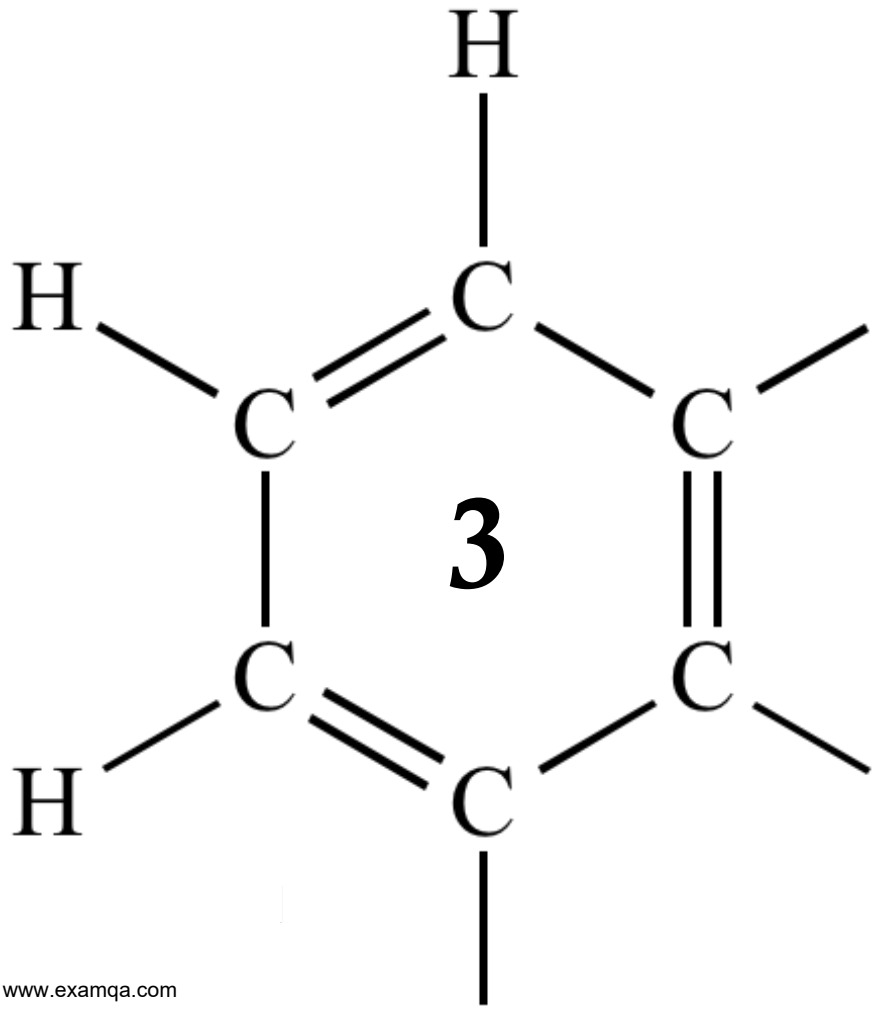
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

SYNTHESIS ~ ANALYSIS

N.M.R



1 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)

2 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)

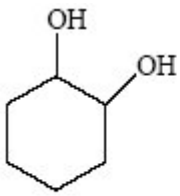
(f) Using the information in parts (a), (b) and (d) deduce the structure of compound **Q.**

(1)

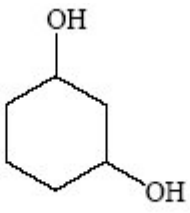
(g) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1)
(Total 10 marks)

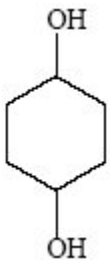
3 Three cyclic alcohols, cyclohexan–1,2-diol, cyclohexan–1,3-diol and cyclohexan–1,4-diol were compared using ^{13}C n.m.r. spectroscopy.



cyclohexan-1,2-diol

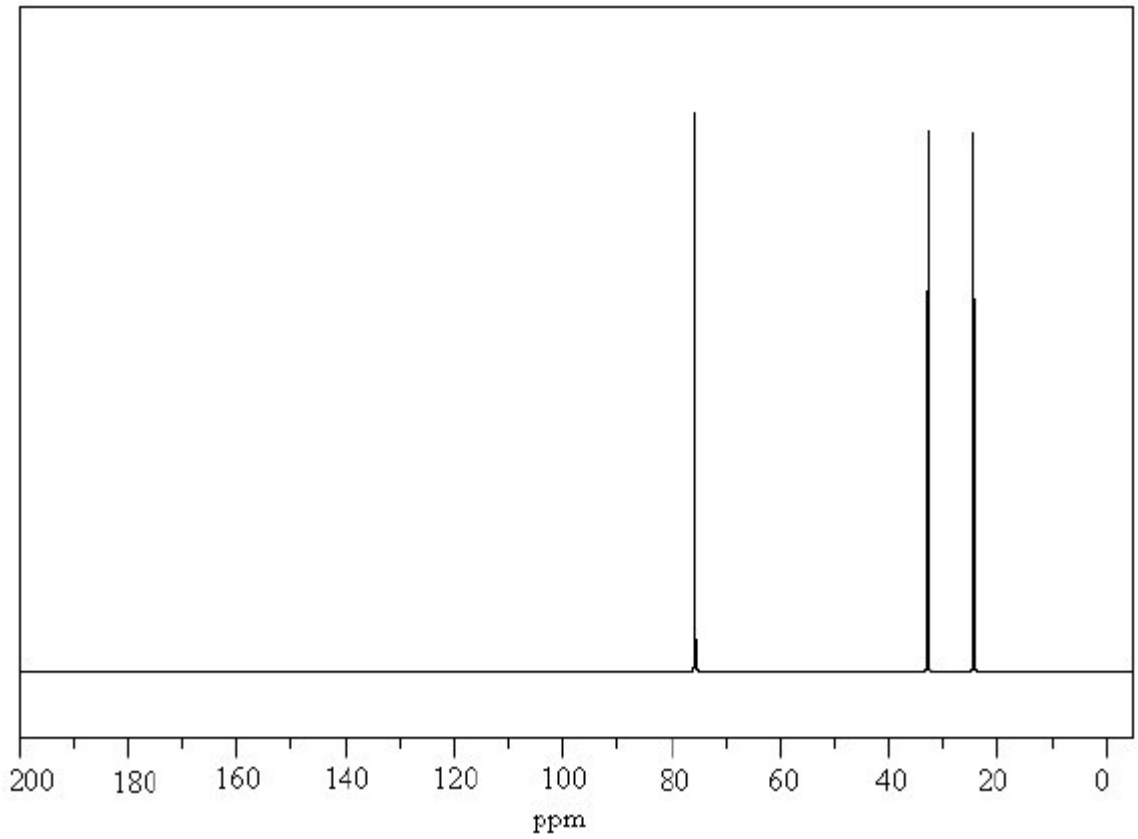


cyclohexan-1,3-diol



cyclohexan-1,4-diol

The ^{13}C n.m.r. spectrum of cyclohexan-1,2-diol is shown below.



(a) (i) Explain why there are three peaks.

.....

.....

.....

(ii) Proton n.m.r. chemical shift data is shown in Table 1 on the reverse of the Periodic Table. Chemical shift values for ^{13}C vary similarly with chemical environment.

Suggest the δ value of the peak in the spectrum above which corresponds to the absorption for carbon atom 1 in cyclohexan-1,2-diol.

.....

(b) (i) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan-1,3-diol.

.....

(ii) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan-1,4-diol.

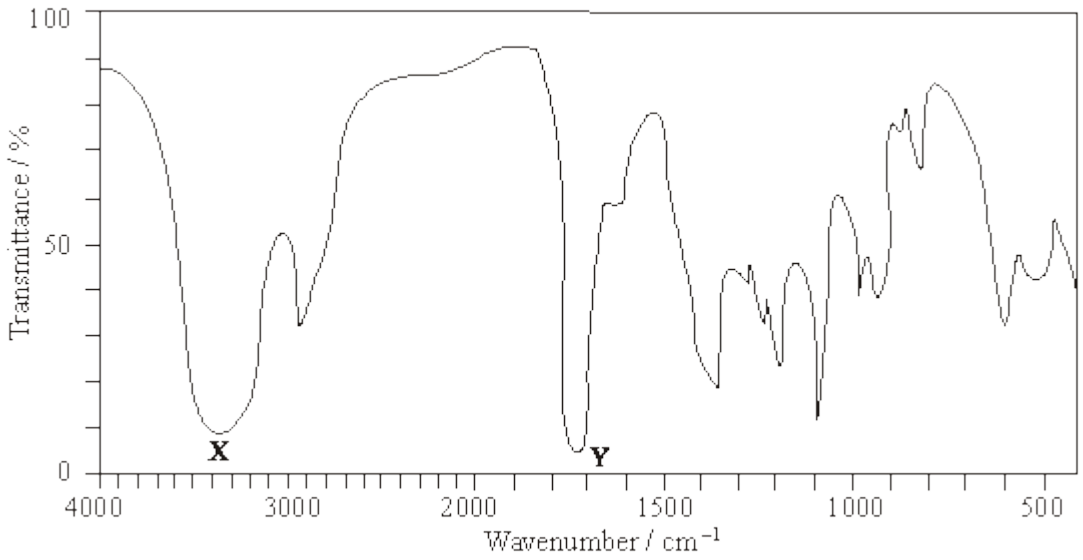
.....

(c) Suggest why the structures drawn above represents several stereoisomers.

.....

(Total 5 marks)

4 (a) The infra-red spectrum of compound **A**, $C_3H_6O_2$, is shown below.



Identify the functional groups which cause the absorptions labelled **X** and **Y**.

Using this information draw the structures of the three possible structural isomers for **A**.

Label as **A** the structure which represents a pair of optical isomers.

(6)

(b) Draw the structures of the three **branched-chain** alkenes with molecular formula C_5H_{10}

Draw the structures of the three dibromoalkanes, $C_5H_{10}Br_2$, formed when these three alkenes react with bromine.

One of these dibromoalkanes has only three peaks in its proton n.m.r. spectrum. Deduce the integration ratio and the splitting patterns of these three peaks.

(10)
(Total 16 marks)

5 Which one of the following pairs of reagents reacts to form an organic product that shows only 2 peaks in its proton n.m.r. spectrum?

A butan-2-ol and acidified potassium dichromate(VI)

B ethanoyl chloride and methanol

C propanoic acid and ethanol in the presence of concentrated sulphuric acid

D ethene and hydrogen in the presence of nickel

(Total 1 mark)

6 This question concerns four isomers, **W**, **X**, **Y** and **Z**, with the molecular formula $C_5H_{10}O_2$

(a) The proton n.m.r. spectrum of **W** shows 4 peaks.
The table below gives the chemical shifts, δ values, for each of these peaks, together with their splitting patterns and integration values.

δ/ppm	2.18	2.59	3.33	3.64
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	3	2

State what can be deduced about the structure of **W** from the presence of the following in its n.m.r. spectrum.

(i) The singlet peak at δ = 2.18

.....

(ii) The singlet peak at δ = 3.33

.....

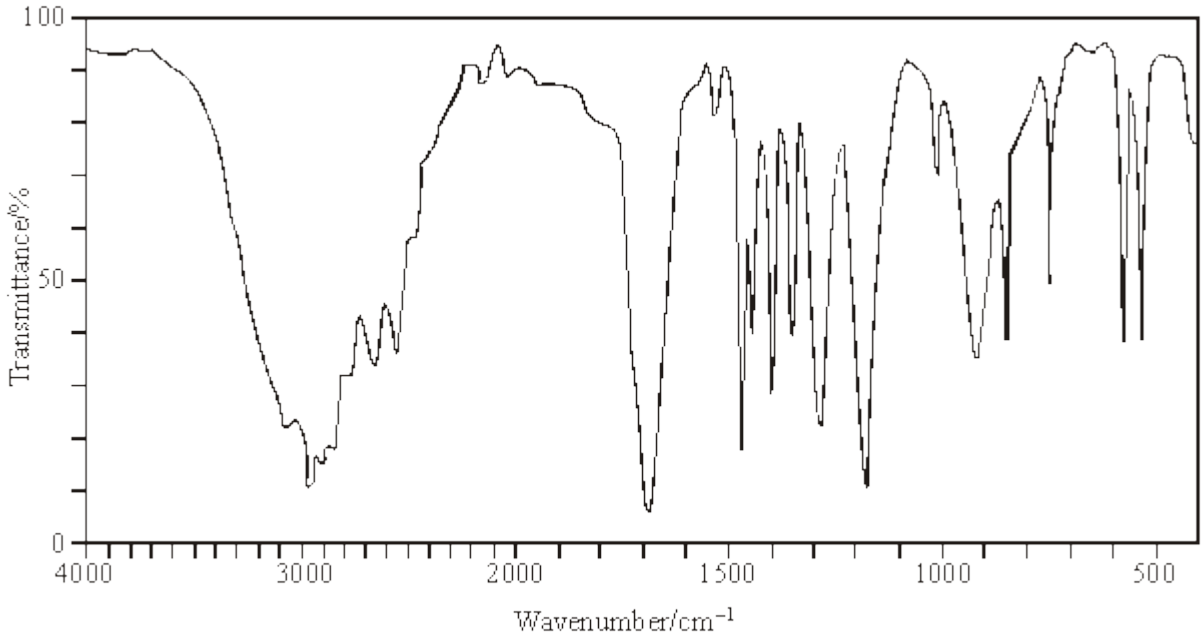
(iii) Two triplet peaks.

.....

(iv) Hence, deduce the structure of **W**.

(4)

(b) The infra-red spectrum of **X** is shown below.



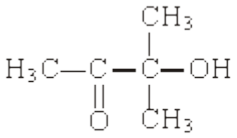
(i) What can be deduced from the broad absorption centred on 3000 cm^{-1} in the infra-red spectrum of **X**?

.....

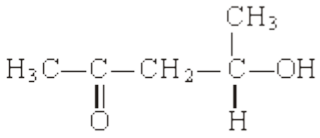
(ii) Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

(2)

(c) Isomers **Y** and **Z** have the structures shown below.



Y



Z

Identify the two reagents you could use in a simple chemical test to distinguish between **Y** and **Z**. State what you would observe when each of **Y** and **Z** is tested with a mixture of these two reagents.

Reagents .....

*Observation with **Y*** .....

*Observation with **Z*** .....

(3)

(Total 9 marks)

7 Which one of the following pairs reacts to form an organic product with only 2 singlets in its proton n.m.r. spectrum?

A ethene and bromine

B propan-2-ol and acidified potassium dichromate(VI)

C ethanol and concentrated sulphuric acid

D epoxyethane and water in the presence of dilute sulphuric acid

(Total 1 mark)

8 Each of the parts (a) to (e) below concerns a different pair of isomers.

Draw one possible structure for each of the species **A** to **J**, using Table 2 on the Data Sheet where appropriate.

(a) Compounds **A** and **B** have the molecular formula C_5H_{10}
A decolourises bromine water but **B** does not.

A **B**

(2)

(b) Compounds **C** and **D** have the molecular formula $C_2H_4O_2$

Each has an absorption in its infra-red spectrum at about 1700 cm^{-1} but only **D** has a broad absorption at 3350 cm^{-1}

C **D**

(2)

(c) Compounds **E** and **F** are esters with the molecular formula $C_5H_{10}O_2$

The proton n.m.r. spectrum of **E** consists of two singlets only whereas that of **F** consists of two quartets and two triplets.

E **F**

(2)

(d) Compounds **G** and **H** have the molecular formula $C_3H_6C_{l2}$ **G** shows optical activity but **H** does not.

G **H**

(2)

(e) Compounds **I** and **J** have the molecular formula C_6H_{12}

Each has an absorption in its infra-red spectrum at about 1650 cm^{-1} and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

I **J**

(2)
(Total 10 marks)