IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2009, for Internal Students of the
Imperial College of Science, Technology and Medicine

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

ADVANCED CHEMISTRY THEORY IIIB

Paper 3

Friday 8th May 2009, 2.00 – 5 pm

Answer ONE question from each attended course

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

3.I8 – Solvents and Solvent Effects

Answer part (a) **AND** part (b) and **EITHER** part (c) **OR** part (d).

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

In most industrial settings a process solvent is exposed to ambient moisture from the air. This can have a measurable effect on the solvent's solvatochromic properties as water in the solvent can interact with the dyes. State whether **EACH** of the following would increase or decrease upon exposure to water:

(i)   The π^* value of *N,N*-dimethylformamide

(ii)   The α value of *N,N*-dimethylformamide

(iii)   The β value of *N,N*-dimethylformamide

(iv)   The π^* value of acetonitrile

(v)   The α value of acetonitrile

(vi)   The β value of acetonitrile

(6 marks)

(b)   Answer **ALL** parts of this question.

The following data were obtained for the hydrolysis of benzonitrile in different solvents at 25 °C:

Solvent	π^*	$k\ (s^{-1})$
Hexane	0	1
Toluene	0.5	128
DMSO	1.0	

(i) Assuming the data fit a typical LSER with π^* as the only parameter, what will be the reaction rate in DMSO? Show your workings.

(6 marks)

(ii) A typical organic reaction has an activation energy of around 50 kJ/mol, leading to the common 'rule of thumb' that the reaction rate doubles every 10 degrees. If this rule holds true for this reaction, to what temperature would the reaction in hexane have to be heated in order to obtain a rate of 128 s^{-1} (i.e. the same rate as for toluene at 25 °C)?

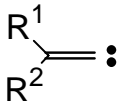(2 marks)

QUESTION 3I8 b) CONTINUED OVER

(iii)What temperature will yield the same rate in hexane as for the reaction in DMSO at 25 °C?

(1 mark)

(iv) Compare these two temperatures against the differences in π^* value. What does this tell you about the relative effects of solvent polarity and temperature on reaction rate for this reaction?

(2 marks)

(c) Describe how solvophobic interactions arise in solution. When are such interactions likely to arise? What will be the sign and relative magnitude of the thermodynamic parameters for solvation (ΔH, ΔG, $T\Delta S$)? Are the solvophobic interactions mainly driven by enthalpic or entropic effects?

(8 marks)

(d) For a simple Diels-Alder reaction, and making reference to its mechanism, explain the predicted effect of changing solvent. How has the Diels-Alder reaction been used to generate the empirical polarity scale Ω? How will Ω vary with solvent polarity?
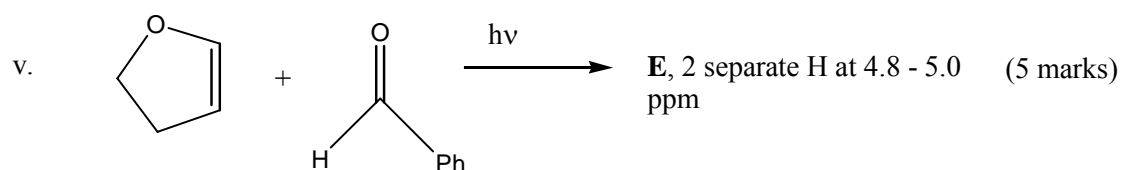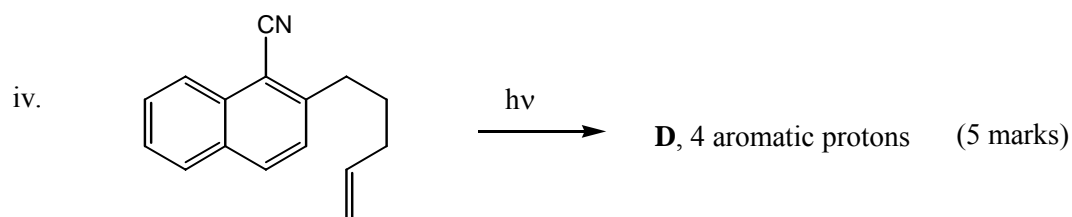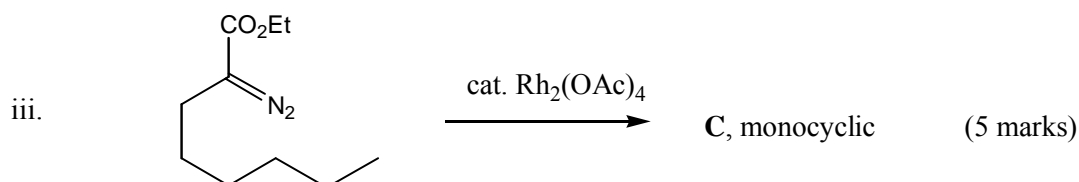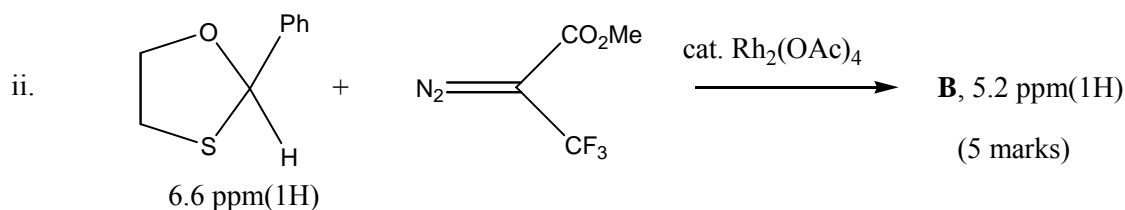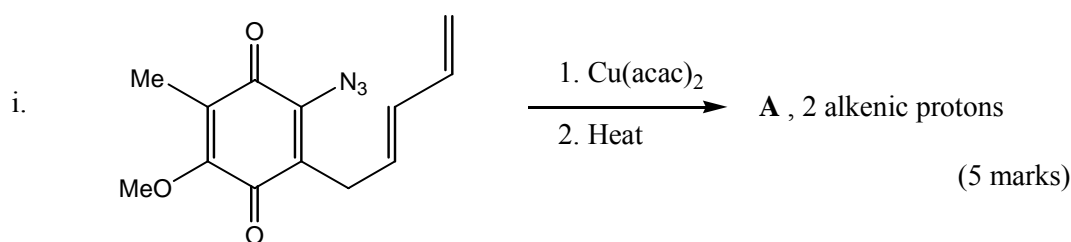
(8 marks)

3.O5 Reactive Intermediates 2 (Carbenes, Nitrenes, Photochemistry)

Answer part (a) and part (b)

Part (a)   Give **TWO** methods for the synthesis of enylidenes of the type:

$$R^1 \diagdown \diagup : \\ R^2$$

Indicate the limitation of each method   (10 marks)

Part (b)   Give the products for **THREE** of the following reactions, noting carefully (a) the spin multiplicity of the reactive intermediate, (b) any other intermediates beyond the carbene, nitrene or photoexcited state and (c) any important regiochemical or stereochemical aspects.

i.

$$\xrightarrow[\text{2. Heat}]{\text{1. Cu(acac)}_2} \textbf{A} \text{ , 2 alkenic protons}$$

(5 marks)

ii.

6.6 ppm(1H) $\xrightarrow{\text{cat. Rh}_2(\text{OAc})_4}$ **B**, 5.2 ppm(1H)

(5 marks)

iii.

$$\xrightarrow{\text{cat. Rh}_2(\text{OAc})_4} \textbf{C}\text{, monocyclic}$$ (5 marks)

iv.

$$\xrightarrow{h\nu} \textbf{D}\text{, 4 aromatic protons}$$ (5 marks)

v.

$$\xrightarrow{h\nu} \textbf{E}\text{, 2 separate H at 4.8 - 5.0 ppm}$$ (5 marks)

3.O10 – Molecular Modelling

Answer **EITHER** part a) **OR** part b).

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

Describe the characteristic features of the molecular mechanics method, including in your answer no more than any **two** of the following aspects:

   i)   An analysis of the four basic equations defining a mechanics force field, including one major limitation and one major strength compared to quantum-mechanical based modelling.

   ii)   How the molecular mechanics steric energy obtained by the sum of the four terms noted above can be used to predict a geometry of a molecule.

   iii)   One case study only, in which the molecular mechanics method can be used to probe the origins of a molecular binding or stability effect, including in your discussion any one aspect which the mechanics method is particularly suited to model, and any one aspect where the mechanics model may be limited. Exact drawings of a complex molecule are not needed, just schematics.

(25 marks)

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

The Ziegler-Natta process involves the polymerisation of e.g. propene, using a titanium catalyst on a magnesium chloride support to give polypropene. Discuss the mechanism of this reaction, and in particular, focus on no more than any **four** of the following aspects:

   i)   What is meant by stereoregular polypropene?

   ii)   What role does the magnesium chloride support play in the mechanism?

   iii)   What role do agostic interactions play in the mechanism?

   iv)   Illustrate using simple arrow pushing what the nature of the basic C-C bond forming transition state is.

   v)   Discuss in terms of the occupancy of the methyl group in propene in the "active site transition state", how this group results in stereocontrol of the polymerisation.

(25 marks)

3.P6 – Molecular Electronic Materials

Answer part a) and **EITHER** part b) **OR** part c).

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

   i) With the aid of a suitable diagram explain the meaning of the following solar cell parameters:

   a) Short circuit current,
   b) Open circuit voltage,
   c) Fill factor

   (1.5 marks)

   ii) The probability of photon to electron conversion [P(photon → electron)] for a solar cell is given by the following equation:

   $$P(photon\ to\ electron) = (1 - e^{-kx}) \times P(CS) \times P(1 - CR)$$

   Explain the physical meaning of each term in the above equation and describe how you would optimize each of the terms.
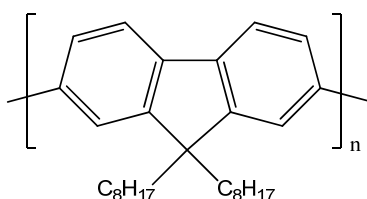
   (7 marks)

   iii) A polymer solar cell is fabricated by sandwiching a thin film of a semiconducting polymer between a transparent indium tin oxide (ITO) electrode and an aluminium electrode. The work functions of ITO and aluminium are 4.7 eV and 4.3 eV respectively. The solar cell device is illuminated by monochromatic light of 550 nm wavelength with an intensity of 25 mW/cm^{-2}. Estimate the maximum theoretical power conversion efficiency that the device can deliver under these illumination conditions. State clearly any assumptions in your calculation. Comment on your answer.

   (4 marks)

   iv) A time-of-flight (ToF) experiment was conducted to determine the hole-mobility of poly-fluorene (structure of polymer is shown below). A 500 nm thick film of the polymer was sandwiched between two electrodes. A transit time (τ) for the holes was found to be 2 microseconds when 1 volt was applied across the electrodes. Using this data calculate the hole mobility for poly-fluorene. Suggest a chemical modification you could make to the structure of the polymer to improve its hole mobility.

   (3.5 marks)

C_8H_{17} C_8H_{17}

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

   i)   With the aid of a suitable diagram explain how molecular dopants may be used to tune the emission colour of a polymer light emitting diode.

   (3 marks)

   ii)   If the fluorescence quantum efficiency for a given polymer is 80% what is the maximum external quantum efficiency achievable in an organic light emitting diode? State clearly any assumptions in your calculation. Comment on your answer.

   (3 marks)

   iii)   Describe the Fowler-Nordheim mechanism for charge injection from a metal electrode into a polymer film.

   (3 marks)

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

   i) Explain what is meant by exciton diffusion length.

   (1 marks)

   ii) Explain why the exciton diffusion length in a polymer film is likely to be larger in the plane of the film than in the perpendicular direction.

   (6 marks)

   iii) With the aid of a suitable diagram explain what is meant by an 'ohmic contact' in an organic light emitting diode.

   (2 marks)

3.P8 – Computational Chemistry and Molecular Modelling

Answer any **TWO** of the three parts a), b) and c)

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

Read the following paragraph – taken from the Computational Methods section of a published paper – and answer i) to iv) below:

"All transition structures were initially optimized with AM1, then reoptimized using B3LYP/6-31G*. Harmonic frequency calculations were carried out at all computed transition structures. Each was shown to have only one vibrational mode with an imaginary frequency. These were animated, to confirm that they were transition structures for the reactions being investigated."

i) Explain how a geometry optimization is carried out. What determines when a geometry optimization has converged? Why are transition structures typically harder to optimise than minima on potential energy surfaces?

(5 marks)

ii) What would be the advantage of using a semi-empirical molecular orbital method such as AM1 initially, as in the above study? Are there any potential disadvantages?

(2 marks)

iii) Explain what a 6-31G* basis set is. What does such a basis set consist of for an oxygen atom? Why are 6-31G* basis sets often used for molecular structure calculations?

(3.5 marks)

iv) Why is it important to check that a transition structure has only a single imaginary vibrational frequency?

(2 marks)

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

The figure below shows how the numerical solution of the electronic Schrödinger equation for a molecule can be made to approach the exact solution.
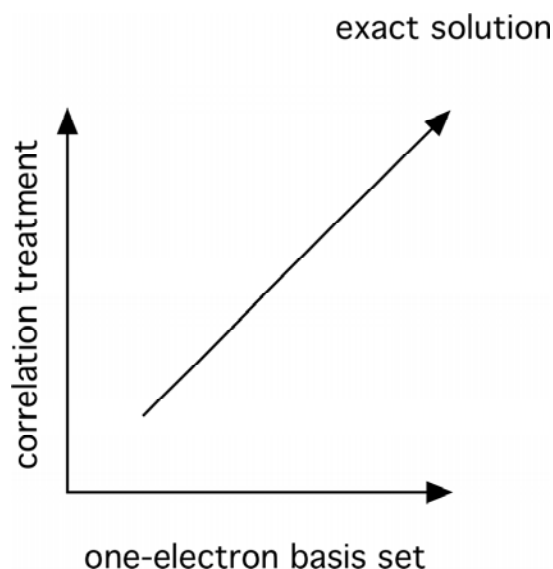
i) Briefly explain what 'Self Consistent Field' means when calculating molecular orbitals.

(2 marks)

ii) What is a minimal basis set? Where would a Hartree Fock Self Consistent Field (SCF) calculation with a minimal basis set appear on the above graph?

(2 marks)

iii) Where on the above graph would a Hartree-Fock MO calculation with a complete basis set appear? What are the problems associated with carrying out such calculations?

(2.5 marks)

iv) Define electron correlation energy with respect to the above figure.

(2 marks)

v) Explain why *dynamic* electron correlation is neglected in an SCF MO calculation. For a closed shell molecule, how can it be systematically treated, using an SCF calculation as a reference?

(2 marks)

vi) What is the significance of the diagonal line indicated on the figure, and how can this be used in practice?

(2 marks)

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

For the isomerization reaction of cyclopropane to propene:

i) How do the molecular mechanics (MM) and self-consistent field molecular orbital (SCF MO) methods for calculating total energies differ?

(3 marks)

ii) For which method would connectivity between atoms need to be specified explicitly, and why? What effect does this have on the calculated relative energies of cyclopropane and propene?

(3 marks)

iii) Which method – MO or MM – would give more accurate bond lengths? Over what range of geometries would the MM and SCF MO methods be applicable for the above isomerization reaction? Would either be able to describe the transition structure(s)?

(6.5 marks)

3.P10 – Soft Condensed Matter

Answer part (a) and **EITHER** part (b) **OR** part (c).

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

i) Viscoelasticity is one of the main properties of soft materials. Define this concept and sketch the dependence of the strain with time in a viscoelastic material. Assume that shear stress is constant. Mark in your diagram the relaxation time.

(4 marks)

ii) Polymer coatings offer an effective approach to stabilize colloidal dispersions. What is the physical principle of this method? What conditions do the polymers need to fulfill to be effective at stabilising the dispersions?

(3.5 marks)

iii) The diffusion coefficient of a colloidal particle can be described by the Stokes-Einstein equation,

$$D = \frac{k_B T}{6\pi \eta a}$$

Explain the physical origin of this equation and estimate the time taken for a polymer particle of 1 μm diameter in water at room temperature to diffuse a distance equal to its own diameter.

You may take the water viscosity as 10^{-3} Pa s

(4.5 marks)

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

The free energy of homogeneous nucleation of a spherical crystal in its melt can be written as:

$$\Delta G(r) = \Delta G_b V(r) + \gamma A(r)$$

i) Sketch the dependence of the free energy with the radius of the crystal, r. How does the nucleation rate change with the crystal-liquid surface tension?

(4 marks)

ii) Show that the critical radius and the free energy barrier for nucleation are given by: $r^* = \frac{-2\gamma^3}{\Delta F_v}$, $\Delta G^*(r^*) = \frac{16}{3}\pi \frac{\gamma^3}{\Delta G_b^2}$

(5.5 marks)

iii) Homogeneous nucleation processes often require strong undercooling, whereas heterogeneous nucleation occurs at temperatures very close to the melting temperature. Explain this observation.

(3.5 marks)

QUESTION 3P10 CONTINUES OVER

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

The freely jointed chain model (FJC) can be used to quantify the end to end distance of a polymer from its degree of polymerization.

    i)   Using the FJC model show that the end to end distance of a polymer made up of N links each of which with length a is $\sqrt{<r^2>} = \sqrt{N}a$

                                                                        (6 marks)

    ii) Using the FJC model estimate the random coil size of a DNA fragment of length 16 micrometers. Assume that the length of the links in the FJC model is 100 nm.

                                                                        (3.5 marks)

    iii) A single molecule experiment shows that a force has to be applied to stretch a DNA fragment beyond its natural random coil end-to-end distance. This force is proportional to the temperature. Explain this observation.

                                                                        (3.5 marks)