Marks

- Glucose labelled with ^{11}C is used to monitor brain function in positron emission tomography (PET) scans. Identify the missing particles in the following nuclear reactions showing the synthesis and decay of ^{11}C. **2**

$$^{14}_{7}N + {}^{1}_{1}H \rightarrow {}^{11}_{6}C + \boxed{{}^{4}_{2}He}$$

$$^{11}_{6}C \rightarrow \boxed{{}^{11}_{5}B} + {}^{0}_{1}e$$

- The intense yellow light emitted from a sodium street lamp has a wavelength of $\lambda = 590$ nm. The light is emitted when an electron moves from a 3*p* to a 3*s* orbital. What is the energy of (a) one photon and (b) one mole of photons of this light? **5**

The energy of a photon with wavelength λ is given by $E = hc / \lambda$. Hence:

$$E = (6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1}) / (590 \times 10^{-9}\ \text{m}) = 3.4 \times 10^{-19}\ \text{J}$$

This is the energy per photon. The energy per mole is therefore:

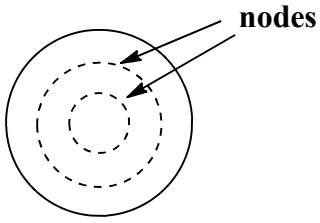
$$E = (6.022 \times 10^{23}\ \text{mol}^{-1}) \times (3.4 \times 10^{-19}\ \text{J}) = 2.0 \times 10^{2}\ \text{kJ mol}^{-1}$$

(a) Answer: **3.4×10^{-19} J**

(b) Answer: **2.0×10^{2} kJ mol^{-1}**

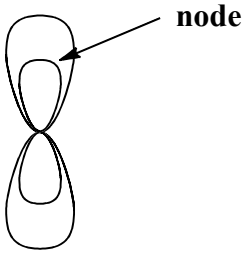
Sketch the shape of a 3*s* and a 3*p* orbital and label any spherical nodes that may be present.

3*s* orbital



3*s* orbital

3*p* orbital



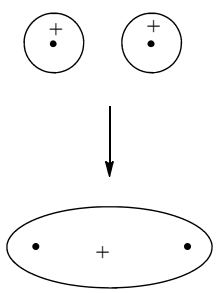
3*p* orbital

What does a node represent?

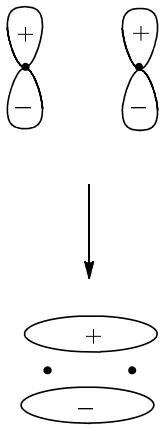
A node represents the region where there is zero probability of finding the electron.

Marks

- Consider the σ-bond of a hydrogen molecule and the π-bond of ethylene ($H_2C=CH_2$). Sketch the shapes of the molecular orbitals of these bonds and the shapes of the atomic orbitals from which they arise. **2**

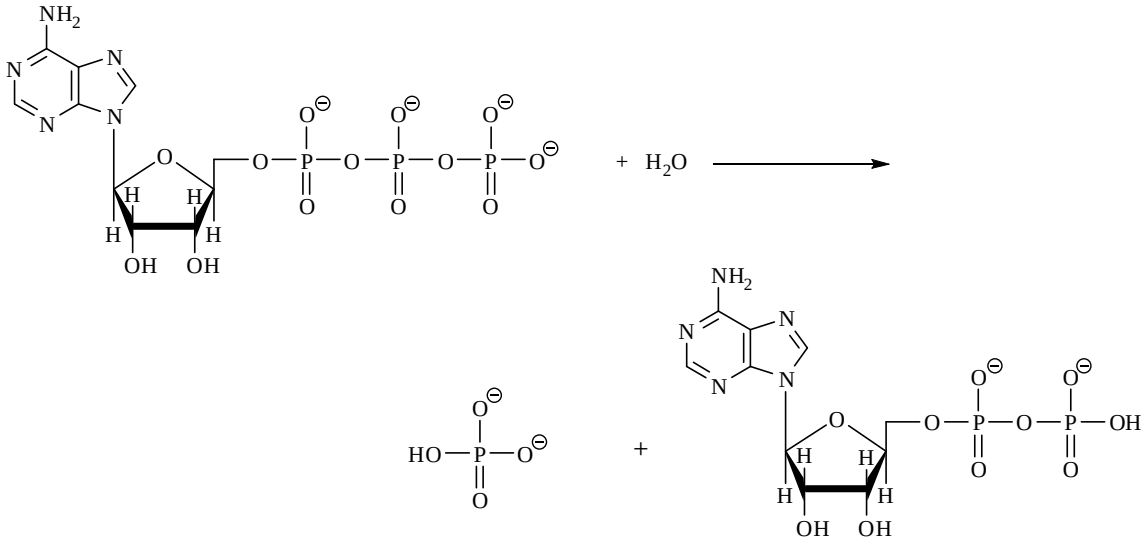


hydrogen



ethylene

- ATP is used as an energy source in the body. Hydrolysis releases ADP, HPO_4^{2-} and energy, according to the equation: **2**



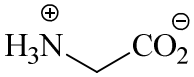
Suggest **two** reasons why this reaction is a good energy source.

There is an increase in resonance stabilisation energy when a free HPO_4^{2-} ion is produced.

ATP is a high energy molecule due to the 4 negative charges near each other. This is reduced when it's converted to ADP which has only 2 close negative charges.

Marks 7

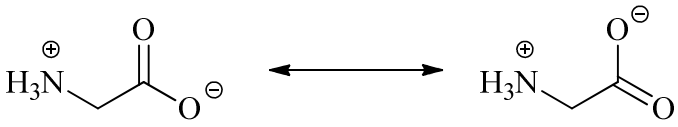
- Glycine, NH_2CH_2COOH, is the simplest of all naturally occurring amino acids. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. Draw a structure that indicates the charges on the molecule at the physiological pH of 7.4.



This pH is much *greater* than the pK_a value of the acid group: it is *deprotonated*.

This pH is much *lower* than the pK_a value of the amino group: it is *protonated*.

Use your structure to illustrate the concept of resonance.



What are the hybridisation states and geometries of the two carbon atoms and the nitrogen atom in glycine?

The carbon on the acid group is sp^2 hybridised and the geometry is trigonal planar.

The carbon on the CH_2 group is sp^3 hybridised and the geometry is tetrahedral.

The nitrogen is sp^3 hybridised and the geometry is tetrahedral.

Propionic acid, CH_3CH_2COOH, has a melting point of –20.7 °C while glycine has a melting point of 292 °C. Suggest a reason why these two molecules have such different melting points.

Propionic acid has strong hydrogen bonds, giving it a relatively high melting point.

However, glycine has very strong ionic bonds between the NH_3^+ and CO_2^- groups giving it *very* high melting point.

- Explain the terms '*weak*' and '*strong*' and the terms '*dilute*' and '*concentrated*' in the context of acids and bases.

Marks 2

A weak acid or base is one which only partially dissociates in water:

e.g. $\mathbf{CH_3COOH(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)}$

A strong acid or base is one which completely dissociates in water:

e.g. $\mathbf{HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)}$

Concentrated and dilute are terms that can be used in reference to any solute, describing the number of moles of solute relative to the volume of solvent. A concentrated solution has a high solute : solvent ratio, whilst a dilute solution has a low solute:solvent ratio.

- Hydrogen bond strength increases in the order N–H::::N < O–H::::O < F–H::::F. Use this information and the data given in the table to explain the differences in boiling point of ammonia, water and hydrogen fluoride.

2

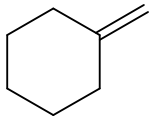
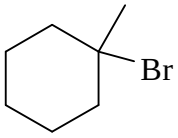
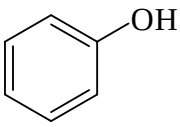
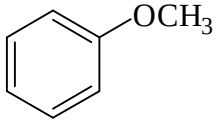
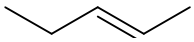
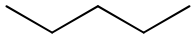
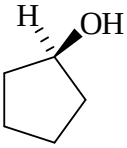
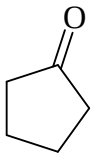
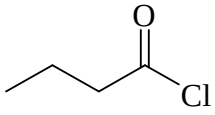
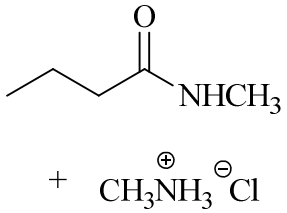
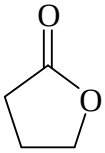
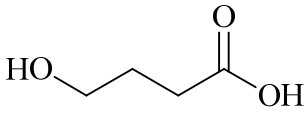
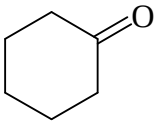
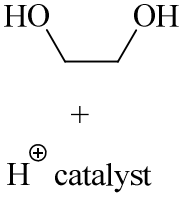
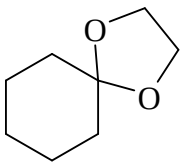
Compound	NH_3	H_2O	HF
Boiling point / °C	–33	100	20

NH_3 and HF both have two H-bond per molecule and their boiling points are in the expected order - HF has the stronger H-bonds and the higher boiling point.

H_2O has 4 H-bonds per molecule, so although the bonds are not as strong as those of HF, there are twice as many of them. As a result the boiling point of H_2O is greater than that of HF.

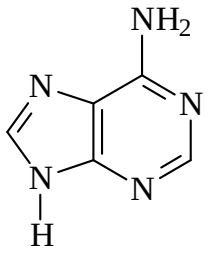
Marks 11

- Complete the following table. Make sure you complete the name of the starting material where indicated.

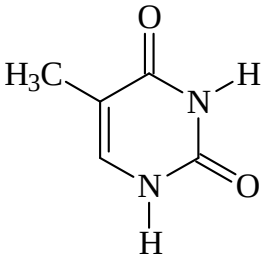
STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	HBr / CCl_4 (solvent)	
	**1. NaOH** **2. CH_3I**	
 **Name: (*E*)-2-pentene**	H_2/Pd	
	$Cr_2O_7^{2\ominus} / H^{\oplus}$	
	excess CH_3NH_2	
	$H^{\oplus}$ / H_2O / heat	
 **Name: cyclohexanone**		

Marks 4

- Adenine and thymine have the structures shown below.

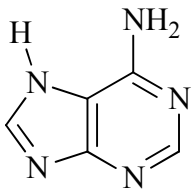


adenine



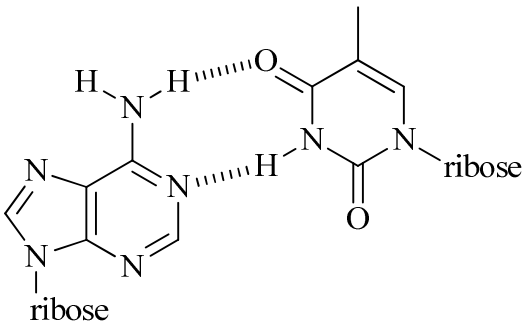
thymine

Draw a tautomer of the shown structure of adenine.



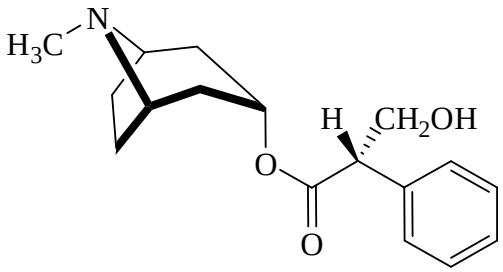
In DNA, adenine forms a "base pair" with thymine. Explain what is meant by "base pair" and indicate the point(s) of interaction between adenine and thymine.

DNA consists of a double strand of polynucleotides. The strands are complementary with C, G, A and T on one strand being paired with G, C, T and A respectively on the other. C (cytosine) and G (guanine) are therefore known as a base pair. Similarly A (adenine) and T (thymine) are another base pair. The two DNA strands are held together by H-bonding between the bases in a base pair.



Marks 7

- The tropane alkaloid (-)-hyoscyamine is found in certain plants of the *Solanaceae* family. It is an anticholinergic agent that works by blocking the action of acetylcholine at parasympathetic sites in smooth muscle, secretory glands and the central nervous system.



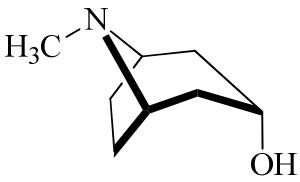
Give the molecular formula of (-)-hyoscyamine. **$C_{17}H_{23}O_3N$**

List the functional groups present in (-)-hyoscyamine.

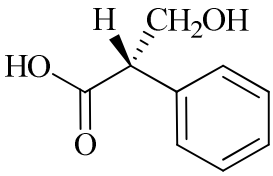
amine, alcohol, ester, aromatic ring (arene)

Hydrolysis of (-)-hyoscyamine results in two fragments, tropine and tropic acid. Draw each of these fragments.

tropine



tropic acid



What is the stereochemistry at the tropic acid stereocentre? Write (*R*) or (*S*). **(*S*)**

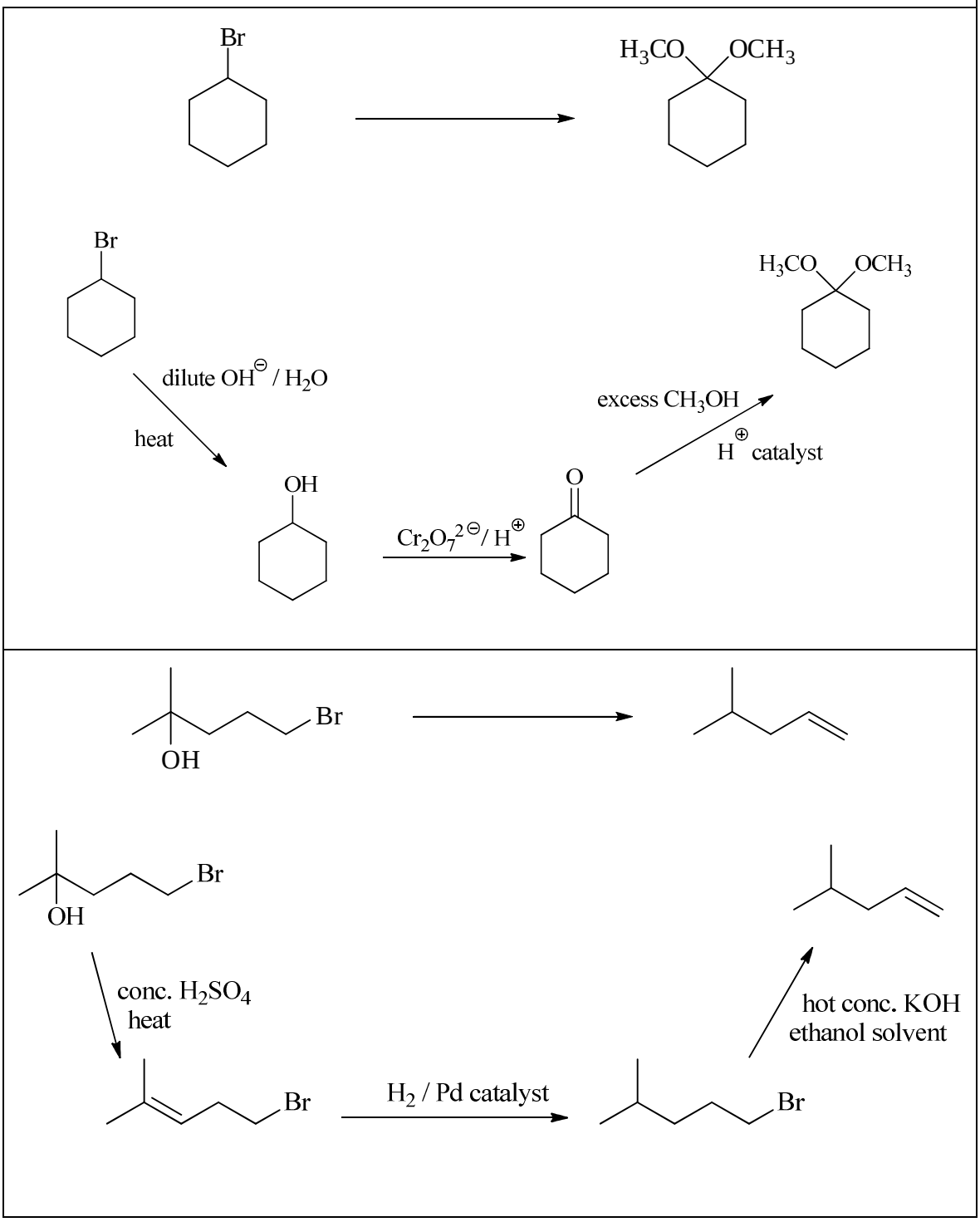
Is tropine optically active? Explain your answer.

No. It is a *meso*-isomer (*i.e.* has a plane of symmetry) and therefore optically inactive.

It is superimposable on its mirror image.

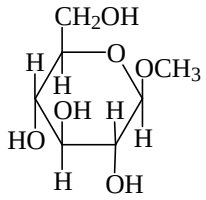
Marks 6

- Show clearly the reagents you would use to carry out the following chemical conversions. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

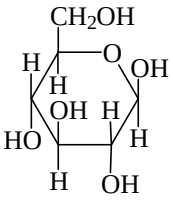


Marks 8

- Consider the following two monosaccharides, (**L**) and (**M**).



(**L**)



(**M**)

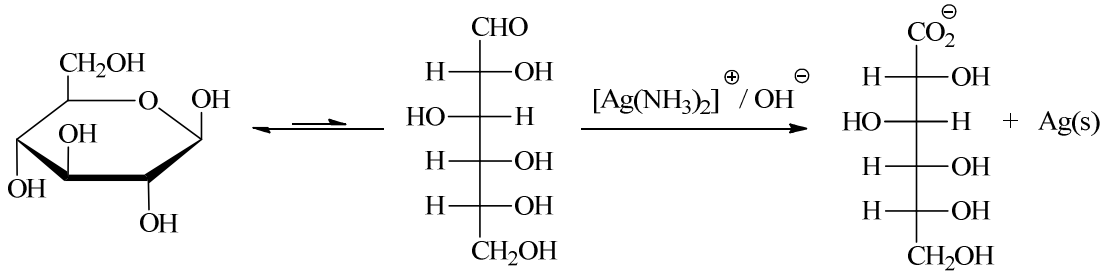
methyl β-D-glucopyranoside

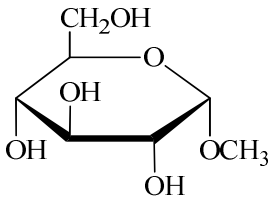
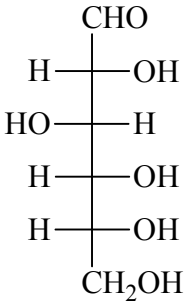
β-D-glucopyranose

Describe a chemical test that could be used to distinguish (**L**) from (**M**). Include in your answer, the reagent you would use, what would be observed and a chemical equation that explains what is occurring in the reaction.

Tollens reagent, $[Ag(NH_3)_2]^+/OH^-$.

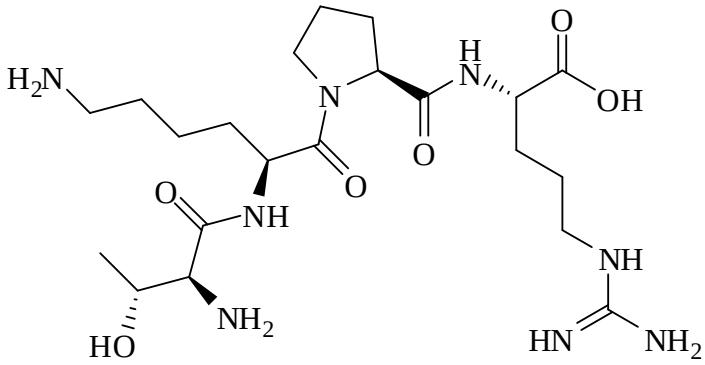
This will give no reaction with (L), but will oxidise (M). In the process, the $[Ag(NH_3)_2]^+$ ion is reduced to metallic Ag which deposits as a silver mirror.



Give the reagents to convert (**L**) to a mixture of (**M**) and the α-anomer of (**M**).	**H^+/H_2O/heat**
Give the reagents to convert (**M**) to (**L**).	**excess CH_3OH / H^+ catalyst**
Give the structure of the isomer of (**L**) also produced in the preceding reaction.	
Sugar (**M**) exists in equilibrium with an open chain form. Give the Fischer projection of this open chain form.	
List the functional groups present in (**L**).	**primary and secondary alcohol, acetal**

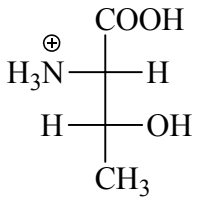
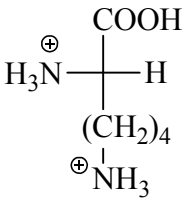
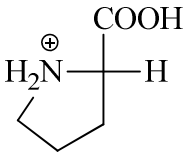
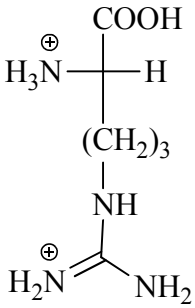
Marks 6

- Tuftsin is a tetrapeptide (Thr-Lys-Pro-Arg) produced by enzymatic cleavage of the Fc-domain of the heavy chain of immunoglobulin G. It is mainly produced in the spleen and its activity is related primarily to immune system function.



tuftsin

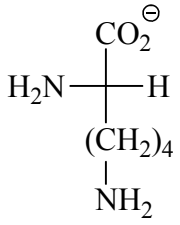
Draw the Fischer projections of the four L-amino acids that result from the acid hydrolysis of tuftsin.

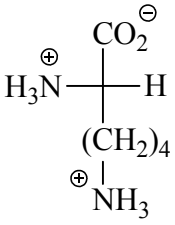
Marks 4

What is the major species present when lysine (Lys) is dissolved in water at pH 12 and pH 5.6. The pK_a values of lysine are 1.82 (α-COOH), 8.95 (α-$NH_3^{\oplus}$) and 10.53 (side chain).

pH 12

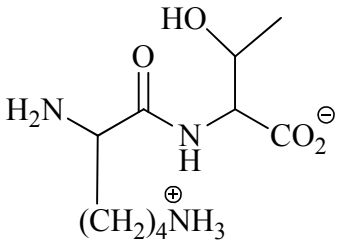


pH 5.6



Give the constitutional formulas for the following dipeptides in their zwitterionic states. The pK_a values of proline (Pro) are 1.95 and 10.64.

Lys-Thr



Pro-Lys