M.Sc. 3rd Semester Examination, 2010

CHEMISTRY

(Physical Special/Inorganic/Organic Special)

PAPER—CH-2101

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Physical Special*)

Answer any four taking two from each Group

GROUP—A

Answer any **two** of the following

1. (*a*) Give definition (*i*) relative percentage error (*ii*) absolute error (*iii*) round off the following number to four significant figures : 0·04356 5

(*b*) Obtain trapezoidal rule for numerical integration. 5

2. (*a*) If the product of two matrices A and B is a null matrix, show with an example that neither of them is a null matrix. 5

(*b*) If $ABC = D$ then show with an example $d_{ij} = \sum_{k} \sum_{l} a_{ik} b_{kl} c_{lj}$ 5

3. (*a*) Derive the matrix representation of $\hat{S}_z$ operator. 5

(*b*) Find out the normalised eigenfunction of $\hat{S}_x$ and $\hat{S}_y$ operator. 5

4. Derive the total electronic energy of a many electron atom in terms of Hartree orbital energy with a short discussion of essential features of Hartee SCF theory. 10

GROUP–B

Answer any **two** of the following

5. (*a*) If ϕ_1 and ϕ_2 are two orthonormal space orbitals supplied then how many two electron functions can be constructed ? Convert any one of them to slater determinant. 5

(*b*) Derive the normalisation constant of a 2N electron closed-shell system. 5

6. Discuss in details the basic differences between Hartree and Hartree-Fock self-consistant field method. 10

7. (*a*) What do you mean by linear vector space and linear function space? Give one example for each. 2

(*b*) Obtain the general form of transformation matrix which can transform one base vector to another in a given linear function space. 5

(*c*) Each nondegenerate molecular orbital of a molecule belonging to a particular point group serves as a basis for a one-dimensional IR of the point group. Explain. 3

8. Use group theoretical principle to obtain the splitting of *d*-orbitals of a transition metal ion in

an octahedral environment. Following is the character table for rotational subgroup 'O'. 10

'O'	E	$6C_4$	$3C_2$	$8C_3$	$6C_2'$		
A_1	1	1	1	1	1		$(X^2 + Y^2 + Z^2)$
A_2	1	-1	1	1	-1		
E	2	0	2	-1	0		$(2Z^2 - X^2 - Y^2, X^2 - Y^2)$
T_1	3	1	-1	0	-1	(X, Y, Z) (R_X, R_Y, R_Z)	
T_2	3	-1	-1	0	-1		(XY, YZ, ZX)

(*Inorganic*)

Paper – CH-2101

Answer any **four** questions

1. For *trans*-dichloro bis-ethylenediamine cobalt (111) complex the ground state is $^1A_{1g}$ and excited singlet states are $^1A_{2g}$, ^1E_g and $^1B_{2g}$. Show that : 4 + 6

(*i*) $^1A_{1g} \rightarrow {}^1A_{2g}$ transition is vibronically allowed with (x, y) polarized light but forbidden with z-polarized light.

(*ii*) $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ transitions are vibronically allowed with (x, y) and z-polarized light.

(Given below the character table for D_{4h} point group).

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

2. Use group theoretical principle to determine the symmetry of vibrational modes of *cis*-[Pt Cl_2 X_2] molecule using Cartesian coordinate method and internal coordinate method. Comment on the results. Determine the missing modes in internal coordinate method. Identify the symmetry of 1R and Raman active mode in this molecule. (Given below the character table for C_{2v} point group).

3 + 3 + 1 + 2 + 1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

3. (*a*) With the help of group theory determine the symmetrics of the ligand group of orbitals which are effective for σ-bond formation in $[PtCl_4]^{2-}$ ion. Construct a qualitative σ-bonding molecular orbital energy level diagram for $[PtCl_4]^{2-}$ ion. (Use the character table of D_{4h} point group given in **question No. 1**). 7

(*b*) Find out the hybridization of Co atom in $[CoCl_4]^{2-}$ ion. 3
(Given below the character table for T_d point group).

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, yz, zx)

4. (*a*) Write the energy expression of NQR spectroscopy explaining each term. 2

(*b*) The ^{11}B NMR spectrum of $B_3H_8^-$ is nonet. Explain. 2

(*c*) Discuss the XPS of Pd metal explaining the energy levels. 3

(*d*) What is dipolar and contact shifts in NMR spectroscopy. 3

5. (*a*) What do you mean by "Exclusion rule"? Justify this rule using *trans*-N_2F_2 as an example. (Given below the character table for C_{2h} point group). 6

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

(*b*) Determine the symmetrics of the vibrational modes in H_2O. (Use the character table of C_{2v} point group given in **Q. No. 2.**) 4

6. (*a*) How would you predict the structure of $PFCl_4$ from its NQR spectrum? 3

(*b*) What is "electric field gradient"? 2

(*c*) How would you predict the binding mode of thiocyanate ion by meant of 1R spectroscopy? 3

(*d*) Predict ^{19}F spectrum of $[SiF_6]^{2-}$. 2

7. (*a*) How spin-orbit coupling splits the spectral level in photoelectron spectroscopy? 4

(*b*) What is the major application of Ultraviolet photoelectron spectroscopy. 2

(*c*) What is So special about ^{19}F spectrum of IF_5? How paramagnetic nuclei would help to improve the situation? 4

(*Organic Special*)

Paper–CH-2101

Answer any **five** questions taking atleast **two** from each Group

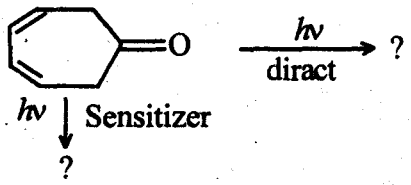
GROUP–A

Answer any **two** of the following

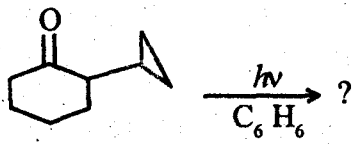
1. (*a*) What is Norrish type-I and type-II reactions. Explain the mechanism of these reactions with suitable examples. 2 + 2

(*b*) Predict the product/s of the following reactions with mechanism (attempt any *one*): 2

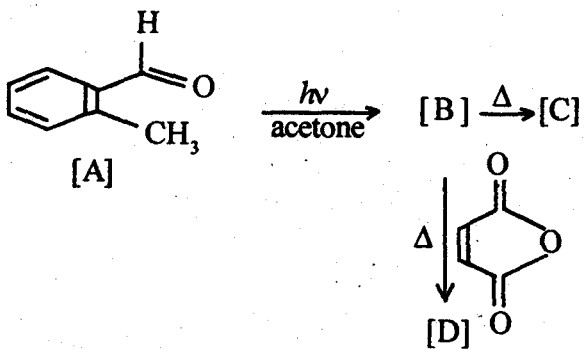
(*i*)



(*ii*)

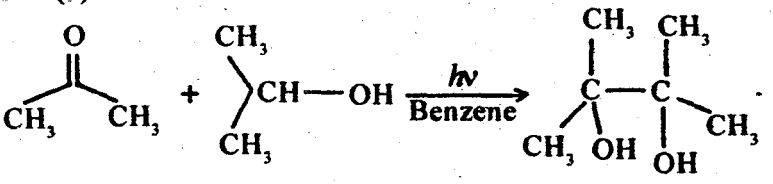


(*c*)



Identify the products *B*, *C* and *D*. 2

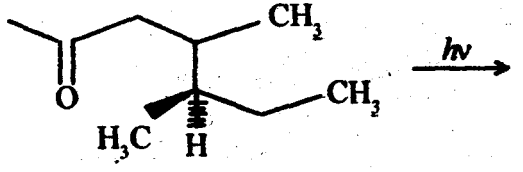
2. (*a*)



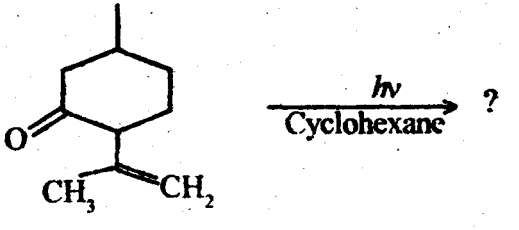
Quantum yield (ϕ) for the above reactions was observed '1'. Explain the mechanism of the reaction and establish this observation. 2

(*b*) Predict the product/s of the following reactions with proper explanation and mechanism (attempt any *three*): 2 x 3

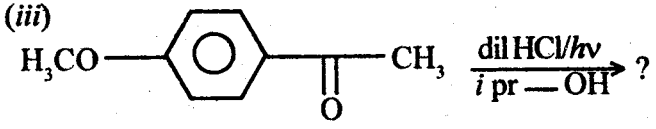
(*i*)



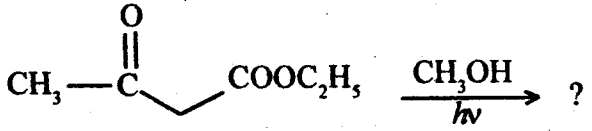
(*ii*)



(*iii*)

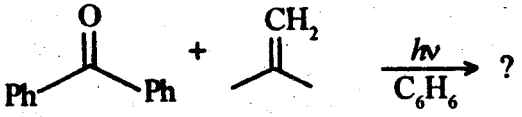


(*iv*)

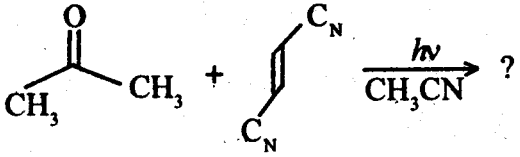


3. (*a*) **Predict the product/s of the following reaction showing mechanistic difference in each case, with explaination;** 2 + 2

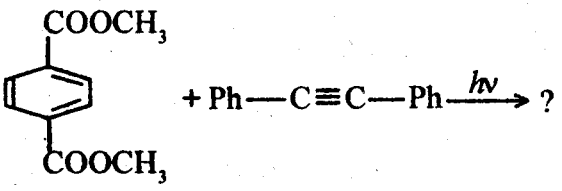
(*i*)



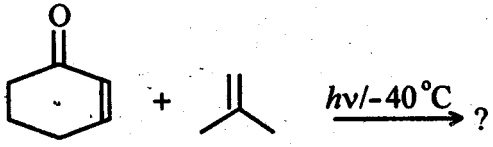
(*ii*)



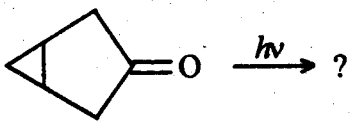
(*b*) (*i*) **Predict the products with mechanism (attempt any *two*):** 2 x 2



(*ii*)

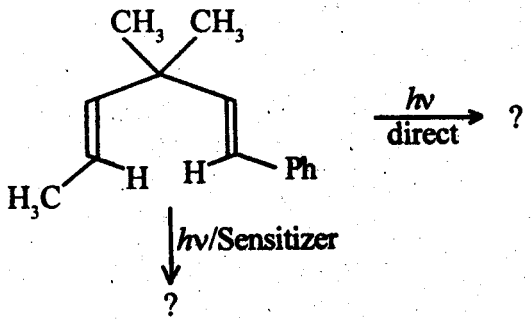


(*iii*)

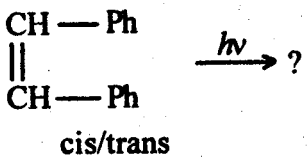


4. (*a*) Predict the product/s of the following reactions and indicate mechanism in each case; $2\frac{1}{2} \times 2$

(*i*)



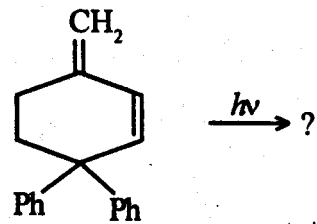
(*ii*)



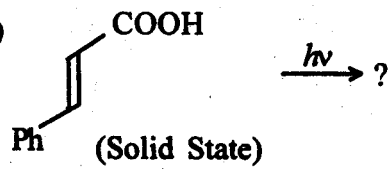
(*Continued*)

(*b*) Predict the products with mechanism (attempt any *two*) : $1\frac{1}{2} \times 2$

(*i*)

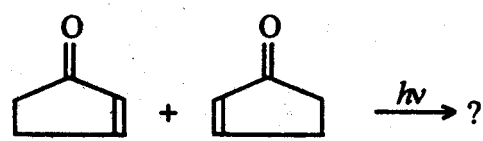


(*ii*)



(Solid State)

(*iii*)

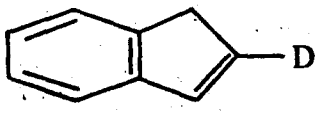


5. (*a*) Write down the Woodward-Hoffmann rules for *H* and *C*-migration in sigmatropic reactions. 3

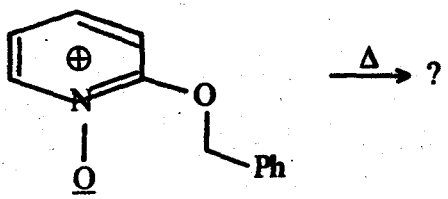
(*b*) "1, 3-H migration is difficult to achieve"– explain the statement. 1

(*c*) Predict the product of the following with Frontier orbital interaction (attempt any *two*) : 2 x 2

(*i*)



(*ii*)



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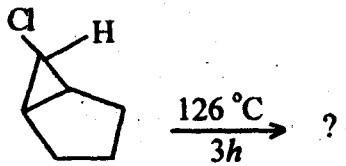

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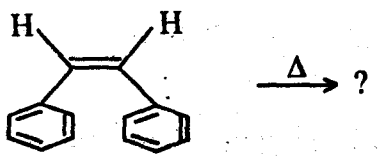


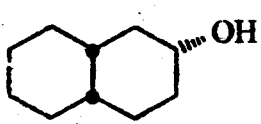
(*Continued*)

GROUP–B

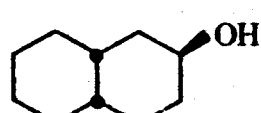
6. Deduce from the first principle the Curtain-Hammett principle (with the help of a potential energy diagram) for a case where the more stable conformer gives rise to the predominant product. Illustrate with an example, how you can find out $\Delta G^{\neq}$. 6+2

7. Answer any *two* of the following: 4x2

(*a*) Name the compounds (1) and (2) with their absolute configuration. Using the Winstein-Holness equation explain the relative rates of saponification of their *p*-nitrobenzoate esters in terms of their conformations.



(1)

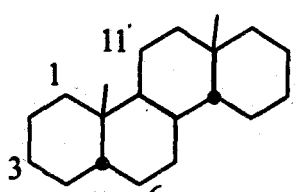


(2)

(*b*) (*i*) Comment on the optical activity of cyclohexene and 4-methylcyclohexene in terms of their conformations.

(*ii*) Explain the relative stability of the two isomers of 2-phenyl-4-*t*-butylcyclohexanone. Explain the salient points in the steps for the complete conversion (100%) of the more stable isomer into the less stable one.

(*c*) Correctly draw the conformation of the diastereomer (**3**) of cyclopentanoperhydrophenanthrene, Comment on the relative rates of CrO_3 oxidation of its three monohydroxy derivatives having OH at 3β-, 6β - and 11β- positions.



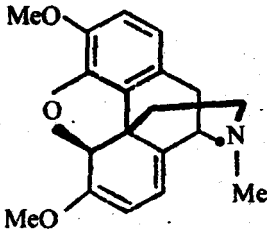
(**3**)

(*Continued*)

8. Write down the flipped conformers of 9 (S), 10 (R)-9-methyl-*cis*-2-decalone. Find out the signs of the torsion angles at the ring fusion bond in both rings directly from the conformations by application of a relevant rule, and hence label the steroid and nonsteroid forms. Explain the nomenclature of the conformers. 8

9. (*a*) Derive the expression for the equilibrium constant K of a monosubstituted cyclohexane by use of ^{1}H NMR spectroscopy. Illustrate it in case of methyl cyclohexanecarboxylate. 4

(*b*) Explain the following reactions sequence with mechanism Designate the absolute configuration of (C) according to the new CIP convention. 4



(--)-Thebaine

$$\xrightarrow{PhMgBr} (A) \xrightarrow[Ag_2O]{MeI} (B) \xrightarrow[Ag_2O]{MeI} (C)$$