Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME	

CENTRE NUMBER						CANDIDATE NUMBER					

4457571208

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2016**

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.

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.

This document consists of **18** printed pages and **2** blank pages.

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

1 Transition elements are important metals because of their characteristic properties.

(a) Define what is meant by a *transition element*.

....

.... [1]

(b) **(i)** For each of the following complexes, state the co-ordination number and the oxidation number of the transition element present.

	co-ordination number	oxidation number
$[Ni(CN)_2(NH_3)_2]$		
$[CrCl_2(H_2O)_4]^+$		

[2]

(ii) State the type of bonding that exists between the ligand and the metal ion in these complexes.

.... [1]

(iii) Suggest the structure of $[Ni(CN)_2(NH_3)_2]$ and name its shape.

name of shape ....

[2]

(c) The complex ion $[Cr(H_2O)_6]^{3+}$ can be converted into $[CrCl_2(H_2O)_4]^+$.

(i) Suggest a suitable reagent for this conversion.

.... [1]

(ii) State the *type of reaction* in **(i)**.

.... [1]

(d) The $[CrCl_2(H_2O)_4]^+$ complex ion shows stereoisomerism.

(i) Name this type of stereoisomerism.

.... [1]

(ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[CrCl_2(H_2O)_4]^+$.

[3]

[Total: 12]

2 Most car air bags contain a capsule of sodium azide, NaN_3. In a crash, the NaN_3 decomposes into its elements.

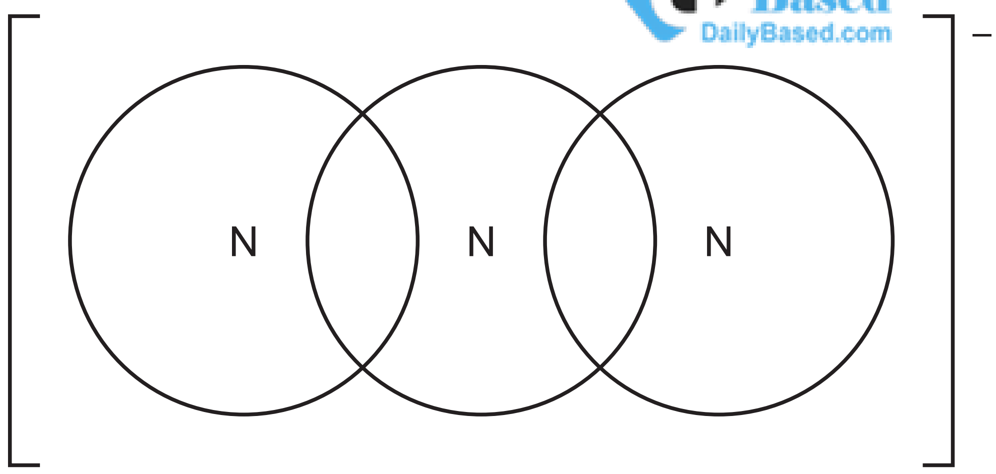
(a) Write an equation for the decomposition of NaN_3.

.... [1]

(b) Complete the 'dot-and-cross' diagram for the azide ion, N_3^-.

Use the following key for the electrons.

- ● electrons from central nitrogen atom
- × electrons from the other two nitrogen atoms
- ◻ added electron(s) responsible for the overall negative charge



[3]

(c) Lattice energies are always negative showing that they represent exothermic changes.

(i) Explain what is meant by the term *lattice energy*.

....

....

.... [2]

(ii) Explain why lattice energy represents an exothermic change.

....

.... [1]

(iii) Use the following data and any relevant data from the *Data Booklet* to calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $NaN_3(s)$.
Include a sign in your answer. Show all your working.

lattice energy, $\Delta H_{latt}^\ominus$, of $NaN_3(s)$	–732 kJ mol^{-1}
standard enthalpy change of atomisation, $\Delta H_{at}^\ominus$, of Na(g)	+107 kJ mol^{-1}
standard enthalpy change, $\Delta H^\ominus$, for $1\frac{1}{2}N_2(g) + e^- \rightarrow N_3^-(g)$	+142 kJ mol^{-1}

$\Delta H_f^\ominus$ of $NaN_3(s)$ = ... kJ mol^{-1} [3]

(iv) The lattice energy, $\Delta H_{latt}^\ominus$, of $RbN_3(s)$ is –636 kJ mol^{-1}.

Suggest why the lattice energy of $NaN_3(s)$, –732 kJ mol^{-1}, is more exothermic than that of $RbN_3(s)$.

....

.... [1]

[Total: 11]

3 Iron has atomic number 26.

(a) Complete the electronic configuration for the iron atom and the iron ion in the +3 oxidation state.

- iron atom [Ar] ....
- iron ion in the +3 oxidation state [Ar] ....

[2]

(b) Fe^{3+} can act as a homogeneous catalyst in the reaction between peroxodisulfate ions ($S_2O_8^{2-}$) and iodide ions.

(i) What is meant by a *homogeneous* catalyst?

....

.... [1]

(ii) Write an equation for the overall reaction between $S_2O_8^{2-}$(aq) and I^-(aq).

.... [1]

(iii) Suggest why, in the absence of a catalyst, the activation energy for this reaction is high.

....

.... [1]

(iv) Write two equations to show how Fe^{3+}(aq) ions can catalyse the reaction between $S_2O_8^{2-}$(aq) ions and I^-(aq) ions.

equation 1 ....

equation 2 ....

[2]

(c) Iron(III) oxide can be reduced to iron metal using carbon monoxide at a temperature of 1000 °C.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^{\ominus} = -43.6\,kJ\,mol^{-1}$$

Some relevant standard entropies are given in the table.

substance	$Fe_2O_3(s)$	CO(g)	Fe(s)	$CO_2(g)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	+90	+198	+27	+214

(i) What is meant by the term *entropy*?

....

.... [1]

(ii) Calculate the standard entropy change, $\Delta S^{\ominus}$, of this reaction.

$\Delta S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ [2]

(iii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 25 °C.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [2]

(iv) Suggest why a temperature of 1000 °C is usually used for this reaction, even though the reaction is spontaneous (feasible) at 25 °C. Explain your answer.

....

....

.... [1]

[Total: 13]

4 **(a)** Explain why compounds of transition elements are usually coloured.

....

....

....

.... [3]

(b) Copper is used to make alloys such as brass. The percentage of copper in a sample of brass can be determined by dissolving the sample in concentrated nitric acid and reacting the mixture with potassium iodide. The resulting solution is then titrated.

A 1.75 g sample of the brass was dissolved in excess concentrated nitric acid.

The reaction of the copper metal in the brass with the concentrated nitric acid released a brown gas and formed a green-blue solution.

(i) Write an equation for this reaction.

.... [2]

The resulting solution was neutralised and made up to 250 cm^3 in a volumetric flask with distilled water.

An excess of aqueous potassium iodide was added to a 25.0 cm^3 portion of this solution to liberate iodine.

The resulting solution required 22.40 cm^3 of 0.100 mol dm^{-3} aqueous sodium thiosulfate solution to react with the iodine produced.

The reactions taking place in this titration are shown.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(ii) Calculate the percentage of copper, by mass, in the sample of brass to **three** significant figures.

% of copper = ... [4]

[Total: 9]

5 The phosphate buffer system operates in biological cells. The buffer contains dihydrogen phosphate, $H_2PO_4^-$, which acts as a weak acid.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

(a) Write an expression for the K_a of $H_2PO_4^-$.

K_a =

[1]

(b) **(i)** Explain what is meant by the term *buffer solution*.

....

....

.... [2]

(ii) Write **two** equations to show how a solution containing a mixture of $H_2PO_4^-$ and HPO_4^{2-} acts as a buffer.

....

.... [2]

(c) The pH in many living cells is 7.40.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_a = 6.31 \times 10^{-8}\,mol\,dm^{-3}$$

Calculate the value of $[HPO_4^{2-}]/[H_2PO_4^-]$ needed to give a pH of 7.40 in the cells.

$[HPO_4^{2-}]/[H_2PO_4^-]$ = ... [3]

(d) **(i)** The $H_2PO_4^-$ ion can also act as a base.

Write an equation to show $H_2PO_4^-$ acting as a base.

.... [1]

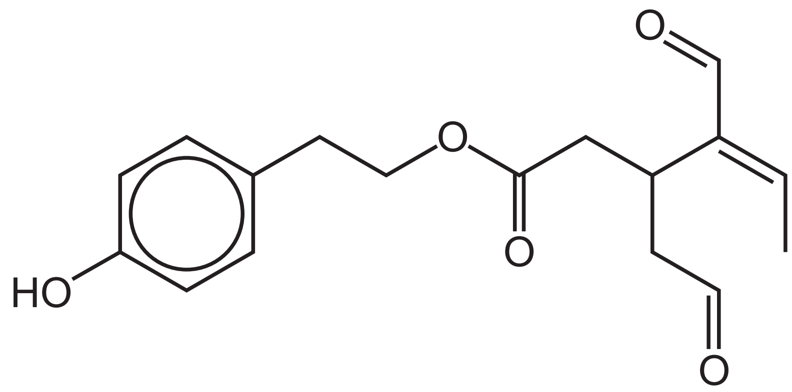
(ii) The HPO_4^{2-} ion can also act as an acid.

Write an equation to show HPO_4^{2-} acting as an acid.

.... [1]

[Total: 10]

6 Oleocanthal, **Q**, is a natural compound found in olive oil. It has antioxidant and anti-inflammatory properties and is thought to have a protective effect against Alzheimer's disease.



Q

(a) **Q** shows optical and cis-trans isomerism.

On the structure of **Q** above, **circle** the functional group that shows cis-trans isomerism and indicate with an **asterisk** (*) the chiral carbon atom. [1]

(b) **Q** can be isolated from olive oil by partitioning between two solvents.

(i) Explain what is meant by the term *partition coefficient*.

....

....

.... [2]

(ii) When 40.0 cm^3 of hexane was shaken with 10.0 cm^3 of a solution containing 0.25 g of **Q** in 10.0 cm^3 of methanol, it was found that 0.060 g of **Q** was extracted into the hexane.

Calculate the partition coefficient, $K_{partition}$, of **Q** between hexane and methanol.

$K_{partition}$ = ... [2]

(c) Complete the following table to show the structures of the products formed when **Q** reacts with the three reagents.

reagent	structure of product(s)		type of reaction
excess $Br_2(aq)$			
$NaBH_4$			
excess hot $NaOH(aq)$			

[6]

(d) When a sample of **Q** synthesised in a laboratory was compared to a natural sample from olive oil, it was found that the therapeutic activity of the synthetic sample was lower.

Suggest a reason for this.

....

.... [1]

[Total: 12]

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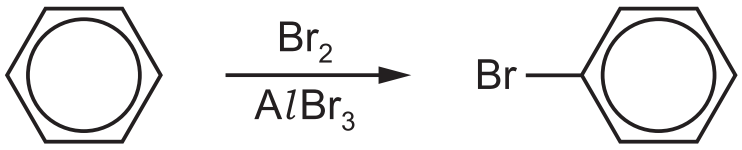
7 (a) Bromobenzene can be prepared from benzene as shown.



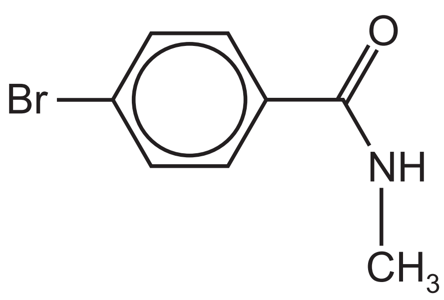
(i) Name the mechanism of this reaction.

.... [1]

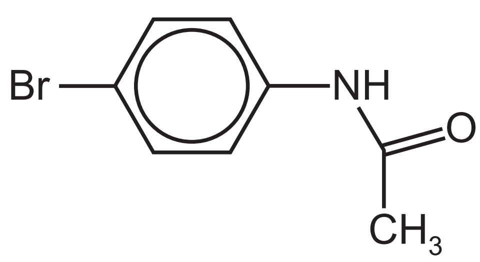
(ii) Draw the mechanism of this reaction. Include all relevant curly arrows, any dipoles and charges.

[4]

(b) Two isomeric aromatic compounds, **V** and **W**, each contain three functional groups, two of which are shown in the table.



V



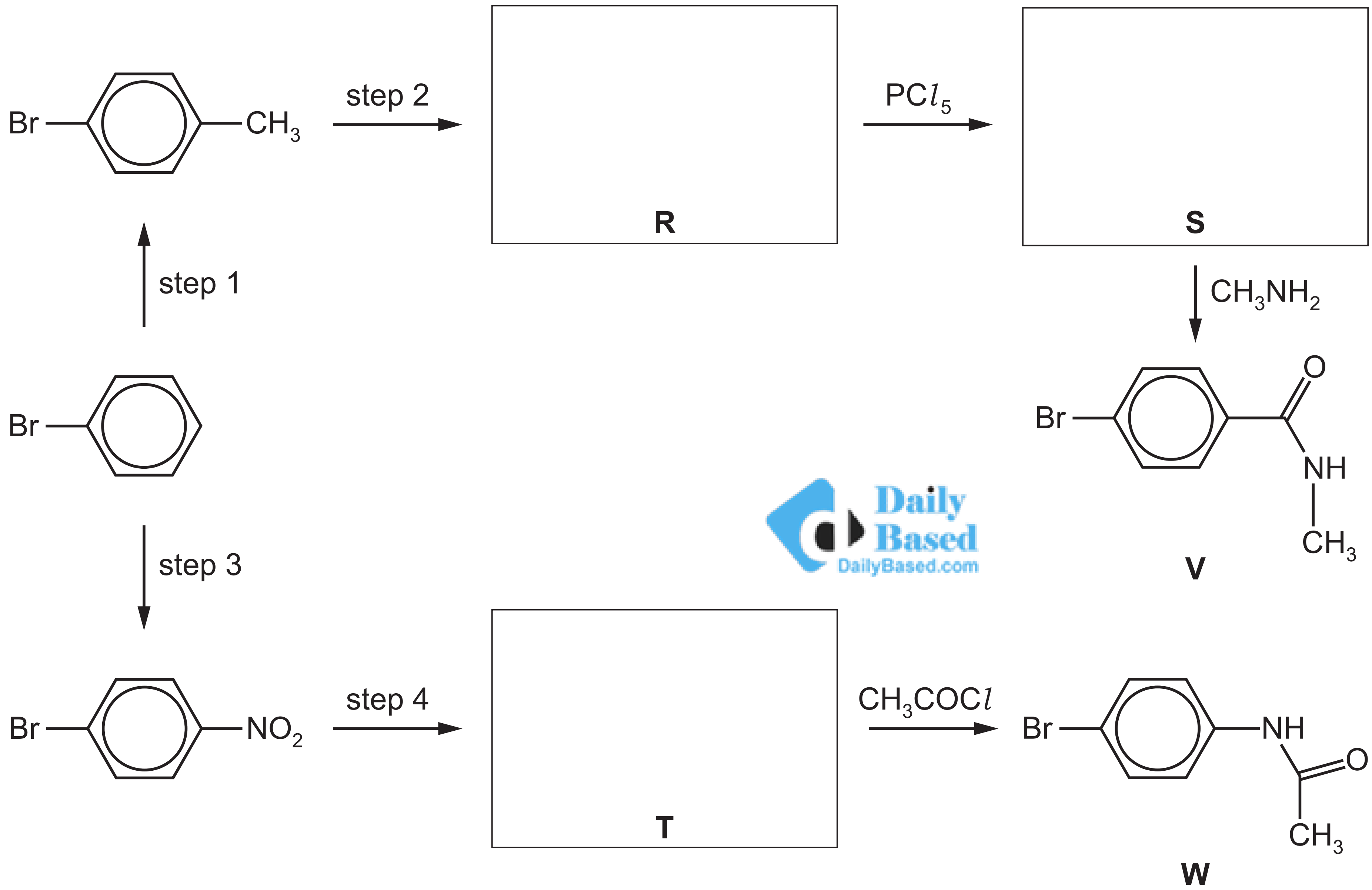
W

Complete the table with the **other** functional groups present in **V** and **W**.

substance	functional groups present		
V	bromo group	aryl (benzene) group	....
W	bromo group	aryl (benzene) group	....

[1]

(c) Compounds **V** and **W** can be synthesised from bromobenzene by the following routes.



(i) Suggest reagents for each of the steps 1–4.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

[4]

(ii) Deduce structures for **R**, **S** and **T** and draw their structural formulae in the boxes. [3]

(d) **(i)** Draw the structures of the two organic products from the reaction of **V** and **W** with $LiAlH_4$.

product from **V**	product from **W**

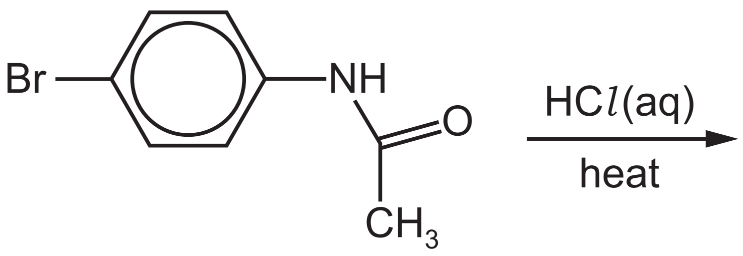
[2]

(ii) Name the *type of reaction* occurring between $LiAlH_4$ and **V** or **W**.

.... [1]

(e) **V** and **W** can be hydrolysed using hot HCl(aq).

(i) Draw the structures of the two organic products of the hydrolysis of **W**.



W

+

[2]

(ii) The products formed from the hydrolysis of **W** are soluble in aqueous acid, whereas a precipitate, **X**, is formed on hydrolysing **V**.

Draw the structure of compound **X**.

X

[1]

(iii) Suggest why **X** is insoluble in water.

....

.... [1]

[Total: 20]

8 Compound **F** is a carboxylic acid.

(a) Compound **F** contains 31.4% oxygen by mass and its mass spectrum has a molecular ion peak at *m* / *e* = 102.

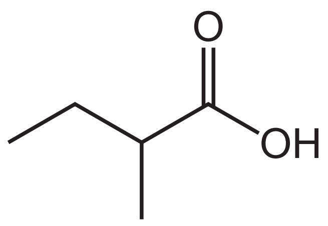
Use all of this information to show that the molecular formula of compound **F** is $C_5H_{10}O_2$. Show all your working.

[1]

(b) There are **four** possible structural isomers of $C_5H_{10}O_2$ that are carboxylic acids.

(i) The first isomer has been drawn.

Draw the skeletal formulae of the three **other** structural isomers.



isomer 1

isomer 2

isomer 3

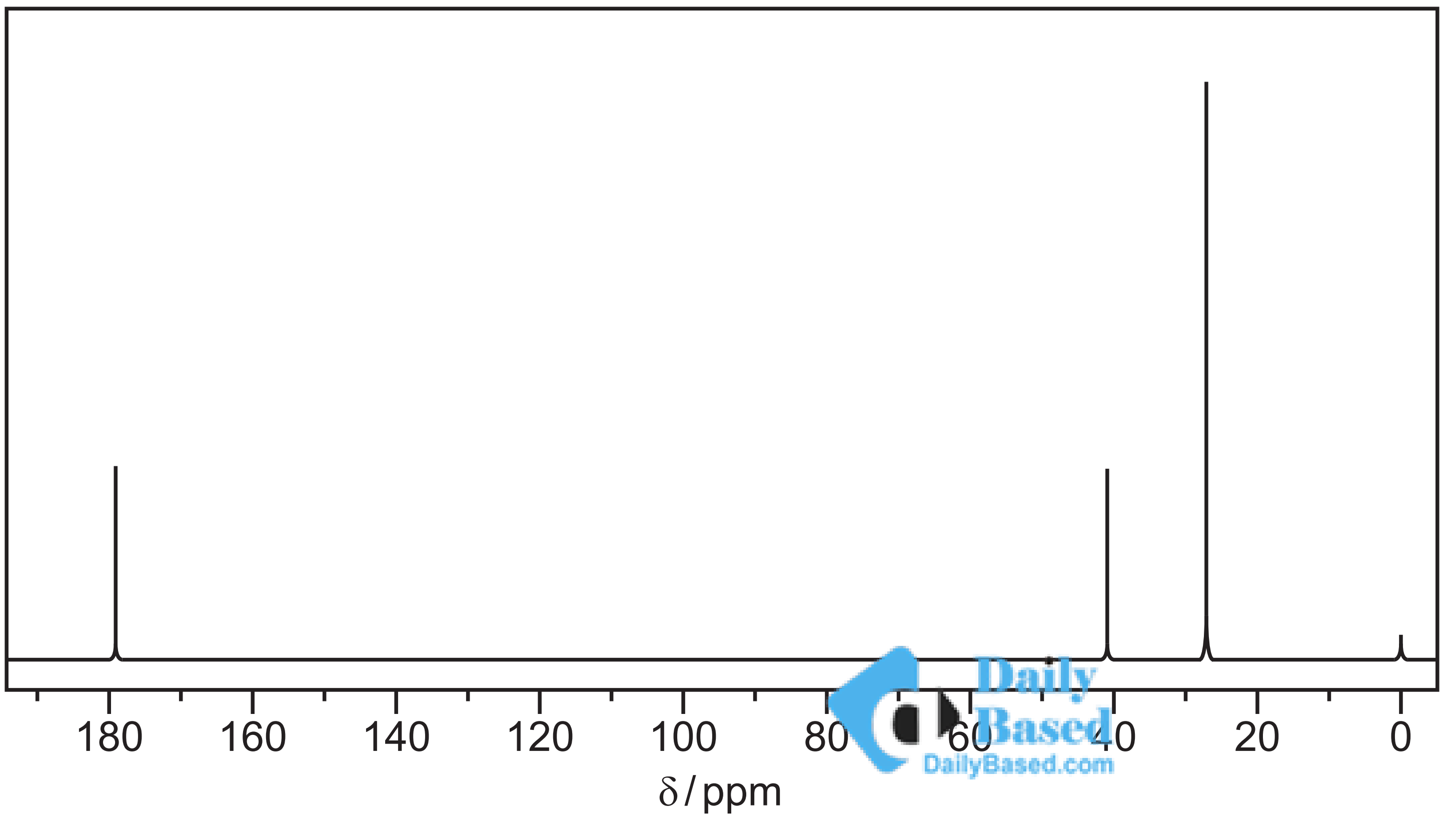
isomer 4

[2]

(ii) State the systematic name of isomer 1.

.... [1]

(c) **F** is one of the four structural isomers in **(b)(i)**. A carbon-13 NMR spectrum of **F** is shown.



(i) Use the spectrum to identify isomer **F**. Draw its structure in the box below.

F

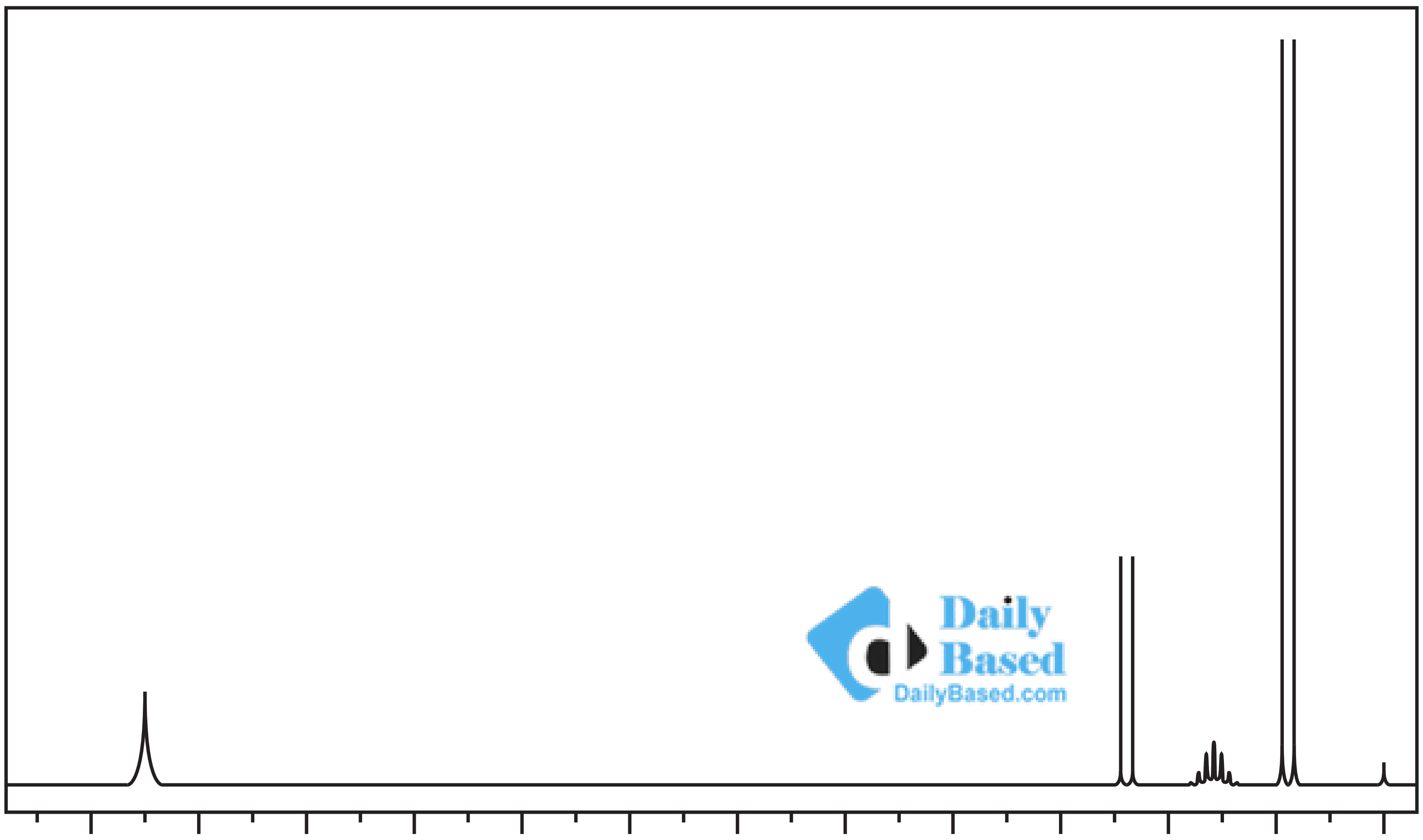
[1]

(ii) Use the *Data Booklet* and your knowledge of carbon-13 NMR spectroscopy to identify the environments and hybridisations of the carbon atoms responsible for each of the three absorptions.

δ / ppm	environment of the carbon atom	hybridisation of the carbon atom
27		
41		
179		

[2]

(d) **G** is another of the four structural isomers in **(b)(i)**. The proton NMR spectrum of **G** is shown.



(i) Use the *Data Booklet* and the spectrum to complete the table below.

The actual chemical shifts for the four absorptions in **G** and the splitting pattern at δ = 1.6 ppm have been added for you.

δ / ppm	type of proton	number of protons	splitting pattern
0.9			
1.6			multiplet
2.4			
11.5			

[4]

(ii) Deduce which isomer is **G** and draw its structure in the box.

G

[1]

(e) Name or give the formula of a suitable solvent for obtaining a proton NMR spectrum.

.... [1]

[Total: 13]

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