

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2015, for Internal Students of
the Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the
Associateship**

1A PAPER TWO

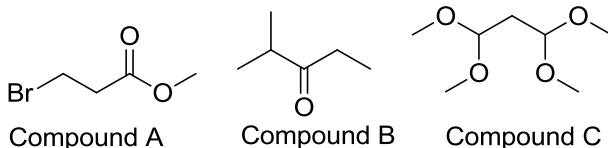
Friday 16th January 2015, 14:00-16:15

**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

1.I9 – Spectroscopy and Characterisation

Answer part a) and **EITHER** part b) **OR** part c) of this question.

- a) Sketch and explain the ^1H NMR spectra which would be observed for compounds A, B and C (the structures are illustrated below). Describe the spectra, paying attention to the chemical shifts, integrals and multiplicity of the resonances. [Assume that ^1H , $I=1/2$, 100% abundant and all other nuclei are NMR inactive. Coupling occurs through 3 bonds or fewer].



(15 marks)

- b) Answer **BOTH** parts of this question.

- i) The infra-red spectra of CDCl_3 and CHCl_3 show absorptions at 2256 cm^{-1} (CDCl_3) and 3020 cm^{-1} (CHCl_3). Assign the absorptions. Calculate the force constants for the bonds and discuss the differences between the absorptions. [$\text{D} = ^2\text{H}$]

(8 marks)

- ii) Explain why CDCl_3 is a commonly used solvent for ^1H NMR spectroscopy.

(2 marks)

- c) Compound D shows the following spectroscopic characteristics.

The IR spectrum shows strong absorptions at 2900 and 1720 cm^{-1} .

The ^1H NMR spectrum shows a quartet (1:3:3:1) at 2.4 ppm , of relative intensity 2, a singlet at 2.1 ppm , of relative intensity 3, and a triplet (1:2:1) at 1.1 ppm , of relative intensity 3.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows signals at 8 , 29 , 37 and 210 ppm .

The mass spectrum shows a molecular ion at m/z : 72 amu . There are also major fragmentation peaks at m/z : 57 , 43 and 29 amu .

Identify D and explain the data. Your answer should include a full assignment of all the data and a sketch of the structure.

(10 marks)

1.O1 – Structure, Mechanism and Reactivity

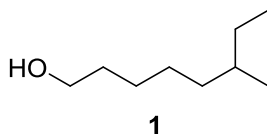
NB. 'Half a question' (out of 12.5 marks).

This is a multiple choice question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

Answer **ALL** parts of this question.

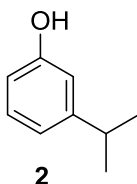
- 1) What is the systematic name for the compound with structure **1**?

(2 marks)



- A) 6-Ethylheptan-1-ol
B) 3-Methyloctan-8-ol
C) 2-Ethylheptan-7-ol
D) 6-Methyloctan-1-ol
- 2) Which of the following is **NOT** a reasonable name for compound **2**?

(2 marks)

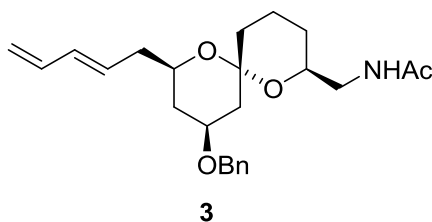


- A) 3-Isopropylphenol
B) *meta*-Isopropylphenol
C) *para*-Isopropylphenol
D) 3-(2-propyl)hydroxybenzene

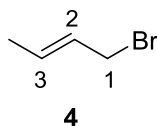
QUESTION CONTINUED OVERLEAF

- 3) Which of the following sets of functional groups is present, amongst others, in compound **3**?

(2 marks)



- A) Acetal, amide, ether, conjugated diene
- B) Benzene ring, amine, ether, conjugated diene
- C) Amide, ester, acetal, non-conjugated diene
- D) Amine, ester, ether, conjugated diene
- 4) Which statement is correct with regards to the predominant reactivity of compound **4**? (3 marks)

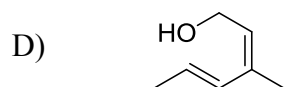
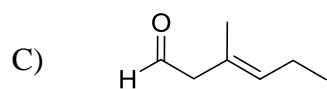
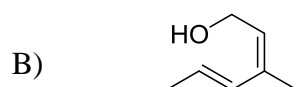
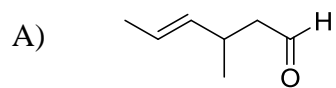
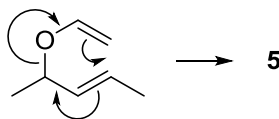


- A) Compound **4** is likely to act as an electrophile. The carbon labelled 1 is an electrophilic centre, but not carbons 2 or 3.
- B) Compound **4** is likely to act as a nucleophile, because of the presence of non-bonding electron pairs on the bromine atom.
- C) Compound **4** is likely to act as an electrophile. The carbon labelled 2 is an electrophilic centre.
- D) Compound **4** is likely to act as an electrophile. The carbons labelled 1 and 3 are both electrophilic centres.

QUESTION CONTINUED OVERLEAF

- 5) Which of the following structures correctly represents the product **5** from the reaction mechanism drawn below?

(3.5 marks)



1.O6 – Stereochemistry

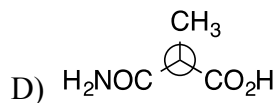
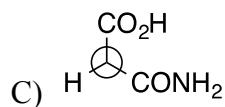
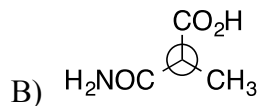
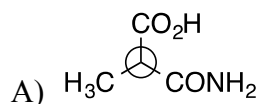
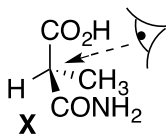
NB. 'Half a question' (out of 12.5 marks).

This is a multiple choice question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

Answer ALL parts of this question.

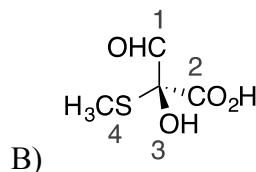
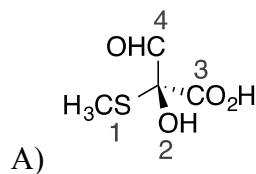
1) Based on diagram X, which is the correct Newman projection?

(2 marks)

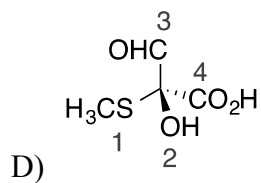
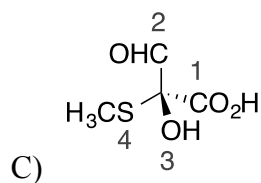


2) For which one of the molecules below has the correct order of priority been assigned?

(2 marks)

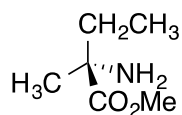


QUESTION CONTINUED OVERLEAF



3) What is the correct stereochemical assignment of the molecule below?

(3.5 marks)



A) achiral

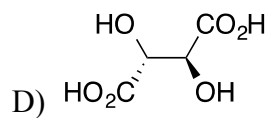
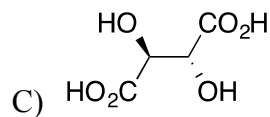
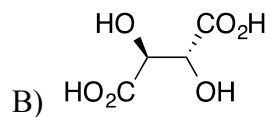
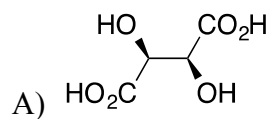
B) *meso*

C) *S*

D) *R*

4) Which of the following molecules is chiral and dissymmetric?

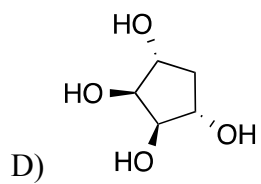
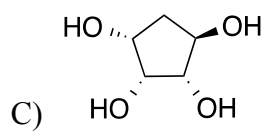
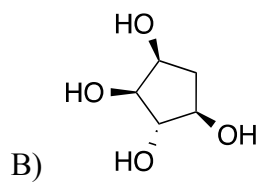
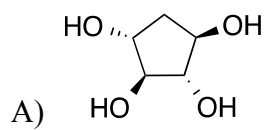
(2.5 marks)



QUESTION CONTINUED OVERLEAF

5) Which of the following molecules is *meso*?

(2.5 marks)



1.P4 – Spectroscopy

Answer part a) and **EITHER** part b) **OR** part c) of this question.

The following facts may be useful:

Charge on an electron is $1.602 \times 10^{-19} \text{C}$

Planck's constant has a numerical value of 6.626×10^{-34}

Speed of light has a numerical value of 2.998×10^8

(Note that some units have been omitted)

a) Answer **ALL** parts of this question.

- i) For the following equations relating to the properties of light, define the meaning of each symbol

$$E = h\nu; c = \lambda\nu$$

(2 marks)

- ii) What are the conventional units for each symbol in the equations of a) i)?

(2 marks)

- iii) The carbonyl stretch of benzaldehyde absorbs electromagnetic radiation at a wavelength of 5.845 microns. Calculate the following.

- a. The energy of a 5.845 μm photon in units of Joules.

(1 mark)

- b. The energy of a 5.845 μm photon in units of electron volts.

(1 mark)

- c. The wavenumber corresponding to 5.845 μm .

(1 mark)

- iv) If a beam of 5 μm photons is shone on the molecule, it will not be absorbed by the carbonyl stretch. Why not?

(2 marks)

- v) Will increasing the intensity of the beam of 5 μm photons from a hot wire source cause the carbonyl stretch to absorb the photons? Explain your reasoning.

(2 marks)

- vi) Sketch an absorption spectrophotometer, identifying the key components and their function.

(4 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **BOTH** parts of this question.

The Beer-Lambert law is: $I = I_0 10^{-\epsilon [J] L}$

i) Define all of the symbols in the Beer-Lambert law above. (2 marks)

ii) Derive the Beer-Lambert law, starting from first principles. (8 marks)

c) Answer **ALL** parts of this question.

The Boltzmann distribution is: $\frac{N_i}{N_j} = \exp\left(-\frac{\Delta E}{k_b T}\right);$

The Boltzmann constant is 1.38×10^{-23} J/K; $e = 2.72$

i) Define all of the symbols in the Boltzmann distribution. (2 marks)

ii) Sketch two graphs, one of the Boltzmann distribution as a function of ΔE at room temperature (298 K) and the other of the distribution as a function of T at a ΔE of 0.025 eV. Mark on both graphs any key features such as axis intercepts, limiting values and the values for which $N_i/N_j = e^{-1}$. (4 marks)

iii) Explain why the strength of the applied magnetic field affects the sensitivity of NMR spectroscopy. (2 marks)

iv) $k_B T$ at room temperature is $\sim 6 \times 10^{-21}$ J. How much more sensitive would a 1 GHz NMR spectrometer be when compared with a 500 MHz spectrometer? Explain your reasoning. (2 marks)