M.Sc. 3rd Semester Examination, 2013

CHEMISTRY

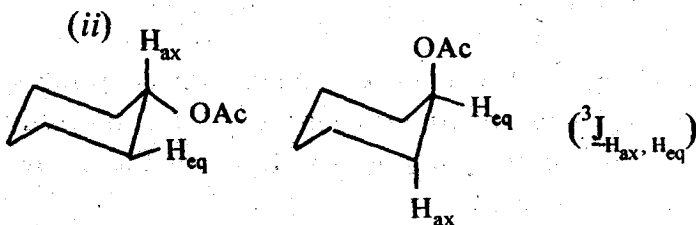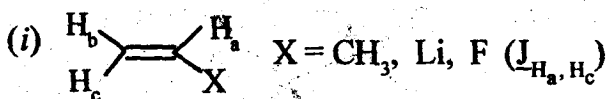PAPER—CEM-303

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Organic Special*)

Answer any **five** questions

1. (*a*) Arrange the following compounds in increasing order of the ^3J values :   3

(*i*) $X = CH_3$, Li, F (J_{H_a, H_c})

(*ii*) $(^3J_{H_{ax}, H_{eq}})$

(b) State three ways of getting information on δ, $\underline{J}$ and multiplicities in the case of non-first order spectra. 3

(c) Write the name and structure of the internal standard for ^{15}N NMR and external standard for ^{31}P NMR spectroscopies. 2

2. (a) What are the stereochemical relationships between the H_a and H_b in the following compounds : 4

(i)

OH   OH

(ii)

HO_2C HO_2C OH CO_2H
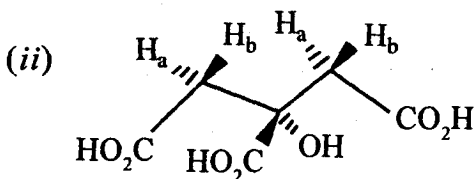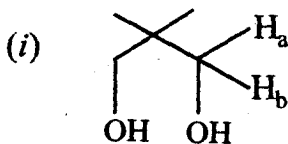
(b) Write down the equation that correlates J_{vic}- with dihedral angle (φ) in saturated aliphatic compounds. Explain the terms involved. 2

(Continued)

(c) Write down the structure of *either* (R)-MTPA *or* (R)-PFE. What is it used as ? 2

3. (a) (i) What is the full form of NOE ? 1

   (ii) Calculate maximum possible η (%) in the case of homonuclear NOE experiment. 2

   (iii) In $[^{29}Si - \{^1H\}$ experiment, what would be the fate of ^{29}Si signal ? 2

   (b) What is the role of Fourier Transform in FT NMR spectroscopy ? 3

4. (a) Fill in the blanks in the following sentences : 4

   (i) The three sets of methylene protons in $ClCH_2CH_2CH_2CO_2H$ constitute _____ spin system (Pople notation).

   (ii) Free Induction Decay is a _____ domain spectrum.

(*Turn Over*)

(*iii*) The coupling between the 1, 3-diequa-
torial protons in cyclohexane is called
_____ coupling.

(*iv*) In PND ^{13}C NMR spectra, the ^{13}C
nuclei experience _____.

(*b*) Separately calculate the $\delta \overset{\div}{C}H$ and $\delta \overset{\neq}{C}H$ in
the following compound :
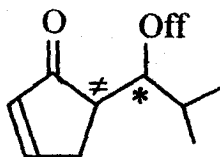
Given, increments for $\beta - O - = 10.1$;
$\alpha - O - = 49.0$; $\beta - C = O = 3.0$; $\gamma\text{-sp}^2 - C =$
-2.1; branching corrections for $3°(3°) = -9.5$;
δCH_2 $\alpha-$ to $C = O$ in cyclopent-2-en-1-one
is 34.1. $2 + 2$

5. (*a*) Determine the structure of the compound,
C_9H_{12} ; UV : $\lambda_{max} 286$ nm ($\epsilon = 480$); IR : 1608,

1473 cm^{-1}; ^{1}H NMR : δ $2 \cdot 26$ (s) and $6 \cdot 79$

(s) with integration ratio 3 : 1.   4

(b) Deduce the structure of the compound, $C_4H_8O_2$ UV : λ_{max} 206 nm ($\epsilon = 50$); IR : 1736 cm^{-1}(s), 1445 cm^{-1}(m); ^{1}H NMR : δ $0 \cdot 95$ (3H, t, $\underline{J} = 7$ Hz), $1 \cdot 67$ (2H, sexfet, $\underline{J} = 7$ Hz), $4 \cdot 12$ (2 H, t, $\underline{J} = 7$ Hz), $8 \cdot 07$ (1H, s).   4

6. (a) Explain $90°$ pulse in terms of rotating frame of reference (r.f.r.).   4

(b) Explain spin-lattice relaxation again in terms of r.f.r.   4

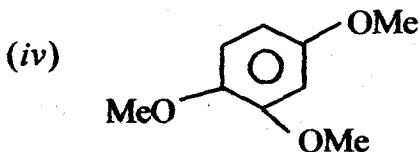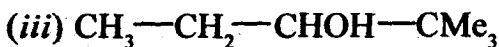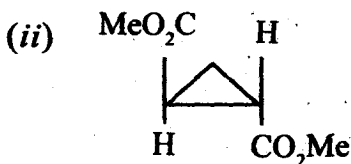7. (a) What are lanthanide shift reagents ?   1

(b) Write down the structures of Eu(dpin)$_3$ and Eu(fhd)$_3$.   3

(c) Name two lanthanides which cause deshielding and two lanthanides which cause

shielding of signals when they are used in
lanthanide shift reagents.　　　　　　　4

8. (a) How many ^1H NMR signals would you
　　　expect for the following Mark them by
　　　different numbers (1, 2, 3 etc.).　　　4

(i)　MeO_2C　CO_2Me

　　　H　　H

(ii)　MeO_2C　H

　　　H　　CO_2Me

(iii) CH_3—CH_2—$CHOH$—CMe_3

(iv)

OMe

MeO　　OMe

　　　　　　(Continued)
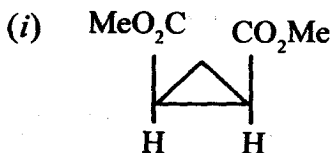
(b) How many ^{13}CNMR signals would the following show ? 4

(i) MeO —⟨O⟩

(ii) Me —⟨O⟩— Me

(iii)

(iv)
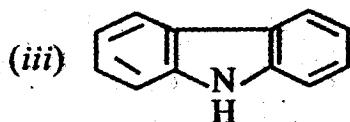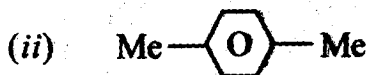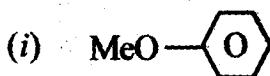
9. (a) What is Mc Lafferty rearrangement ? Show the mass fragmentation pattern. 2

(b) Illustrate the mass fragmentation pattern of retro — Diels-Alder cleavage. 2

(c) Differentiate the following isomeric pairs of compounds from mass spectral fragmentation pattern (any *one*) : 4

(i)

and

(ii) $CH_3 - (CH_2)_3 - CH - (CH_2)_9 - CH_3$
$\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad CH_3$

and

$CH_3(CH_2)_5 - CH - (CH_2)_5 - CH_3$
$\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad (CH_2)_2$
$\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad CH_3$
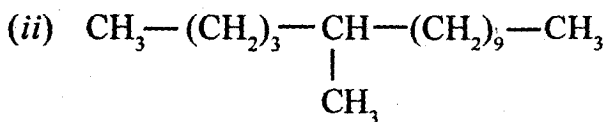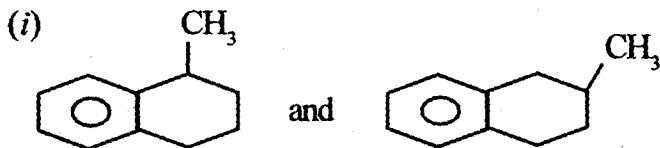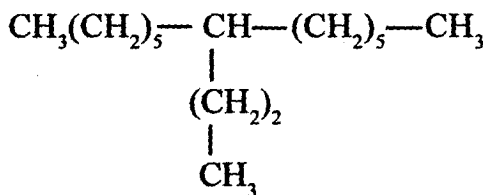
(*Inorganic Special*)

Answer any **five** questions taking at least
two from each Group

GROUP – A

1. (a) What is the basic difference between
    distribution co-efficient and distribution
    ratio ?   4

(*Continued*)

(b) If a distribution ratio for a certain solute in water-carbon tetrachloride system is 20, calculate the per cent of solute extracted from 20 ml aqueous solution by 50 ml CCl_4 divided into two equal parts and used for extraction one after another.   4

2. (a) Find the equilibrium concentration of Schotky defects in an ionic crystal at a temperature T.   4

(b) Find an expression of $\Delta S + h$ i.e. thermal entropy change per vacancy in a solid.   4

3. (a) Write briefly about Sol-Gel technique an MBE technique.   3

(b) What is the working principles of probe microscope ?   2

(c) What kind of information will come out from the following instruments ?   3

   (i) LEED
   (ii) SEM
   (iii) TEM.

4. (*a*) Define limiting current in polarography. How is it useful in analytical chemistry ?   2 + 2

   (*b*) What is polarographic maxima ? Why is oxygen to be expected from the polaro-graphic cell before the experiment ?   2 + 2

GROUP – B

5. (*a*) How does HPLC differ from GLC ?   3

   (*b*) What is super critical fluid ?   2

   (*c*) Write down the characteristics of HPLC detector.   3

6. (*a*) What is a colour centre ? Describe in details the mechanism of formation of a colour centre.   5

   (*b*) Clearly distinguish between metal, insulator, and semiconductor.   3

7. Answer any *four* :   2 × 4

   (*a*) Differentiate 3D and 1D structure.

          (*Continued*)

(b) Why the nanomaterials are different from their bulk counter part ?

(c) Give the idea of CVD technique for thin film preparation ?

(d) What is "top-down" approach of nano-science ? Give example.

(e) What do you mean by e-lithography ?

(f) Give the difference between chemical ethcing and electro-etching.

8. (a) Why X-Ray is appropriate for crystal structure information while electron micro-scope is suitable for surface morphology study ?   3

(b) Why the electron microscope is superior to optical microscope in nanomaterials study ?   2

(c) Calculate the energy difference between the conduction band and Fermi energy in an intrinsic Si sample at 300 K.   3

Given $m_e^* = 1 \cdot 1 \, m$

$m_n^* = 0 \cdot 59 \, m$

Eg of Si = $1 \cdot 1$ eV

(12)

(*Physical Special*)

Answer **four** questions taking **two** from Group-A
and **one** each from Group−B and Group−C

GROUP − A

Answer any **two** of the following :

1. (*a*) Spectroscopic transition probability from
    state 'n' to 'K' under a constant perturbing
    field H' is given by

    $$W_{n \to k} = \frac{4|H'_{Kn}|^2}{\hbar^2} \frac{\sin^2(w_{Kn}t/2)}{w^2_{Kn}}.$$

    Use the above expression to deduce Fermi
    Golden rule. Comment on your result.   5

    (*b*) Use rigid rotator model to obtain the
    selection rule for rotational spectroscopy.
    Recursion formula for Associated Legendre
    function is given below :   5

    $$(2J+1) P_J^{|M|}(x) = (J-|M|+1) P_{J+1}^{|M|}(x) +$$
    $$(J+|M|) P_{J-1}^{|M|}(x).$$

2. What is meant by Homogeneous and inhomogeneous broadening of spectral lines. Consider the motion of vibrating charge as damped oscillator and hence obtain the expression for line shape function. What is FWHM of spectral transition band ? $3+6+1$

3. (a) "Inversion of population is an essential criterian for a system to show Lasing activity."— Explain.   2

   (b) "Inversion of population can not be achieved in a three level system." Justify or criticize the statement.   5

   (c) Describe the principle to obtain second Harmonic frequency (2γ) from a given frequency (γ) of radiation.   3

4. (a) State and explain the factors responsible for radiationless transition in molecular electronic spectroscopy.   5

(b) Show that,

$$F = \phi_f I_0 (2 \cdot 303) \in_\lambda Cl$$

where F: fluorescence intensity, ϕ_f: quantum yield of fluorescence emission, I_0: Intensity of incident radiation, $\in_\lambda$: molar extinction co-efficient, C: Concentration, l = path length. "Fluorescence emission spectra is the approximate mirror image of absorption spectra." — Explain.   3 + 2

GROUP — B

Answer any **one** of the following :

5. What is meant by dynamic quenching of a fluorophore ? Deduce the following form of Stern-Volmer equation,

$$\frac{\tau^\circ}{\tau} = 1 + K_{sv}[Q]$$

where symbols have their usual significances. How do you obtain the dynamic quenching constant using the principle of Half quenching method ?   2 + 5 + 3

(*Continued*)

6. Write down the steps involved and the rate of each step for Unimolecular photophysical processes.

   Show that,

$$K_{ISC} = \frac{1}{\tau_f^{\circ}} \left(\frac{1 - \phi_f}{\phi_f} \right)$$

   where symbols have their usual significances.

   (Assume, $\phi_f + \phi_p + \phi_{ISC}^{T} \cong 1$).   4 + 6

GROUP – C

Answer any **one** of the following :

7. Write down the magnetic interaction Hamiltonian and the spin wave functions for A—X system. Obtain the zero order as well as first order correction to energy and hence show the frequency of all possible transitions.   2+3+3+2

8. (a) Show that the frequency of NMR transition for hydrogen atom (having shielding

constant σ_H) in presence of an external magnetic field is given by,

$$\gamma_H = \frac{\gamma B_0}{2\pi}(1 - \sigma_H).$$
3

(b) What do you understand by chemical shift in NMR transition ? State its advantages.   3

(c) What are first order and second order NMR transitions ? Give examples.   4

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