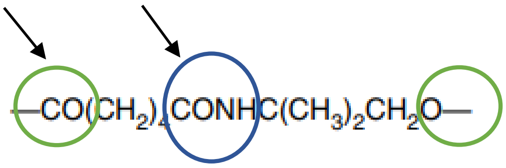
(d) Polymer **J** has been recently developed by scientists. The repeat unit of polymer **J** is shown below.

$$—CO(CH_2)_4CONHC(CH_3)_2CH_2O—$$

polymer J

(i) What are the functional groups in polymer **J**? [1]

Polymer J has an **ester** and **amide**



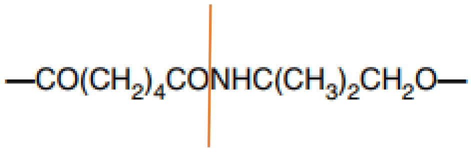
(ii) Two different monomers react to form polymer **J**.

Draw the structures of the two monomers in the boxes below.

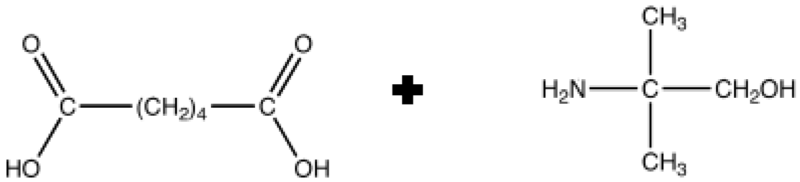
Display the functional groups in each monomer. [2]

Since there is an amide link in the middle of the polymer, one of the monomers has a COOH group (which has lost its -OH) and the other contains an NH_2 group (which has lost an H) – as can be seen either side of the divide in the structure below.

At either side of the polymer repeating unit is two halves of an ester link. On the left-hand side, the -OH from a COOH group has been removed and on the right-hand side, the H from an OH group has been removed. Splitting polymer J at the point shown below and replacing the removed Os and Hs gives:



$$\text{—CO(CH}_2)_4\text{CO|NHC(CH}_3)_2\text{CH}_2\text{O—}$$



(iii) Polymer **J** is used in hair spray. It can be washed away easily with hot water.

Suggest why polymer **J** is able to be washed away easily with hot water. [1]

Polymer J can be **washed easily with hot water** as the molecule can be **hydrolysed** and the two monomers can form hydrogen bonds with water.

[Total 20 Marks]

Question 6

This question looks at the properties and chemistry of some α-amino acids. The general formula of an α-amino acid is $RCH(NH_2)COOH$.

(a) In the α-amino acid alanine, $CH_3CH(NH_2)COOH$, R is CH_3.
The isoelectric point of alanine is at pH 6.0.

(i) What is meant by the term *isoelectric point?* [1]

Amino acids have at least two potentially charged groups (COOH and NH_2 / COO^- and NH_4^+).

The isoelectric point is **the pH** at which both groups are charged and the zwitterion exists.

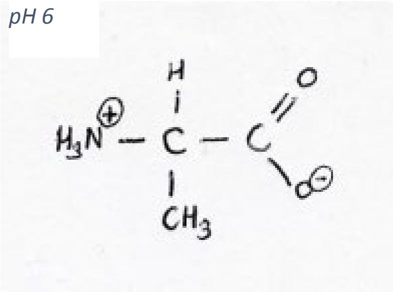
In a zwitterion, the carboxyl becomes deprotonated (negative) and the amine becomes protonated (positive) so there **is no overall charge across** the molecule.

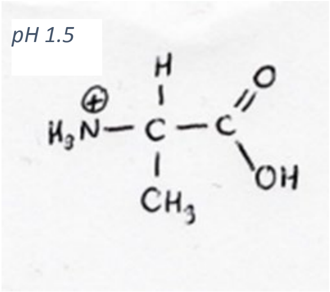
(ii) Draw the structures of the ions formed by alanine at pH 6.0 and at pH 1.5. [2]

At pH 6, the zwitterion exists, and both the **amine and carboxyl groups will be charged**.

At pH 1.5 there is a high $[H^+]$ meaning **both groups will be protonated**.

R = CH_3 for alanine, structure: $CH_3CH(NH_2)COOH$





(iii) Different R groups in α-amino acids result in different isoelectric points.

Suggest the functional group, in the R group, that results in the isoelectric point being lower than pH 3 and higher than pH 10. [2]

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R groups that can accept or donate protons can **alter the isoelectric point** of an amino acid.

If the **R group is a proton acceptor** (e.g. NH_2) it will have potential to be protonated and add positive charge to the molecule at low pH.

This means **a higher pH will be needed** to achieve no overall charge (the isoelectric point).

Similarly, if the **R group is a proton donor**, it can **add negative charge** at a high pH, so the isoelectric point will be lowered.

pH < 3: COOH pH > 10: NH_2

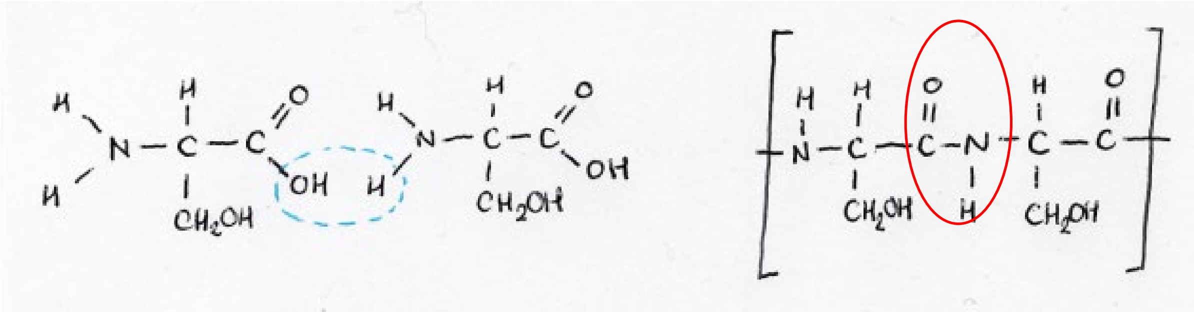
(b) The α-amino acid serine, where R is CH_2OH, readily forms a condensation polymer containing peptide links.

Draw a section of poly(serine), showing **two** repeat units.

Display the peptide linkage. [2]

Draw 2 serine monomers

emoval of water to condense into a polymer. Peptide linkage shown in red:



(c) Apart from glycine, where R is H, all α-amino acids show optical isomerism.

(i) Why does glycine **not** show optical isomerism? [1]

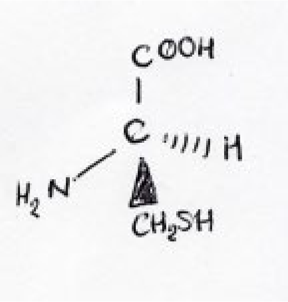
Optical isomerism occurs when **4 different functional groups** are bonded to a central carbon.

Glycine has 1 COOH, 1 NH_2 and **2 hydrogen atoms** bound to the central carbon.

There is **no chiral centre** or asymmetry within the molecule.

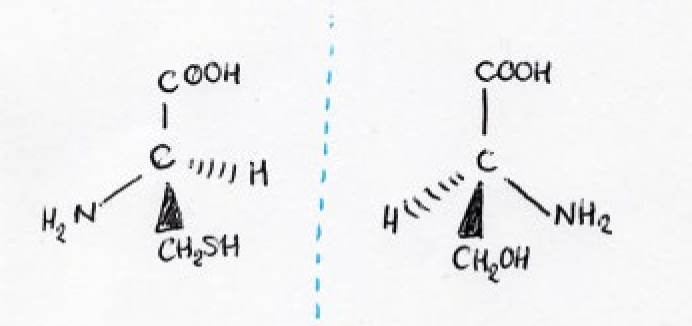
(ii) Draw 3-D diagrams for the two optical isomers of the α-amino acid cysteine, where R is CH_2SH. [2]

Draw one isomer in 3D wedge form.



Draw a **line of reflection** and a central carbon with mirrored bonds

Fill out the functional groups so that the molecule is a **direct reflection** of the first molecule.



(iii) α-Amino acids are being used in the development of peptide-based pharmaceuticals. Optical isomerism has been found to be significant in the action of some pharmaceuticals.

- State **two** possible disadvantages of synthesising a peptide-based pharmaceutical that contains a mixture of optical isomers.
- State **two** methods that are used by manufacturers to synthesise pharmaceuticals containing just the required optical isomer.

In your answer, you should use appropriate technical terms, spelled correctly. [4]

Disadvantages

Most biomolecules are chiral, so different stereoisomers of a drug may have different effects.

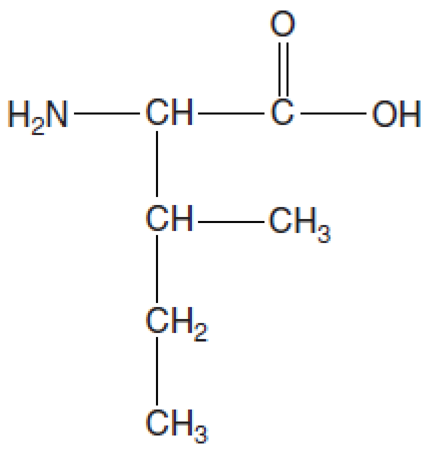
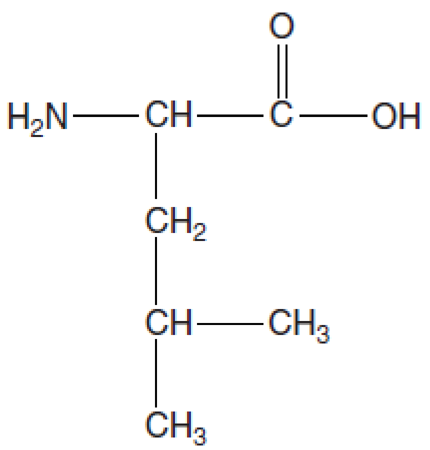
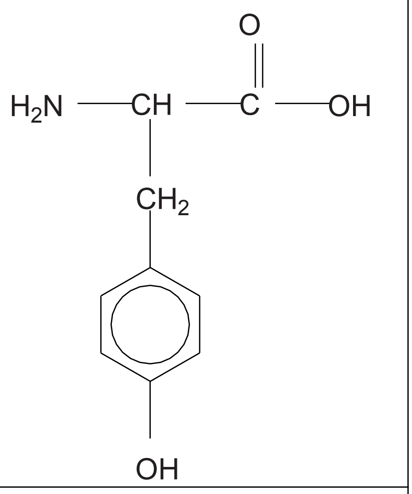
One stereoisomer **may cause adverse side effects** or may just not contribute to the drug's effectiveness, so the **drugs overall activity will be reduced**.

It can also be **difficult and costly to separate stereoisomers**, as they have very similar physical properties.

Methods

To **only synthesise one optical isomer** during manufacturing, **chiral molecules** must be used. Examples of these are **chiral catalysts**, **enzymes** and natural chiral molecules such as L-amino acids.

(d) The structures of the α-amino acids isoleucine, leucine and tyrosine are shown below.

		
isoleucine	**leucine**	**tyrosine**

Predict the number of peaks in the carbon-13 spectrum of each of these α-amino acids.

α-amino acid	**isoleucine**	**leucine**	**tyrosine**
number of peaks			

[3]

C13 NMR spectra peaks occur due to **carbons in different environments**.

For each structure, count how many different carbon environments there are.

Isoleucine – each carbon is in a different environment, as there are **no planes of symmetry**. This totals 6 peaks.

Leucine – the **2 CH_3** groups are in the **same environment**, so will not give distinct peaks.

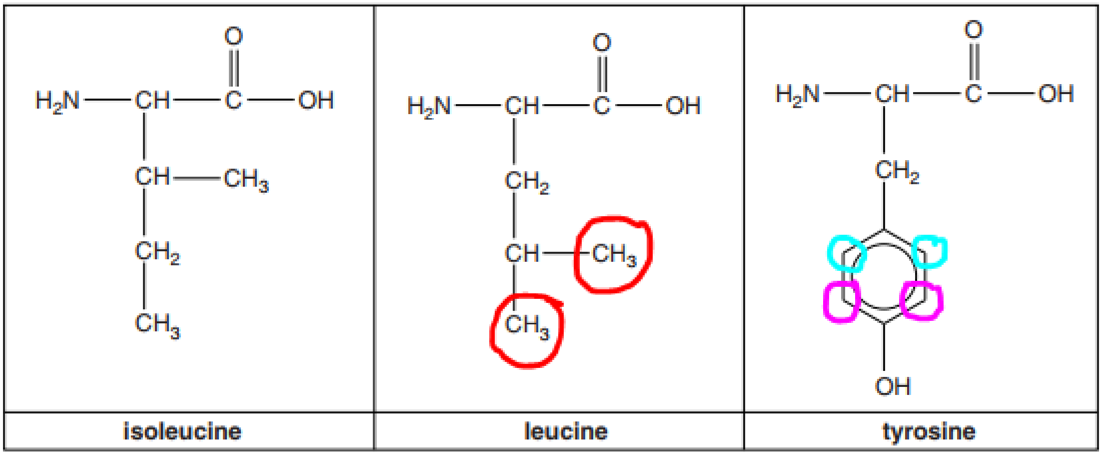
There are **5 different carbon environments** so 5 peaks.

Tyrosine – there is **symmetry across the benzene ring** in tyrosine.

2 pairs of carbons are in the same environment so will appear as one peak.

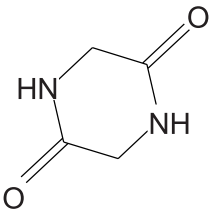
Overall there are 7 different carbon environments, so 7 peaks.

This diagram shows the carbons in the same environment circled in the same colour.

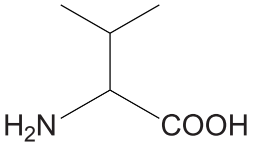


(e) When strongly heated, an α-amino acid can form a cyclic 'dimer' in a condensation reaction.

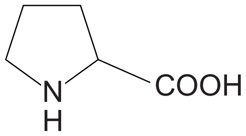
For example, glycine, where R is H, forms the cyclic dimer shown below.



Draw the structures of the cyclic dimers that could be formed from the α-amino acids valine and proline, shown below.



valine



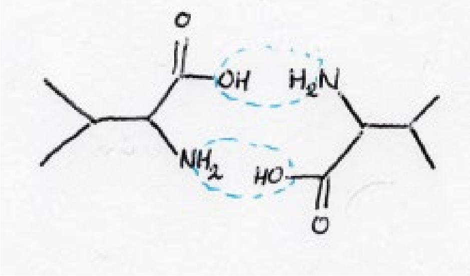
proline

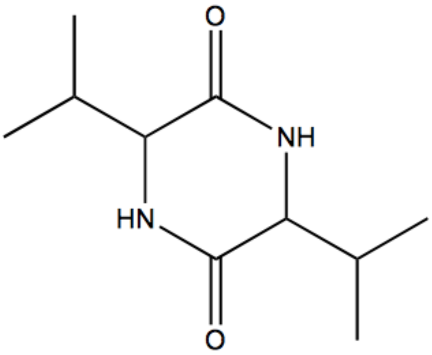
[2]

These cyclic dimers form from **condensation of the COOH and NH_2** groups to form **amide links.**

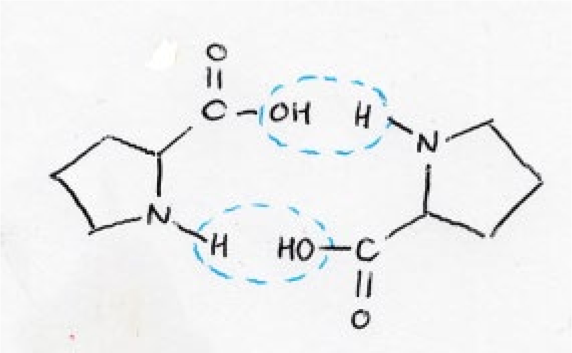
To draw them, draw 2 molecules with the COOH and NH_2 **groups facing each other** (i.e. one flipped) and circle the H_2O that will be removed.

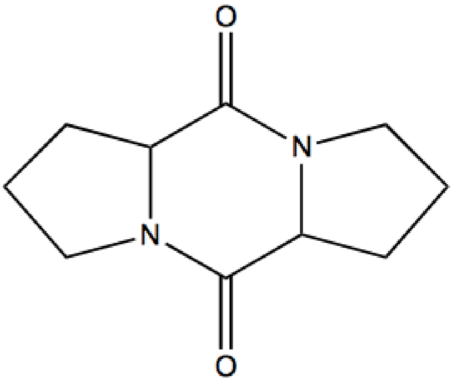
Valine





Proline





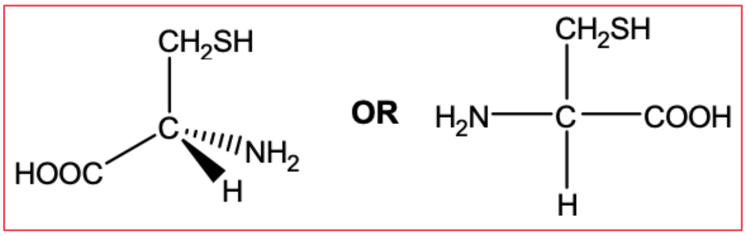
[Total 19 Marks]

The general formula of an α-amino acid is $RCH(NH_2)COOH$.

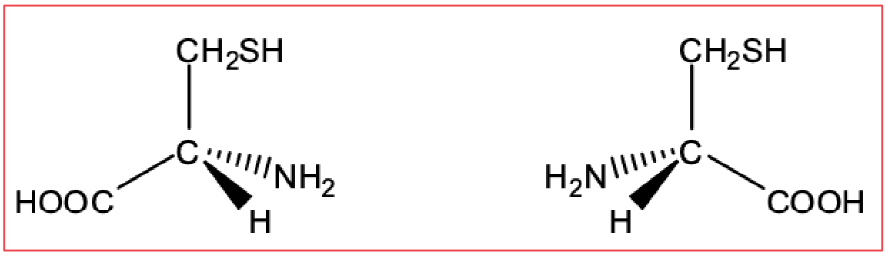
(a) The α-amino acid cysteine ($R = CH_2SH$) shows optical isomerism.

Draw 3-D diagrams to show the optical isomers of cysteine. **[2]**

Correct groups attached to chiral C of cysteine seen **once** e.g. Either diagram is fine but for purposes of consistency it is better to use stereo bonds for chiral carbon atoms.



Two **3D structures** of cysteine that are mirror images with correct connectivity in both, double check to make sure that you have attached the groups in the right order.



Exam Tip

Optical Isomers

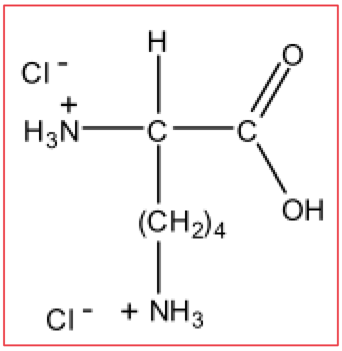
Start with the chiral centre and add on the stereo bonds first. One bond goes back into the page (hashed line), one bond comes out towards you (wedge line) and two more are in the plane of the page (the straight lines). You should always double check that they are correct by confirming their mirror images cannot superimpose on each other.

(b) The α-amino acid lysine (R = $(CH_2)_4NH_2$) reacts with an excess of dilute hydrochloric acid to form a salt.

Draw the structure of the salt formed in this reaction.

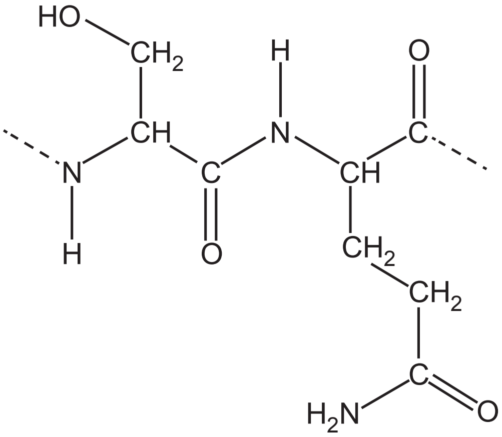
[2]

Correct salt of lysine with both amine groups protonated with **positive charges** on the N atoms in both groups. The Cl^- ion should also be clearly included as the questions states to draw the structure of the salt.



(c) α-Amino acids can react to form proteins.

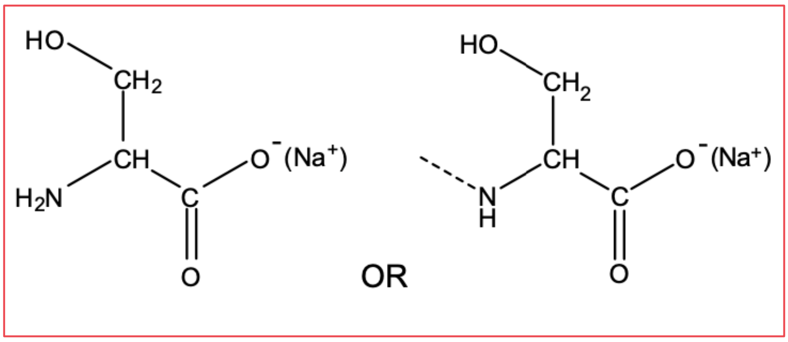
A short section of a protein chain is shown below.

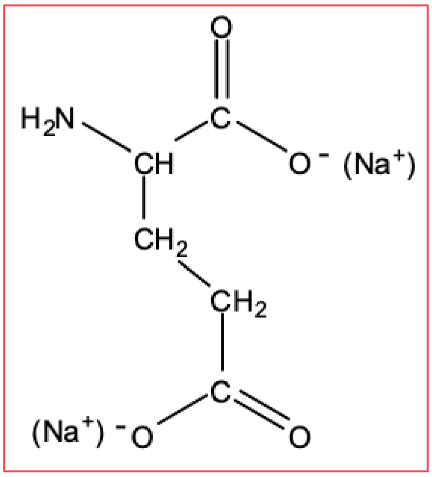


A student hydrolyses the protein with hot NaOH(aq).

Draw the structures of the organic products formed from this section of the protein.

[3]





Proteins undergo hydrolysis in alkaline conditions:

$$\text{R-CH(NH}_2\text{)-COOH} + \text{NaOH} \longrightarrow \text{R-CH(NH}_2\text{)-COO}^-\text{Na}^+ + \text{H}_2\text{O}$$

(Total 7 marks)