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CHEMISTRY

9701/43

Paper 4 Structured Questions

May/June 2014

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Section A

Answer **all** questions.

Section B

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

| For Examiner's Use | |
|--------------------|--|
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |
| 6 | |
| 7 | |
| 8 | |
| Total | |

This document consists of **19** printed pages and **1** blank page.

* 2 4 6 9 1 4 8 7 7 3 *

Section A

Answer **all** the questions in the spaces provided.

- 1 (a) (i) State how the melting point and density of iron compare to those of calcium.

melting point of iron:

density of iron:

- (ii) Explain why these differences occur.

melting point:

.....

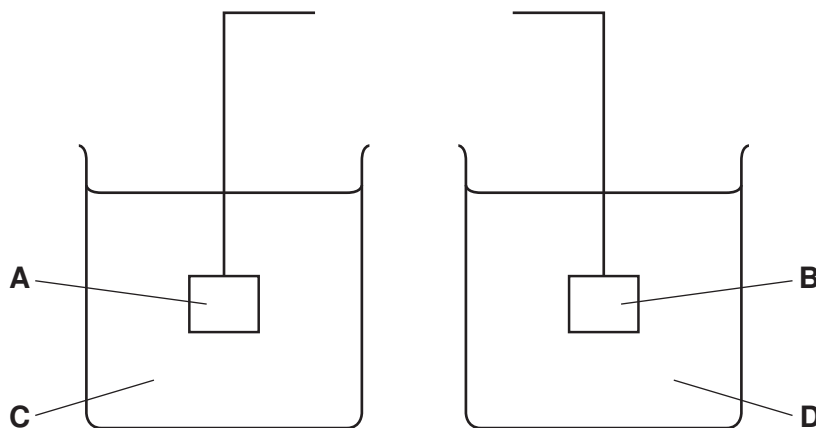
density:

.....

[4]

- (b) The following diagram shows the apparatus used to measure the standard electrode potential, E^\ominus , of a cell composed of a Cu(II)/Cu electrode and an Fe(II)/Fe electrode.

- (i) Finish the diagram by adding components to show the complete circuit. Label the components you add.



- (ii) In the spaces below, identify or describe what the four letters **A-D** represent.

A

B

C

D

(iii) Use the *Data Booklet* to calculate the E^\ominus for this cell.

.....

(iv) Predict how the size of the overall cell potential would change, if at all, as the concentration of solution **C** is increased.
Explain your reasoning.

.....

.....

.....

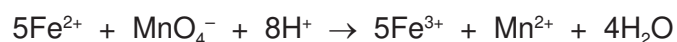
[8]

(c) The iron(II) complex *ferrous bisglycinate hydrochloride* is sometimes prescribed, in capsule form, to treat iron deficiency or anaemia.

A capsule containing 500 mg of this iron(II) complex was dissolved in dilute H_2SO_4 and titrated with $0.0200 \text{ mol dm}^{-3} \text{ KMnO}_4$.

18.1 cm^3 of KMnO_4 solution were required to reach the end point.

The equation for the titration reaction is as follows.



(i) Describe how you would recognise the end point of this titration.

.....

(ii) Calculate

- the number of moles of Fe^{2+} in the capsule,

- the mass of iron in the capsule,

- the molar mass of the iron(II) complex, assuming 1 mol of the complex contains 1 mol of iron.

[4]

[Total: 16]

2 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) (i) State what is meant by the terms:

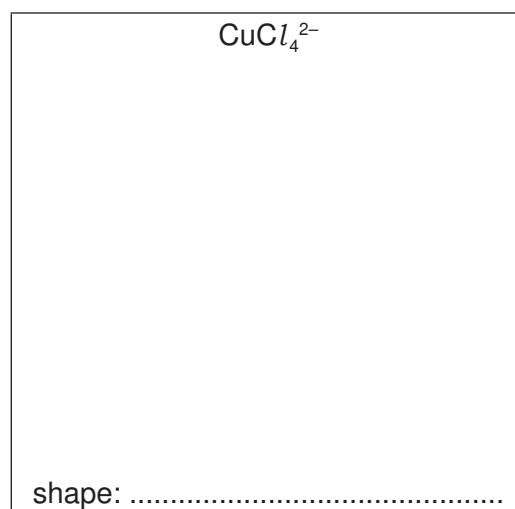
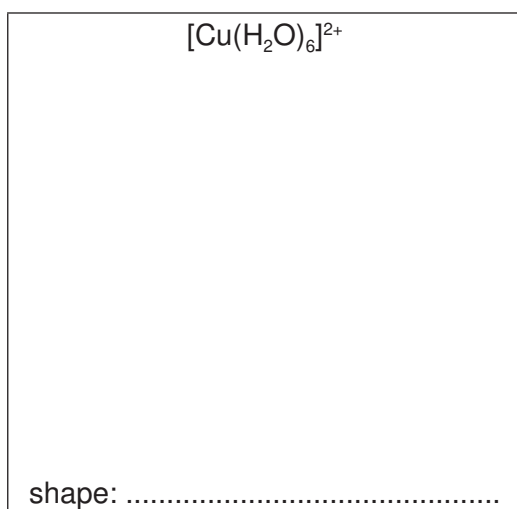
complex,

.....

ligand.

.....

(ii) Two of the complexes formed by copper are $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and CuCl_4^{2-} .
Draw three-dimensional diagrams of their structures in the boxes and name their shapes.

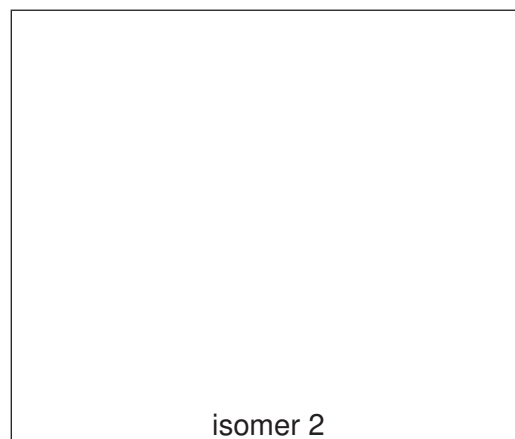
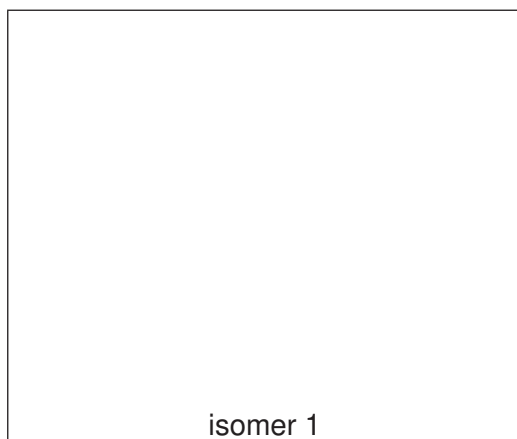


(iii) Platinum forms square-planar complexes, in which all four ligands lie in the same plane as the Pt atom.

There are two isomeric complexes with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

Suggest the structures of the two isomers, and, by comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here.

Structures of isomers:



Type of isomerism:

[7]

(b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

(i) Complete the electronic structures of these ions.

Cu(II) [Ar]

Cu(I) [Ar]

(ii) Use these electronic structures to explain why

copper(II) salts are usually coloured,

.....
.....
.....
.....

copper(I) salts are usually white or colourless.

.....
.....

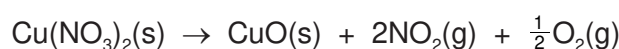
[5]

- (c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the ΔH_f^\ominus values for some compounds.

| compound | $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ |
|-------------------------------|-------------------------------------------|
| $\text{Cu}_2\text{O(s)}$ | -168.6 |
| CuO(s) | -157.3 |
| $\text{Cu(NO}_3)_2\text{(s)}$ | -302.9 |
| $\text{NO}_2\text{(g)}$ | +33.2 |

- (i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable ΔH_f^\ominus values from the table to calculate the ΔH^\ominus for this reaction.



$$\Delta H^\ominus = \dots\dots\dots \text{kJ mol}^{-1}$$

- (ii) Copper(I) oxide can be produced from copper(II) oxide.

- Use suitable ΔH_f^\ominus values from the table to calculate ΔH^\ominus for the reaction.



$$\Delta H^\ominus = \dots\dots\dots \text{kJ mol}^{-1}$$

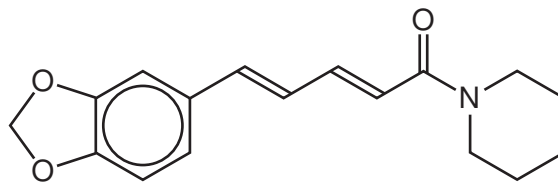
- Hence suggest whether a low or a high temperature of oxidation would favour the production of copper(I) oxide. Explain your reasoning.

.....

[4]

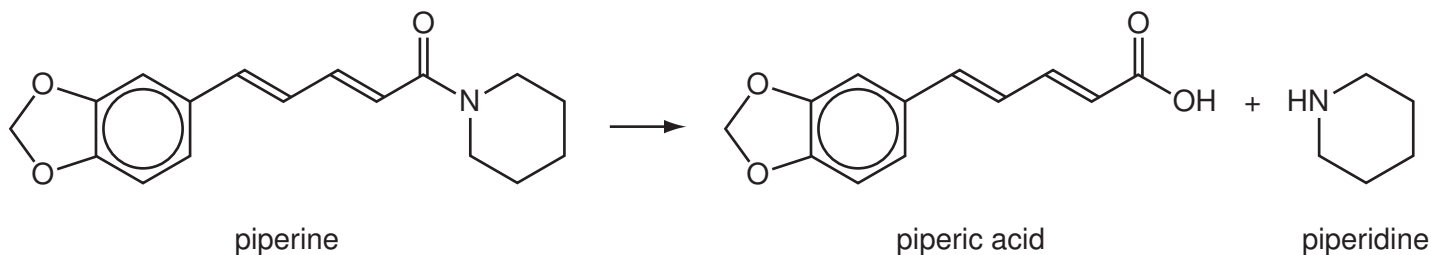
[Total: 16]

- 3 Piperine is the compound responsible for the hot taste of black pepper.



piperine

Piperine is an amide and can be broken down as follows:



- (a) Suggest reagents and conditions for this reaction.

..... [1]

- (b) (i) How many stereoisomers are there with the same structural formula as piperic acid (including piperic acid itself)?

.....

- (ii) Draw the skeletal structure of a stereoisomer of piperic acid, different to the one shown above.

- (iii) Suggest structures for the compounds that would be formed when piperic acid is treated with an **excess** of hot concentrated acidified KMnO_4 .

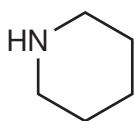
[4]

(c) (i) Write the expression for K_w .

.....

(ii) Use your expression and the value of K_w in the *Data Booklet* to calculate the pH of $0.150 \text{ mol dm}^{-3} \text{ NaOH(aq)}$.

(iii) The pH of a $0.150 \text{ mol dm}^{-3}$ solution of piperidine is 11.9.



piperidine

Suggest why this answer differs from your answer in (c)(ii).

.....

.....

(iv) How would you expect the basicity of piperidine to compare to that of ammonia?
Explain your reasoning.

.....

.....

[5]

(d) 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ HCl was slowly added to a 10.0 cm^3 sample of $0.150 \text{ mol dm}^{-3}$ piperidine. The pH was measured throughout the addition.

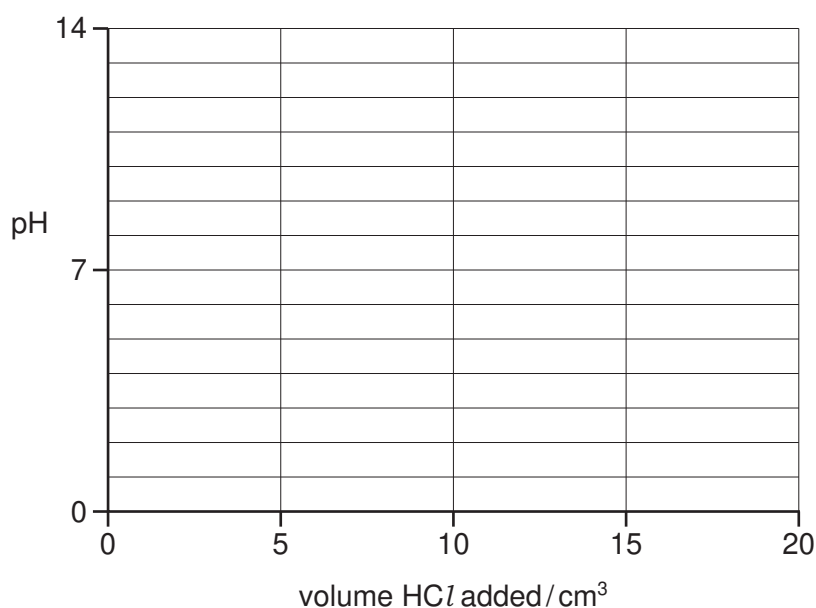
(i) Calculate the number of moles of HCl remaining at the end of the addition.

moles of HCl =

(ii) Hence calculate the $[\text{H}^+]$ and the pH at the end of the addition.

pH =

(iii) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ HCl. Mark clearly where the end point occurs.



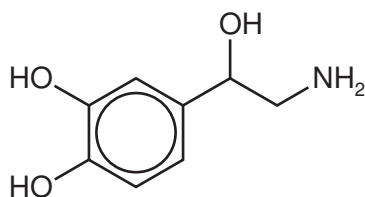
(iv) From the following list of indicators, put a tick in the box by the side of the indicator most suitable for this titration.

| indicator | pH at which colour changes | place one tick only in this column |
|-----------|----------------------------|-------------------------------------------|
| A | 0 - 1 | |
| B | 3 - 4 | |
| C | 11 - 12 | |
| D | 13 - 14 | |

[6]

[Total: 16]

- 4 Noradrenaline is a hormone and neurotransmitter, which is released during stress to stimulate the heart and increase blood pressure.



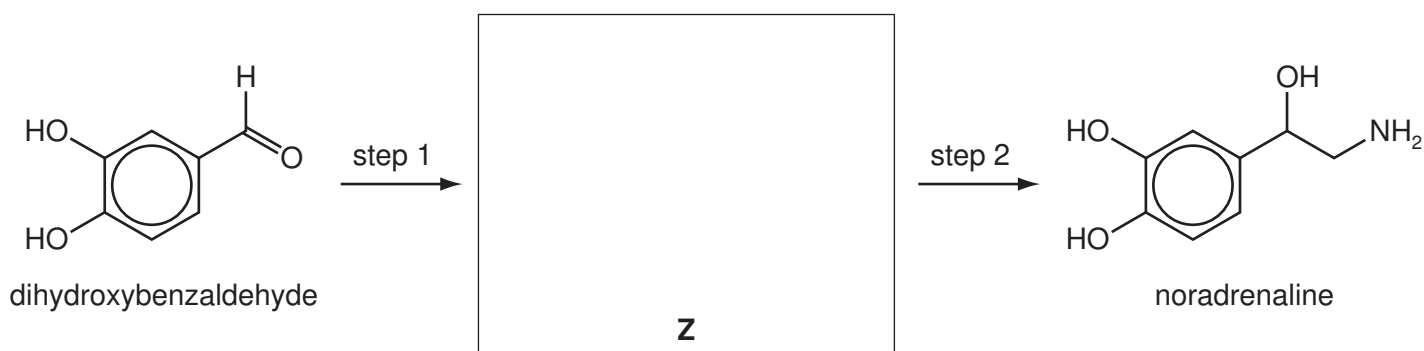
noradrenaline

- (a) State the **names** of **three** functional groups in the noradrenaline molecule.

.....

 [3]

- (b) (i) Consider the following two-stage synthesis of noradrenaline from dihydroxybenzaldehyde.



- Draw the structure of the intermediate **Z** in the box.
- Suggest reagents for steps 1 and 2.

step 1

step 2

(ii) Dihydroxybenzaldehyde reacts with $\text{Br}_2(\text{aq})$.

- Describe what you would see during this reaction.

.....

- Draw the structure of the product.

[5]

(c) Draw the structures of the products when noradrenaline is reacted with

(i) dilute $\text{NaOH}(\text{aq})$,

(ii) dilute $\text{HCl}(\text{aq})$,

(iii) an excess of ethanoyl chloride, CH_3COCl .

[4]

(d) Name the **new** functional groups formed in the reaction in (c)(iii).

.....

..... [2]

[Total: 14]

- 5 The two compounds **V** and **W** are isomers with the molecular formula C_4H_8O , and show the following properties and reactions.
- Both compounds react with sodium metal, and both decolourise bromine water.
 - Compound **V** forms a yellow precipitate with alkaline aqueous iodine, whereas compound **W** does not.
 - When reacted with cold $KMnO_4(aq)$, both **V** and **W** produce the same neutral compound **X**, $C_4H_{10}O_3$.
 - Both **V** and **W** exist as pairs of stereoisomers.

(a) Suggest which functional groups are responsible for the reactions with

(i) sodium,

.....

(ii) bromine water,

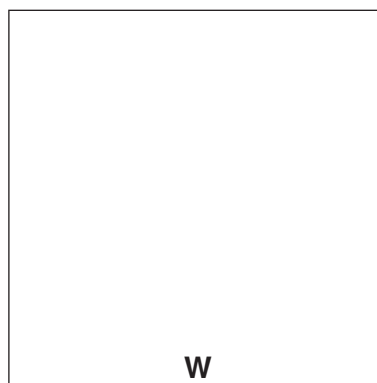
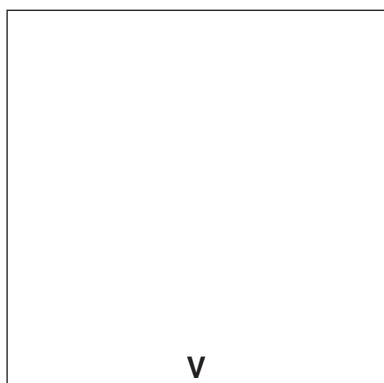
.....

(iii) alkaline aqueous iodine.

.....

[3]

(b) Suggest structures for **V** and **W**.

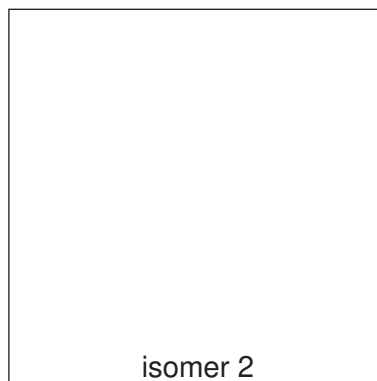
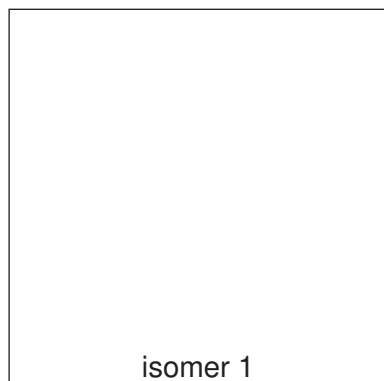


[2]

- (c) State the type of stereoisomerism shown by compound **V** and draw the structures of the stereoisomers.

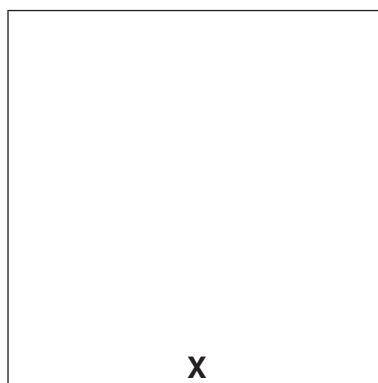
type of stereoisomerism

structures of stereoisomers



[2]

- (d) Suggest the structure of the neutral compound **X**.



[1]

[Total: 8]

Section B

Answer **all** the questions in the spaces provided.

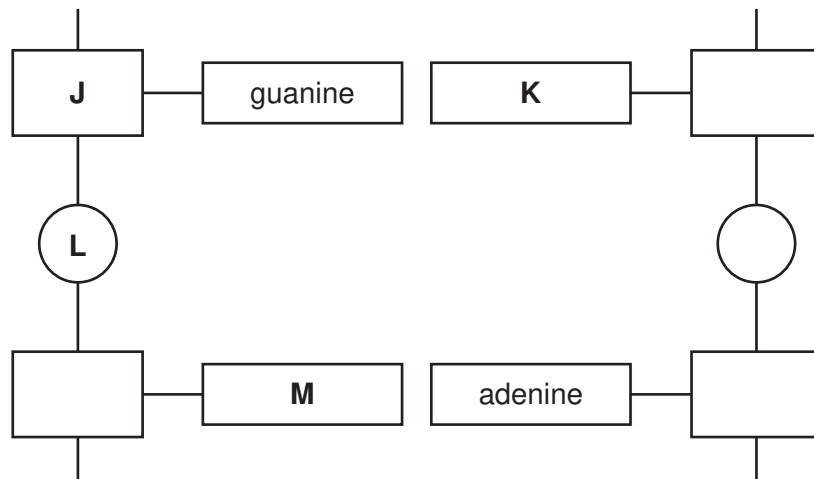
- 6 Proteins and deoxyribonucleic acid, DNA, are two important polymers that occur within living organisms.

- (a) Proteins have a number of 'levels' of bonding: primary, secondary and tertiary.
 Complete the table to indicate the level of bonding responsible for the features described.

| feature | level of bonding |
|------------------------------|------------------|
| formation of α -helix | |
| formation of disulfide bonds | |
| formation of ionic bonds | |
| linking amino acids | |

[3]

- (b) The diagram shows part of a DNA molecule. Study the diagram and give the correct names for the blocks labelled **J**, **K**, **L** and **M**.



| block letter | name |
|--------------|------|
| J | |
| K | |
| L | |
| M | |

[4]

(c) The DNA molecule is formed from two polymer strands which are held together until DNA replication occurs.

(i) What type of bonding holds the strands together?

.....

(ii) Explain why this type of bonding allows the base pairs within the strands to separate during replication at normal body temperature.

.....

.....

[2]

(d) In the polymer RNA, the identities of two of the blocks, **J**, **K**, **L** or **M**, are different.

For **one** of these blocks that are different, give its correct name in DNA and in RNA.

DNA:

RNA:

[1]

[Total: 10]

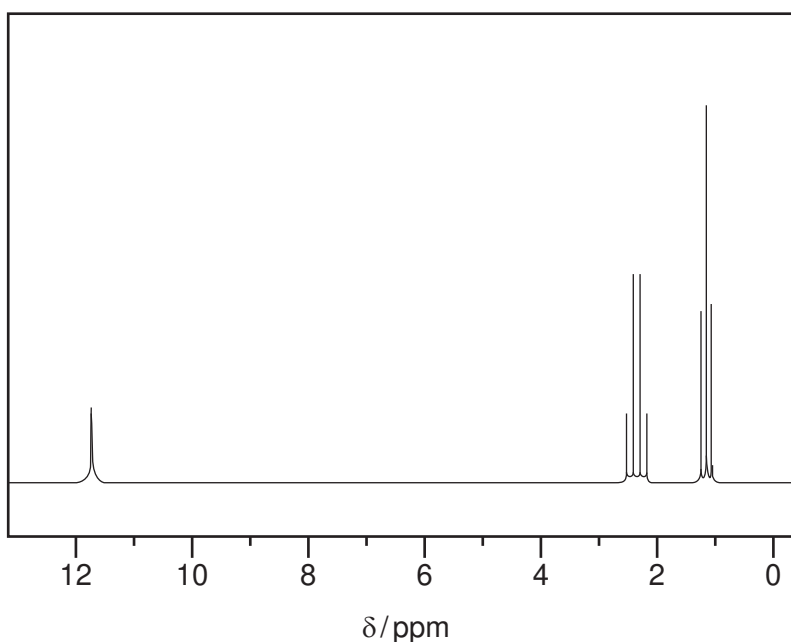
7 The combination of mass spectroscopy and NMR spectroscopy provides a powerful method of analysis for organic compounds.

(a) The mass spectrum of a compound **G** contains M and $M+1$ peaks in the ratio of their heights of 74 : 2.5.

Use these data to calculate the number of carbon atoms present in **G**. Show your working.

[2]

(b) The NMR spectrum of compound **G** is shown.



(i) Use the *Data Booklet* and your knowledge of NMR spectroscopy to identify the type of proton responsible for each of the three absorptions.

| δ /ppm | type of proton |
|---------------|----------------|
| 1.1 | |
| 2.2 | |
| 11.8 | |

(ii) The addition of D_2O causes one of these absorptions to disappear. Explain why this happens and state which absorption is affected.

.....

(iii) Draw the structural formula of **G**.

[6]

(c) Several structural isomers of **G** exist.

(i) Draw the structural formula of an isomer of **G** with only two absorptions in its NMR spectrum.

(ii) Use the *Data Booklet* to suggest where these absorptions would occur.

| peak | δ /ppm |
|------|---------------|
| 1 | |
| 2 | |

[3]

[Total: 11]

8 (a) Many common drugs are taken orally, but some medications, such as those based on protein molecules, are injected to prevent them being broken down in the digestive system.

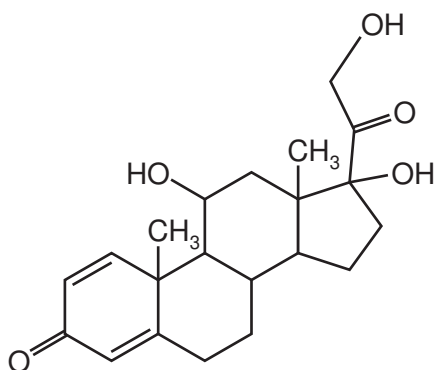
(i) **Name** a functional group present in drug molecules that might be broken down by acid in the stomach.

.....

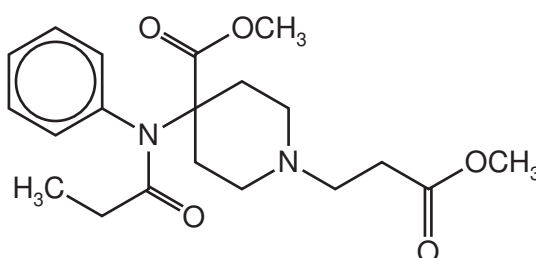
(ii) State the *type of reaction* that would cause such a breakdown.

.....

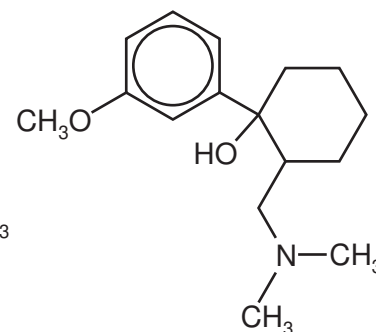
(iii) Which **one** of the following compounds would **not** be suitable to be taken orally?



A



B



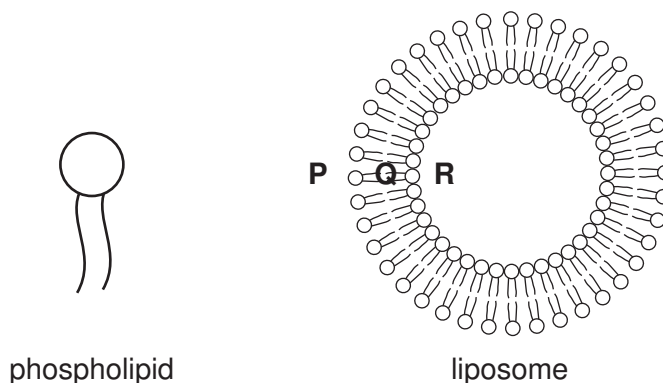
C

compound

(iv) On the structure of your chosen compound in (iii), circle **all** the functional groups that might be broken down by acid.

[5]

- (b) One way of protecting drug molecules that are taken orally is to enclose them in liposomes. These are artificially created spheres made from phospholipids which have an ionic phosphate ‘head’ and two hydrocarbon ‘tails’.



- (i) State and explain in which location, **P**, **Q** or **R**, a hydrophobic drug could be carried.

.....

- (ii) By considering the nature of the functional groups in **A**, **B** and **C**, explain why these drugs can be carried at position **R** in the liposome.

.....

[2]

- (c) Another method of protecting drug molecules is to ‘trap’ them inside gold nano-cages. When they reach the site where they are needed, such as a tumour, the drug is released by exposing the site to infra-red radiation.

- (i) Suggest the size of the nano-cages **in metres**.

.....

- (ii) Suggest why infra-red, rather than higher frequency radiation is used.

.....

[2]

[Total: 9]

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