NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/02
Paper 2 Structured Questions
28 August 2023
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

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 on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use paper clips, highlighters, glue or correction fluid.

Answers **all** questions.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/9
2	/10
3	/12
4	/13
5	/13
6	/18
Paper 2 Total	/75

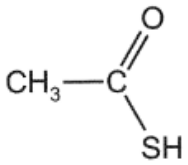
	Marks	Weightings
Paper 1	/30	**15%**
Paper 2	/75	**30%**
Paper 3	/80	**35%**
Paper 4	/55	**20%**

Overall Percentage	
Grade	

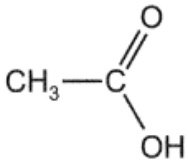
This document consists of **22** printed pages.

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

1 **(a)** Thioacetic acid, CH_3COSH, and ethanoic acid, CH_3COOH, both act as weak acids in solution.



thioacetic acid



ethanoic acid

(i) An equilibrium is set up when CH_3COSH is added to water.

Write the equation for this equilibrium.

……..

[1]

(ii) 0.150 mol of CH_3COSH dissolves in 250 cm^3 of distilled water to produce a solution of pH 1.79.

Calculate the pK_a of CH_3COSH.

[2]

(iii) CH_3COOH has a pK_a value of 4.76. With reference to the *Data Booklet*, explain the difference in the pK_a values of CH_3COOH and CH_3COSH.

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[2]

(b) **(i)** State the type of reaction involved when $CH_2ClCOOH$ and $CH_2BrCOOH$ are synthesized from CH_3COOH.

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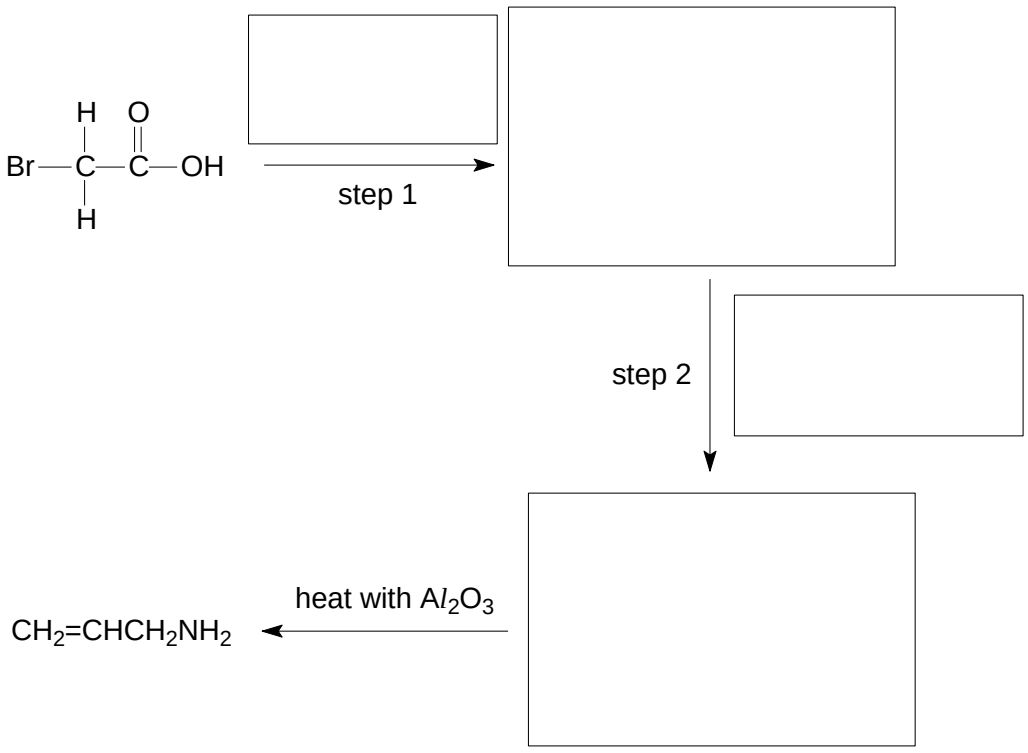
[1]

(ii) Prop-2-en-1-amine, $CH_2=CHCH_2NH_2$, commonly used as a pharmaceutical intermediate, can be synthesized from $CH_2BrCOOH$.

Complete the following synthetic route for the conversion of $CH_2BrCOOH$ into $CH_2=CHCH_2NH_2$. Suggest the structure of the intermediate compounds, and reagents and conditions for step 1 and 2.



[3]

[Total: 9]

2 **(a)** A student studies the reaction of $CH_3CHClCOOH$ with aqueous NH_3 to determine the reaction mechanism. The student finds that when $CH_3CHClCOOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.

reaction I $\quad CH_3CHClCOOH + NH_3 \longrightarrow CH_3CHClCOO^- + NH_4^+$

Identify the conjugate acid-base pairs in reaction I.

conjugate acid-base pair 1: ……

conjugate acid-base pair 2: ……

[1]

(b) In an excess of NH_3, $CH_3CHClCOO^-$ undergoes a nucleophilic substitution reaction.

reaction II $\quad CH_3CHClCOO^- + NH_3 \longrightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

(i) Describe the effect of an increase in temperature on the rate of reaction of $CH_3CHClCOO^-$ and NH_3, illustrating your answer using the Boltzmann distribution curve.

[3]

A student mixes $CH_3CHClCOO^-$ with a large excess of NH_3 and monitored the $[CH_3CHClCOO^-]$ with time. The graph in Fig. 2.1 shows the results obtained.

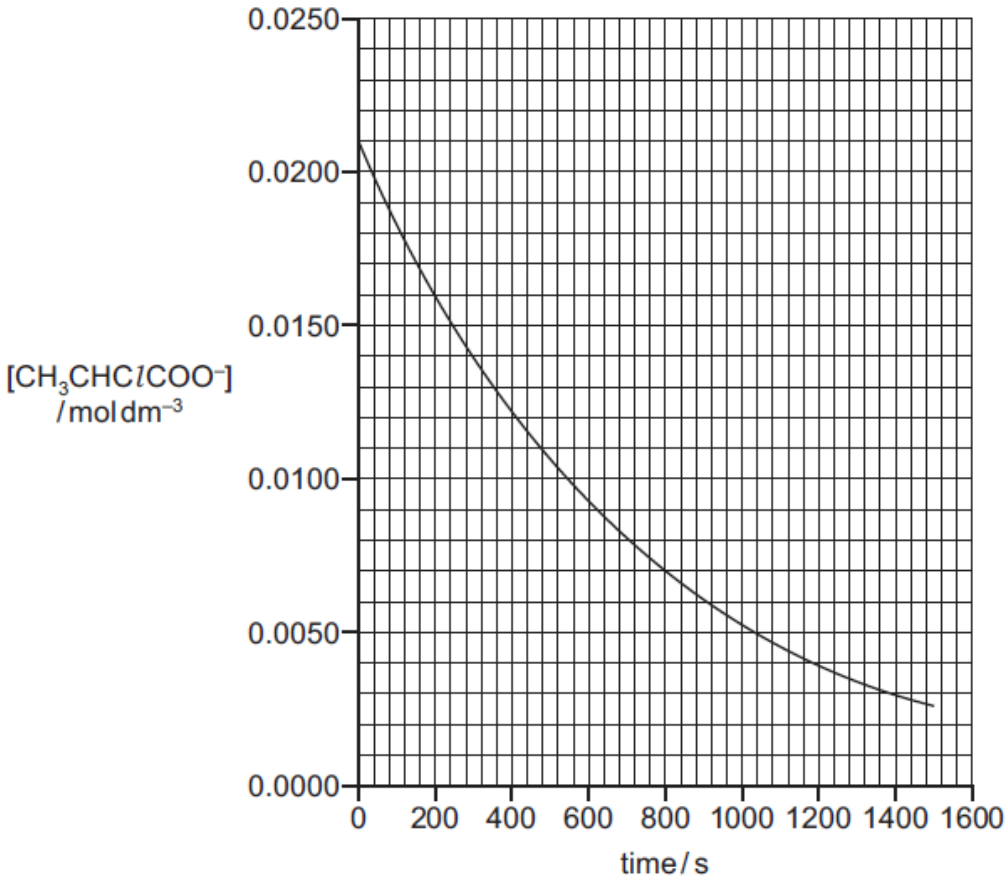


Fig. 2.1

(ii) Use the graph in Fig. 2.1, deduce the order of reaction with respect to $CH_3CHClCOO^-$ in reaction II.

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[2]

(iii) Explain why a large excess of NH_3 needs to be used to obtain the results in Fig. 2.1.

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[1]

(iv) The student measured the effect of changing concentration of NH_3 on the rate of reaction II. Table 2.1 shows the results obtained.

Table 2.1

experiment	$[CH_3CHClCOO^-]$ / mol dm^{-3}	$[NH_3]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.00120	0.00300	1.47×10^{-5}
2	0.00120	0.00450	2.21×10^{-5}

Use the information in Table 2.1 and your answer in **b(ii)** to determine whether the nucleophilic substitution reaction proceeds via S_N1 or S_N2 mechanism.

Explain your answer.

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[2]

(v) When an excess of $CH_3CHClCOO^-$ is used in reaction II, further substitution reactions occur. One product has the formula $C_6H_9NO_4^{2-}$, suggest its structure.

[1]

[Total: 10]

3 This question is related to the properties of Group 17 elements and their compounds.

(a) Table 3.1 shows the reactions between concentrated sulfuric acid and sodium halides.

Table 3.1

halide	reaction
NaC*l*	$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$
NaBr	$2NaBr + 2H_2SO_4 \longrightarrow Br_2 + SO_2 + Na_2SO_4 + 2H_2O$
NaI	$8NaI + 5H_2SO_4 \longrightarrow 4I_2 + H_2S + 4Na_2SO_4 + 4H_2O$

(i) Suggest the role of concentrated sulfuric acid in its reaction with NaC*l*.

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[1]

(ii) By considering the changes in oxidation states of S, deduce whether NaBr or NaI is a stronger reducing agent.

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[2]

(iii) ΔH_1, is defined as the energy required to remove one mole of electrons from one mole of gaseous halide ions to form one mole of gaseous halogen atom.

$$X^-(g) \longrightarrow X(g) + e^- \qquad \Delta H_1$$

With reference to the ionic radii in the *Data Booklet*, suggest a reason for the trend of ΔH_1 shown in Table 3.2.

Table 3.2

halide ion	ΔH_1 / kJ mol^{-1}
Cl^-(g)	+349
Br$^-$(g)	+324
I$^-$(g)	+295

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[2]

(iv) Given the following data, construct an energy level diagram and calculate ΔH_2

$$NaF(s) \longrightarrow Na^+(g) + \tfrac{1}{2}F_2(g) + e^- \qquad \Delta H_2$$

1st electron affinity of fluorine	= −328 kJ mol^{-1}
enthalpy change of atomisation of fluorine	= +79 kJ mol^{-1}
lattice energy of sodium fluoride	= −902 kJ mol^{-1}

[3]

(b) Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

(i) Suggest one reason why CFCs were originally used for these purposes.

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[1]

(ii) Briefly explain how CFCs destroy the ozone layer.

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[1]

(iii) The percentage of O_3 in a gaseous mixture can be determined by its reaction with aqueous KI.

$$O_3 + KI + H_2O \longrightarrow I_2 + O_2 + 2KOH$$

The iodine formed can be determined by its reaction with sodium thiosulfate.

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

When 250 cm^3 of a gaseous mixture containing O_3 at s.t.p. was passed into an excess of aqueous KI, 15.0 cm^3 of 0.050 mol dm^{-3} sodium thiosulfate was required to react with the iodine produced.

Calculate the percentage of O_3 in the gaseous mixture.

[2]

[Total: 12]

PLEASE TURN OVER

4 **(a)** Compound **G** has the molecular formula $C_7H_{14}O$. Treating **G** with hot acidified $KMnO_4(aq)$ produces two compounds **H**, C_4H_8O, and **J**, $C_3H_4O_3$. These three compounds were tested using the reagents shown in the Table 4.1 below.

Table 4.1

test reagent	result of test with		
	compound **G**	compound **H**	compound **J**
$Br_2(aq)$	Br_2 decolourises	no reaction	no reaction
Na(s)	effervescence observed	no reaction	effervescence observed
alkaline aqueous iodine, warm	no reaction	yellow precipitate	yellow precipitate
2,4-dinitrophenylhydrazine	no reaction	orange precipitate	orange precipitate

(i) Name the type of reaction occurring when compounds **H** and **J** react with 2,4-dinitrophenylhydrazine.

……..

[1]

(ii) Based on the results of the tests in the table, suggest the structure for compounds **H** and **J**.

compound **H**	compound **J**

[2]

(iii) Compound **G** exists as two stereoisomers, **G1** and **G2**.

Draw the structure of the two isomers and state the type of stereoisomerism involved. Hence, explain how this type of stereoisomerism arises.

isomer **G1**	isomer **G2**

Type of stereoisomerism: ……..

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[4]

(iv) Compound **G** reacts with $H_2(g)$ in the presence of Ni catalyst but not with Li$Al$$H_4$. Explain why.

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[1]

(b) Compound **K**, an alcohol, has a relative molecular mass of 60.0. The mass ratio of carbon to hydrogen to oxygen is 9 : 2 : 4.

(i) Deduce the molecular formula of compound **K**.

[2]

(ii) A 20 cm^3 mixture containing CH_4 and compound **K**, was burnt completely in excess oxygen. On passing the residual gas through aqueous sodium hydroxide, there was a reduction in volume by 25 cm^3. All volumes were measured at room temperature and pressure.

Calculate the percentage by mass of CH_4 in the mixture.

[3]

[Total: 13]

5 **(a)** Pyridine, C_5H_5N, and benzene, C_6H_6, have similar structures.

pyridine

(i) Identify the hybridization of orbitals in C and N atoms in pyridine and use a labelled diagram to show how the orbitals overlap to form the bonds between C and N in pyridine.

[3]

(ii) Pyridine reacts with Cl_2 in the presence of $AlCl_3$ as shown in Fig. 5.1.

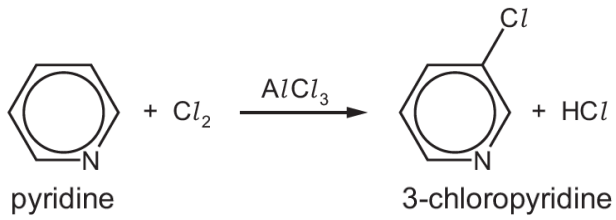

Fig. 5.1

The mechanism of this reaction is similar to that of the chlorination of benzene.

Describe the mechanism for the reaction shown in Fig. 5.1. Include all relevant charges, dipoles, lone pairs of electrons and curly arrows as appropriate.

[3]

(iii) Suggest how the basicity of 3-chloropyridine might compare to that of pyridine. Give a reason for your answer.

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[2]

(b) **(i)** Addition of hydrogen iodide gas to but-1-ene gives a racemic mixture.

Draw the 2 enantiomers and explain how a racemic mixture is obtained in this reaction.

[2]

(ii) Reaction of but-1-ene with bromine in the presence of aqueous sodium chloride gives a mixture of products.

Draw the structure of three possible products and name the compounds.

[3]

[Total: 13]

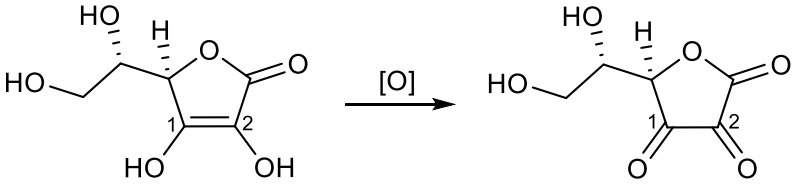
6 Haemoglobin reacts with oxygen to form oxyhaemoglobin as follows.

$$Hb + O_2 \rightleftharpoons HbO_2$$

In order for haemoglobin to absorb oxygen, iron must be present. Iron makes up 4% by mass of the haemoglobin molecule. A healthy person should have 30 mg of haemoglobin per million red blood cells.

Approximately 10,000 million new blood cells are formed in the bone marrow daily. Components of the red blood cells are recycled by the liver at the end of their life cycle.

Iron is taken into the body in the diet as Fe^{3+}. In the presence of vitamin C, Fe^{3+} is converted to Fe^{2+} and incorporated into the haemoglobin structure. Vitamin C itself is oxidized in the process as follows.



Vitamin C

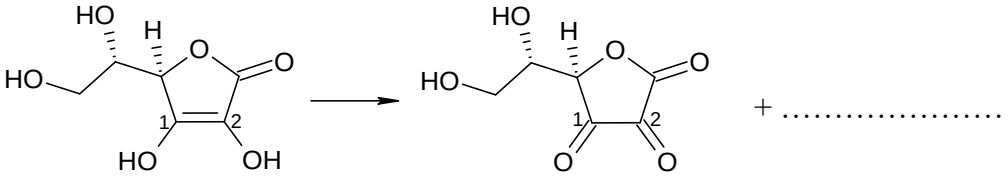
(a) **(i)** State the oxidation state of C_1 of vitamin C before and after oxidation.

Oxidation state of C_1 in vitamin C : …….

Oxidation state of C_1 after oxidation : ……..…

[1]

(ii) Hence or otherwise, complete the half equation for the oxidation of vitamin C below.



[1]

(b) **(i)** Calculate the mass of iron that needs to be available each day within the bone marrow for the production of new red blood cells.

[2]

(ii) According to Health Science Authority, the recommended daily dietary intake of iron is lower than the value calculated in **(b)(i)**. Suggest a reason for this.

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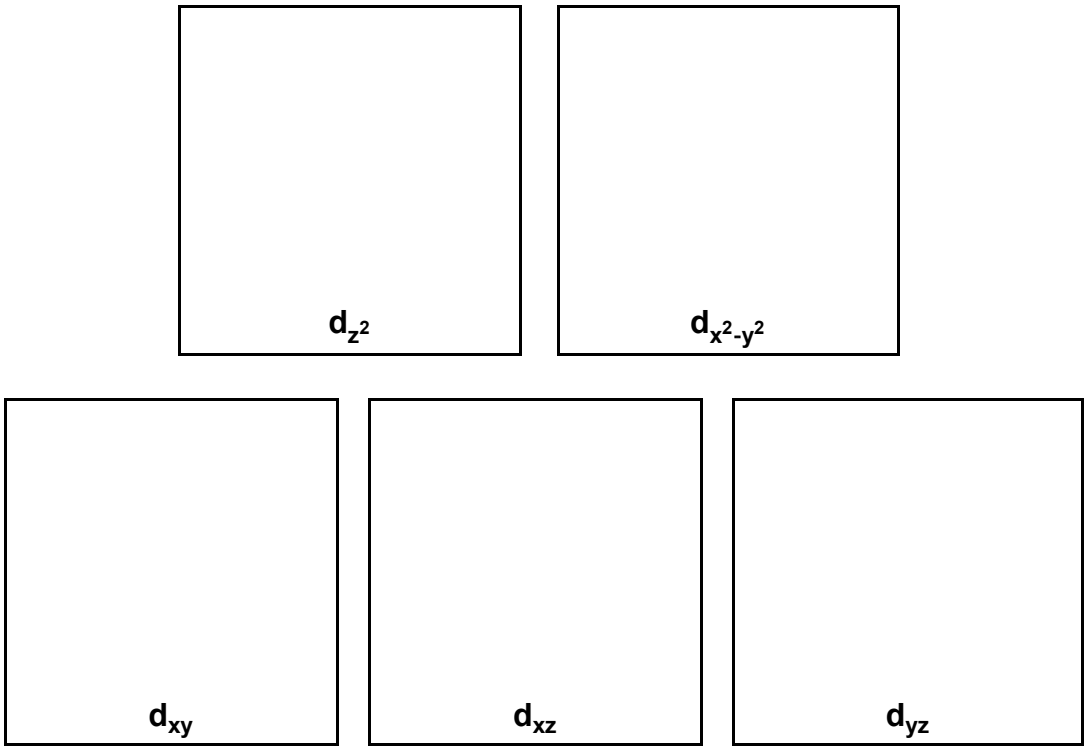
……..

[1]

(c) **(i)** In the space provided below, draw the shapes of all the 3d orbitals. Label the axes clearly.



[3]

(ii) Account for the red colouration of blood.

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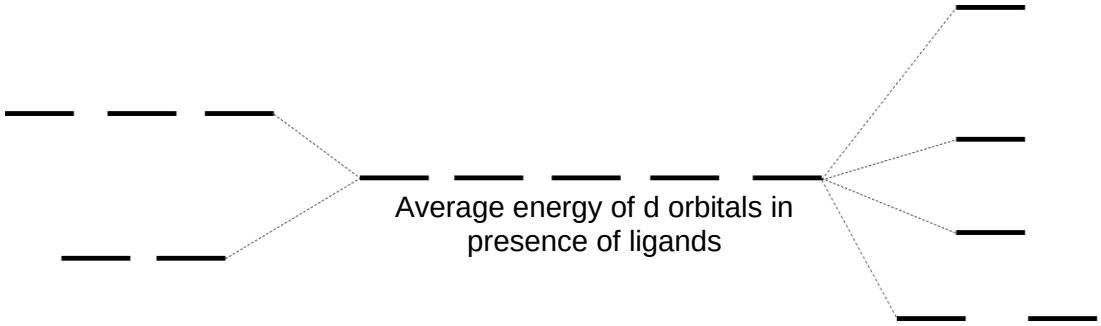
[3]

(d) Complexes of Ni^{2+} are commonly found to have coordination number of 4, and exist either as tetrahedral or square planar complexes.

Fig. 6.1 shows the splitting of the energy levels of d orbitals for tetrahedral and square planar complexes.



tetrahedral complex square planar complex

Fig. 6.1

(i) Complete the electronic configuration for Ni^{2+}.

$1s^2\ 2s^2\ 2p^6$ ……..

[1]

(ii) The Aufbau principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.

On the energy levels provided in Fig. 6.1, show the electronic arrangement of the 3d electrons of Ni^{2+} in the tetrahedral and square planar complex.

[2]

(iii) Complex ions with only paired electrons are considered to be diamagnetic while those with at least one unpaired electron are considered to be paramagnetic.

A Ni^{2+} complex $[NiX_4]^{2-}$ is found to be diamagnetic, with reference to your answer in **(d)(ii)**, state the shape of this complex ion.

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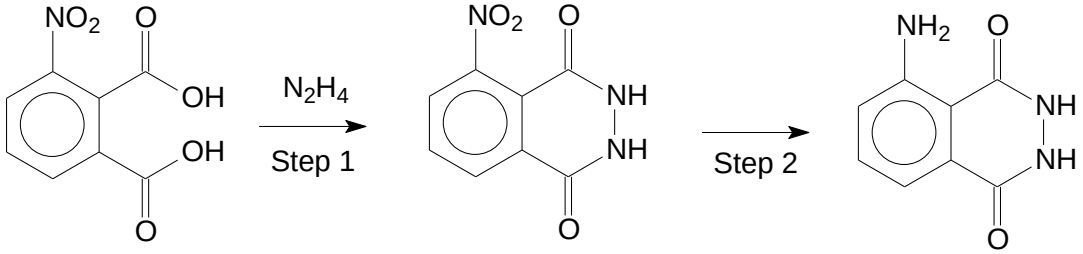
[1]

(e) Forensic investigators use luminol to detect traces of blood at crime scenes, as it reacts with the iron in haemoglobin. Luminol can be synthesized using the following route.



Compound **X** luminol

(i) State the type of reaction for Step 1 and Step 2.

Step 1: ……

Step 2: ……

[2]

(ii) A research student used the following reagent for Step 2.

Sn, conc HCl, heat, followed by excess NaOH(aq)

Suggest a reason why his method will not give luminol as the product.

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[1]

[Total : 18]