

**M.Sc. 4th Semester Examination, 2013**

**CHEMISTRY**

**PAPER—CEM - 403**

*Full Marks : 40*

*Time : 2 hours*

*The figures in the right-hand margin indicate marks*

*( Organic Special )*

Answer any *five* questions

1. (a) "As keto and enol coupling leads to formation of carbocyclic rings so does the mine and enamine coupling, leading to of alkaloids". Justify the statement with an example.  
  
(b) Give the most recent synthesis of Tryptamine using ortho-Nitroluene as the starting material.

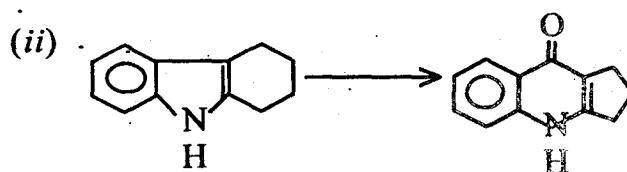
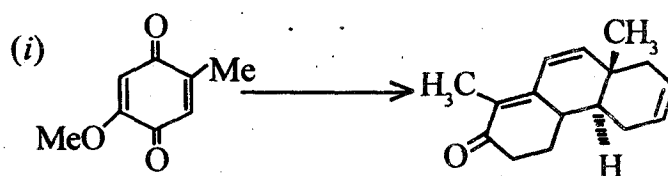
*( Turn Over )*

- (c) Give plausible mechanism for the conversion of Thebaine  $\rightarrow$  Morphothebaine. 3 + 3 + 2
2. (a) How the position and stereochemistry of  $\text{CO}_2\text{Me}$  and OH groups in yohimbine has been established ?
- (b) "Although cinchona and Indole alkaloids possess entirely different structures yet biogenetically they originate from the same precursor". Explain the statement with a biogenetic scheme. 4 + 4
3. (a) How the absolute stereochemistry of  $\text{C}_{15}\text{H}$  and  $\text{C}_{20}\text{H}$  of yohimbine were established.
- (b) Experimentally show that the configurations at  $\text{C}_3$  and  $\text{C}_4$  of all cinchona alkaloids are same and hence deduce their configurations. 4 + 4
4. (a) Give the Retrosynthetic analysis for construction of non-nitrogenous part of yohimbine and hence show the structure of appropriate synthon.

- (b) Delineate the nature, position and configuration of  $-\text{CO}_2\text{H}$  group in abietic acid. (3 + 1) + 4
5. (a) How can you show that abietic acid contains a homoannular diene system with an isopropyl group.
- (b) Show how Barbier-Wieland degradation has been used in determining the nature and position of attachment of the side chain in cholesterol. 4 + 4
6. (a) What does the term "Transannular cyclisation" mean? Apply this concept to show that caryophyllene is a macrocyclic sesquiterpene having a nine-membered ring.
- (b) Show how the nature and position of  $-\text{OH}$  group in cholesterol has been determined. 5 + 3
7. (a) What are 'acetogenins'? With an example show that phenolic coupling can lead to a large number of oxygenated natural products.

(b) How can you show that catechin and epicatechin are diastereoisomers and hence deduce their relative stereochemistry. (1 + 3)+ 4

8. Carry out the following transformation and give plausible mechanism where possible. 5 + 3



( Inorganic Special )

Answer any *four* questions

1. (a) "Thermodynamically non-spontaneous reactions also may take place spontaneously in presence of light" – Explain.

(b) The parity selection rule for radiationless

transitions is precisely opposite to the selection rule for radiative transitions. Explain.

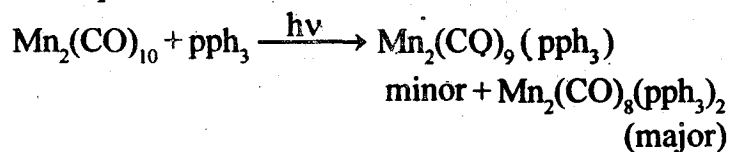
(c) Write short notes on :

(i) Spontaneous emission

(ii) photo dissociation reactions.

2 + 2 + (4 + 2)

2. (a) Suggest plausible mechanism for the following photochemical reaction :



(b) Write the essential criteria for developing a photochemical energy-storage cycles. What do you mean by THEXI and DOSENCO states ?

(c) What do you mean by "photosensitization" ?

(d) What are photochemical reactions ? How do they differ from thermal reactions ?

2 + (2 + 2) + 2 + 2

3. (a) Define supramolecular chemistry.
- (b) What do you mean by ion-ion interaction and ion-dipole interaction ?
- (c) What is van der Waals interaction ?
- (d) What do you mean by self-assembly ?  
2 + (2 + 2) + 2 + 2
4. (a) Write down the differences between 4f and 5f orbitals.
- (b) Discuss luminescence of lanthanoid complexer.
- (c) How uranium is extracted from its ore ?  
3 + 4 + 3
5. (a) Draw a flow diagram for extraction of the lanthanoid metals from monazite.
- (b) Write down the separation of lanthanoid metal ion.
- (c) Write short notes on :
- (i) Oxidation state of actinoids
- (ii) Lanthanide Contraction. . . . . 4 + 3 + 3

6. (a) Find the density of states applying sommerfield model in the metal. Hence find an expression for Fermi Energy.
- (b) How will you determine Fermi temperature and Dibe temperature. (5 + 2) + 3
7. (a) What is Hall effect ?
- (b) Explain how the current becomes steady in a normal metal and a super conductor.
- (c) Mention the important characteristics of a superconductor. 4 + 2 + 4

( *Physical Special* )

GROUP – A

Answer any *one* of the following

1. What do you understand by twisted intramolecular charge transfer (TICT) emission ? Write down the characteristic features of TICT emission. What is  ${}^1L_a$  and  ${}^1L_b$  state ? "It is the TICT rather than the reversal of  ${}^1L_a$  and  ${}^1L_b$  state, responsible for stoke shifted broad emission of dimethyl

amino benzonitrile (DMABN) in polar solvent".  
Justify or criticize the statement. What is static and dynamic polarity effect in TICT processes? State and explain the effect of solvent polarity on TICT emission.  $1 + 2 + 1 + 2 + 2 + 2$

2. What is excimer emission? Give one such example. Draw a schematic potential energy diagram to explain, that the excimer emission is broad and red shifted compare to its monomer emission. What is exciplex emission. Give one such example. Use MO diagram to explain the stability of exciplex formation.  $2 + 3 + 1 + 4$

### GROUP – B

Answer any *one* of the following

3. What is excited state acidity constant ( $P^{k_a}$ ) of an organic acid? How do you obtain ground and excited state acidity constant of salicylic acid experimentally? Describe Fröster cycle to obtain excited state acidity constant of salicylic acid. Give a schematic potential energy diagram for the ground and 1st excited state of salicylic acid along its proton transfer co-ordinate.  $1 + 2 + 2 + 3 + 2$



4. (a) What is meant by stimulated Raman scattering. Give a schematic energy level diagram to explain the stimulated Raman scattering.
- (b) What is coherent anti-stokes Raman scattering? Write down the principle involved for the generation of second Harmonic from a given frequency of radiation. (2 + 3) + (2 + 3)

GROUP – C

Answer any *one* of the following

5. Write down the magnetic interaction Hamiltonian and spin wave functions for hydrogen atom. Obtain the expression for zero order energy and energy with 1st order correction using Fermi contact term as perturbing term to its Hamiltonian. State the selection rule for ESR transition and hence show the possible transitions and their frequencies for ESR transition in H-atom. 6 + 4

6. (a) What is optically detected magnetic resonance (ODMR) spectroscopy? Depict the splitting of triplet level of naphthalene in the absence of an external magnetic field, at 1.2 K. What are zero field splitting parameter.
- (b) Draw the energy levels with possible  $M_l$  and  $M_s$  values for  $\dot{\text{C}}\text{H}_3$  radical and hence show the possible ESR transitions. (1 + 3 + 2) + 4

GROUP – D

Answer any *one* of the following

7. (a) Write down the advantages of time resolved fluorescence spectroscopy over the steady state fluorescence spectroscopy.
- (b) Define fluorophore. BSA can be used as intrinsic fluorophore. – Explain.
- (c) What do you understand by Stokes' shift and mirror image relationship in electronic spectroscopy? State Kasha's rule.  
(2 + (1 + 2) + (2 + 2 + 1))

8. (a) What is meant by fluorescence anisotropy?  
Show that

$$I_{\parallel} = 3I_{\perp}$$

where  $I_{\parallel}$  and  $I_{\perp}$  are the fluorescence intensity at the parallel and perpendicular direction of the z-axis.

- (b) A special alignment of the emission polarizer is required during fluorescence anisotropy measurement. – Explain.

- (c) What is fluorescence resonance energy transfer (FRET)? (1 + 4) + 3 + 2