Marks

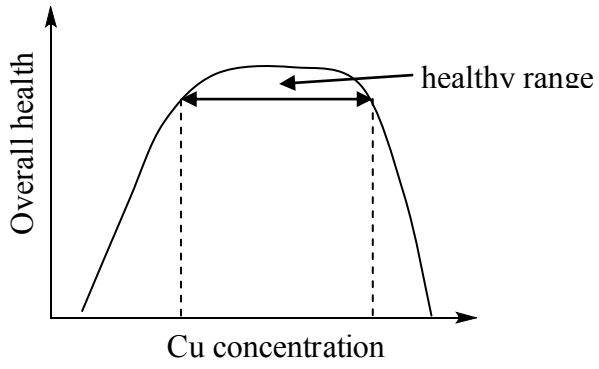
- Complete the following table, giving either the systematic name or the molecular formula as required. **2**

Formula	Systematic name
SO_2	**sulfur dioxide**
$CoCl_2 \cdot 6H_2O$	**cobalt(II) chloride-6-water**
Ag_2CrO_4	silver chromate
$KHCO_3$	potassium hydrogencarbonate

- Complete the following table, providing the ground state electron configuration for each of the following species. **3**

Species	Ground state electron configuration
nitrogen atom	**$1s^2\ 2s^2\ 2p^5$ or [He] $2s^2\ 2p^3$**
chloride ion	**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or [Ne] $3s^2\ 3p^6$**
manganese(II) ion	**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$ or [Ar] $4s^0\ 3d^5$**

- Copper is an essential element in human biology, deficiencies leading to blood disorders. Excess copper can occur in cases of poisoning or in Wilson's disease. Draw a graph showing the relationship between overall health and the level of copper in the body and identify the 'healthy' range. **4**



Describe one biological function of copper.

Copper enzymes are involved in electron transport systems due to the ability of copper to change its oxidation state.

In some organisms, copper enzymes are involved in oxygen transport.

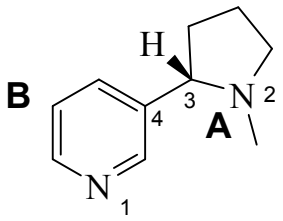
ANSWER CONTINUES ON THE NEXT PAGE

Suggest one approach for treating an excess level of copper.

Treatment with a complexing agent such as EDTA leads to the formation of stable water-soluble complex that can be excreted from the body.

Marks 8

- The molecular structure of nicotine, the addictive component of tobacco, is shown below.



List the types of intermolecular interactions that each of the following sites on nicotine would be involved in when it is dissolved in water.

A – H bonding and dipole-dipole interactions

B – dispersion forces and dipole-induced dipole

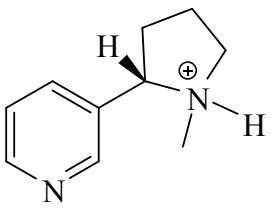
Provide the requested information for each of the indicated atoms in nicotine.

Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry around the atom
N-1	**trigonal planar**	***sp*^{2}**	**bent (~120°)**
N-2	**tetrahedral**	***sp*^{3}**	**trigonal pyramidal**
C-3	**tetrahedral**	***sp*^{3}**	**tetrahedral**
C-4	**trigonal planar**	***sp*^{2}**	**trigonal planar**

The pK_b of N-1 is 10.88 and the pK_b of N-2 is 5.98. Draw the structure of the predominant form of nicotine that exists in the human body at pH 7.4.

For N-1, the pK_a of the protonated form (the conjugate acid) is (14.00 – 10.88) = 3.12. As the pH is *higher* than the pK_a, the conjugate acid is deprotonated: *very* little protonation occurs.

For N=2, the pK_a of the protonated form is (14.00 – 5.98) = 8.02. As the pH is *lower* than the pK_a, the conjugate acid form dominates: protonation occurs.

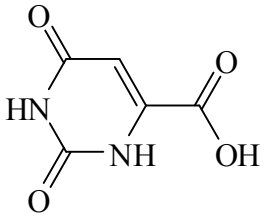


Marks 4

- Lithium salts, especially lithium carbonate, are commonly used in the treatment of bipolar disorder. Write the net ionic equation for the reaction which occurs between lithium carbonate and hydrochloric acid in the stomach.

$Li_2CO_3(s) + 2H^+(aq) \rightarrow 2Li^+(aq) + H_2O(l) + CO_2(g)$

Lithium orotate (as a monohydrate salt, $LiC_5H_3N_2O_4 \cdot H_2O$) is a controversial alternative formulation sold in some health food stores. The orotate ion is the conjugate base of orotic acid, whose structure is shown below.



orotic acid

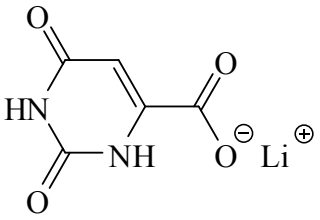
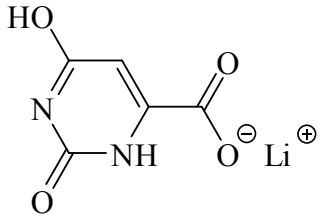
Like the carbonate, lithium orotate is taken orally. Using an equation, comment on any differences between the form in which lithium is bioavailable from these two lithium salts.

When lithium orotate, $LiC_5H_3N_2O_4$, dissolves in water, it forms $Li^+(aq)$ ions and orotate ions:

$LiC_5H_3N_2O_4(s) \rightarrow Li^+(aq) + C_5H_3N_2O_4^-(aq)$

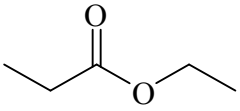
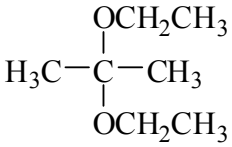
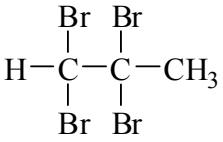
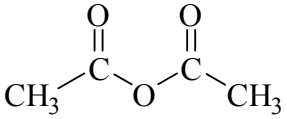
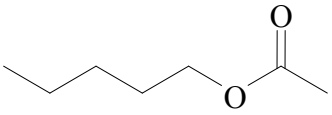
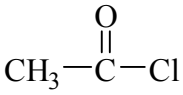
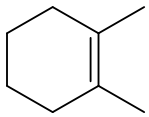
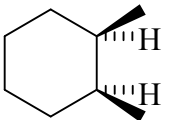
Both lithium carbonate and lithium orotate thus give rise to the same form of lithium, $Li^{2+}(aq)$, when taken orally.

Like three of the bases found in DNA and RNA, orotic acid is a derivative of pyrimidine. Also like those bases, orotic acid and its salts have tautomers. Draw the structural formula of a tautomer of lithium orotate.

lithium orotate	tautomer of lithium orotate
	

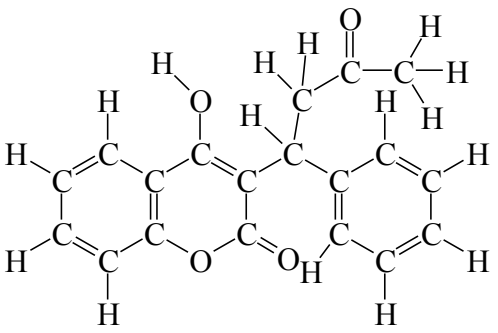
- Complete the following table. Make sure you indicate any relevant stereochemistry.

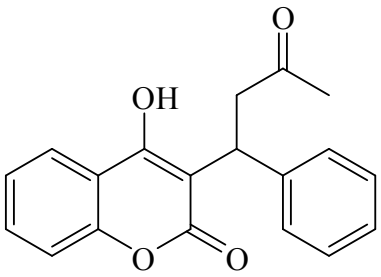
Marks 7

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
CH_3CH_2COOH	1. $SOCl_2$ 2. CH_3CH_2OH	
	dilute $H^{\oplus}$	 + CH_3CH_2OH
$H-C\equiv C-CH_3$	excess Br_2 in diethyl ether solvent	
$CH_3CH_2CH_2CH_2CH_2OH$	 conc. H_2SO_4 catalyst	 + CH_3COOH
	H_2O	CH_3COOH
	H_2 / Pd / C ethanol solvent	

- A structural formula for Warfarin, an anticoagulant, showing all atoms and bonds is shown below. Draw a stick representation of the formula in the adjacent box.

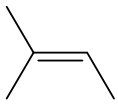
Marks 1





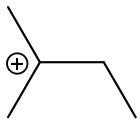
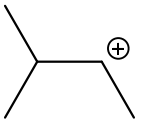
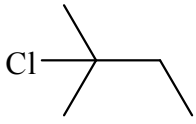
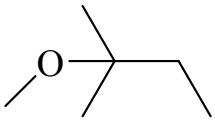
- Consider the alkene, 2-methyl-2-butene (**B**).

4



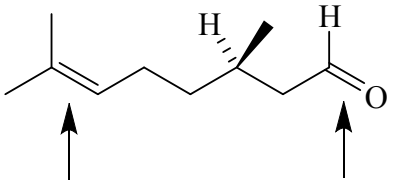
(**B**)

When (**B**) is treated with hydrogen chloride in methanol, two carbocations can be formed. The major carbocation reacts with nucleophiles that are present in the reaction to give an alkyl halide and an ether. Provide constitutional formulas of these intermediates and products in the appropriate boxes below.

major carbocation	minor carbocation
 **H^+ attaches to the less substituted end of the double bond leaving a positive charge is on the more substituted end of the double bond where it is stabilized.**	 **H^+ attaches to the more substituted end of the double bond leaving a positive charge is on the less substituted end of the double bond where it is less stabilized.**
alkyl halide product	ether product
 **Cl^- attaches to the carbon with the positive charge in the major carbocation.**	 **CH_3OH attaches to the carbon with the positive charge in the major carbocation. It then loses H^+ to make the ether shown.**

Marks 5

- (+)-Citronellal is a widely occurring natural product present in citronella oil, lemon and lemon grass. It is used as a soap perfume and in insect repellents.



citronellal

alkene **aldehyde**

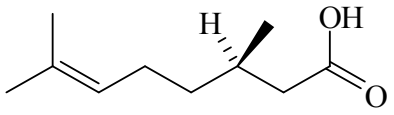
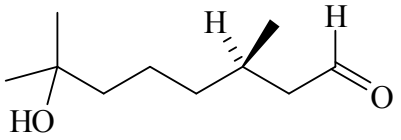
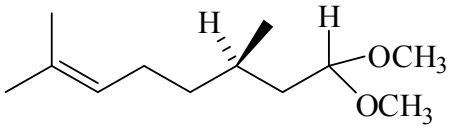
Give the molecular formula of citronellal.

$C_{10}H_{18}O$

Identify the functional groups present in citronellal.

Alkene and aldehyde (see structure above)

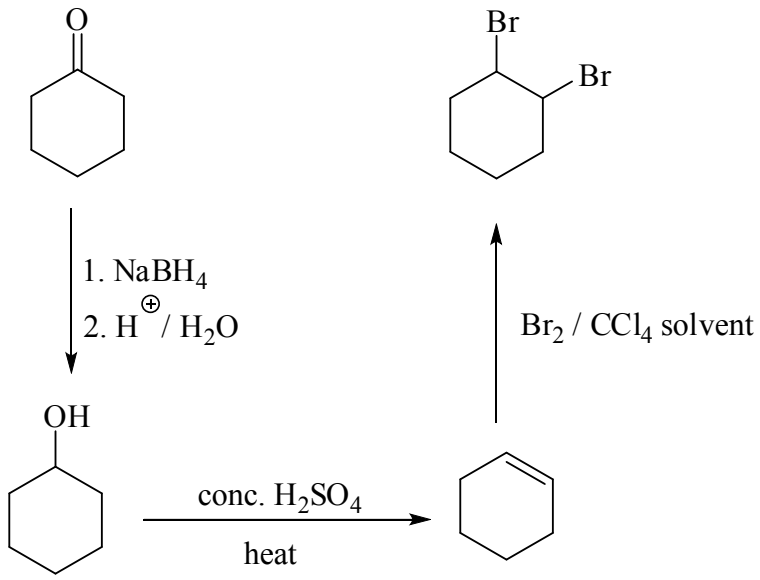
Draw the constitutional formula of the product(s) formed when citronellal is treated with each of the following reagents.

$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
3 M H_2SO_4	
excess CH_3OH / catalytic amount H_2SO_4	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

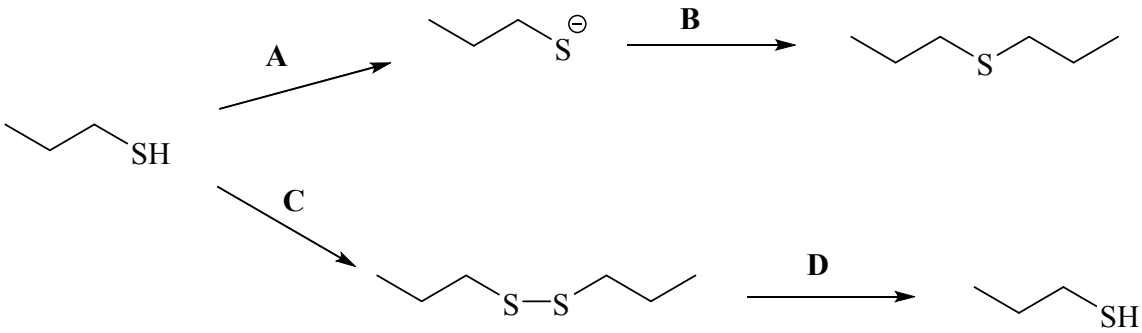
- Devise a synthesis of 1,2-dibromocyclohexane from cyclohexanone. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

Marks
3



- Indicate the reagents used in the laboratory to undertake the following transformations.

4

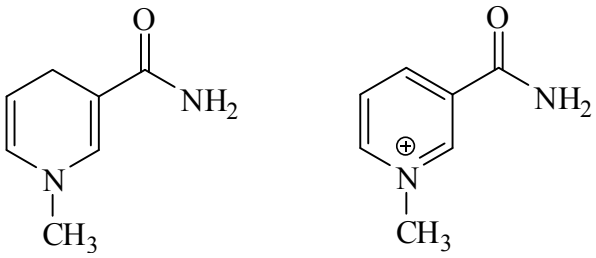


A:	**NaOH (deprotonation of RSH by strong base)**
B:	**$CH_3CH_2CH_2Br$ (nucleophilic attack by RS^- with substitution of Br^-)**
C:	**I_2 (formation of disulfide bridge by oxidation)**

Provide a description for transformation **B**.	**nucleophilic substitution**
Provide a description for transformation **D**.	**reduction**

- Using a spectroscopic technique, how would you distinguish between the following pairs of compounds? Indicate the observations you would make.

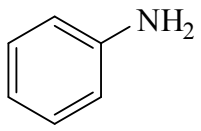
Marks **2**

Compounds	Technique and observation
	**^{1}H NMR** **This can detect different numbers of H's attached to the ring. The first compound has 3 olefinic resonance (each 1H) and 1 aliphatic resonance (2H) whilst the second compound has 4 aromatic resonances (each 1H).**
	**IR.** **The first compound will give intense absorption at about 1740 cm^{-1} due to the C=O group. The second compound will have no absorption in that region.**

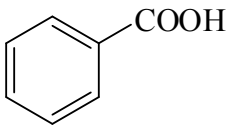
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Aniline, benzoic acid and benzamide are all insoluble in water, but soluble in ether. Explain how, by using simple laboratory reagents and equipment, each compound could be separated and recovered from a mixture of all three.

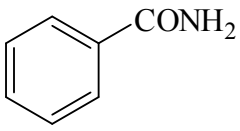
Marks
5



aniline



benzoic acid

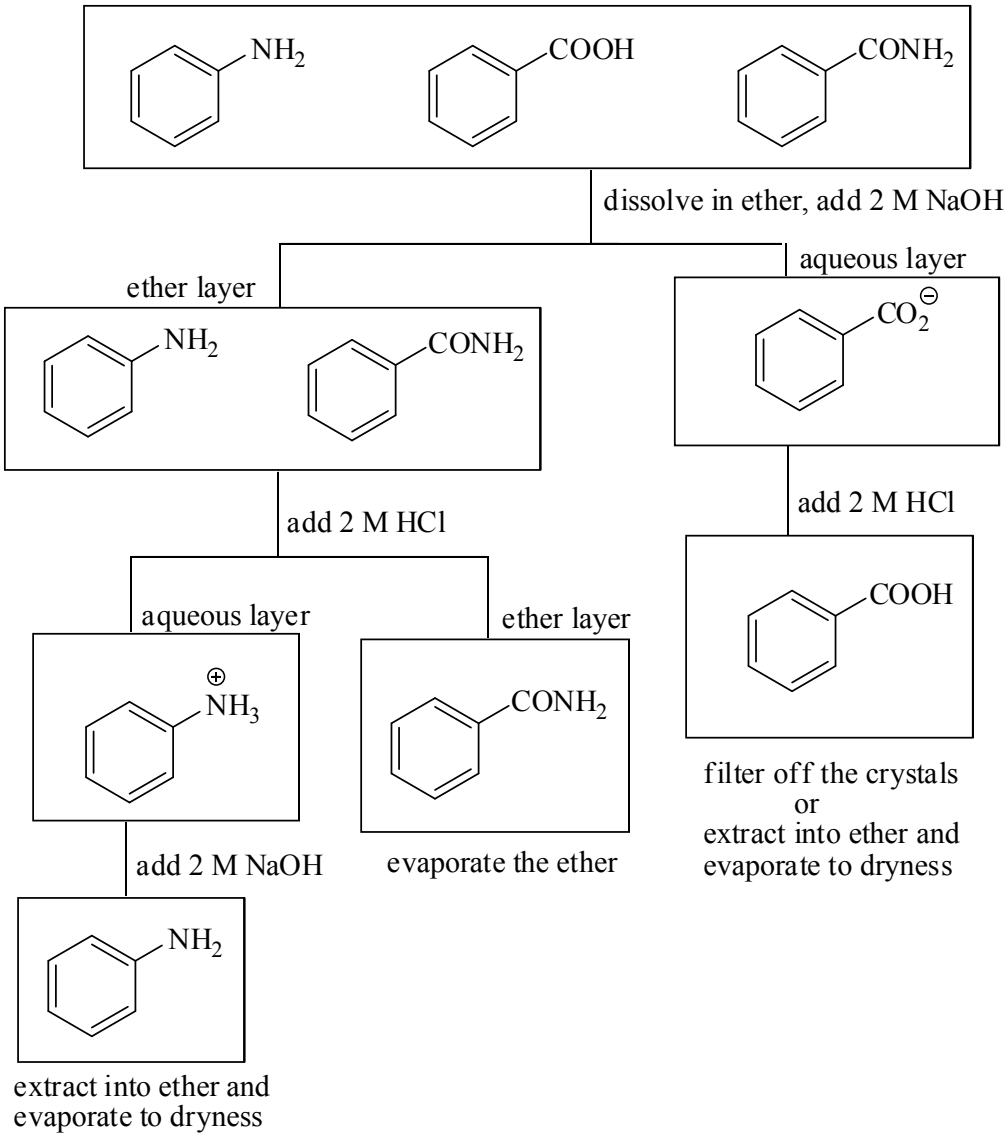


benzamide

All of the compounds are neutral and will dissolve in an organic solvent like ether.

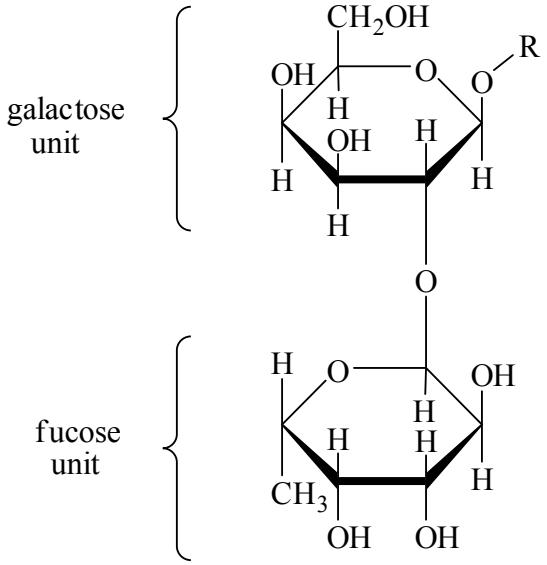
Benzoic acid is a weak acid and will react with a strong base to form an anion which will dissolve in water.

Aniline is a weak base (whereas benzamide is a *very* weak base) and will be deprotonated by reaction with a strong acid to form a water soluble cation.



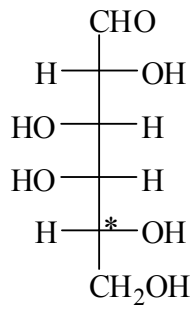
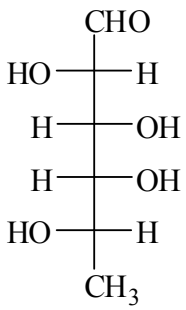
Marks 6

- An important group of oligosaccharides is the blood group antigens. The blood group antigen of humans with blood group O can be represented by the partial structure below, in which R is a glycoprotein.



Specify the fucose unit as a furanose or a pyranose.	**pyranose**
Specify fucose as a hexose, a pentose or a tetrose.	**hexose**

The type O blood group antigen can be hydrolysed to galactose, fucose and a glycoprotein unit. Give the Fischer projections of the open chain form of galactose and fucose.

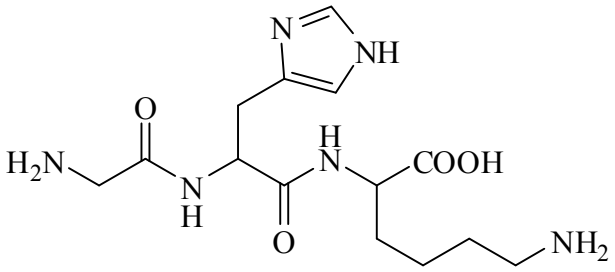
Fischer projection of galactose	Fischer projection of fucose
	

On your Fischer projection of galactose indicate with an asterisk (*) the carbon atom used in the D/L convention.

Specify the galactose from blood antigen as D-galactose or L-galactose.	**D-galactose**
Specify the fucose from blood antigen as D-fucose or L-fucose.	**L-fucose**

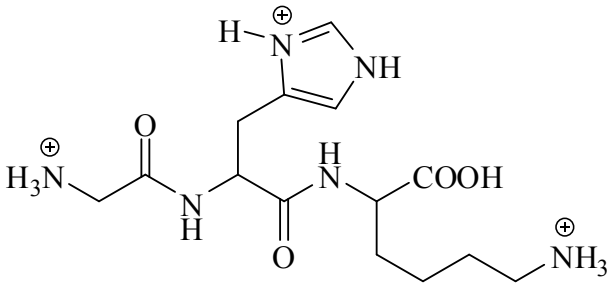
Marks 7

- The tripeptide glycyl-L-histidyl-L-lysine (**M**) is a liver growth factor.

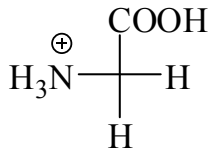
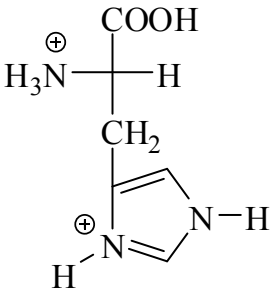
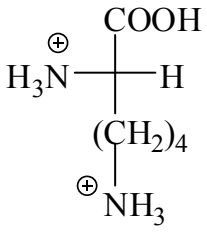


(**M**)

At pH 4 this tripeptide exists mainly as a species (**N**) with three positive charges. Give the constitutional formula for (**N**).



Vigorous acid hydrolysis of tripeptide (**M**) gives three amino acids: glycine, L-histidine and L-lysine. Give constitutional formulas of these amino acids obtained after hydrolysis of (**M**) with 6 M HCl. Make sure you show the products in the appropriate ionic states and with the correct stereochemistry.

glycine	L-histidine	L-lysine
		

Why does histidine have an "L" descriptor, but glycine does not?

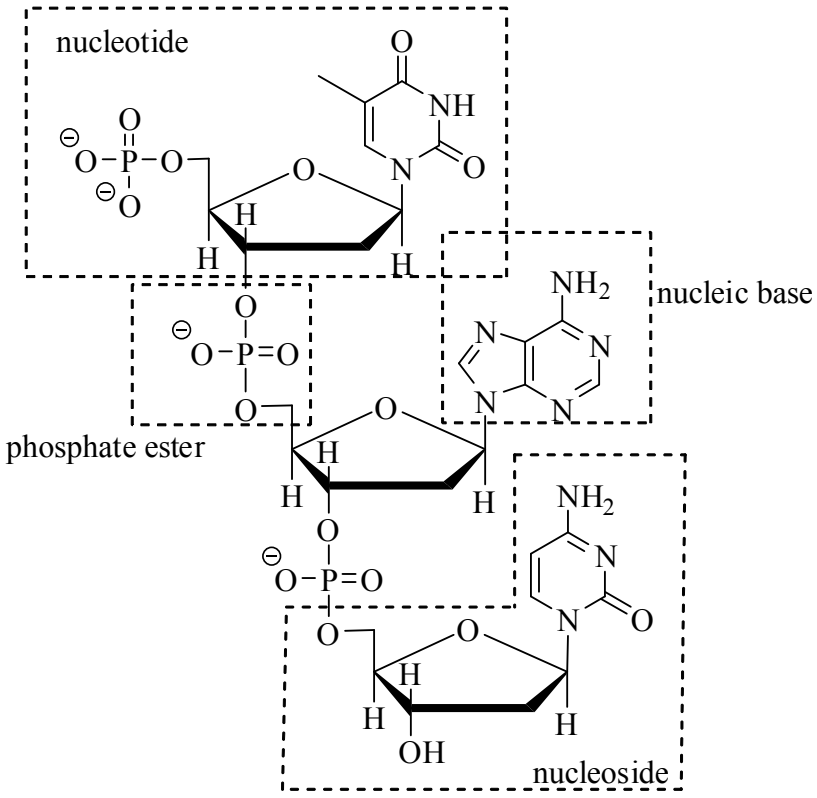
Glycine is achiral, whilst lysine contains a stereogenic carbon with the L-configuration.

- Is the following structure a fragment of DNA or RNA? Give two reasons.

Marks 6

It is a fragment of DNA:

- **It contains the nucleic base thymine (RNA contains uracil instead).**
- **The sugar present is deoxyribose (RNA contains ribose instead).**



Clearly identify on the above structure one example of each of the following subunits.

phosphate ester

nucleic base

nucleoside

nucleotide

See structure above