

University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 464 CHEM 474
Paper Title:	Contemporary Topics in Chemistry Special Topic

Time Allowed: **THREE HOURS**

Number of pages: **EIGHT**

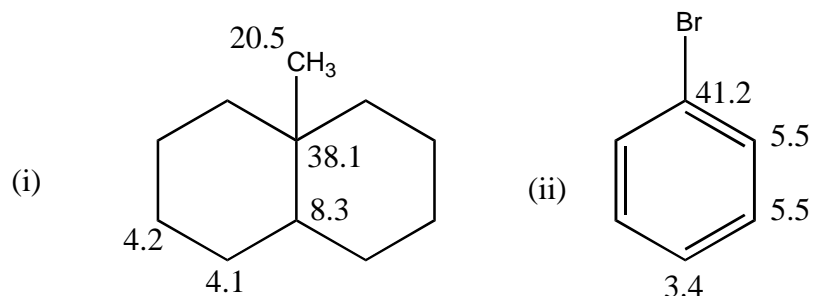
Answer **FIVE** questions out of **SEVEN**.

All questions are of equal value

TURN OVER

1. (a) (6 marks)

Account for the differences within each structure that are responsible for the measured ^{13}C T_1 values(s) shown for each of structures (i) and (ii).



(b) (14 marks)

In ^1H -NMR spectroscopy, a problem is frequently encountered in which multiplets from protons in a structure are overlapping due to similarities in chemical shifts.

Discuss what structural information could be extracted from these multiplets if they could be resolved from each other.

Describe a strategy, involving as many 1D- and 2D-NMR experiments as possible, that could be used to reveal each multiplet separated from its overlapping partners. For each experiment that you refer to, briefly describe the underlying principles of the technique used in the experiment.

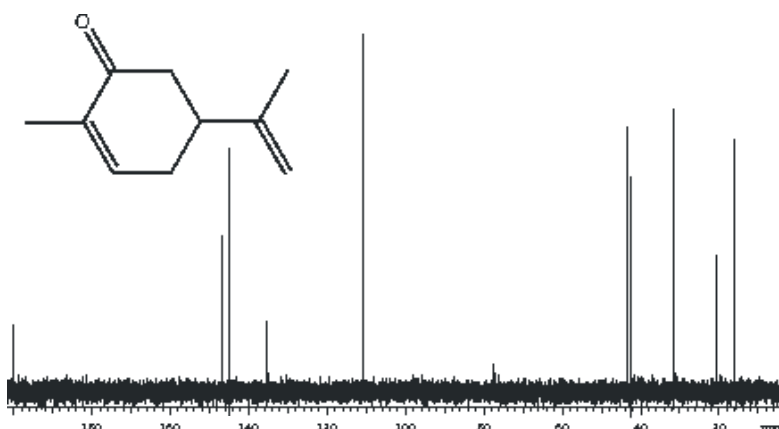
TURN OVER

2. (a) (14 marks)

The ^{13}C -NMR spectrum of carvone (below) was obtained using the repetitive pulse Fourier transform method, with the following acquisition parameters:

Acquisition time	1.3 s
Pulse delay	0 s
Flip angle	54°
Temperature	296 K
Number of transients	32

Explain why the peaks show different intensities, and describe methods for obtaining a spectrum in which all peaks would be of equal intensity for equal numbers of carbons.



(b) (6 marks)

Describe methods that could be used to determine which of the signals in the ^{13}C -NMR spectrum of carvone (above) arise from CH_3 , CH_2 , CH or C type carbons. Comment on the advantages and disadvantages of the methods you describe.

3. In radical polymerization kinetics there have recently been major advances made in the understanding of the INITIATION, PROPAGATION and TERMINATION reactions.

Discuss these advances in **TWO** of these three cases.

In your discussion you should outline:

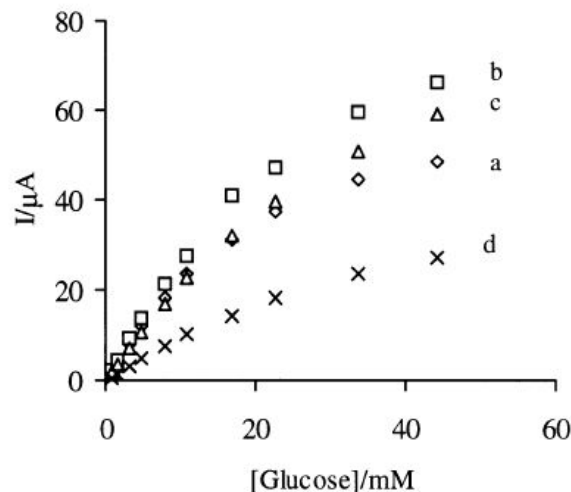
- the previous understanding that prevailed;
- the recent experimental data that called this previous understanding into question;
- the experimental technique by which these recent data were obtained; and
- the more refined understanding that has now been arrived at.

(Of course your discussion may range wider than this if you so wish.)

4. (a) Biosensors have the potential to allow analyses to be performed by the general public without any training in measurement science. Explain, in general terms, how this is achieved with a biosensor and discuss what criteria the device must fulfil to be able to be reliably used by the general public. Give an example of a biosensor that fulfils these criteria and explain how it works.
- (b) The sensitivity and dynamic range of enzyme electrodes are affected by a number of parameters. What are these parameters and how do variations in these parameters influence the dynamic range and sensitivity of an enzyme electrode?
- (c) Explain how a recognition molecule, such as an enzyme, strand of DNA, or peptide, can be attached to a gold surface by a self-assembled monolayer. Include diagrams where appropriate and ensure that the functional groups through which links are made are identified. Discuss the reasons why a longer or shorter linking molecule might be chosen.

5. (a) What are the two main classes of biosensor? Give an example of each class. Explain how the link between biorecognition and transduction is achieved; that is, how your example of each class of biosensor works.
- (b) (i) What are the important criteria immobilisation must achieve in any biosensor?
- (ii) The calibration curves below are from the first paper you studied in class. They show the variation in response of a glucose oxidase based enzyme electrode as the amount of glutaraldehyde cross-linking agent used is increased from **a** to **d**. In **a** no glutaraldehyde is used.

Explain why the current signal first increases with the addition of glutaraldehyde and then decreases when more glutaraldehyde is used.

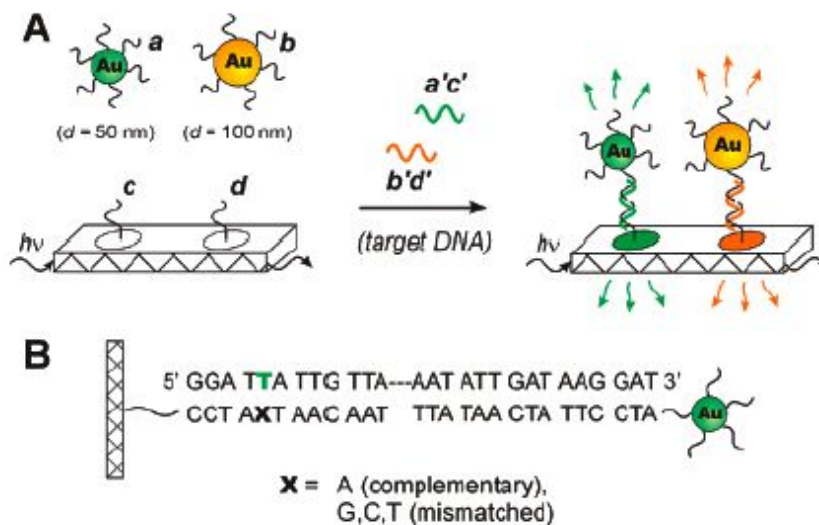


- (c) In scheme 1 (on the following page), the biosensor relies on a sandwich assay for detecting DNA. Answer the following in relation to this biosensor
- (i) Explain how this sandwich assay is performed. What are the advantages and disadvantages of using a sandwich configuration with regards to ease of use and biosensor response time?
- (ii) The longer the sequences of DNA, the more favourable the thermodynamics of binding. What would be the effect of using longer strands of DNA on the concentration range in which the DNA biosensor would operate?

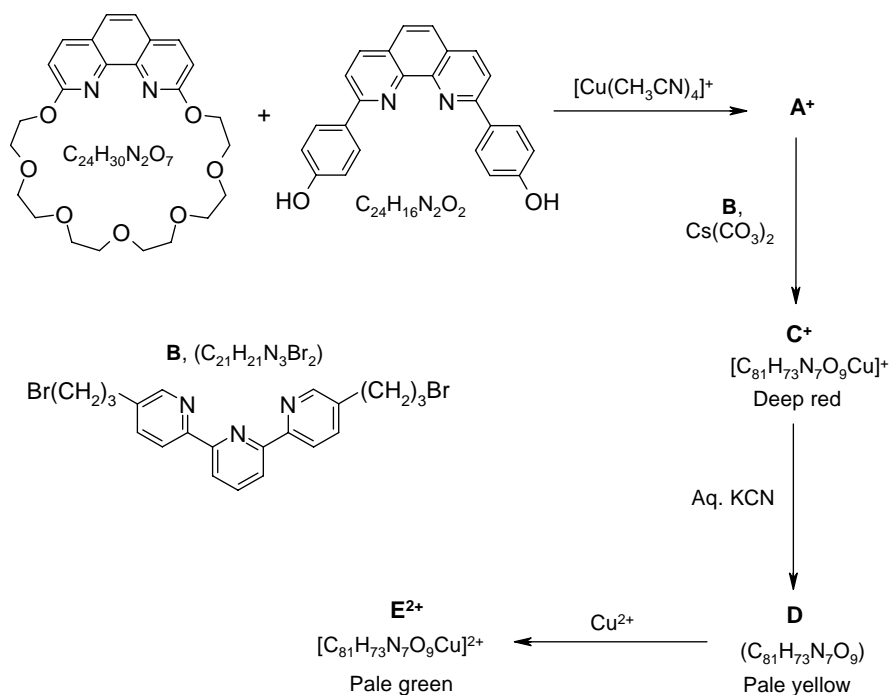
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Question 5 continued

Scheme 1

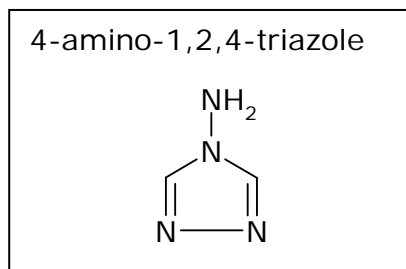
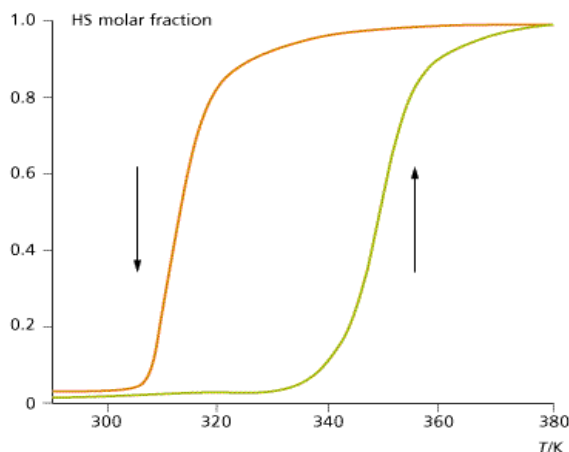


6. (a) What is a [2]-rotaxane? By using appropriate examples to illustrate your answer, discuss the synthetic strategies employed in the preparation of [2]-rotaxanes.
- (b) **A**⁺, **C**⁺ and **D** all exhibit well resolved ¹H-NMR spectra in the 0-10 ppm range; **E**²⁺ has a magnetic moment of 1.73 B.M. Schematically illustrate the most likely structures for **A**⁺, **C**⁺, **D** and **E**²⁺.

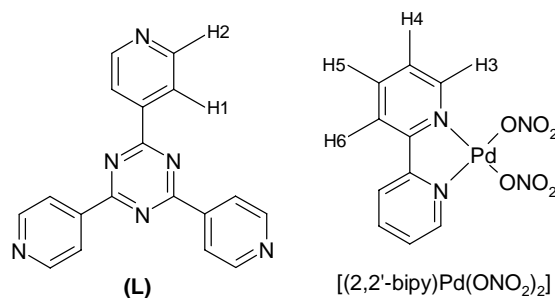
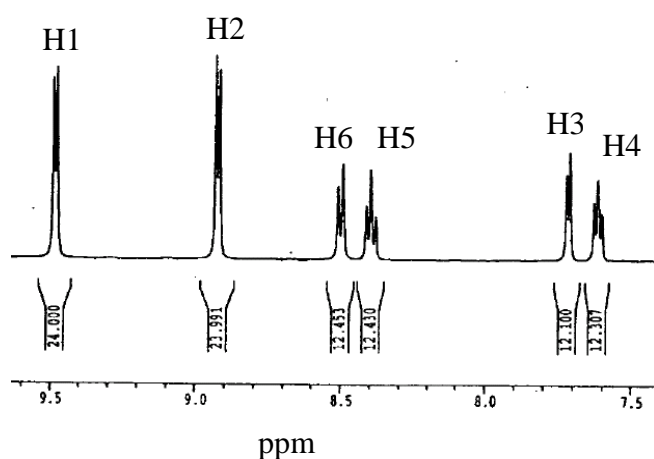


TURN OVER

7. (a) Shown below is the temperature-dependence of the high-spin (HS) molar fraction (γ_{HS}) of $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ (NH_2trz = 4-amino-1,2,4-triazole). Interpret this figure as fully as possible accounting for the spin behaviour and suggesting possible structures for this compound. Explain, with reasoning, any technological applications within which this compound might find use.



- (b) A crystalline product (**A**) formed in quantitative yield when $[(2,2'\text{-bipy})\text{Pd}(\text{ONO}_2)_2]$ (shown below) and 2,4,6-tri(4-pyridyl)-1,3,5-triazine (**L**, shown below) were combined in water in a 3:2 stoichiometry. A $^1\text{H-NMR}$ spectrum (shown below) indicated the presence of a single product in D_2O solution. Suggest, with the aid of diagrams, a plausible structure for **A** that is consistent with these data.



END OF PAPER