## Topics in the June 2012 Exam Paper for CHEM1611

Click on the links for resources on each topic.

2012-J-2:

- Atomic Structure
- The Periodic Table

2012-J-3:

- Chemical Bonding
- The Shapes of Molecules
- Acids and Bases

2012-J-4:

- Chemical Bonding
- The Shapes of Molecules

2012-J-5:

- Atomic Structure
- Chemical Bonding

2012-J-6:

- Alkenes
- Alcohols, Phenols, Ethers and Thiols
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2012-J-7:

- Introduction to Organic Chemistry
- Stereochemistry

2012-J-8:

- Alkenes
- Aldehydes and Ketones
- Alcohols, Phenols, Ethers and Thiols
- Organic Halogen Compounds

2012-J-9:

- Carbohydrates

2012-J-10:

- Amino Acids, Peptides and Proteins

2012-J-11:

- Amino Acids, Peptides and Proteins

2012-J-12:

- Heterocyclic Compounds

Marks

- $^{11}C$ is used in positron emission tomography – PET. It is synthesised by bombarding a $^{14}N$ target with protons. Write a nuclear equation for the formation of $^{11}C$ and thus identify the by-product of this synthesis. **2**

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

$^{11}C$ undergoes positron decay with a half life of 20.3 minutes. Write a nuclear equation to identify the product of this decay reaction.

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

- Calculate the wavelength of light (in nm) emitted when an electron moves from the $n = 4$ to $n = 2$ energy levels in a hydrogen atom. **3**

**The energy of an orbital in an 1-electron atom or ion is given by**

$$E_n = -Z^2 E_R (1/n^2)$$

**The energy difference between two levels is therefore:**

$$\Delta E = E_{n1} - E_{n2} = [-Z^2 E_R (1/n_1^2)] - [-Z^2 E_R (1/n_2^2)] = Z^2 E_R (1/n_2^2 - 1/n_1^2)$$

**The energy emitted when an electron moves from $n = 4$ to $n = 2$ for H with $Z = 1$ is therefore:**

$$\Delta E = (1)^2 E_R (1/2^2 - 1/4^2)$$
$$= E_R \times (3/16) = (3/16) \times 2.18 \times 10^{-18}\ J = 4.09 \times 10^{-19}\ J$$

**Using $E = hc / \lambda$, this corresponds to a wavelength of:**

$$\lambda = hc / E = (6.626 \times 10^{-34}\ J\ s)(2.998 \times 10^{8}\ m\ s^{-1}) / (4.09 \times 10^{-19}\ J)$$
$$= 4.86 \times 10^{-7}\ m$$
$$= 486\ nm$$

Answer: **486 nm**

What is the energy of this radiation (in kJ $mol^{-1}$)?

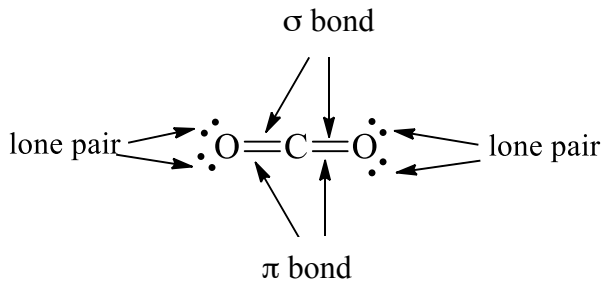
The energy of each photon is **$4.09 \times 10^{-19}$ J. Therefore, per mol:**

**energy of radiation = $(6.022 \times 10^{23}\ mol^{-1}) \times (4.09 \times 10^{-19}\ J) = 246\ kJ\ mol^{-1}$**

Answer: **246 kJ $mol^{-1}$**

- Draw the Lewis structure of carbon dioxide and label the electron pairs as either 'σ-bond' or 'π-bond' or 'lone pair'.

**Marks 4**




What is the hybridisation of the carbon atom and the oxygen atoms?

| | |
|---|---|
| C: ***sp*** | O: ***sp*²** |

Does carbon dioxide have a permanent dipole moment? Explain your reasoning.

**As oxygen is more electronegative than carbon. The shared electrons in this bond lie more towards the oxygen. Each C–O bond is polar.**

**However, the symmetry of the molecule means that the 2 bond moments cancel each other. Overall, there is no permanent dipole moment.**

**3**

- In a standard acid-base titration, 25.00 mL of 0.1043 M NaOH solution was found to react exactly with 28.45 mL of an HCl solution of unknown concentration. What is the pH of the unknown HCl solution at 25 °C?

**The reaction follows the equation $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ so that the number of moles of $H^+$ that reacts is equal to the number of moles of $OH^-$.**

**For $OH^-$:**

**number of moles = concentration × volume**
**= 0.1043 mol $L^{-1}$ × 0.02500 L = 0.002608 mol**

**This is equal to the number of moles of $H^+(aq)$ in 28.45 mL, so:**

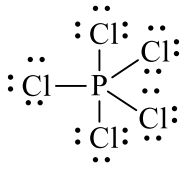
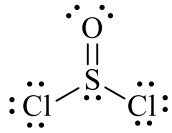
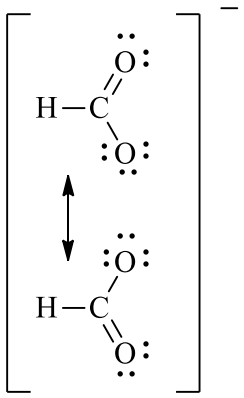
**concentration of $H^+(aq)$ = number of moles / volume**
**= 0.002608 mol / 0.02845 L = 0.09165 mol $L^{-1}$**

**Using $pH = -\log_{10}[H^+(aq)]$:**

**$pH = -\log_{10}(0.09165) = 1.04$**

pH = **1.04**

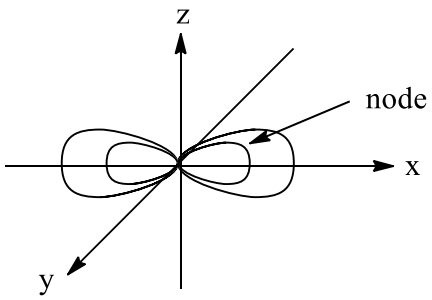
• Complete the following table, include resonance structures if appropriate. The central atom is underlined. **Marks 7**

| Formula | $\underline{P}Cl_5$ | $\underline{S}OCl_2$ | $H\underline{C}OO^-$ |
|---|---|---|---|
| Lewis structure |  |  |  |
| Arrangement of electron pairs around the underlined atom | **trigonal bipyramidal** | **tetrahedral** | **trigonal planar** |
| Molecular geometry | **trigonal bipyramidal** | **trigonal pyramidal** | **trigonal planar** |
| Intermolecular forces present | **dispersion** | **dispersion and dipole-dipole** | |

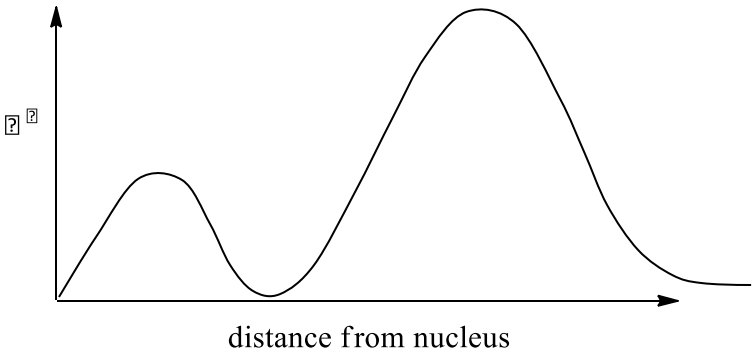
**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks 4**

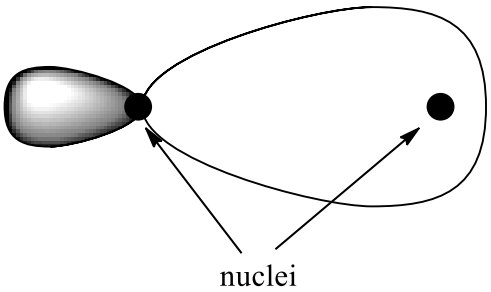
- Sketch the shape of a $3p_x$ orbital.




Sketch the radial probability ($\psi^2$) of an electron in a $3p_x$ orbital.

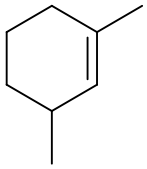
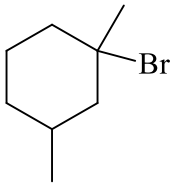
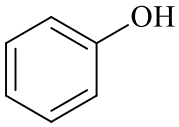
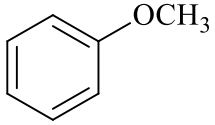
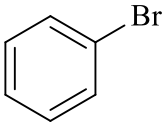
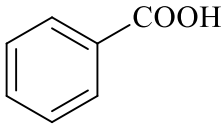
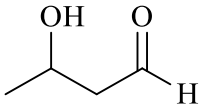
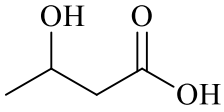
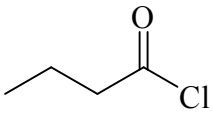
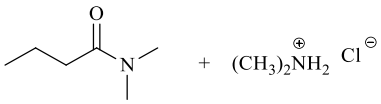
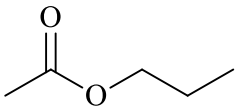
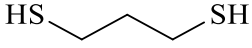



Sketch the shape of the σ orbital formed by overlap of a $3p_x$ orbital and an *s* orbital. Clearly show the position of the two nuclei.



**Marks 11**

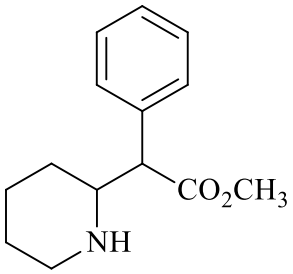
- Complete the following table. Make sure you complete the name of the starting material where indicated.

| STARTING MATERIAL | REAGENTS/ CONDITIONS | CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S) |
|---|---|---|
|  | $HBr / CCl_4$ (solvent) |  |
|  | 1. NaOH<br>2. $CH_3I$ |  |
|  | 1. Mg / dry ether<br>2. $CO_2$<br>3. $H^{\oplus}$ / $H_2O$ |  |
|  <br>**Name: 3-hydroxybutanal** | 1. $[Ag(NH_3)_2]^+$ / $OH^-$<br>2. $H^+$ |  |
|  | excess $(CH_3)_2NH$ |  |
|  <br>**Name: 1-propyl acetate** | 3 M NaOH |  |
|  | **Zn / $H^+$** |  |

**Marks 7**

- Methylphenidate, also known as Ritalin, is a psychostimulant drug approved for treatment of attention-deficit disorder. It belongs to the piperidine class of compounds and increases the levels of dopamine and norepinephrine in the brain through reuptake inhibition of the monoamine transporter.

methylphenidate



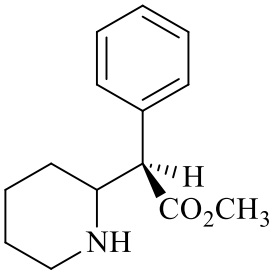

Give the molecular formula of methylphenidate. **$C_{14}H_{19}NO_2$**

List the functional groups present in methylphenidate.

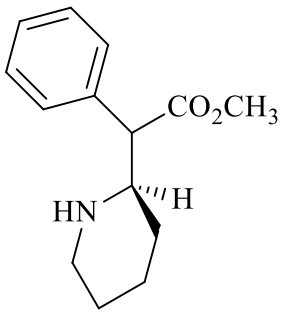
**Aromatic ring, ester, secondary amine**

How many stereogenic (chiral) centres are there in methylphenidate? **2**

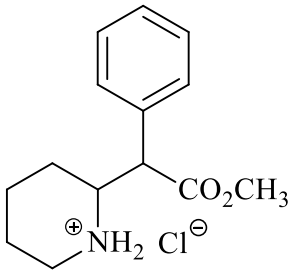
Using a stereogenic centre you have identified, draw the (*R*)-configuration of that centre.




or




Ritalin is generally sold as the hydrochloride salt. Draw the structure of this salt and suggest why this is the preferred compound for sale.

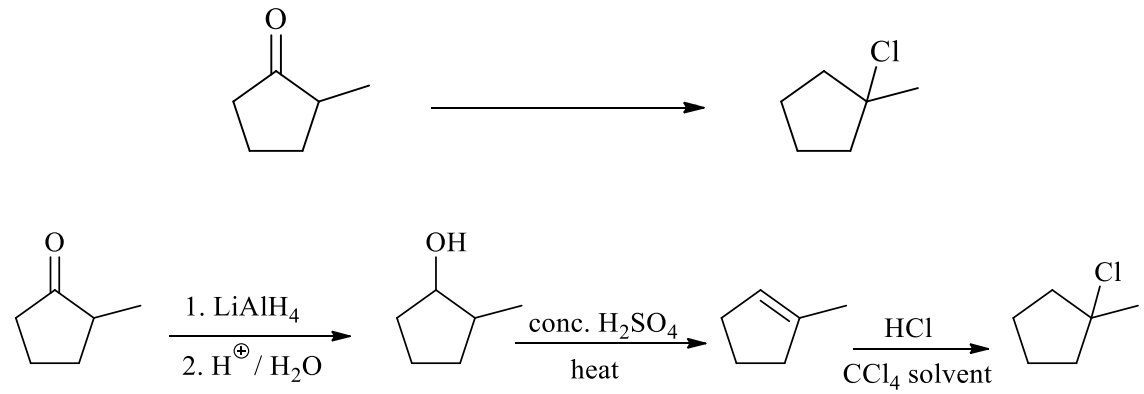


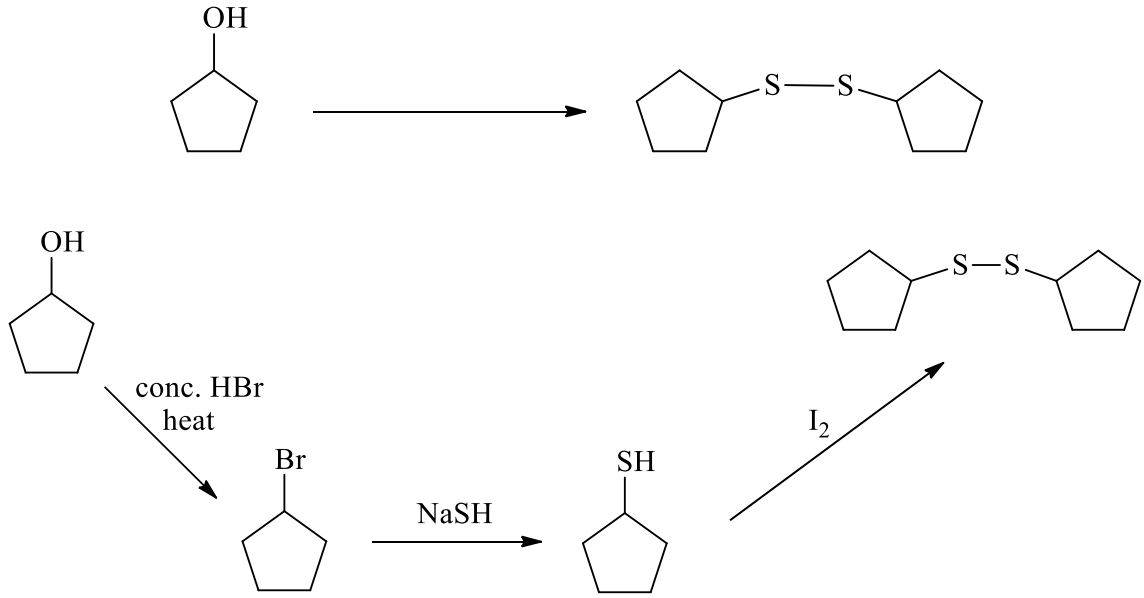

**The hydrochloride salt is soluble in water, which generally means better bioavailability.**

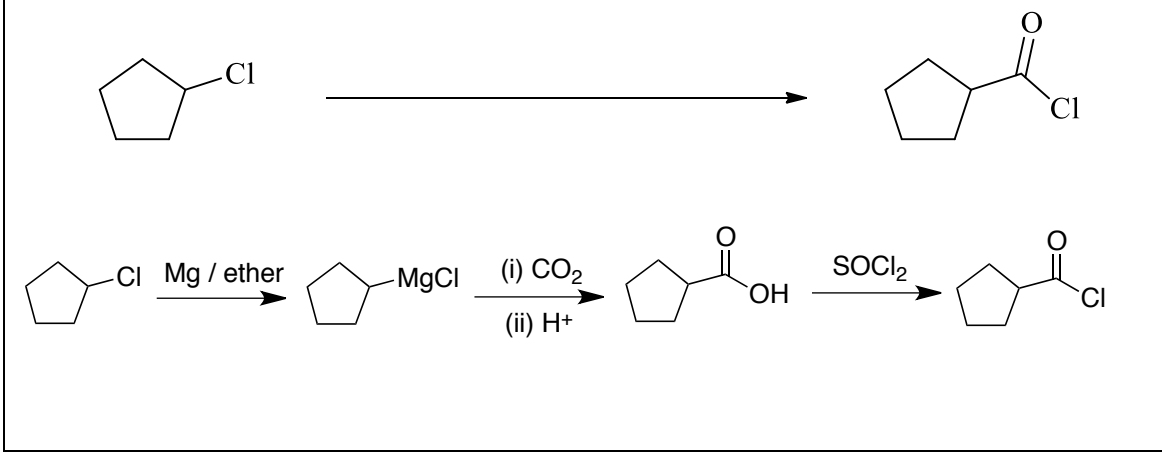
**Salt will have better stability - amines prone to aerial oxidation.**

- 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
**7**



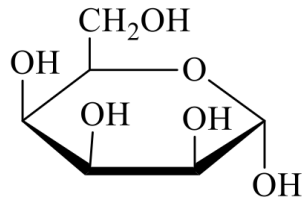



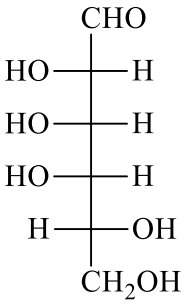



**Marks 7**

- The open chain form of D-talose is in equilibrium with two pyranose forms (**L**) and (**M**). Draw Haworth projections of (**L**) and (**M**).

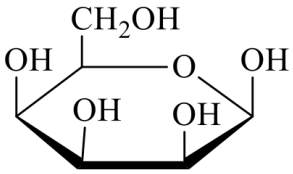
(**L**)



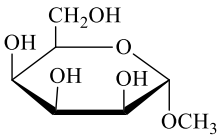


D-talose

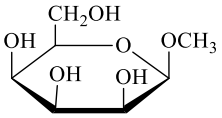
(**M**)



Give the Haworth stereoformula of one of the products obtained when D-talose is treated with excess methanol in the presence of an acid catalyst.

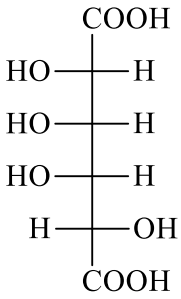


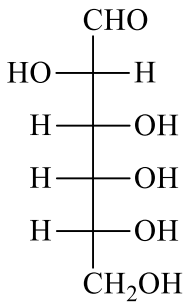
or



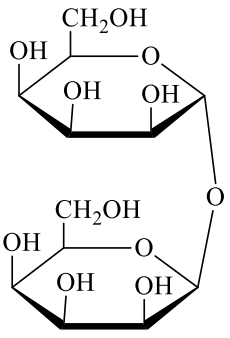
Concentrated $HNO_3$ oxidises aldehydes and primary alcohols to carboxylic acids, but does not oxidise secondary alcohols. Treatment of either D-talose or the aldohexose D-altrose with concentrated $HNO_3$ gives the diacid (**N**). Give the Fischer projection of D-altrose.

(**N**)



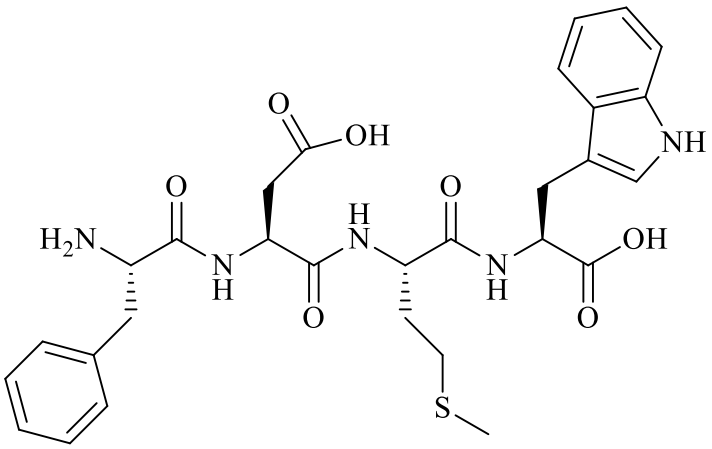


Draw the Haworth stereoformula of a non-reducing disaccharide formed from D-talose.



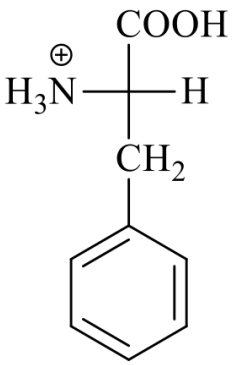
**Marks 6**

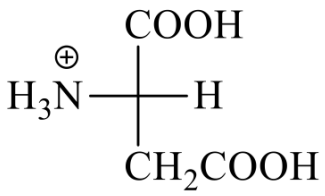
- Cholecystokinin tetrapeptide (CCK-4), (Phe-Asp-Met-Trp) is a peptide fragment derived from the larger peptide hormone cholecystokinin. Unlike cholecystokinin, which has a variety of roles in the gastrointestinal and central nervous systems, CCK-4 acts primarily in the brain as an anxiogenic.

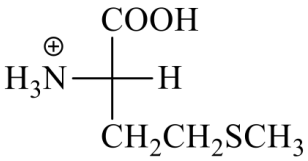


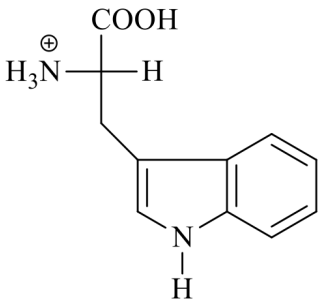
CCK-4

Draw the Fischer projections of the four L-amino acids that result from the acid hydrolysis of CCK-4.







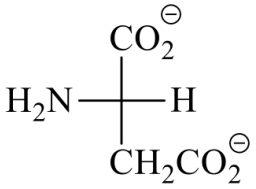


**THIS QUESTION CONTINUES ON THE NEXT PAGE.**

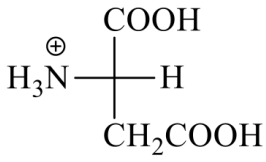
What is the major species present when aspartic acid (Asp) is dissolved in water at pH 12 and pH 1? The p$K_a$ values of aspartic acid are 1.88 (α-COOH), 9.60 (α-$NH_3^{\oplus}$) and 3.65 (side chain).

**Marks 4**

pH 12

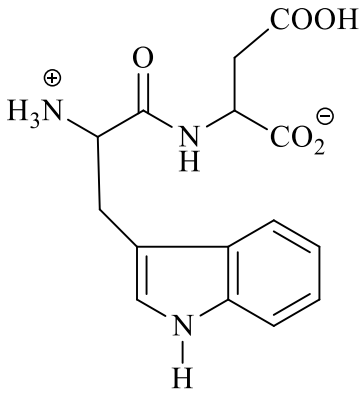


pH 1

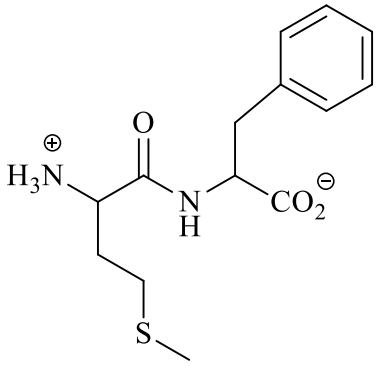


Give the constitutional formulas for the following dipeptides in their zwitterionic states.

Trp-Asp



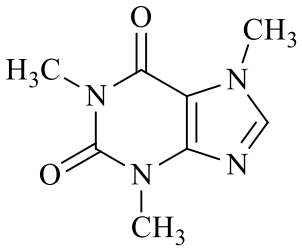
Met-Phe



**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

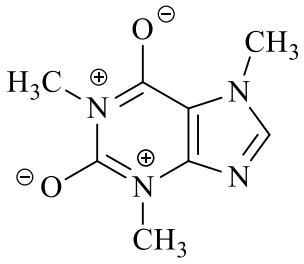
**Marks 5**

- Shown below is the structure of caffeine.

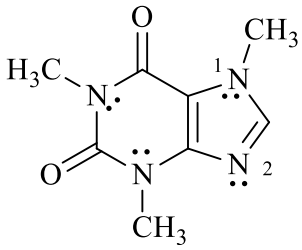


caffeine

Draw the structure of a 10 π–electron aromatic resonance contributor to the structure of caffeine.



Only one of the nitrogen atoms in caffeine is basic. Indicate which of the nitrogen atoms is basic and explain why it is basic and why the others are not.



**$N^1$ is $sp^2$ hybridised. The "lone pair" is in the unhybridised *p* orbital and is part of the aromatic system so is unavailable to act as a proton acceptor.**
**$N^2$ is also $sp^2$ hybridised, but here the lone pair is in the $sp^2$ hybrid orbital pointing away from the ring system. It is able to act as a proton acceptor, so this N is basic.**

**The "lone pairs" on the two N's in the 6-membered ring are (at least partially) involved in the resonance stabilisation of the amides and the aromatic system as shown in the first part of this question. These electrons are delocalised and hence not available to act as proton acceptors.**

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