CHEMISTRY 2

PAPER 1

Monday 14th August 2006, 9.30 am – 12.30 pm

Answer ALL questions.

Please answer each question in a separate book.

[The bracketed numbers shown against part of a question are only a guide to the likely allocation of marks in that question.]

This examination will be marked anonymously.

**Please enter your student examination number on each answer book.**

A data sheet is provided with this examination paper.

Unassembled molecular model kits may be used in this examination.

Only the calculator provided may be used in this examination.

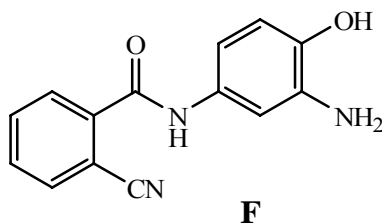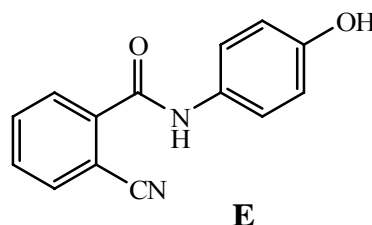1. Answer **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).

(a) Draw all the resonance structures of the carbocation intermediates that might reasonably be generated by electrophilic substitution reactions of 2-cyano-*N*-phenylbenzamide, **A**. Then, using the resonance structures, predict the position(s) of electrophilic substitution of benzamide, **A**. **[10]**

A
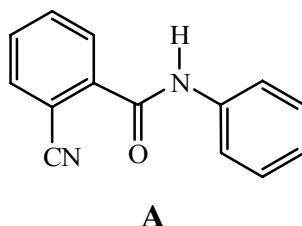
(b) Devise syntheses for *o*-cyanobenzoic acid, **B**, and aniline, **C**, using benzene (C_6H_6) or toluene ($C_6H_5CH_3$) as starting materials and any necessary reagents. Assume that *ortho* and *para* isomers can be separated. Then, suggest a way to prepare benzamide, **A**. **[10]**

B

C
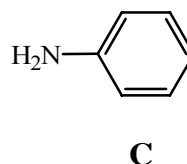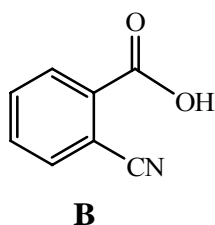
(c) Outline syntheses of **D**, **E** and **F** commencing with benzamide, **A**. Use any appropriate reagents and assume that *ortho* and *para* isomers can be separated. **[10]**

D

E

F
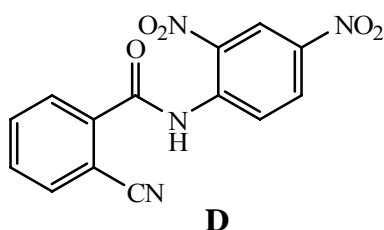
2.   Answer **all** of part (a) and **ANY TWO** of parts (b), (c) **and** (d).

(a)   Draw a fully labelled molecular-orbital diagram for the molecule N_2, showing all valence-shell molecular orbitals and the atomic orbitals from which they are derived, and indicate how the electrons are distributed among the molecular orbitals.   **[8]**

(b)   (i)   Explain the meaning of the term *degenerate orbitals*. Illustrate your answer with an appropriate diagram for the molecule N_2.

      (ii)   Sketch the anti-bonding σ orbital formed from a $2p$ orbital on each nitrogen atom of the molecule N_2.

      (iii)   Explain, giving reasons, what would happen to the vibrational frequency for stretching of the N-N bond when an electron is added to the N_2 molecule, and when an electron is removed.   **[6]**

(c)   (i)   Explain the origin of *vibrational fine structure* in the photo-electron spectra of diatomic molecules.

      (ii)   Describe what you would observe in the He(I) photo-electron spectrum of N_2.   **[6]**

(d)   (i)   Explain how and why the molecular-orbital diagram for CO would differ from that for N_2 in part (a).

      (ii)   Explain briefly how the similarities and differences of the diagrams for N_2 and CO are reflected in their abilities to act as ligands with transition metals.   **[6]**

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

(a) For the complex $[Fe(CN)_6]^{3-}$:

(i) draw a diagram to show the energy splitting of the $3d$ orbitals, including appropriate symmetry labels for the orbitals, the occupancy of the orbitals with electrons and the crystal-field splitting parameter, **[7]**

(ii) calculate the crystal-field stabilisation energy in multiples of the crystal-field splitting parameter, **[3]**

(iii) calculate the spin-only magnetic moment. **[2]**

(b) (i) Give one example each of a π-donor ligand, π-acceptor ligand and σ-only ligand. For each kind of ligand, give one example of a complex formed by the ligand. **[6]**

(ii) Explain why nickel forms the tetracarbonyl $[Ni(CO)_4]$ whereas iron forms the pentacarbonyl $[Fe(CO)_5]$. **[2]**

(c) (i) Explain the relative rates of reaction expected for a given transition-metal ion with a macrocyclic ligand or an analogous open-chain ligand. **[2]**

(ii) Show with the aid of a diagram why $[Co(en)_3]^{2+}$ has two enantiomers $[en = NH_2CH_2CH_2NH_2]$. **[2]**

(iii) Explain why Zn(II) complexes are typically colourless whereas Cu(II) complexes are coloured. **[2]**

(iv) Explain why the metal orbital angular moment is usually neglected when calculating the magnetic moment of a transition-metal complex. **[2]**

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

(a) A particle of mass m is confined to a three-dimensional cubic box of length L. The allowed energy levels are determined by the equation

$$E = \frac{\left(n_x^2 + n_y^2 + n_z^2\right)h^2}{8mL^2}$$

where $n_x, n_y, n_z = 1,2,3,\ldots$ are quantum numbers.

(i) Explain why none of the quantum numbers can be equal to zero. **[3]**

(ii) Sketch an energy-level diagram for the particle, including all quantum states up to $n_x = n_y = n_z = 2$. Indicate the zero of energy, the zero-point energy, and, for each energy level, the degeneracy. **[5]**

(iii) Calculate the wavelength of radiation corresponding to the lowest-energy transition for an electron confined to a cubic box of length $L = 10$ nm. **[2]**

(b) The Schrödinger equation for the particle in the cubic box from part (a) is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi = E\Psi .$$

The wavefunctions are given by

$$\Psi(x,y,z) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right)\sin\left(\frac{n_z \pi z}{L}\right).$$

(i) Show that the wavefunctions satisfy the Schrödinger equation, and hence confirm the energy-level formula given in part (a). **[6]**

(ii) Explain the significance of the prefactor $\sqrt{8/L^3}$ in $\Psi(x,y,z)$. **[2]**

(iii) Determine the average position and momentum of the particle. **[2]**

(c) The allowed energy levels for the electron in a hydrogen atom are given by

$$E_n = -\left(\frac{R_{\mathrm{H}}}{n^2}\right)$$

where $R_{\mathrm{H}} = 13.6$ eV is the Rydberg constant, and $n = 1,2,3,\ldots$

(i) Sketch an energy-level diagram for the electron. The diagram should include all distinct quantum states in the first three energy levels, the degeneracy of each of those energy levels, and the zero of energy. **[5]**

(ii) List the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the type of orbital (e.g. 1s) for each of the quantum states belonging to the energy level with $n = 3$. **[3]**

(iii) Calculate the frequency of radiation required to ionise a hydrogen atom initially in its ground electronic state. **[2]**

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

    (a) (i)   In which region of the electromagnetic spectrum do rotational transitions occur? **[2]**

        (ii) State which of the following molecules will show a rotational spectrum:
Cl_2 NO   HF.
Justify your answer. **[3]**

        (iii) Sketch the multiplet structure of the CH_3 resonance in the ^1H NMR spectrum of diethyl ether, $(CH_3CH_2)_2O$. Explain your answer. **[5]**

    (b) The wavenumbers of the lines observed in the emission spectrum of the Li^{2+} ion can be calculated using the following equation,

$$\bar{v} = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where Z is the atomic number, $R = 109729$ cm^{-1} is the Rydberg constant for Li^{2+}, and n_1 and n_2 are principal quantum numbers.

        (i)   Calculate the wavenumber of the first line in the Paschen series of transitions in the emission spectrum of Li^{2+}. **[4]**

        (ii) Explain which of the following transitions will be observed in the emission spectrum of Li^{2+}: $4p$ to $3d$; $3d$ to $1s$; $3p$ to $2s$; $4p$ to $3s$. **[3]**

        (iii) Identify the transition in part (b)(ii) that belongs to the Balmer series. **[1]**

        (iv) Identify the transitions in part (b)(ii) that emit light of the same wavelength. **[2]**

    (c) The $^1H^{35}Cl$ molecule absorbs infrared radiation of wavelength 3.346 μm.

        (i)   Calculate the vibrational frequency of the $^1H^{35}Cl$ bond. **[2]**

        (ii) Calculate the force constant of the $^1H^{35}Cl$ bond. **[5]**

        (iii) Explain why the transition from $v = 1$ to $v = 2$ is not observed in the infrared spectrum of $^1H^{35}Cl$ at a temperature of 298 K. **[3]**