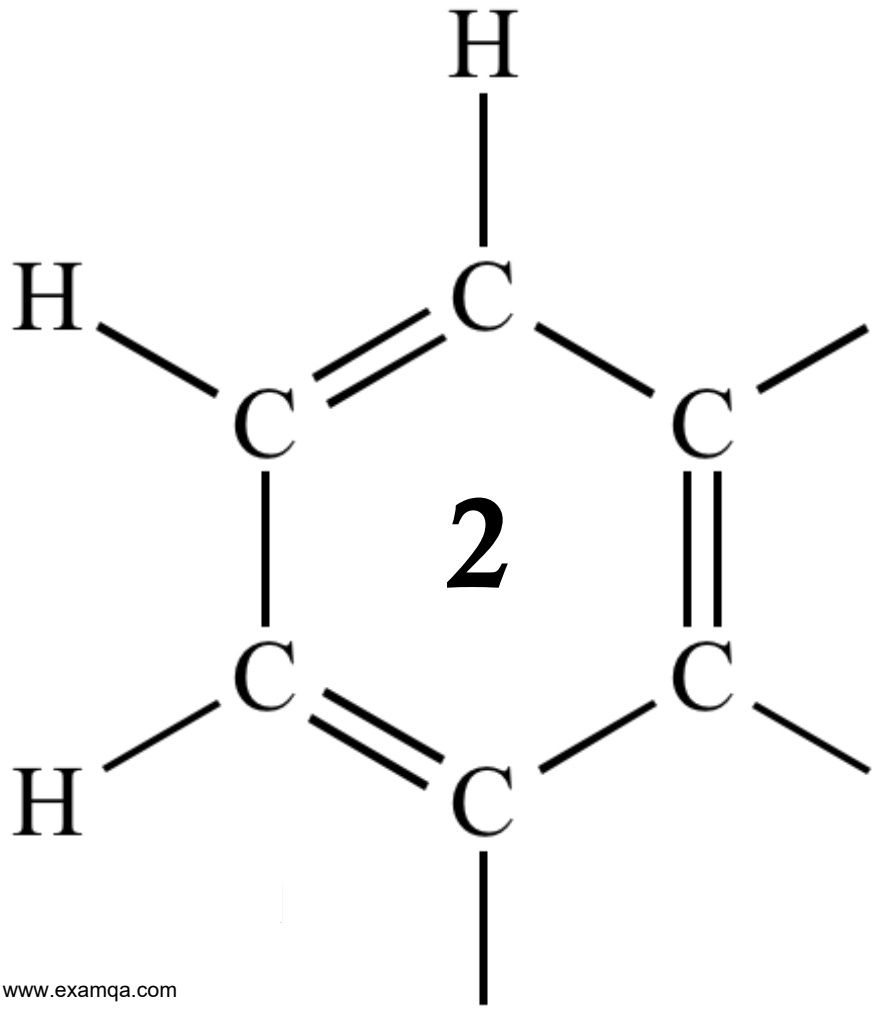
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

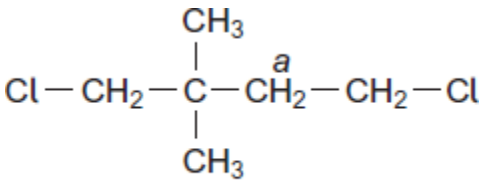
SYNTHESIS ~ ANALYSIS

N.M.R



1 N.m.r. spectroscopy can be used to study the structures of organic compounds.

(a) Compound **J** was studied using ^{1}H n.m.r. spectroscopy.



J

(i) Identify a solvent in which **J** can be dissolved before obtaining its ^{1}H n.m.r. spectrum.

.....

(1)

(ii) Give the number of peaks in the ^{1}H n.m.r. spectrum of **J**.

.....

(1)

(iii) Give the splitting pattern of the protons labelled *a*.

.....

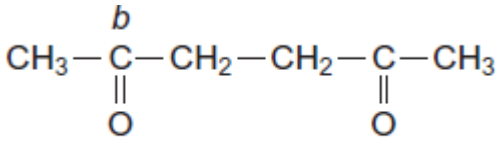
(1)

(iv) Give the IUPAC name of **J**.

.....

(1)

(b) Compound **K** was studied using ^{13}C n.m.r. spectroscopy.



K

(i) Give the number of peaks in the ^{13}C n.m.r. spectrum of **K**.

.....

(1)

(ii) Use **Table 3** on the Data Sheet to suggest a δ value of the peak for the carbon labelled *b*.

.....

(1)

(iii) Give the IUPAC name of **K**.

.....

(1)

(Total 7 marks)

2 This question concerns isomers of $C_6H_{12}O_2$ and how they can be distinguished using n.m.r. spectroscopy.

(a) The non-toxic, inert substance TMS is used as a standard in recording both ^{1}H and ^{13}C n.m.r. spectra.

(i) Give **two** other reasons why TMS is used as a standard in recording n.m.r. spectra.

Reason 1 .....

.....

Reason 2 .....

.....

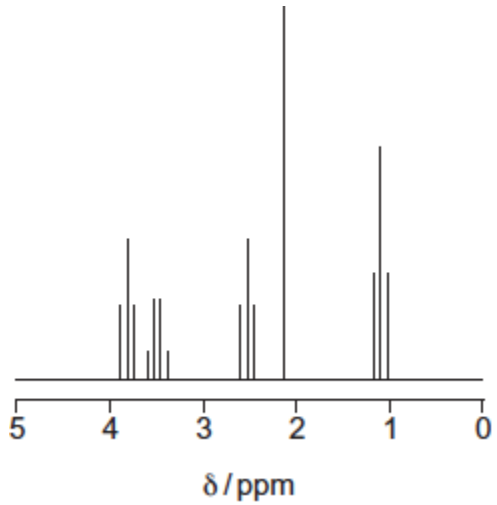
(2)

(ii) Give the structural formula of TMS.

(1)

(b) The proton n.m.r. spectrum of compound **P** ($C_6H_{12}O_2$) is represented in **Figure 1**.

Figure 1



The integration trace gave information about the five peaks as shown in **Figure 2**.

Figure 2

δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3

(i) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peak at δ 2.2.

(1)

(ii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.5 and 1.2.

(1)

(iii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.8 and 2.6.

(1)

(iv) Deduce the structure of **P**.

(1)

(c) These questions are about different isomers of **P** ($C_6H_{12}O_2$).

(i) Draw the structures of the two esters that both have only two peaks in their proton n.m.r. spectra. These peaks both have an integration ratio of 3:1.

Ester 1

Ester 2

(2)

(ii) Draw the structure of an optically active carboxylic acid with five peaks in its ^{13}C n.m.r. spectrum.

(1)

(iii) Draw the structure of a cyclic compound that has only two peaks in its ^{13}C n.m.r. spectrum and has no absorption for C = O in its infrared spectrum.

(1)

(Total 11 marks)

3 Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

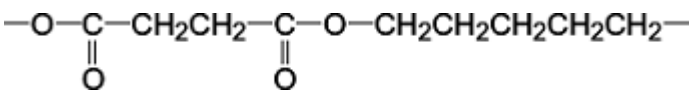
(a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

Mechanism

Name of organic product .....

(5)

(b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



(i) Name the diol used.

.....

(1)

(ii) Draw the displayed formula of the diacyl chloride used.

(1)

(iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction .....

Explanation .....

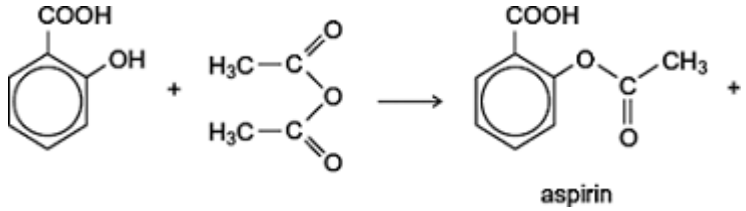
.....

.....

.....

(3)

(c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



aspirin

.....

(1)

(ii) Suggest a name for the mechanism for the reaction in part (c)(i).

.....

(1)

(iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 .....

.....

.....

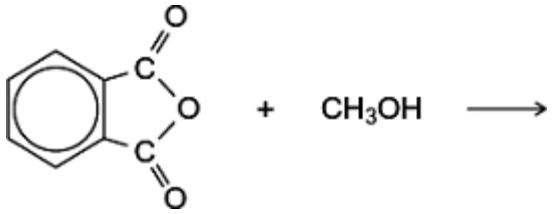
Advantage 2 .....

.....

.....

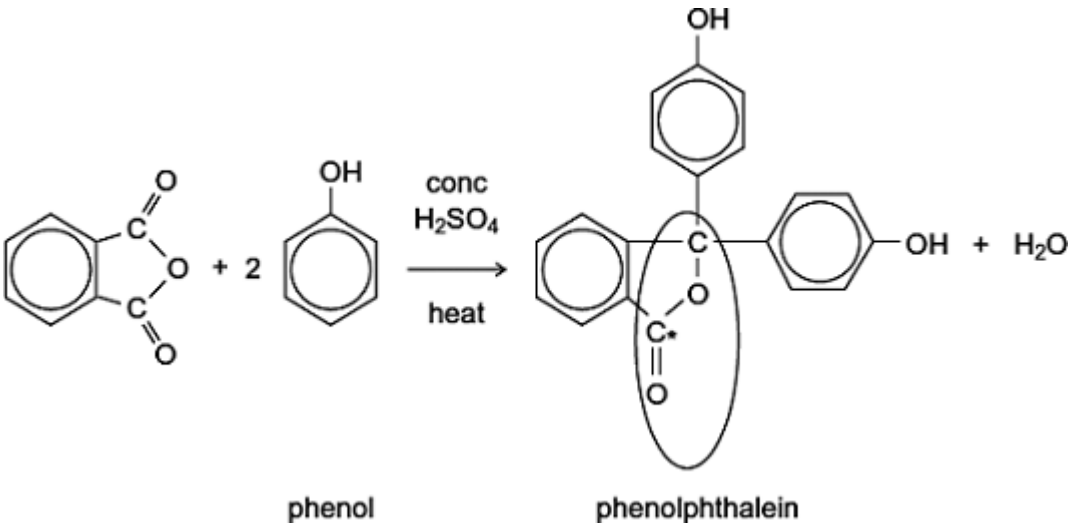
(2)

(d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product



(1)

(e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



(i) Name the functional group ringed in the structure of phenolphthalein.

.....

(1)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of phenolphthalein.

.....

(1)

(iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

.....

(1)

(f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

(i) For **each** acid.alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	**Alkali**	**Tick box (✓)**
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2)

(ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

.....

(1)
(Total 21 marks)

4 When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts (a) to (d).

(a) Compounds **F** and **G** have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.

F has two peaks in its ^{13}C n.m.r. spectrum.

G has three peaks in its ^{13}C n.m.r. spectrum.

F **G**

(2)

(b) Compounds **H** and **J** have the molecular formula C_6H_{12}.

Both have only one peak in their ^1H n.m.r. spectra.
H reacts with aqueous bromine but **J** does not.

H **J**

(2)

(c) **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$.

Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

K **L**

(2)

(d) Compounds **M** and **N** have the molecular formula $C_6H_{15}N$.

M is a tertiary amine with only two peaks in its ^1H n.m.r. spectrum.

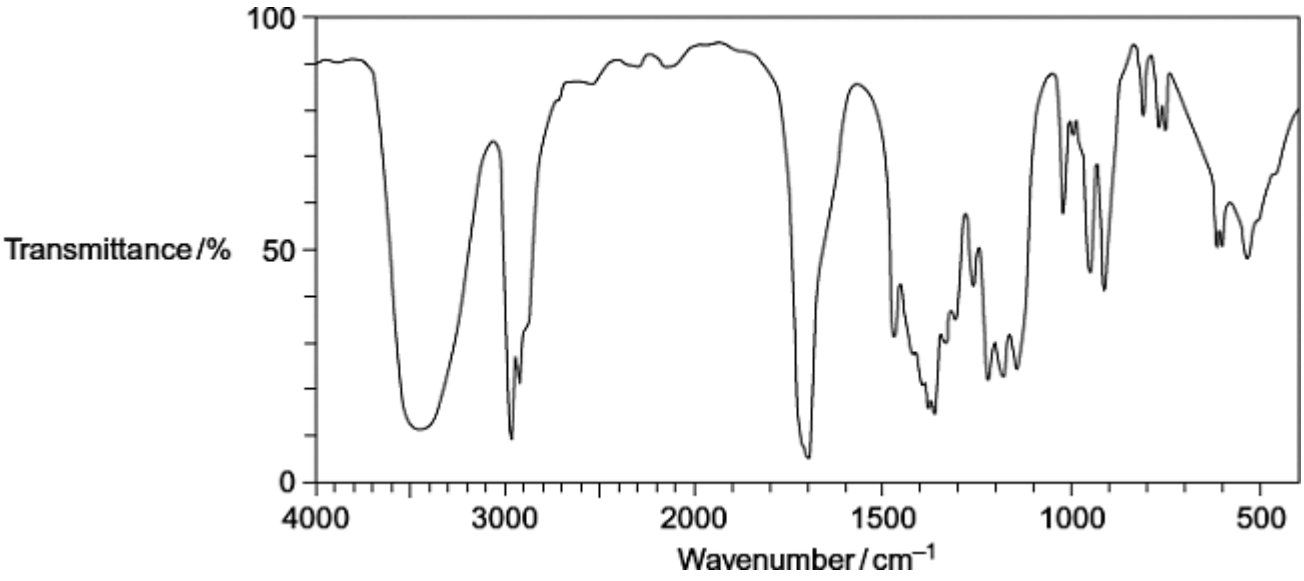
N is a secondary amine with only three peaks in its ^1H n.m.r. spectrum.

M **N**

(2)
(Total 8 marks)

5 Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

(a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450cm^{-1} in the spectrum.

.....

(1)

(b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ /ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

(i) The peak at δ = 2.6

.....

(1)

(ii) The peak at δ = 2.2

.....

(1)

(iii) The peak at δ = 1.2

.....

(1)

(iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

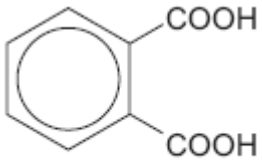
(1)

(Total 5 marks)

6 Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

(a) Give the IUPAC name for phthalic acid.

.....

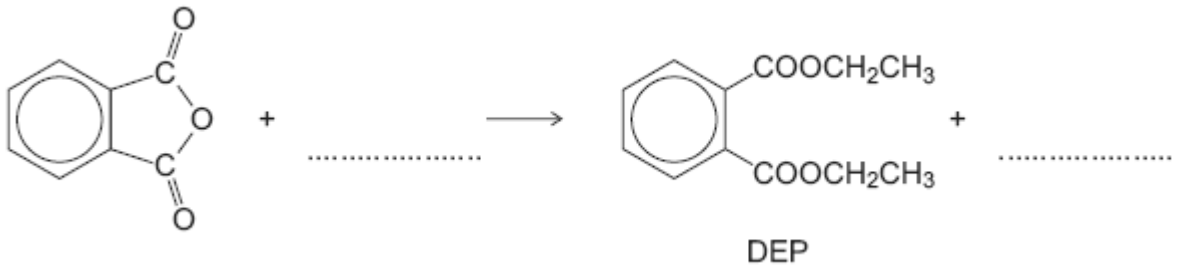
(1)

(b) Draw the displayed formula of the repeating unit of poly(chloroethene).

(1)

(c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

(i) Complete the following equation showing the formation of DEP from phthalic anhydride.



DEP

(2)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

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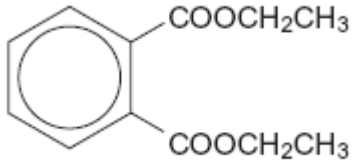
(1)

(iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at δ = 62 ppm.

Table 3 on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1)

(d) The mass spectrum of DEP includes major peaks at *m/z* = 222 (the molecular ion) and at *m/z* = 177

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at *m/z* = 177

.....

(2)

(e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

An organisation that represents the manufacturers of plasticisers asserts that experimental evidence and research findings show that phthalates do not pose a risk to human health because they biodegrade in a short time scale.

According to the organization's research, phthalates do not represent a risk for humans or for the environment and they are biodegradable.

(i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

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(1)

(ii) Suggest what needs to be done so that the public could feel confident that the research discussed above is reliable.

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(Extra space) .....

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(2)
(Total 11 marks)

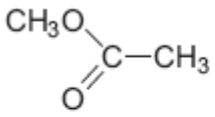
7 Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

(a) The following compounds can be distinguished by observing what happens in test-tube reactions.

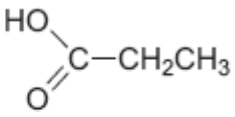
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

(i)



E



F

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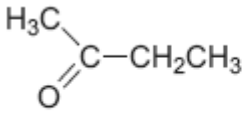
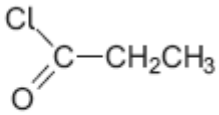
(3)

(ii)



G



H

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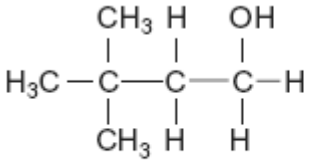
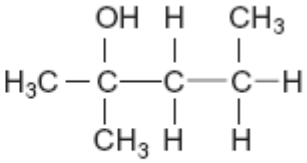
(3)

(iii)



J



K

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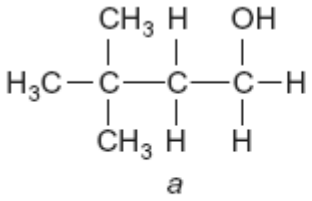
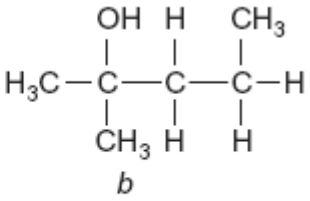
(3)

(b) Compounds **J** and **K** can also be distinguished using spectroscopic techniques such as ^{1}H n.m.r.



a

J



b

K

(i) Name compound **J**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

.....

.....

.....

.....

.....

.....

(3)

(ii) Name compound **K**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

.....

.....

.....

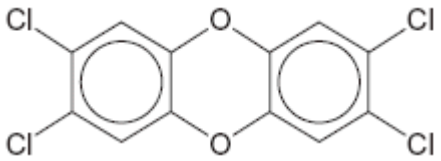
.....

.....

.....

(3)
(Total 15 marks)

8 In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.



In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

(a) Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry.
Suggest how the mixture could be separated.

.....

(1)

(b) The molecular formula of TCDD is $C_{12}H_4O_2Cl_4$

Chlorine exists as two isotopes ^{35}Cl (75%) and ^{37}Cl (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m/z* value of the most abundant molecular ion peak.

Number of molecular ion peaks .....

.....

m/z value of the most abundant molecular ion peak .....

.....

(2)

(c) Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

.....

.....

(1)

(d) TCDD can also be analysed using ^{13}C n.m.r.

(i) Give the formula of the compound used as the standard when recording a ^{13}C spectrum.

.....

(1)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TCDD.

.....

(1)
(Total 6 marks)