Q1. Organic chemists use a variety of methods to identify unknown compounds. When the molecular formula of a compound is known, spectroscopic and other analytical techniques are used to distinguish between possible structural isomers. Use your knowledge of such techniques to identify the compounds described below.

Use the three tables of spectral data on the Data Sheet where appropriate.

Each part below concerns a different pair of structural isomers.
Draw **one** possible structure for each of the compounds **A** to **J**, described below.

(a) Compounds **A** and **B** have the molecular formula C_3H_6O
A has an absorption at 1715 cm^{-1} in its infrared spectrum and has only one peak in its ^1H n.m.r. spectrum.
B has absorptions at 3300 cm^{-1} and at 1645 cm^{-1} in its infrared spectrum and does **not** show *E*–*Z* isomerism.

A **B**

(2)

(b) Compounds **C** and **D** have the molecular formula C_5H_{12}
In their ^1H n.m.r. spectra, **C** has three peaks and **D** has only one.

C **D**

(2)

(c) Compounds **E** and **F** are both esters with the molecular formula $C_4H_8O_2$
In their ^1H n.m.r. spectra, **E** has a quartet at δ = 2.3 ppm and **F** has a quartet at

δ = 4.1 ppm.

E **F**

(2)

(d) Compounds **G** and **H** have the molecular formula $C_6H_{12}O$
Each exists as a pair of optical isomers and each has an absorption at about 1700 cm^{-1} in its infrared spectrum. **G** forms a silver mirror with Tollens' reagent but **H** does not.

G **H**

(2)

(e) Compounds **I** and **J** have the molecular formula $C_4H_{11}N$ and both are secondary amines. In their ^{13}C n.m.r. spectra, **I** has two peaks and **J** has three.

I **J**

(2)
(Total 10 marks)

Q2. It is necessary to use several analytical techniques to determine the structure of an unknown compound.

An analytical chemist was asked to determine the structure of compound **Q** which was found in a waste tank in a mixture of volatile liquids.

Compound **Q** has the molecular formula C_4H_7ClO. It is a volatile liquid which does not produce misty fumes when added to water.

(a) Suggest how the chemist could obtain a sample of **Q** for analysis from the mixture of volatile liquids.

.....

(1)

(b) The infra-red spectrum of Q contains a major absorption at 1724 cm^{-1}. Identify the bond which causes this absorption.

.....

(1)

(c) The mass spectrum of Q contains two molecular ion peaks at *m/z* = 106 and *m/z* = 108.
It also has a major peak at *m/z* = 43.

(i) Suggest why there are two molecular ion peaks.

.....

(ii) A fragment ion produced from **Q** has *m/z* = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

Fragment ion .....

Equation .....

(3)

(d) The proton n.m.r. spectrum of **Q** was recorded.

(i) Suggest a suitable solvent for use in recording this spectrum of **Q**.

.....

(ii) Give the formula of the standard reference compound used in recording proton
n.m.r. spectra.

.....

(2)

(e) The proton n.m.r. spectrum of Q shows 3 peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting patterns.

	Peak 1	Peak 2	Peak 3
Integration value	3	3	1
Splitting pattern	doublet	singlet	quartet
Number of adjacent, non-equivalent protons	1		

(1)

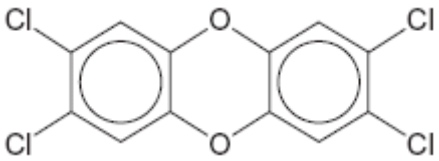
(f) Using the information in parts (a), (b) and (d) deduce the structure of compound **Q.**

(1)

(g) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1)
(Total 10 marks)

Q3. 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.

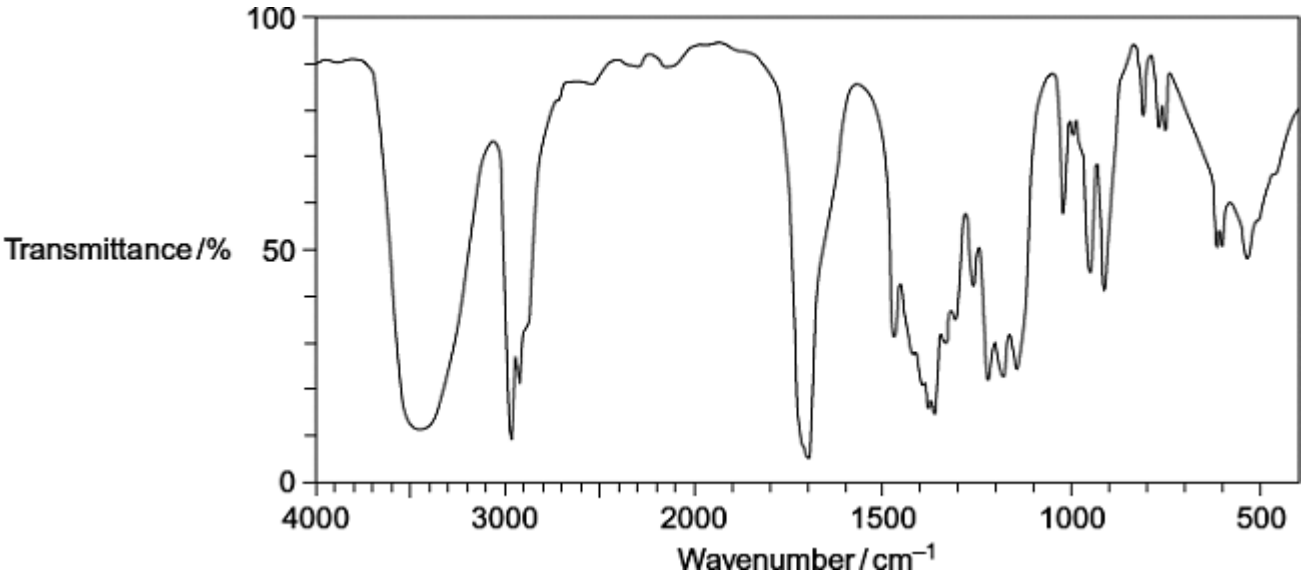
.....

(1)

(Total 6 marks)

Q4. 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.

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(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

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(1)

(ii) The peak at δ = 2.2

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(1)

(iii) The peak at δ = 1.2

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(1)

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

(1)
(Total 5 marks)

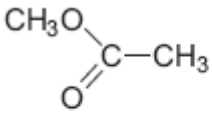
Q5. Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

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

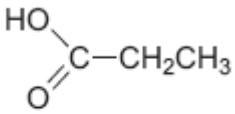
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

(i)



E



F

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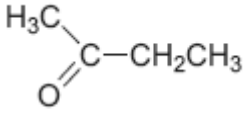
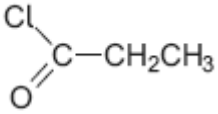
(3)

(ii)



G



H

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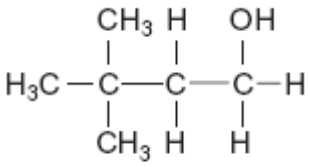
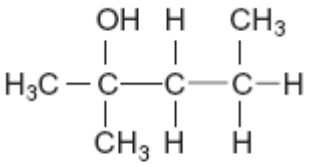
(3)

(iii)



J



K

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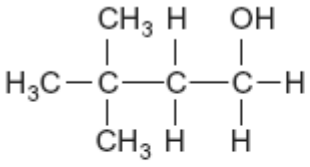
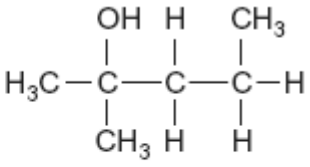
(3)

(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*.

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(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*.

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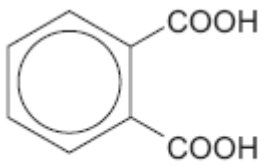
(3)
(Total 15 marks)

Q6. 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.

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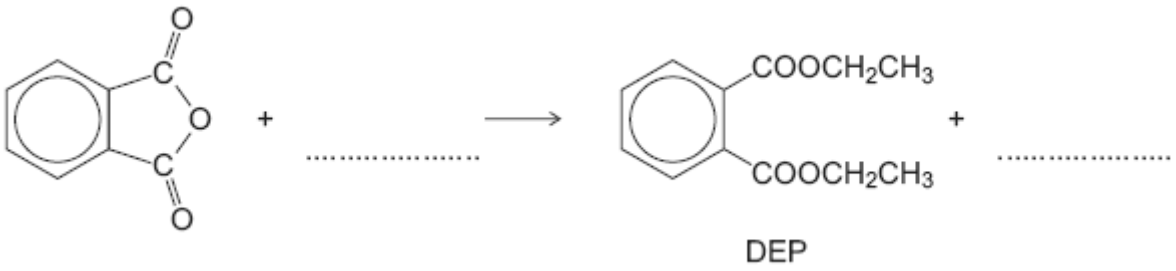
(1)

(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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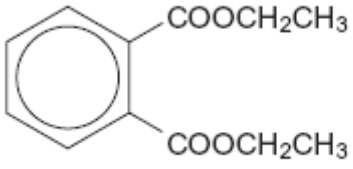
(1)

(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)