# 2014

## M.Sc. Part–II Examination

## CHEMISTRY

### PAPER—VII

**Full Marks : 75**

**Time : 3 Hours**

*The figures in the margin indicate full marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

*Illustrate the answers wherever necessary.*

### (Physical Special)

Answer any *five* questions taking at least *two* from each group.

### Group—A

1. (a) Write down the steps involved and the rate of each step for Unimolecular photophysical processes.

   Assuming $\phi_p + \phi_f + \phi_{ISC}^T \cong 1$ for a unimolecular photophysical process, Show that,

   $$K_{ISC}^T = K_P \left[ \frac{1-\left(\phi_p+\phi_f\right)}{\phi_p} \right]$$

   where symbols have their usual significance.     4+6

   (b) Write a short note on p-type delayed emission.     5

2. What is meant by static and dynamic quenching of fluorophore? How do you obtain the rate constant of dynamic and static quenching where both the quenching take place simultaneously for a fluorophore?  3+6+6

3. (a) What is meant by Twisted Intramolecular Charge Transfer (TICT) emission? Give one such example.  2+1

   (b) Write down the characteristic features of TICT emission. Explain the effect of polarity and viscosity of medium on TICT emission.  3+6

   (c) What is meant by static and dynamic polarity effect on TICT processes?  3

4. (a) What is anharmonicity effect?  3

   (b) What is Coriolis interaction, overtones and combination band?  2×3

   (c) Rotational spectra of 1-deutropropyne were studied in five different electric field ($\epsilon$) at 20°C for J = +1 to + 2 and $M_J$ = ±1→ =1 transition and the following results were reported:  3

| Electric field ($\epsilon$) | Shift lines for $|M_J| = 1$  $|K| = 1$ $\Delta\gamma$ MC/S |
|---|---|
| 50.36 | 6.84 |
| 64.16 | 8.12 |
| 90.59 | 11.40 |
| 96.95 | 12.30 |
| 144.94 | 18.23 |

   Calculate the dipole moment of $CH_3C \equiv CD$ molecule.

   (d) Draw and explain normal vibrational mode of $SiF_2$ and $CO_2$ molecule.  3

(Continued)

5. (a) Derive Debye Equation and from its derive union of Debye and Lorentz Equation.  5+3

   (b) For $SO_2(g)$ at 273(K) and 1 atm pressure. dielectric constant is 1.00993. This molecule has a permanent dipole moment of 1.63D. Assuming that $SO_2$ behaves as an ideal gas, calculate per molecule of (i) total, (ii) orientation, (iii) induced polarization and (iv) distortion polarizability.  4

   (c) Give molecular interpretation of diamagnetism and paramagnetism.  3

### Group—B

6. (a) Write down the characteristic features of LASER radiation.

   'Inversion of population can not be achieved for a two level system' — Explain.  2+8

   (b) Write a short note on Q-switching of LASER.  5

7. Write down the magnetic interaction Hamiltonian and spin wave function 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.  3+5+5+2

8. (a) What is meant by spin-spin and spin-lattice relaxations in NMR Spectroscopy?  2+2

   (b) Why are these relaxation processes are essential to observe NMR transitions?  4

(Turn Over)

(c) 'The net effect of spin lattice relaxation is to depopulate the higher spin state than to populate it' — Explain.                                     7

9. (a) Write the magnetic interaction Hamiltonian of free radical in presence of an external magnetic field. How do you obtain Lande 'g' factor from ESR transition of a free radical ?                                     2+3

   (b) Deduce the selection rule for ESR transition. Depict the energy levels and possible ESR tramitions of a free radical having four magnetic nuclei with unequal coupling.                                     4+6

10. Write the magnetic interaction Hamiltonian and the spin wavefunctions of H-atom.                                     2

   Use perturbation theory to obtain first order correction to wavefunction for second order correction to energy.                                     4

   Show that $\psi_1$ (lowest level) $\longrightarrow$ $\psi_4$ (highest level) is a forbidden tramition for zero as well as first order transitions but it is allowed for second order tramition.                                     3+3+3

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(Organic Special)

Answer any five questions taking at least two from each group.

Group—A

1. (a) Predict the theoretical number of non-equivalent proton in each of the following compounds :     2

   1,2-dichloropropane, 3-chloropropene, trans-1,2-dichlorocyclopropane, 2-chloro-3-methylbutane.

   (b) What is Nuclear Overhauser Effect ? Explain the reason for this effect.                     4

   (c) A compound having molecular formula $C_9H_{11}Br$ showed the following signals in $^1H$ NMR data :

   $\delta2.25$ (2H, m), $\delta2.75$ (2H, t), $\delta3.38$ (2H, t), $\delta7.22$ (5H, s)

   Determine the structure of the compound with justification.                     6

   (d) 'The magnetically equivalent nuclei are chemically equivalent nuclei but the reverse is not true'— Explain.                     3

2. (a) 3-methylcyclopentadiene shows a singlet for the methyl protons in its $^1H$ NMR spectroscopy — explain.                     3

   (b) How would you distinguish between intra and inter-molecular hydrogen bonding on the basis of PMR spectroscopy?                     3

   (c) The uncertainty in the NMR frequency of a compound in liquid state (relaxation time = 10 s) is 0.1 Hz. What is the uncertainty in the frequency (in Hz) of same compound in solid state (relaxation time = $10^{-5}s$).     2

(d) An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following $^1H$ and $^{13}C$ NMR spectral data :

$^1H$ NMR : $\delta$ 2.4 (6H, s), 7.2 (4H, d, J = 8 Hz), 7.7 (4H, d, J = 8Hz).

$^{13}C$ NMR : $\delta$ 21.0, 129.0, 130.0, 136.0, 141.0, 190.0

Determine the structure of the compound and assign these $\delta$ values to various hydrogen and carbon atoms of the compound.     7

3. (a) A compound having molecular formula $C_9H_{18}O$ showed only one singlet in its $^1H$ NMR spectrum but three $^{13}C$ NMR signals in the intensity ratio 1:2:6. Determine the structure of the compound.     3

(b) A compound having molecular formula $C_4H_6O$ showed the following signals in $^1H$ NMR data.

$\delta$6.20 (1H), $\delta$6.0 (1H), $\delta$5.8 (1H), $\delta$2.2 (3H)

Determine the structure of the compound and assign these $\delta$ values to various hydrogen of the compound.     4

(c) The $^1H$ NMR spectrum of $A_3X$ exhibits lines at $\delta$ = 4.1 and 4.3 ppm (for A type protons) and $\delta$ = 2.1, 2.3, 2.5 and 2.7 ppm (for X type protons), measured from TMS with an instrument operating at 300 MHz. What are the chemical shift (in ppm) of A and X protons and coupling constant (in Hz)?     3

(d) How a complex spectrum is simplified by using high field FT-NMR spectroscopy?     3

(e) Distinguish the following compounds using PMR spectroscopy?     2

and
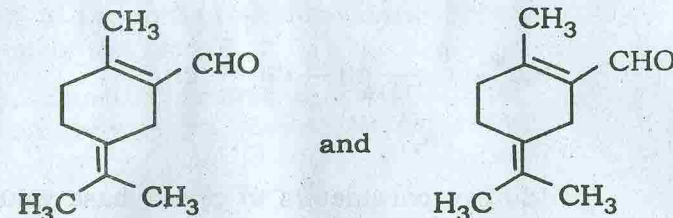
4. (a) What are the advantages of Fourier Transform (FT-NMR) technique over CW-NMR technique?     3

(b) Give the most plausible structure of the $C_4H_8O$ isomer with the following $^1H$ NMR data:

$\delta$1.84 (2H), $\delta$3.73 (4H)

Determine the structure of the compound and assign these $\delta$ values to various hydrogens of the compound.     3

(c) What is spin decoupling in NMR spectroscopy? How it is carried out? Illustrate the phenomenon with pure ethanol.     4
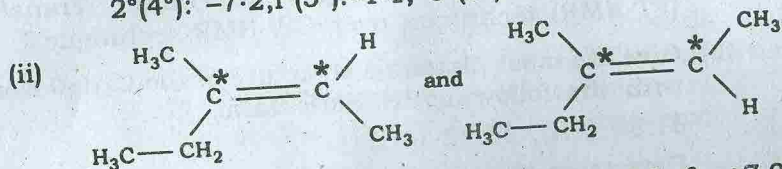
(d) Can $^1H$ NMR spectroscopy distinguish between enantiomeric pair?     1

(e) Calculate the $\delta_C$ values of the carbon atoms marked with asterisk of the following pairs of isomeric compounds and show how they can be distinguished from each other.     2+2

(i)   and
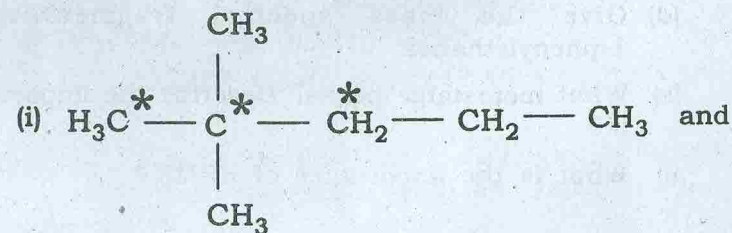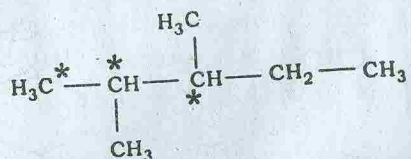
Additive parameters in ppm : base value : $-2.5$; $\alpha$, $\beta$ and $\gamma$-effects have their usual values ; $\delta$-effect : $+0.3$, $1°(4°)$: $-3.4$; $4°(2°)$: $-8.4$; $2°(4°)$: $-7.2$; $1°(3°)$: $-1.1$; $3°(3°)$: $-9.5$; $3°(2°)$; $-3.7$]

(ii)



[Additive parameters in ppm : $\alpha$ : $+10.6$, $\beta$ : $+7.2$; $\gamma$ : $-1.5$, $\alpha$ : $-7.9$, $\beta$ : $-1.8$, $\gamma$ : $-1.5$, Z(cis) correction : $-1.1$, E (trans) correction: 0, Two alkyl substituent at Cl(two $C\alpha$): $-4.8$; Base value 123.3 ppm]

5. (a) What do you understand by Nitrogen rule in mass spectrum ?  **2**

(b) What do you mean by the base peak and the molecular ion peak ?  **2**

(c) What is typical in the mass spectrum of a compound containing (i) one bromine atom (ii) one chlorine atom ?  **2**

(d) Give the mass spectral fragmentation of 1-phenylethanol.  **2**

(e) What metastable peaks? Describe the importance of it ?  **2+2**

(f) What is the importance of HRMS ?  **2**

(Continued)

(g) Which of the following molecule gives most intense molecular ion peak ?  **1**

(i) 3,3-dimethyl hexane (ii) tert-Butanol
(iii) anthracene (iv) 3-methylcyclohexene.

### Group—B

6. (a) How would you distinguish between the following pairs of isomeric compounds from their mass spectral fragmentations? Answer any four:  **2×4**

(i) 2-hexene and cyclohexene ;

(ii) 3,3-dimethyl heptanes and n-heptane ;

(iii)



and

(iv)



and
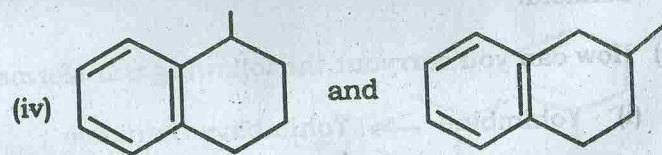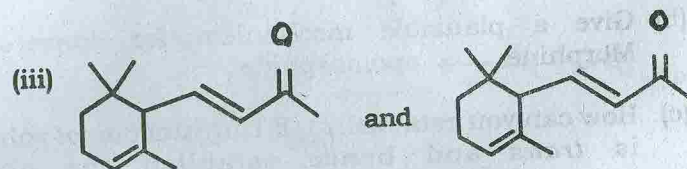
(b) Determine the structure of the compound whose m/e values are m/e 74 (Molecular ion), 56, 43 and 31 (base peak). Justify the signals.  **4**

(c) What is McLafferty rearrangement ? Give example of it.  **3**

7. (a) Alkylation of Indole at $C_2$-Occurs via migration from $C_3$. Justify the statement with an experimental observation.

(Turn Over)

(b) How can you carryout the synthesis of tryptamine from *ortho* nitrotoluene.

(c) Write the structure of most effective synthon necessary for building non-nitrogeneous part of yohimbine. Show the possible retro-synthetic scheme for preparation of such a synthon.

(d) Although structurally altogether different, Indole and quinine alkaloids orginate from same biogenetic precursor. Justify the statement.        3+4+4+4

8. (a) How can you show that all Cinchona alkaloids have the same stereochemistry at $C_3$ and $C_4$ and hence deduce their absolute configurations.

(b) Give a plausible mechanism for conversion of Morphine $\longrightarrow$ apomorphine.

(c) How can you establish D/E ring junction of yohimbine is *trans* and hence establish the absolute stereochemistry of $C_{15}$ and $C_{20}$ centre of such an alkaloid.

(d) How can you carryout the following transformations :

(i) Yohimbine $\longrightarrow$ Yohimbine Oxiindole ;

(ii)



4+2+3+2×3
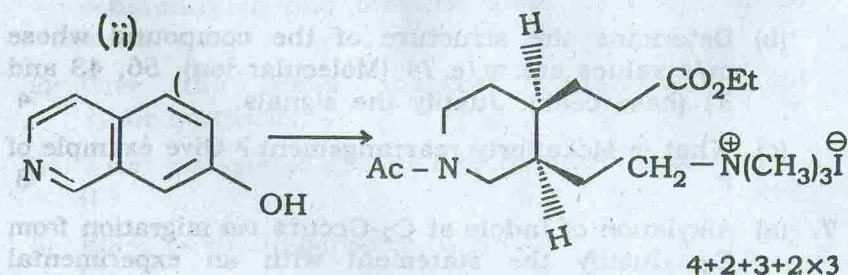
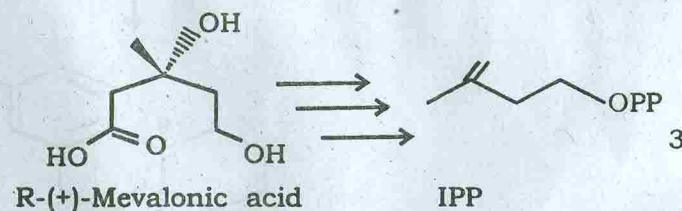9. (a) What is biogenesis ?        2

(b) Delineate the following biogenetic conversion :

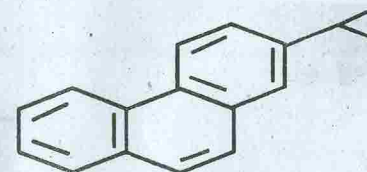(i) Acetyl coenzume to IPP ;

(ii) FPP to Squalene.        4+4

(c) How the nature, position and stereo-chemistry of – COOH group in abietic acid were established ?        5

10. (a) How would you justify the participation of three molecules of ATP during the following conversion :



R-(+)-Mevalonic acid        IPP        3

(b) Abietic acid $\xrightarrow{\text{Se}}$



How much information could be procured from the above conservasion regarding the structure of abietic acid ?        3

(c) Propose mechanism for the formation of $\alpha$-terpineol and limonene from geranyl pyrophosphate (GPP).        3

(d) Explain the following conversion :　　　　3+3