NATIONAL JUNIOR COLLEGE
SH2 Preliminary Examination
Higher 3

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9813/01

Paper 1

Friday 17 September 2021

Candidates answer on the Question Paper
Additional Materials: Data Booklet
Insert

2 hours 30 minutes

READ THE INSTRUCTIONS FIRST

Write your subject class, registration 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.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **two** questions.

The use of an approved scientific calculator is expected, where appropriate.
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	
Section A	
1	/13
2	/18
3	/12
4	/17
Section B (circle the attempted questions)	
5	/20
6	/20
7	/20
Percentage	/100

This document consists of **28** printed pages.

[Turn over

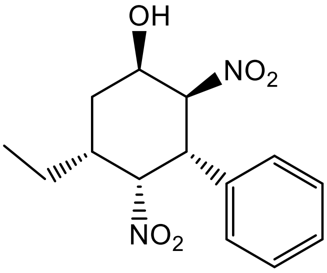
Section A

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

1 **The information provided in the insert is taken from a number of published scientific articles. Other published articles may not agree with all of this information.**

You should read the whole insert before you start to answer any questions and use the information it contains to answer the questions.

(a) Cyclohexanol **4a** is the major stereoisomer formed in the screening experiments.



4a

(i) Draw the structure of the organocatalyst most suitable for the synthesizing cyclohexanol **4a**. [1]

(ii) Based on the mechanism in *figure 1*, write a balanced equation for the reaction to synthesize cyclohexanol **4a**. [1]

(iii) Suggest the condition(s) best for the formation of highly substituted optically active cyclohexanol **4a**. Explain your answer. [1]

(iv) Suggest three advantages of asymmetric domino reactions using organocatalysts in organic synthesis. [3]

(v) Draw the 2 conformers of cyclohexanol **4a**. Suggest which structure is the major conformer. Explain your answer. [2]

(b) The mechanism for the reaction involves 4 steps.

(i) Using suitable diagram, suggest how the stereochemistry at carbon **d** and **e** in cyclohexanol **4** was introduced. [3]

(ii) Draw a suggested mechanism for step 3. [2]

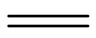
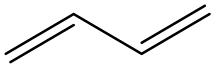
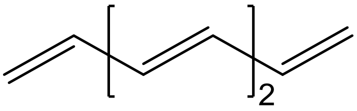
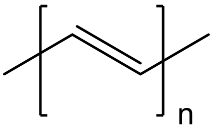
[Total: 13]

2 **(a)** **(i)** Using suitable diagram, calculate the bond order of Li_2^+. [2]

(ii) Suggest whether Li_2^+ exhibits paramagnetism. [1]

(b) Band gap is the energy gap between the valence and conduction band in a conjugated pi system.

The following pi systems have varying band gap as stated.

Pi system		Band Gap (eV)
Ethene		6.7
Buta-1,3-diene		5.8
Octa-1,3,5,7-tetraene		3.1
Polyacetylene		1.5

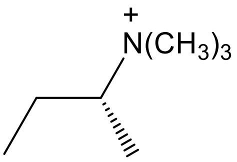
(i) Draw and label the π molecular orbitals for buta-1,3-diene and octa-1,3,5,7-tetraene on the axis given below.

In the same diagram, predict and draw the shape of each molecular orbital. You should indicate the nodes present in each molecular orbital with (|). [4]

(ii) Suggest which molecular orbitals in the polyene contributes to the conduction and valence band respectively. [1]

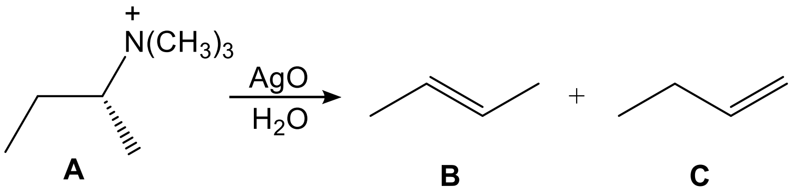
(iii) Polyacetylene is known to be an organic semiconductor. Explain how polyacetylene is able to function as an organic semiconductor. [2]

(c) It is understood that compound, such as compound **A**, bearing charged leaving groups like $–NR_3^+$ and $–SR_2^+$ promotes elimination.



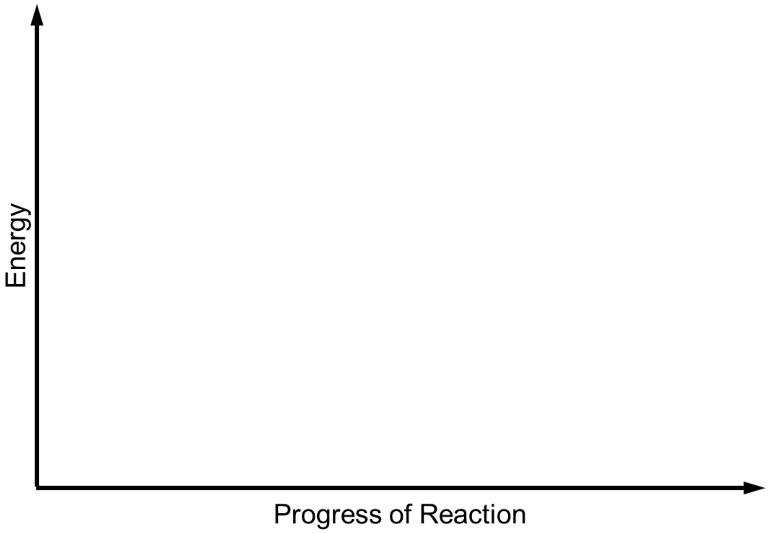
A

(i) Elimination of compound **A** can yield two alkenes **B** and **C**. Two different mechanisms were employed to produce the two alkenes respectively.



Draw the two mechanisms that lead to alkenes **B** and **C** being formed. [3]

(ii) Draw the energy profile diagram for the two mechanisms on the same axis below.

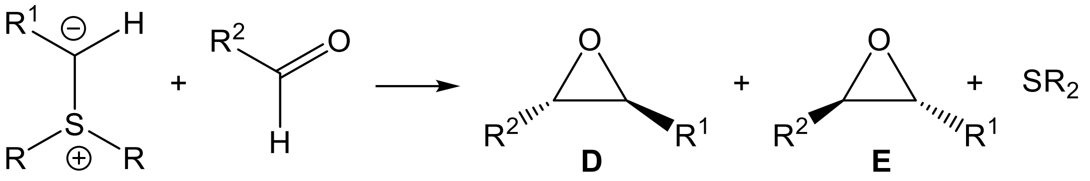


[2]

(iii) Using the information in **(c)**, suggest how buta-1,3-diene can be synthesized from **B**. [3]

[Total: 18]

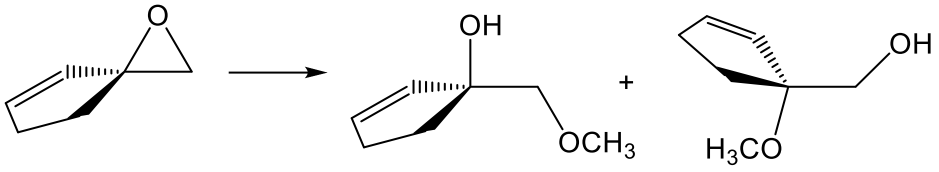
3 **(a)** Ylides are dipolar reagents that can be used to synthesize epoxides. This epoxidation process proceeds in 2 steps. The second step is a substitution via S_N2 mechanism.



(i) Draw the mechanism for the epoxidation. [2]

(ii) Suggest, with suitable diagram, why epoxides **D** and **E** are the only 2 stereoisomers being formed. [2]

(b) Epoxide **F** can be further reacted under different reagent and condition to give compound **G** and **H**.



F **G** **H**

Reaction	Reagents and Conditions	G	H
I	$NaOCH_3$, CH_3OH	86%	5%
II	H_2SO_4, CH_3OH	7%	83%

(i) Using the *R* and *S* convention, assign the absolute configuration of compound **G**. Your answer should include priority assignments as defined by the Cahn-Ingold-Prelog rules. [1]

(ii) Explain the yield of compound **G** and **H** obtained. [2]

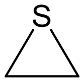
(iii) Suggest a possible side product from this reaction. [1]

(iv) Suggest what changes to the yield of stereoisomers would you expect if the reagent and conditions were changed to the following:

Reaction	Reagents and Conditions
I	$NaOCH_3$, CH_3OH, 80°C
II	H_2SO_4, $(CH3)_3COH$, 10 °C

[2]

(c) Thiiranes are analogue of epoxides.



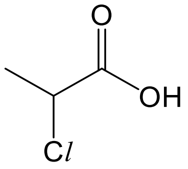
Thiiranes

Given the C–O–C bond in epoxides have a bond angle of 60°, suggest the bond angle of C–S–C in thiiranes. Explain the answer. [2]

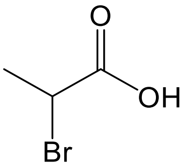
[Total: 12]

4 **(a)** Organic acids are organic compounds which produces an acidic solution when added into water.

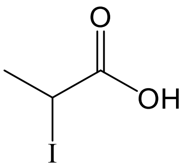
(i) Carboxylic acid functional group is one such example with acidic properties. Rank the pH of 1 mol dm^{-3} solution of the carboxylic acids **I**, **J** and **K** in order of increasing pH. Explain your answer.



I



J



K

[2]

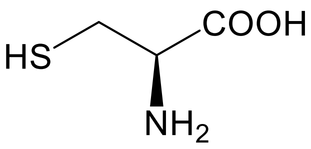
The K_a value of CH_3CH_2SH and CH_3CH_2OH is as follows.

	K_a / mol dm^{-3}
CH_3CH_2SH	2.51×10^{-11}
CH_3CH_2OH	1.26×10^{-16}

(ii) Suggest a reason for the difference in the K_a values of the two compounds. [1]

(iii) With reference to the data booklet, suggest the infra-red absorbance of S–H bond in CH_3CH_2SH. Explain your answer. [1]

Cysteine has the pKa values of 1.92, 8.37 and 10.70.



Cysteine

(iv) Suggest the structure of the dominant species at

- pH 1.52
- pH 2.45
- pH 10.1
- pH 12.2

[2]

(v) Isoelectronic point (pI) is the pH when the molecule is electrically neutral. Based on your structures drawn in part **(vi)**, suggest the pI value for cysteine. [1]

(b) Hydrogen choride, hydrogen bromide and hydrogen iodide are strong acids with different pK_a values.

(i) Rank hydrogen choride, hydrogen bromide and hydrogen iodide in order of increasing pK_a values. Explain your answer. [3]

(ii) Calculate the pH of 0.25 mol dm^{-3} solution of hydrobromic acid. [1]

(c) Currently, air on earth is composed of 412 ppm by volume of carbon dioxide. Carbon dioxide gas is soluble in water.

Equation 4.1 $CO_2(g) \rightleftharpoons CO_2(aq)$ $K_H = 0.800\ \text{mol dm}^{-3}\ \text{atm}^{-1}$

The solubility of carbon dioxide gas in water can be determined by Henry's law give n in equation 4.2.

Equation 4.2 $C_{\text{gas, water}} = K_H P_{\text{gas}}$

Where $C_{\text{gas, water}}$ = solubility of gas in water
K_H = Henry's Law
P_{gas} = partial pressure of gas

Dissolved carbon dioxide then forms carbonic acid which dissociates in water according to the following equations.

Equation 4.3 $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ $K_c = 3.1 \times 10^{-5}$
Equation 4.4 $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $K_{a1} = 4.5 \times 10^{-7}\ \text{mol dm}^{-3}$
Equation 4.5 $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ $K_{a2} = 4.7 \times 10^{-11}\ \text{mol dm}^{-3}$

(i) Using the information given, calculate the pH of 1 dm^3 sample of freshwater in a reservoir at 1 atm. [4]

(ii) Corals produce calcium carbonate to grow their skeletal structures which form the reefs we observe in seas and oceans.

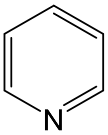
Using the information in **(c)**, suggest the effect global warming due to greenhouse effect has on the coral reefs. [2]

[Total: 17]

Section B

Answer **two** questions from this section.

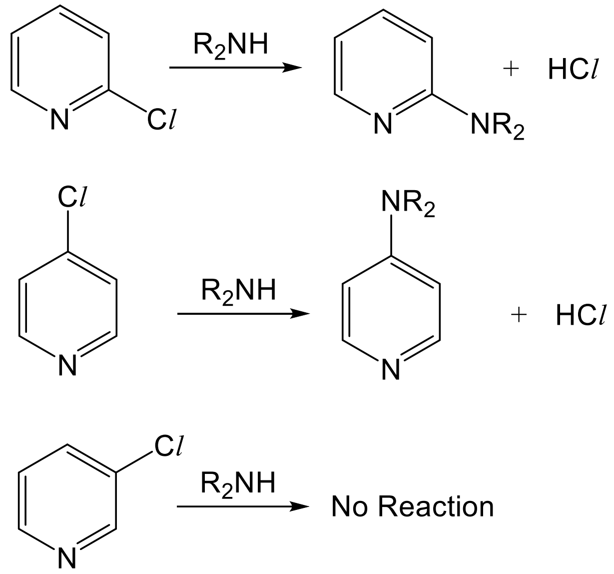
5 **(a)** Pyridine is a common functional group found in many biological molecules. It is aromatic in nature, similar to benzene.



Structure of pyridine

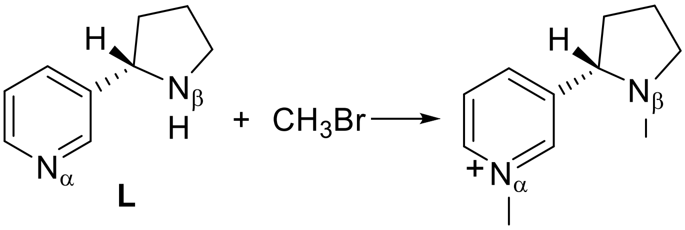
(i) Pyridine has a lower reactivity towards electrophilic substitution as compared to benzene. Suggest a reason for this lowered reactivity. [1]

(ii) 2-chloropyridine and 4-chloropyridine are able to undergo nucleophilic aromatic substitution readily but not 3-chloropyridine. Nucleophilic aromatic substitution consists of a nucleophilic addition followed by elimination process.



With suitable diagram, suggest the reason for this observation. [2]

(iii) Compound **L** contains an amine and pyridine functional group. Pyridine is able to serve as a base and a nucleophile due to the presence of lone pair on nitrogen.



L

With reference to the hybridisation of each nitrogen, suggest the relative rate of methylation on N_α and N_β. Explain your answer. [2]

To promote stability in pH of an organic reaction mixture, a pyridine buffer was considered. (pK_b of pyridine = 8.8).

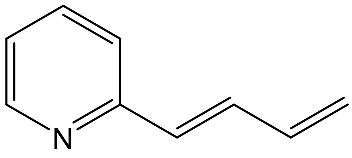
(iv) Describe how you would prepare a 50 cm^3 pyridine buffer at 25 ^oC using a 1 mol dm^{-3} stock solution of pyridine. You are also provided with 1 mol dm^{-3} stock solutions of common laboratory chemicals and glassware. [2]

(v) Reaction **A** to **D** are optimized when reacted under the following pH range.

Reaction	Optimized reaction pH range
A	3.0 – 4.1
B	9.2 – 10.1
C	6.8 – 7.3
D	4.6 – 5.7

Suggest which reaction could a pyridine buffer be used to ensure optimized reaction pH. [1]

Compound **M** is a derivative synthesized from pyridine.

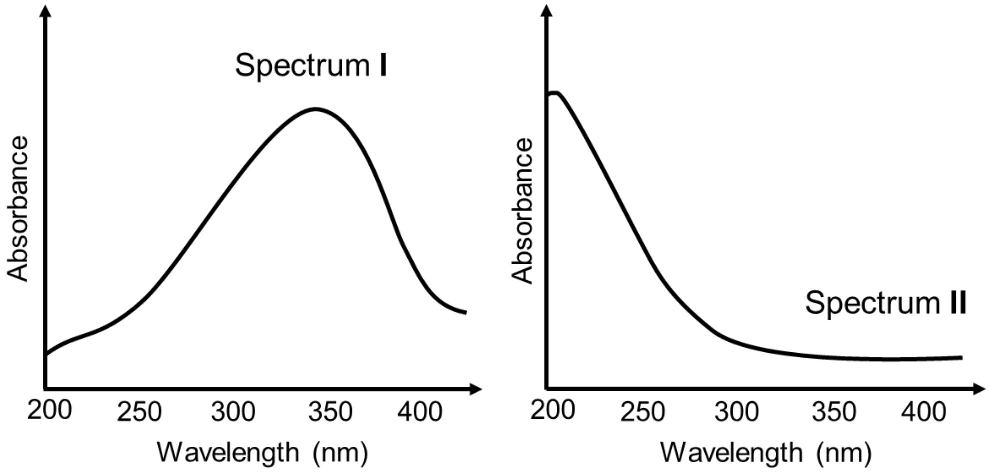


M

Both pyridine and compound **M** can are UV active.

(iv) Explain why pyridine and compound **M** are UV active. [1]

(v) Spectra **I** and **II** are two UV spectra obtained from analysis of separate sample of pyridine and compound **M**

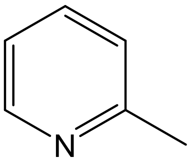


Identify which compound do these spectra belong to. Explain your answer. [2]

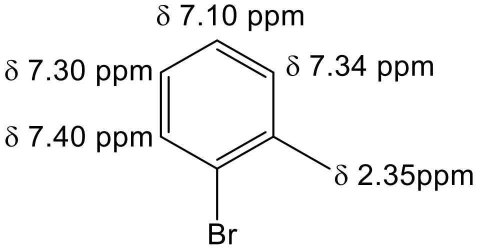
(vi) Using information given in **(v)** and a 0.1 mol dm^{-3} stock solution of pyridine, describe a procedure to determine the concentration of pyridine in a mixture containing both pyridine and compound **M**. [2]

According to a molecular electrostatic potential map study, the 3-position of pyridine has the largest electron density. The electron density of 2- and 4- position of the pyridine ring is affected by the nitrogen.

(vii) Using the ^{1}H NMR data of 1-bromo-2-methylbenzene as a reference, predict the peaks that would be present in the ^{1}H NMR spectrum of compound **N**. You should include the splitting pattern expected from the peaks.



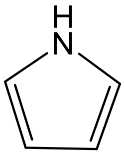
N



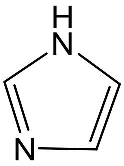
1-bromo-2-methylbenzene

[3]

(b) Pyrroles and imidazoles, like pyridine, is a heterocycle. Pyrroles undergo electrophilic substitution more readily than benzene.



pyrrole



imidazole

(i) Using 'E$^+$' to denote electrophile, draw the mechanism for the electrophilic substitution of pyrrole to explain its increased reactivity as compared to benzene. [2]

(ii) Imidazole is known to be amphoteric in nature. Construct balanced equations to illustrate the amphoteric nature of imidazole. [2]

[Total: 20]

6 **(a)** An organic compound **P** has a molecular formula of $C_xH_yO_z$.

When analysed in a mass spectrometer, compound **P** is found to have molecular ion peaks at m/e value of 102 and 103 at relative abundance of 72% and 4% respectively.

A 1.2 g sample of compound **P** was completely burnt in a vessel containing 2.5 dm^3 of oxygen gas. The resultant gas mixture was passed through a glass U-tube containing anhydrous calcium chloride and 2.08 dm^3 of gas was collected at the end of the process. The mass of calcium chloride increased by 1.06 g. All volumes are measured at room temperature and pressure.

(i) Calculate the number of carbon atoms in compound **P**. [1]

(ii) Determine the molecular formula of compound **P**. [4]

A mixture of (+)-**P** and (–)-**P** has a specific rotation of –40°. Pure (+)-**P** has a specific rotation of +50°. The optical purity of the mixture can be calculated using equation 6.1.

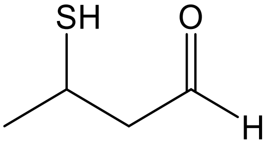
Equation 6.1 $$\text{optical purity} = \frac{\text{specific rotation of mixture}}{\text{specific rotation of pure sample}} \times 100\%$$

(iii) Suggest which is the major stereoisomer in the mixture. [1]

(iii) Calculate the optical purity of the mixture. [1]

(iv) The calculated optical purity is numerically equal to the enantiomeric excess. Explain, using (+)-**P** and (–)-**P** as example, why are optical purity and enantiomeric excess values numerically equal. [2]

(b) Compound **Q** has the following structure. The thiol functional group (–SH) in **Q** is weakly acidic in nature but is more acidic than hydroxy group (–OH) in alcohols.



Q

(i) Draw the structure of four major fragments that would be observed on the mass spectrum of compound **Q**. [2]

(ii) Predict the total number of peaks in the ^1H NMR spectrum of compound **Q** in $CDCl_3$ solvent.

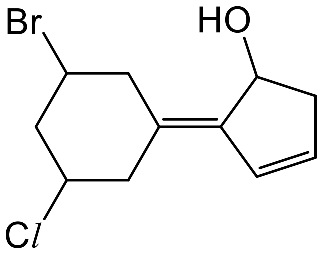
For each peak in the spectrum, you should
- Indicate on a structure of compound **Q** which protons are responsible for the peak,
- Suggest its proton chemical shift value, δ
- Suggest the splitting pattern. [6]

(iii) Explain, with the aid of an equation, what would be observed on the 1H NMR spectrum when the analysis is done using D_2O instead of $CDCl_3$. [1]

(iv) Predict whether thiolates ($R–S^–$) is a stronger nucleophile than alkoxides ($R–O^–$). Explain your answers. [2]

[Total: 20]

7 **(a)** Compound **R** has the following structure.



(i) Using the *E* and *Z* convention, assign the absolute configuration of compound **R**. Your answer should include priority assignments as defined by the Cahn-Ingold-Prelog rules. [1]

(ii) Two samples of compound **R** are prepared by dissolving **R** in small amount and excess dichloromethane solvent respectively. Suggest the difference in the IR absorption of the two samples. Explain your answer. [2]

(b) Diels-Alder reaction forms a cyclic alkene by combining a diene and an alkene as shown below.

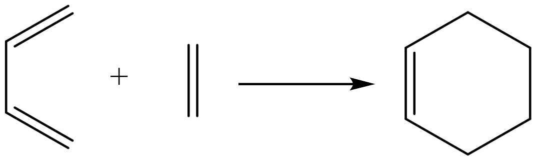
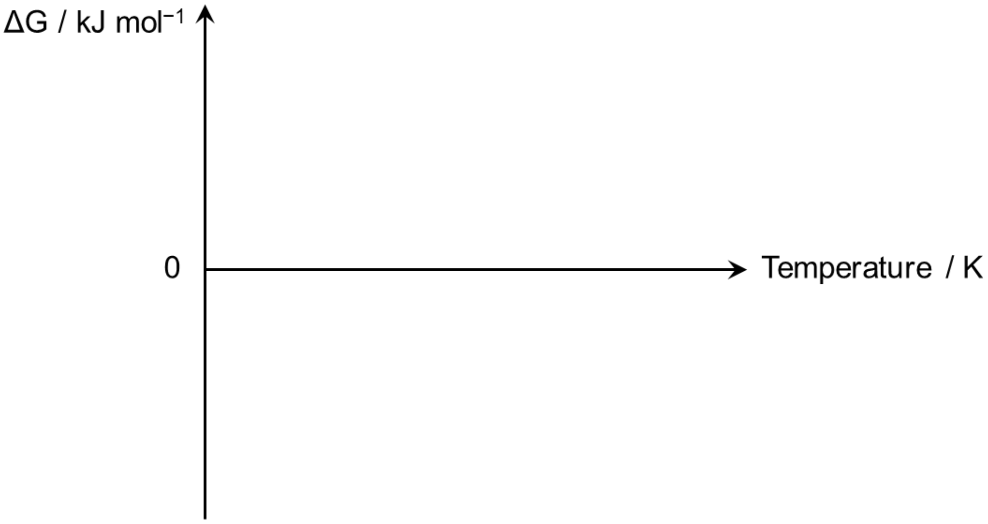


Figure 7.1

(i) Using relevant data from the *Data Booklet*, calculate the enthalpy change of reaction for the diels-alder reaction shown in figure 7.1. [1]

(ii) Using the following axis, draw the trend you would expect for reaction shown in figure 7.1 and explain if Diels-Alder reaction should be conducted at lower or higher temperature. [3]



(c) **(i)** Predict the number of IR absorption for nitrogen dioxide and identify the vibrational modes that gave rise to them. [2]

(ii) Methylamine, CH_3NH_2, and ethanamide, $CH_3C(O)NH_2$, both contain a C–N bond. The C–N bond in methylamine shows an IR absorption at 1100 cm^{-1}.

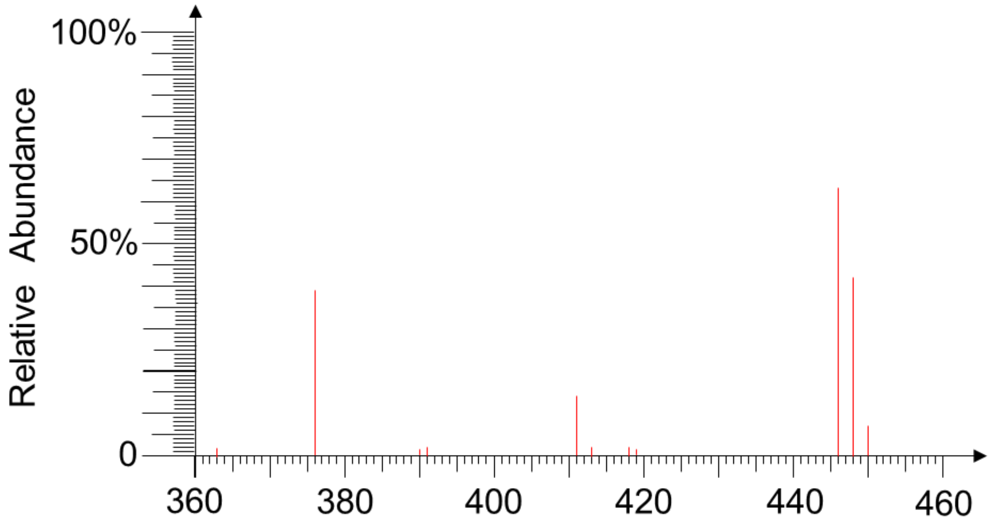
Suggest the IR absorption for C–N bond in ethanamide. Explain your answer. [2]

(d) Compound **S** has elemental composition of 69.8% carbon, 7.2% hydrogen, 7.2% oxygen and 15.9% chlorine.

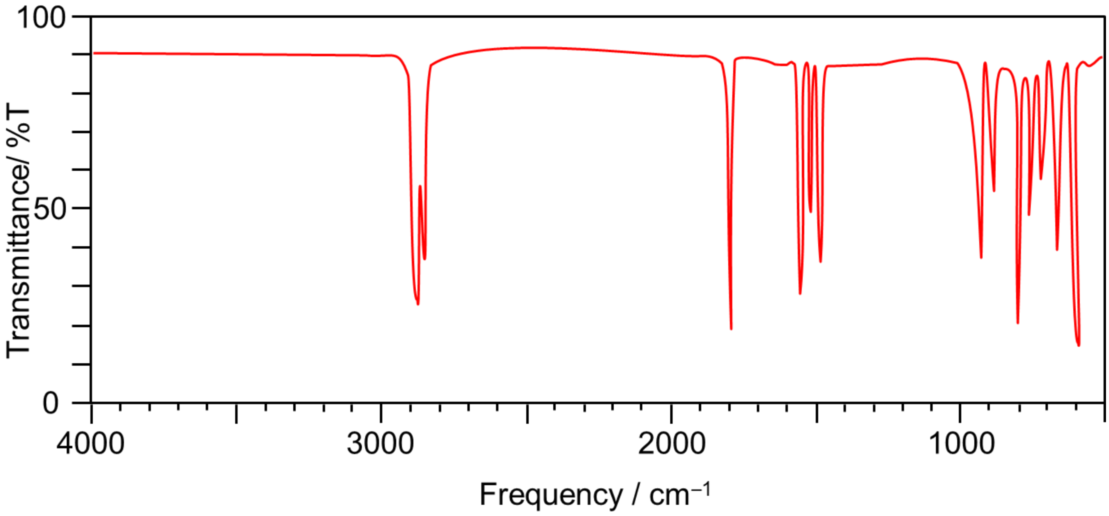
(i) Determine the empirical formula of compound **S**. [1]

A pure sample of compound **S** has the following spectroscopic data.

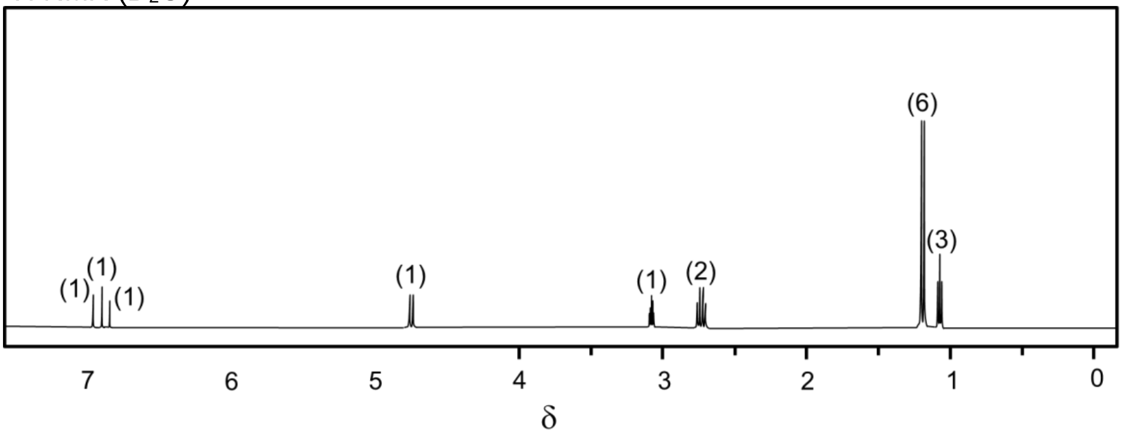
Mass Spectrum



IR Spectrum

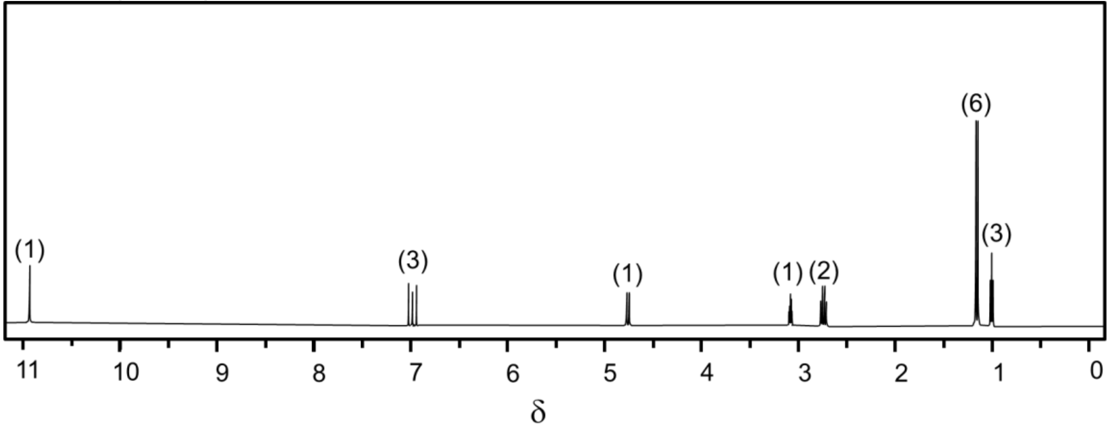


^{1}H NMR (D_2O)



Upon completion of reaction, a reaction mixture containing compound **S** as the only organic product was washed with excess water and extracted with ethyl acetate solvent. The organic ethyl acetate layer was then dry under vacuum and purified under flash chromatography. The purified compound has the following ^{1}H NMR spectrum.

^{1}H NMR ($CDCl_3$)



(ii) Deduce the structure of compound **S**. [8]

[Total: 20]

End of Paper