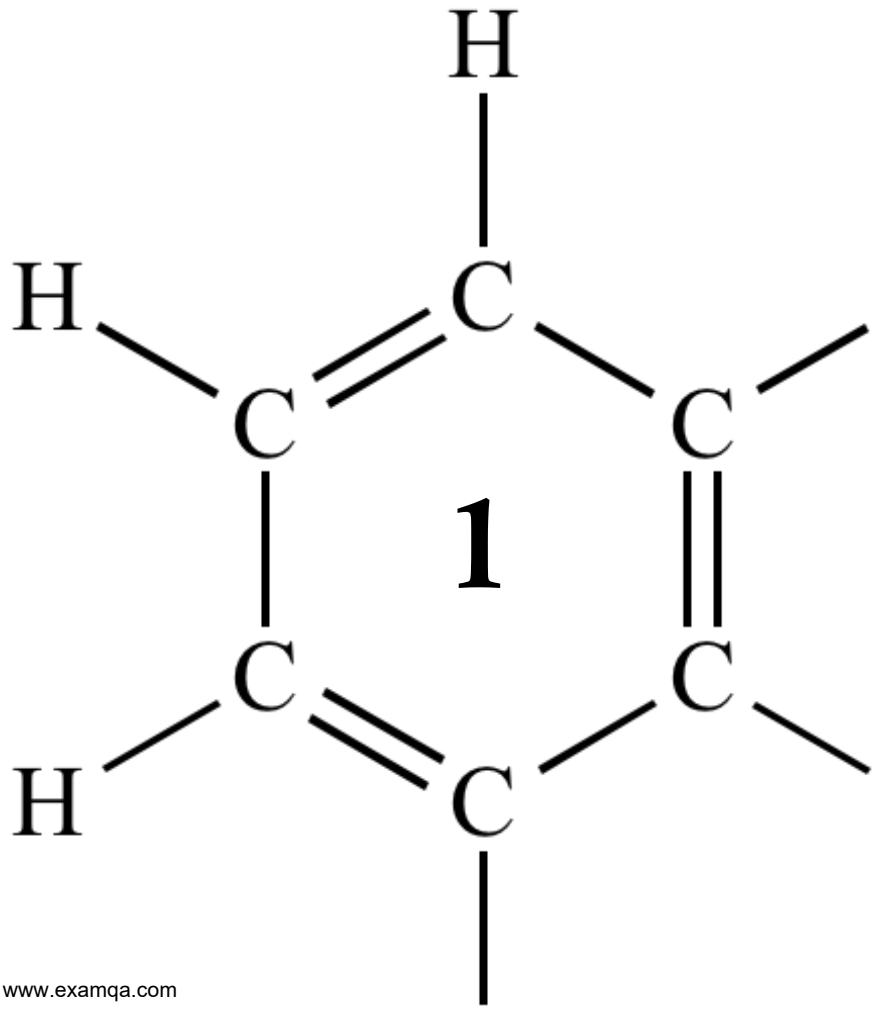
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

AROMATIC ~ AMINES

AMINES



1 The amide or peptide link is found in synthetic polyamides and also in naturally occurring proteins.

(a) (i) Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2)

(ii) In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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(3)

(b) (i) Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2

Name of mechanism.....

Mechanism

(5)

(ii) Give the name of the product containing an amide linkage that is formed in the reaction in part (b) (i).

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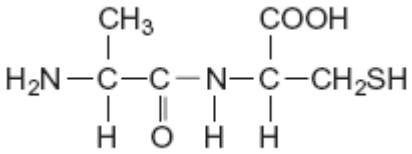
(1)

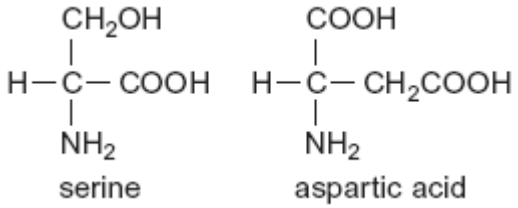
(c) The dipeptide shown below is formed from two different amino acids.



Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1)

(d) The amino acids serine and aspartic acid are shown below.



(i) Give the IUPAC name of serine.

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(1)

(ii) Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1)

(iii) Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

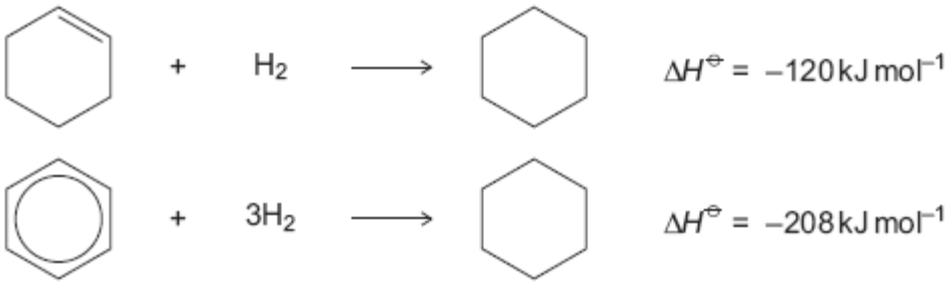
(1)

(iv) Draw the structure of the species formed when serine reacts with an excess of bromomethane.

(1)
(Total 16 marks)

2 The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

(a) The molecule cyclohexatriene does not exist and is described as hypothetical.
Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



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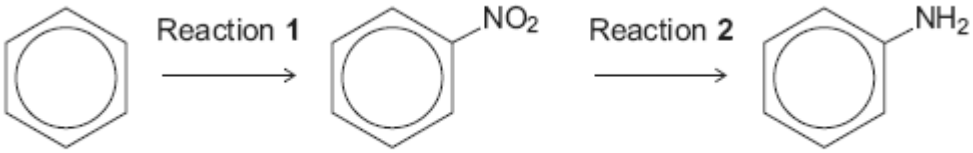
(4)

(b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



U

The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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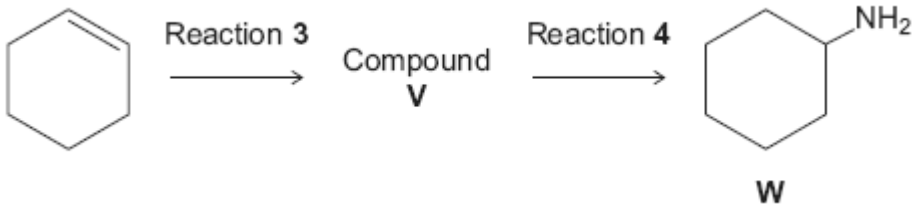
(6)

(c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(Extra space) .....

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(6)

(d) Explain why amine **U** is a weaker base than amine **W**.

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(Extra space) .....

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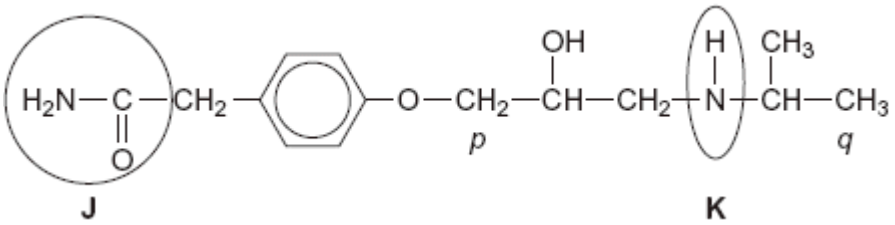
(3)
(Total 19 marks)

3 Atenolol is an example of the type of medicine called a beta blocker. These medicines are used to lower blood pressure by slowing the heart rate. The structure of atenolol is shown below.



(a) Give the name of each of the circled functional groups labelled **J** and **K** on the structure of atenolol shown above.

Functional group labelled **J** .....

Functional group labelled **K** .....

(2)

(b) The ^{1}H n.m.r. spectrum of atenolol was recorded.

One of the peaks in the ^{1}H n.m.r. spectrum is produced by the CH_2 group labelled *p* in the structure of atenolol.
Use **Table 2** on the Data Sheet to suggest a range of δ values for this peak.
Name the splitting pattern of this peak.

Range of δ values .....

Name of splitting pattern ……

(2)

(c) N.m.r. spectra are recorded using samples in solution.

The ^{1}H n.m.r. spectrum was recorded using a solution of atenolol in $CDCl_3$

(i) Suggest why $CDCl_3$ and **not** $CHCl_3$ was used as the solvent.

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(1)

(ii) Suggest why $CDCl_3$ is a more effective solvent than CCl_4 for polar molecules such as atenolol.

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(1)

(d) The ^{13}C n.m.r. spectrum of atenolol was also recorded.

Use the structure of atenolol given to deduce the total number of peaks in the ^{13}C n.m.r. spectrum of atenolol.

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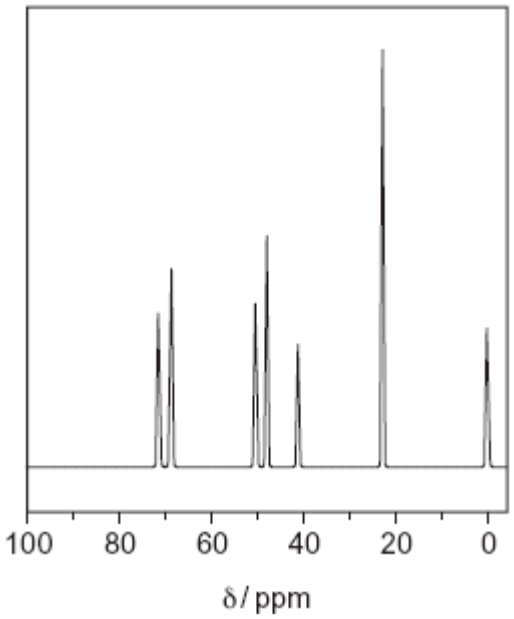
(1)

(e) Part of the ^{13}C n.m.r. spectrum of atenolol is shown below. Use this spectrum and **Table 3** on the Data Sheet, where appropriate, to answer the questions which follow.



(i) Give the formula of the compound that is used as a standard and produces the peak at δ = 0 ppm in the spectrum.

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(1)

(ii) One of the peaks in the ^{13}C n.m.r. spectrum above is produced by the CH_3 group labelled *q* in the structure of atenolol.
Identify this peak in the spectrum by stating its δ value.

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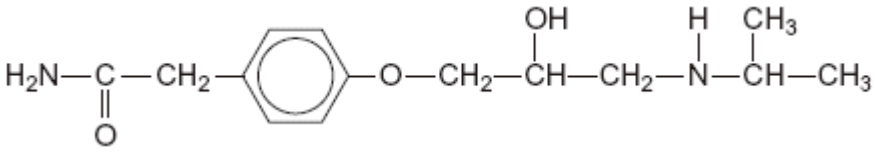
(1)

(iii) There are three CH_2 groups in the structure of atenolol. One of these CH_2 groups produces the peak at δ = 71 in the ^{13}C n.m.r. spectrum above.
Draw a circle around this CH_2 group in the structure of atenolol shown below.



(1)

(f) Atenolol is produced industrially as a racemate (an equimolar mixture of two enantiomers) by reduction of a ketone. Both enantiomers are able to lower blood pressure. However, recent research has shown that one enantiomer is preferred in medicines.

(i) Suggest a reducing agent that could reduce a ketone to form atenolol.

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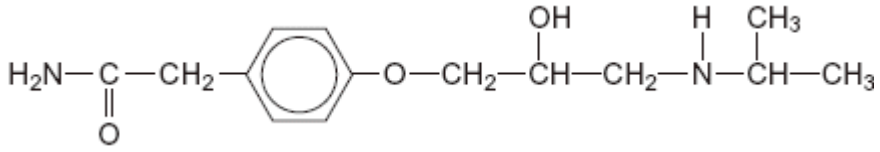
(1)

(ii) Draw a circle around the asymmetric carbon atom in the structure of atenolol shown below.



(1)

(iii) Suggest how you could show that the atenolol produced by reduction of a ketone was a racemate and **not** a single enantiomer.

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(2)

(iv) Suggest **one** advantage and **one** disadvantage of using a racemate rather than a single enantiomer in medicines.

Advantage .....

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Disadvantage .....

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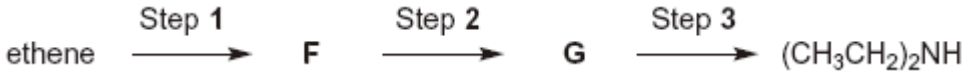
(2)
(Total 16 marks)

4 The compound $(CH_3CH_2)_2NH$ can be made from ethene in a three-step synthesis as shown below.



(a) Name the compound $(CH_3CH_2)_2NH$

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(1)

(b) Identify compounds **F** and **G**.

Compound **F** .....

Compound **G** .....

(2)

(c) For the reactions in Steps **1**, **2** and **3**,

- give a reagent or reagents
- name the mechanism.

Balanced equations and mechanisms using curly arrows are **not** required.

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(6)

(d) Identify **one** organic impurity in the product of Step **3** and give a reason for its formation.

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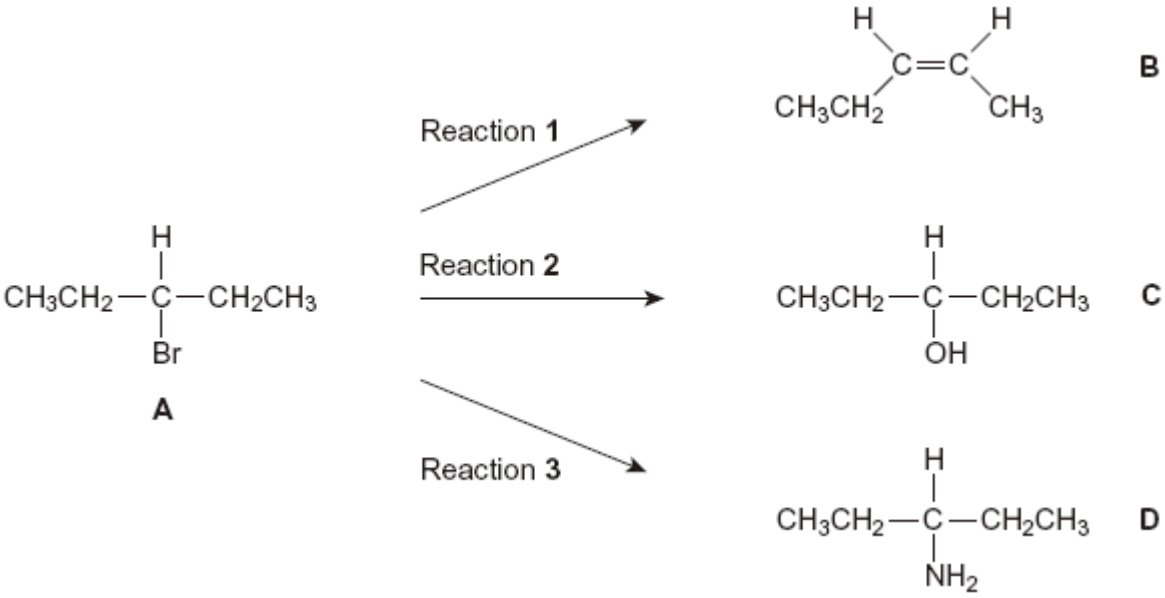
(2)
(Total 11 marks)

5 Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



(a) (i) Draw a **branched-chain** isomer of **A** that exists as optical isomers.

(1)

(ii) Name the type of mechanism in Reaction **1**.

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(1)

(iii) Give the full IUPAC name of compound **B**.

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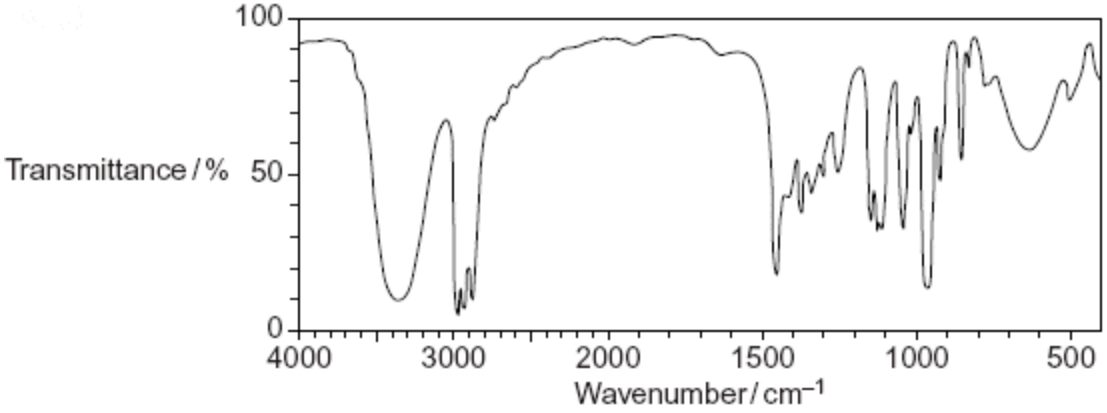
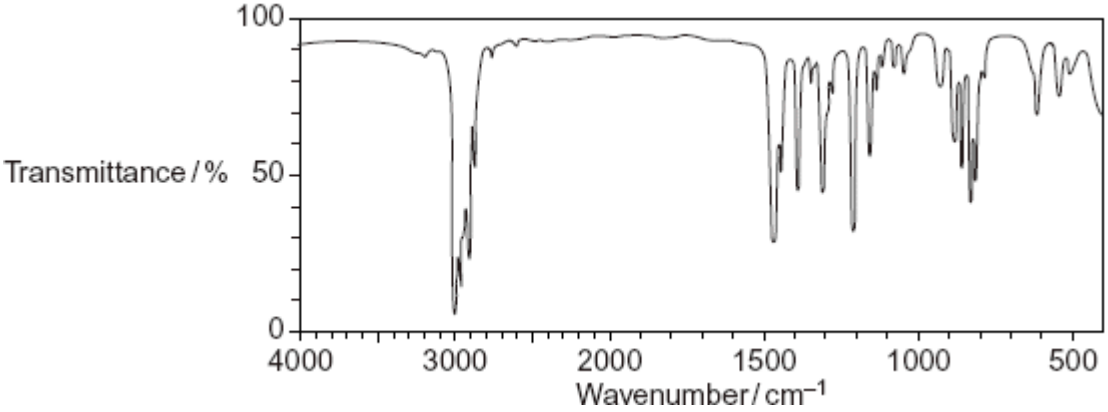
(1)

(b) The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**.
Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

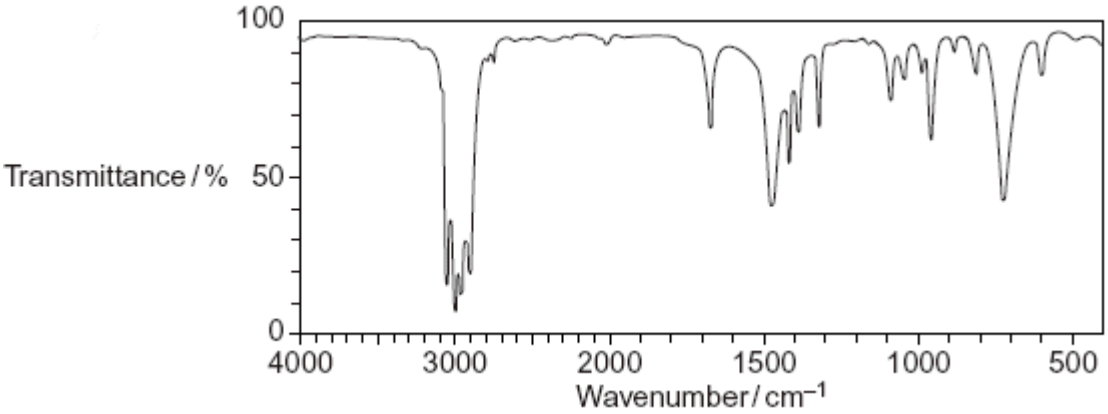
(i)



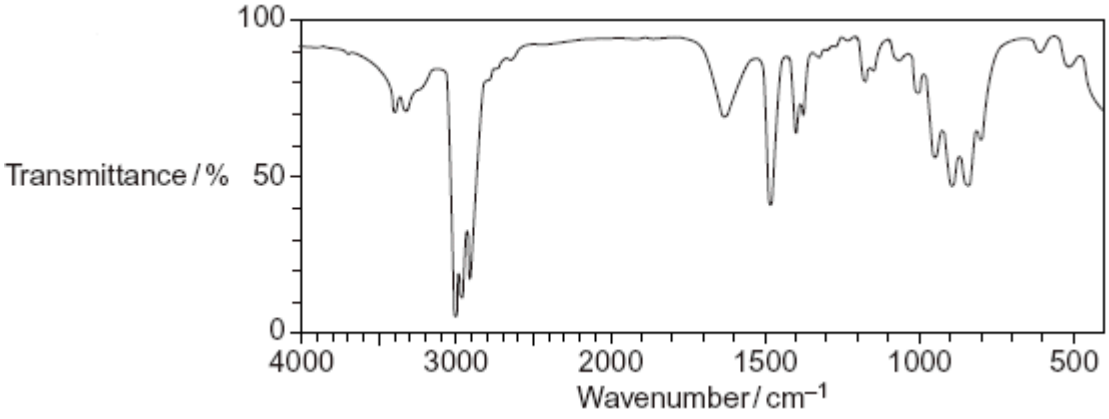
(ii)



(iii)



(iv)



(4)

(c) Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .....

(2)

(d) (i) Outline a mechanism for Reaction **3**.

(4)

(ii) State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

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(1)

(iii) Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

(1)

(e) **D** is a primary amine which has three peaks in its ^{13}C n.m.r. spectrum.

(i) An isomer of **D** is also a primary amine and also has three peaks in its ^{13}C n.m.r. spectrum. Draw the structure of this isomer of **D**.

(1)

(ii) Another isomer of **D** is a tertiary amine. Its ^{1}H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

(1)
(Total 17 marks)