M.Sc. 4th Semester Examination, 2011

CHEMISTRY

(Inorganic Special/Organic Special/ Physical Special)

PAPER—CH-2203

The figures in the right-hand margin indicate marks

(Inorganic Special)

Full Marks : 40

Time : 2 hours

Answer any *four* questions

1. (*a*) Discuss thermodynamic and kinetic limitations on the photochemical conversion and storage of sunlight. 5

(*b*) State the requirements which must be satisfied in order to perform a photochemical experiment. 3

(*c*) How cerium salts function in the process of photochemical splitting of H_2O molecule. 2

2. (*a*) Discuss the photochemical cleavage of water molecule using $[Ru(bPy)_3]^{2+}$ as a sensitizer. 8

(bPy = 2, 2′-bipyridine)

(*b*) Write down the product(s) of the following photochemical reaction and suggest plausible mechanism : 2

$$Mn_2(CO)_{10} + PPh_3 \xrightarrow{h\nu}$$

3. (*a*) Discuss the temperature dependence of photochemical processes. 6

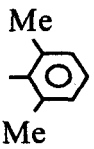
(*b*) Write note on any *one* of the following : 4

(*i*) Oscillator strength and Radiative Life time

(*ii*) Thexi states and DOSE NCO states.

4. (*a*) Draw a quantitative energy level diagram for a lanthanide complex showing transitions from ligand and metal ion excited states. 3

(*b*) Complete the following reactions : 1 + 2 + 1

(*i*) $LaCl_3 + 4$ Li  $\xrightarrow{THF}$?

(*ii*) $LuCl_3 \xrightarrow[Et_2O]{C_5Me_5Li}$? $\xrightarrow{MeLi}$?

(*iii*) $NdF_3 . \frac{1}{2}H_2O \xrightarrow[OR\ 600\ ^\circ C\ /HF]{300\ ^\circ C,\ in\ vacuo}$?

(*c*) Discuss the magnetic properties of lanthanide complexes. 3

5. Write notes on any *two* of the following : 5 + 5

(*i*) Free electron theory of metal

(*ii*) Hall effect

(*iii*) Meissner effect.

6. (*a*) What is π-π stacking interaction ? 1

(*b*) Discuss "ion-ion interaction" and "ion-dipole interaction". 2 + 2

(*c*) What do you mean by the term "Host-Guest chemistry" and "self assembly" ? 2

(*d*) What do you mean by "supramolecular chemistry" ? Schematically present the development of supramolecular system from molecular building blocks. 1 + 2

7. (*a*) How lanthanides are separated ? 2

(*b*) Calculate the ground state term symbol for Pm^{3+}. 2

(*c*) Discuss the structure of LaF_3. 2

(*d*) Explain the role of lanthanides as shift reagents. 4

(*Organic Special*)

Full Marks : 40

Time : 2 hours

Answer any *five* questions

1. Comment on the following :

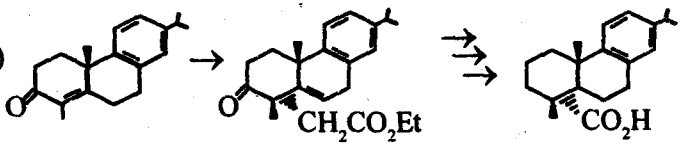
   (*a*) The diene system in abietic acid. 2

   (*b*) Formation of biological isoprene from acetyl coenzyme A. 4

   (*c*) Biogenetic conversion of IPP to FPP. 2

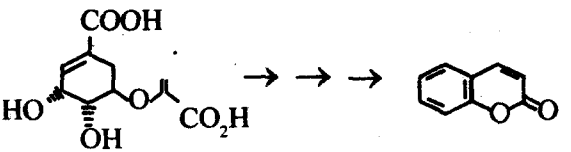
2. Explain the following steps drawing the conformation, whenever necessary : 4 x 2

   (*a*)



   Name the final product.

   (*b*)



3. (*a*) Write down the stereostructures of all the four *cinchona* alkaloids, giving (*R*, *S*) -designation of each chiral center. 3

(*b*) Write down the conversion of quinine to quinotoxine and quintoxine to quinine. 5

4. (*a*) Establish the relative stereochemistry at C3 and C4 of (−) -quinine. 4

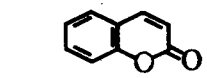
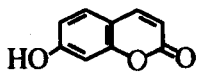
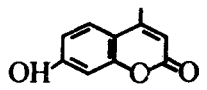
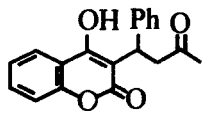
(*b*) In the Woodard-Docring synthesis of quinine mention one or two steps you think strategically important. 4

5. (*a*) Prove that marmesin possesses *S*-configuration at the only chiral center. 5

(*b*) How marmesin is biogenetically converted to psoralen. 3

6. (*a*) Name the precursors of cholesterol in plant and animal systems. Mention the sequence of methyl loss in each case. 2

(*b*) Discuss the synthesis of the following coumarins (any *three*) : 2 x 3

Name the important coumarin derivative used as an anticoagulant.

7. Trytamine is the basic unit present in indole alkaloids. Give two elegant synthesis of trytamine. 8

8. Design suitable experiment to establish the absolute stereochemistry in the following centres of yohimbine (*i*) C_5-H (*ii*) C_{15}-C_{20} ring junction. 4 x 2

(*Physical Special*)

Full Marks : 40

Time : 2 hours

GROUP–A

Answer any *one* of the following

1. (*a*) What do you understand by exciplex and excimer emission ? Give one example for each. Use MO diagram to explain the stability of excimer and exciplex formation. 2 + 3

   (*b*) State and explain the effect of solvent polarity on exciplex emission. 5

2. (*a*) What do you mean by twisted intra-molecular charge transfer (TICT) emission ? Explain with example. 5

   (*b*) State and explain the effect of polarity on TICT emission. 5

GROUP–B

Answer any *one* of the following

3. (*a*) State Decius rule with example to obtain the number of different normal mode of vibrations for both linear and non-linear molecules. 6

(*b*) Use projection operator method to obtain the following orthonormalized set of symmetry co-ordinate for a pyramidal XY_3 molecule.

A_1 species; $S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$

$$S_2 = \frac{1}{\sqrt{3}}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)$$

where 'α' and 'r' are angle and bond vector respectively. 4

4. (*a*) Write down the characteristic features of Morse potential function. Deduce the following expression for the determination

of anharmonicity constant, 'a' from experimental parameter,

$$a=\sqrt{\frac{2\pi^2\gamma^2\mu}{D}}$$

where 'γ' is the harmonic frequency, 'μ' is the reduced mass and 'D' is the dissociation energy. 2 + 4

(*b*) Write short note on any *one* of the following : 4

(*i*) Stimulated Raman spectroscopy

(*ii*) Cavity ring-down spectroscopy.

GROUP–C

Answer any *one* of the following

5. (*a*) Explain nuclear-electron spin coupling and Fermi contact term using hydrogen atom as an example. How do these two terms contribute to the effective Hamiltonian of a hydrogen atom. Write down the effective Hamiltonian of a hydrogen atom is presence of an external magnetic field. $\left(1\frac{1}{2}\times 2\right)+1+1$

(*b*) Write the spin functions of a hydrogen atom. Obtain the zero order magnetic interaction energy of a hydrogen atom in presence of an external magnetic field. 1 + 4

6. (*a*) Write down the magnetic interaction Hamiltonian and sketch the energy level (upto 1st order correction to energy) for a methyl radical ($\dot{C}H_3$) in presence of a magnetic field. Show the possible esr transition and hence the ratio of intensity of those transition. 1 + 2 + 1 + 2

(*b*) What do you understand by ODMR spectroscopy ? Give a qualitative discussion on the splitting of triplet energy level of naphthalene in the absence of an external magnetic field. 1 + 3

GROUP–D

Answer any *one* of the following

7. (*a*) What do you understand by 'intrinsic' and 'extrinsic' fluorophore ? Explain with example. 2 + 2

(*b*) Fluorescence emission intensity is dependent on excitation wavelength but emission wavelength is independent on the excitation wavelength. —Explain. 3

(*c*) Time resolved fluorescence spectroscopy is more informative than steady state fluorescence spectroscopy. —Explain. 3

8. (*a*) What do you mean by fluorescence anisotropy ? Describe the alignment of the polarizer during the measurement of fluorescence anisotropy. 2 + 3

(*b*) Calculate the expected anisotropy of perylene in ethanol at 20 °C. Molecular weight and density of perylene are 252 gm/mole and 1·35 gm/mL respectively. Viscosity of ethanol is 1·194 cP at 20 °C. Assume τ = 6ns and r_0 = 0·36 for perylene. 5
