PG/IIIS/CH - 2101/09

2009

CHEMISTRY

PAPER—CH-2101

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Inorganic*)

Answer any *four* questions

1. In $[Co(NH_3)_6]^{3+}$, the ground state belongs $^1A_{1g}$ representation and two excited states belong to $^1T_{1g}$ and $^1T_{2g}$ representation. Show that the

electronic transition from the ground state to these excited states will be vibronically allowed.

(Given below the character table for O_h point group). 10

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
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		
E_g	2	-1	0	0	2	2	0	-1	2	0		
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	$(2z^2-x^2-y^2,\ x^2-y^2)$
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		(xz, yz, xy)
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

2. With the help of group theory determine the symmetries of the atomic orbitals of F atoms which are effective for σ–bond formation in SF_6 molecule. Construct a qualitative σ–bonding molecular orbital energy level diagram for SF_6 molecule. (Use the character table of O_h point group given in **Question No. 1**). 10

3. Use group theoretical principle to determine the symmetry of vibrational mode of ML_5 (square pyramidal) molecule using Cartesian coordinate method and internal coordinate method. Comment about the results. Identify the symmetry of IR and Raman active mode in this molecule. 4 + 4 + 1 + 1

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2+y^2,\ z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)\ (R_x, R_y)$	(xz, yz)

4. **(*a*)** Establish the relation

$$\chi(\alpha) = \frac{\sin\left(I+\frac{1}{2}\right)\alpha}{\sin \alpha/2}.$$ 6

(*b*) What do you mean by "exclusion rule"? 1

(*c*) With the help of group theory find out the hybridization of *B* atom in BF_3 molecule. 3

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2,\ z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

5. (*a*) Predict ^{19}F nmr spectrum in $9F_5$ molecule. 3

(*b*) Discuss briefly the ^{31}P NMR of $HP_2O_5^{3-}$ molecule. 3

(*c*) Discuss the physical basis of photoelectron spectroscopy. 4

6. (*a*) What is the principle of NQR spectroscopy? 2

(*b*) What do you mean by Fourier transform technique? 2

(*c*) A particular Mössbauer nucleus has spins 3/2 and 1/2 in its excited and ground states, respectively. How will the γ-ray spectrum split up under the following conditions:

(*i*) the nucleus is under the influence of an internal electric field gradient, but no magnetic field is applied.

(*ii*) there is no magnetic field gradient at the nucleus but an external magnetic field is applied.

(*iii*) both an internal electric field gradient and an external magnetic field are present? 2 + 2 + 2

7. (*a*) What is Koopman's theorem? 3

(*b*) The compound $PFCl_4$ can exist in two different isomer, NQR spectroscopy predicts one of them in solid state — discuss. 3

(*c*) ^{31}P resonance in P_4S_3 consists of two peaks with intensity ratios of 3 : 1. The more intense peak is a doublet and the less intense is a quadruplet. Predict the structure of P_4S_3 from above information. 4

(*Organic*)

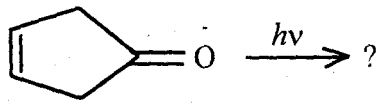
Answer any *five* questions taking at least *two* from each Group

GROUP—A

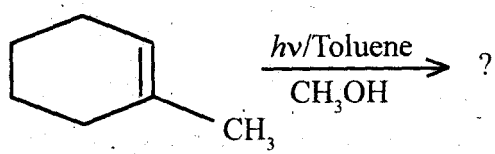
1. (*a*) What is Jablonski diagram? Show various transitions occurring between ground and excited states initiated through photochemical irradiation. (Show the diagram only) 2

(*b*) Predict the product(s) of the following reactions with mechanism (attempt any *four*): $1\frac{1}{2} \times 4$

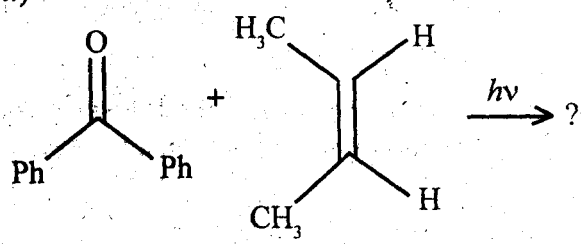
(*i*)



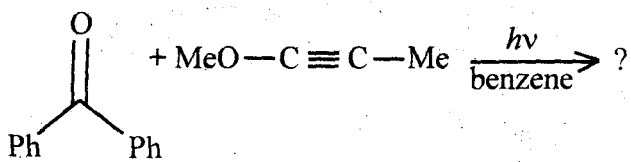
(*ii*)



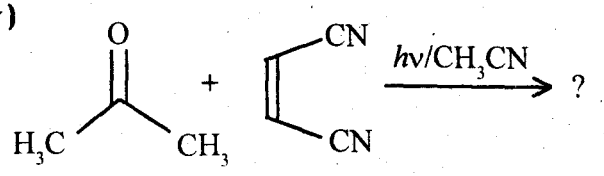
(*iii*)



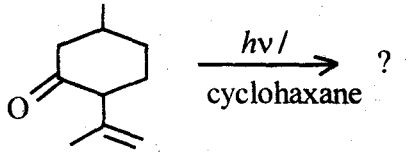
(*iv*)



(*v*)



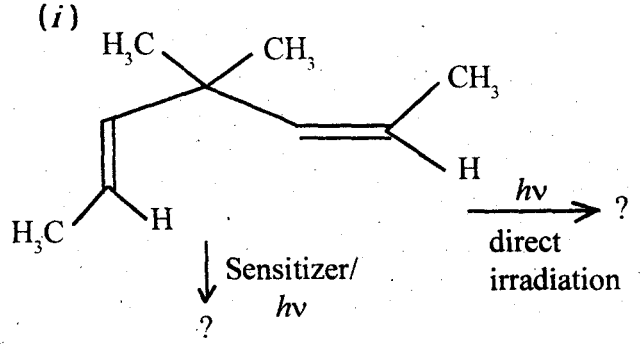
(*vi*)



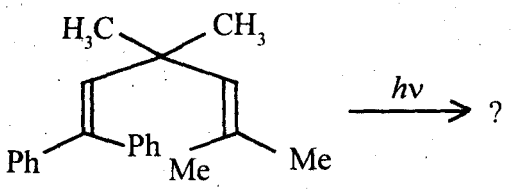
2. (*a*) What is di-π-methane rearrangement reaction? Explain the orbital interactions showing symmetry allowed path for the reaction with suitable example(s). 3

(*b*) What happens when the following compounds are photolysed? (attempt any *one*): 2

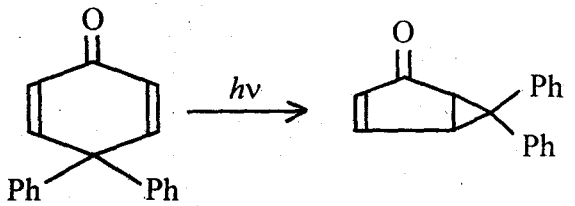
(*i*)



(*ii*)

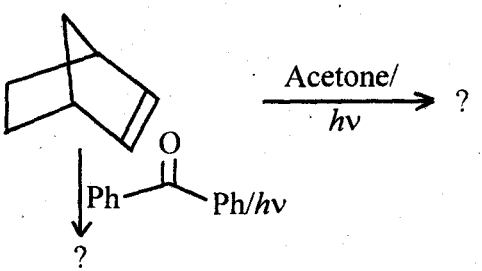


(*c*) Explain the mechanistic path of each of the steps of the following reaction;



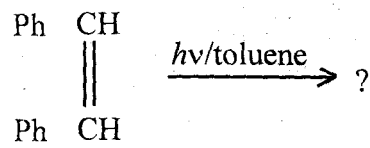
Rationalise that the reaction does not follow di-π-methane rearrangement reaction. 3

3. (*a*) What is Paterno-Buchi addition reaction? Explain the mechanism with suitable example(s) and predict the product of the following reaction; 2 + 2



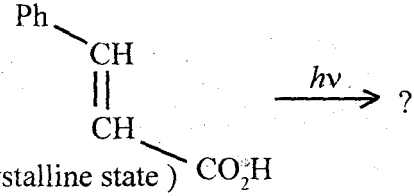
(*b*) Predict the product(s) of the following reactions with mechanism (attempt any *two*): 2 × 2

(*i*)

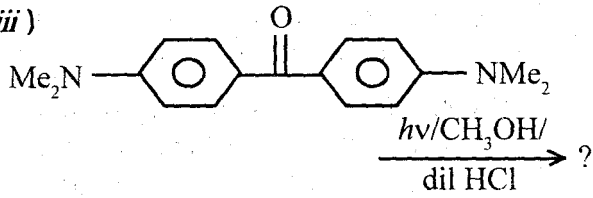


(*ii*)

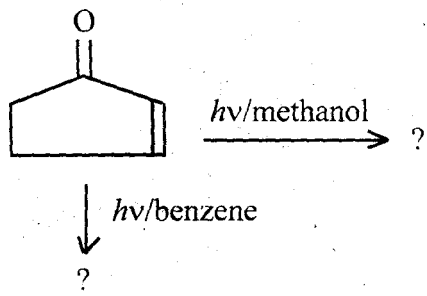
Cis/trans



(*iii*)



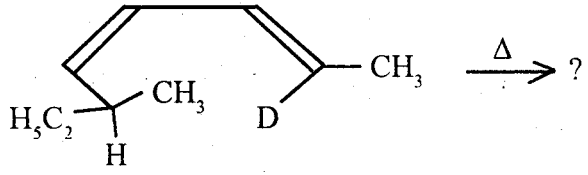
(*iv*)



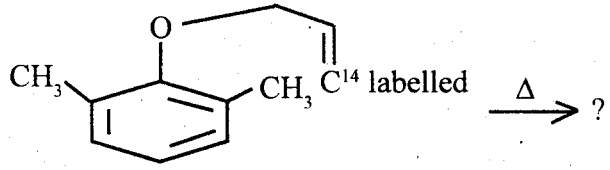
(*Continued*)

4. (*a*) What are supra and antarafacial processes in sigmatropic reactions? What is [*i*, *j*] sigmatropic shifts and hence predict the product of the following reaction with plausible mechanism: (attempt any *one*) 2 + 2

(*i*)

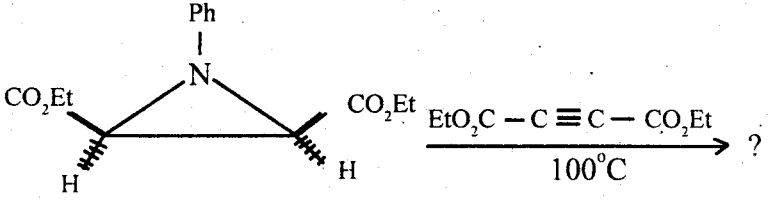


(*ii*)

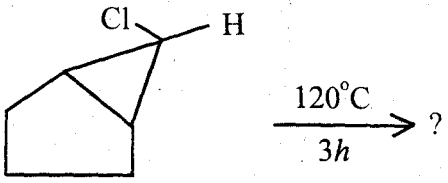


(*b*) Carry out the following transformation indicating F.O.I (any *two*): 2 × 2

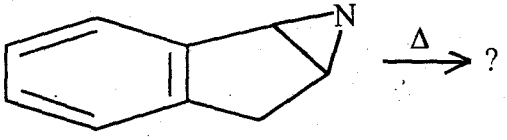
(*i*)



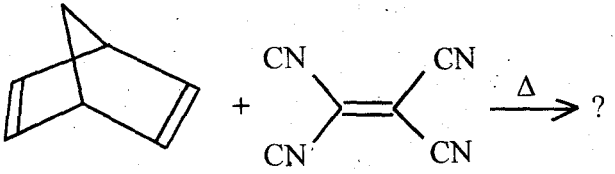
(*ii*)



(*iii*)



(*iv*)



GROUP—B

5. (*a*) Draw the Newman projection formulae of *cis*-decalin (any conformer) and *trans*-decalin to demonstrate the torsion angle signs at both sides of the ring junction of each. 3

(*b*) Justify the names of the conformers of *cis* -decalin. Illustrate the rule by which one can find out the torsion angle sign at the inner side of any chair conformation. 3

(*c*) *cis*-Decalin lacks reflection symmetry, still it is optically inactive, whereas 1- or 2-substituted *cis*-decalin is optically active. Explain. 2

6. (*a*) Deduce the Eliel equation displaying the relationship between equilibrium constant and the different specific rate constants of a mobile system. How can you derive Winstein-Holness equation from the Eliel equation? 5

(*b*) The specific reaction rates of the acetylation (with Ac_2O/Py at 25°C) of *cis*-4-*t*-butylcyclohexanol, *trans*-4-*t*-butylcyclohexanol and *cis*-4-methylcyclohexanol are 2·89, 10·65 and 3·76 units (the unit is 10^{-5} l mol^{-1} sec^{-1}). Find out the conformational equilibrium constant of 4-methylcyclohexanol, and hence calculate ΔG (conformational free energy) for its two conformers. 3

7. (*a*) Comment on the relative stability and optical activity of the two conformers each of the E and Z diastereomers of 2-methylcyclohexylidene acetic acid. $2\frac{1}{2}$

(*b*) Which diastereomer of 2-methyl-4-*t*-butylcyclohexanone is more stable and why? How can you effect the complete (100%) conversion of the more stable diastereomer into the less stable one, explain the steps. 3

(*c*) Comment on the relative rates of CrO_3 oxidations of cholesten-3β-ol and cholesten-6β-ol. $2\frac{1}{2}$

8. (*a*) Complete the following reaction sequence and rationalize mechanistically. Show the involvement of the π-orbitals in the second step. Name $\underline{\underline{A}}$ and $\underline{\underline{C}}$ and designate the absolute configuration of $\underline{\underline{C}}$. 4

$$(\underline{R})\text{-}(-)\text{-MeCHOH.C}\equiv\text{CH} \xrightarrow[H^{\oplus}]{Me_2CHCHO} \underline{\underline{B}} \xrightarrow[\Delta]{SiO_2} (-)\text{-}\underline{\underline{C}}.$$

(*b*) *cis*-2-Decalone upon bromination with bromine in acetic acid forms predominantly the axial 1-bromo derivative. Explain this fact in terms of mechanism, and stereoelectronic and steric factors involved. 4

(*Physical Spl.*)

Answer any *four* questions
taking *two* from each Group

GROUP—A

1. (*a*) Given

x	1	2	3	4	5	6	7	8
$f(x)$	1	8	27	64	125	216	343	512

find $f(1\cdot5)$. 5

(*b*) Evaluate

$$\int_0^1 (4x - 3x^2)\, dx,$$

taking 10 intervals, by Trapezoidal rule. 5

2. (*a*) Find the matrix representation of $\hat{S}y$. 5

(*b*) Write a note on projection operator. 5

3. (*a*) Derive the matrix representation of Schrödinger equation. 5

(*b*) Describe independent particle model and calculate the ground state energy of Li atom using this model. 5

4. (*a*) Derive Hartree-Fock SCF theory. 6

(*b*) Convert the Hartree-Fock equations to pseudo eigenvalue form. 4

5. Obtain the expression for the total energy of a 2N-electronic atom in a closed shell configuration using a slater determinantal wave function. State the meaning of the integrals involved in the expression. 10

GROUP—B

6. (*a*) Discuss unitary transformations with examples. 6

(*b*) Show that Koopman's theorem is valid at the Hartree-Fock SCF level. 4

7. (*a*) Show that

$$<\hat{H}> = \sum_{\mathscr{P}} (-1)^{p} < S_1(1) \ldots S_{2N}(2N) \mid \hat{H} \mid \mathscr{P} S_1(1) \ldots S_{2N}(2N) >$$

for a closed shell configuration. 6

(*b*) Show that Hartree-Fock operator is in variant under unitary transformation. 4

8. (*a*) What do you mean by linear space and basis vector ? Illustrate with an example. 3

(*b*) How do you obtain the representation of a vector from a given basis to another basis within a vector space ? 4

(*c*) Show that, the eigenvector matrix that diagonalises a hermitian matrix is unitary in nature. 3

9. (*a*) Find the rotational matrix in the basis set of (e_1, e_2, e_3) where e_1 and e_2 are unit vectors and are inclined at an angle 'α' to one another and e_3, the unit vector perpendicular to both e_1 and e_2 is the axis of rotation. 4

(*b*) The linear relation between the complex p–wavefunctions and the real p–orbitals are

$$p_{+1} = \frac{1}{\sqrt{2}} p_x + \frac{i}{\sqrt{2}} p_y$$

$$p_{-1} = \frac{1}{\sqrt{2}} p_x - \frac{i}{\sqrt{2}} p_y$$

$$p_0 = p_z$$

If the representation matrices for C_3 and C'_2 of the point group D_3 in the basis set (p_x, p_y, p_z) [Written as a row matrix] be

$$D(C_3) = \begin{pmatrix} -\frac{1}{\sqrt{2}} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$D(C'_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

What will be the corresponding matrices in the bais set (p_{+1}, p_{-1}, p_0)? 6

10. (*a*) Show that for direct product representation of two square matrices

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \text{ and } B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$$

the character $\chi(A + B) = \chi(A)\,\chi(B)$. 5

(*b*) Prove that in the C_{3v} point group,

$$E \times E = A_1 + A_2 + E.$$ 3

(*c*) Diagonalize the σ_3 matrix : 2

$$\sigma_3 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \text{ by}$$

$$X = \begin{pmatrix} \sqrt{3}/2 & 1/2 \\ -1/2 & \sqrt{3}/2 \end{pmatrix}$$

[Given character table for C_{3v} point group :

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

].