



CHE 514 / CHE 515 / CHE 516

M.Sc. (IIIrd SEMESTER) EXAMINATION, 2023-24

(CBCS Mode)

CHEMISTRY

Paper : II A / II B / II C

Time : Three Hours]

[Maximum Marks : 75

1509

CHE 514 : Quantum Chemistry II

Paper : II A

Note : There are three sections (A, B and C) and Candidate has to attempt all questions. Marks are indicated against each section.

Section-A

1. Answer all questions. 5×3=15
- (a) Explain the meaning of invariability of a wave function under symmetry operation.
 - (b) What is difference between slater type orbitals (STOs) and Gaussian type orbitals (GTOs)?
 - (c) Explain why cyclobutadiene molecule is unstable ?
 - (d) What is meant by reducible and irreducible representation of a group ?
 - (e) What do you mean by the term direct product representation ?

Section-B

Note: Answer all questions of the following : $4 \times 5 = 20$

2. (a) Discuss the concept of Aromaticity and Antiaromaticity.

Or

- (b) Explain Density Functional Theory (DFT) and its applications.

3. (a) Derive the condition for the activity of a fundamental modes of vibration of a molecule in IR spectrum.

Or

- (b) Discuss the relative stability of cyclopropenyl cation, radical and its anion.

4. (a) Discuss the assumption of HMO theory.

Or

- (b) Describe Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

5. (a) Explain Moller-Plesset (MP) perturbation theory.

Or

- (b) Write down secular determinant for benzene using HMO theory and calculate its delocalization energy.

Section-C

Note: Answer any two questions of the following : $2 \times 20 = 40$

6. Apply Huckel molecular orbital (HMO) theory for the calculation of π (Pi) electron energy and delocalization energy of 1, 3-butadiene.
7. What is basis set ? Explain types of basis sets with suitable examples.
8. Explain molecular mechanics. Discuss about force-field. Give the advantages and disadvantages of molecular mechanics.
9. What are symmetry operations ? Discuss the construction of π (Pi) molecular orbitals of naphthalene.

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CHE 515 : Chemical Application of Symmetry and Group Theory

Paper : II B

Note : There are three sections (A, B and C) and Candidate has to attempt all questions. Marks are indicated against each section.

Section-A

1. Answer all parts of this questions. 5×3=15
 - (a) Determine the point group in $ML_3 L_3$ (fac), where M is central atom and L and L' stands for the ligands.
 - (b) Define cyclic group with examples.
 - (c) Show all the symmetry elements in D_{6h} point group.
 - (d) Give matrix representation of all the symmetry elements present in C_{3v} point group.
 - (e) With respect to normal mode analysis of Td point group, work out the IRs of lint by internal coordinate method. The character table is given below.

| 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, xz, yz) |

Section-B

Note: Answer all questions of the following : $4 \times 5 = 20$

2. (a) Find out the fundamental vibrational modes of ammonia by Cartesian and internal coordinate methods. Comment on the IR and Raman activities. Draw the diagram of the vibrational modes. The relevant character table is given below :

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | | |
|----------|---|--------|-------------|---------------------|----------------------------|
| A_1 | 1 | 1 | 1 | z | $x^2 + y^2, z^2$ |
| A_2 | 1 | 1 | -1 | R_z | |
| E | 2 | -1 | 0 | $(x, y) (R_x, R_y)$ | $(x^2 - y^2, xy) (xz, yz)$ |

Or

- (b) Give the example of 'Reducible Representation', Selecting the point group of your choice. Reduce the representation into irreducible one.
3. (a) Derive the effect of weak crystal field on 'F' and 'G' spectroscopic terms in On point group the relevant character table is given below :

| 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 | $(2z^2 - x^2 - y^2, x^2 - y^2)$ |
| T_{1g} | 3 | 0 | -1 | 1 | -1 | 3 | 1 | 0 | -1 | -1 | (R_x, R_y, R_z) |
| T_{2g} | 3 | 0 | 1 | -1 | -1 | 3 | -1 | 0 | -1 | 1 | (xy, yz, xz) |
| A_{1u} | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | |
| 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 | |

Or

- (b) What do you understand by "Similarity transformation"? Prove that all the symmetry operations of C_{2v} point group.
4. (a) What is meant by representation of a group? Explain the rules needed for the formation of a group with suitable example.

Or

- (b) Work out the point group symmetry of the following molecules / Ions :
- CO_3^{--}
 - $[PtCl_4]^{--}$
 - B_2H_6
 - SO_2
 - PCl_5

5. (a) Derive matrix for rotation operation by angle $Q = \pi/2$ (clockwise). Assume Z-axis as axis of rotation.

Or

- (b) What do you understand by the term 'Classes'? Explain the rules involved in detail.

Section-C

Note: Answer any two questions of the following. $2 \times 20 = 40$

6. Explain the following giving a suitable example in each case.
- (i) Rotation-reflection axis, S_4
 - (ii) Dihedral plane of symmetry, σ_d
 - (iii) Cubic point group
 - (iv) Abelian group
7. State the 'Great' Orthogonally theorem. Explain its each term in detail.
8. What do you understand by the term "Block Factorisation" of large matrices ? Explain with example.
9. Write short notes on any two :
- (i) Group generating elements
 - (ii) Symmetry operations in O_h point group
 - (iii) Isomorphic groups



CHE 516 – Stereochemistry

Paper : II C

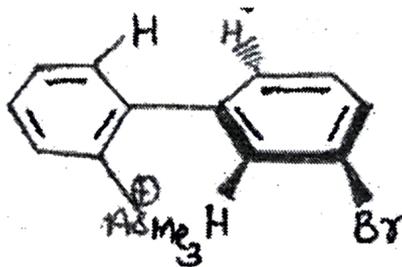
Note : There are three sections (A, B and C) and Candidate has to attempt all questions. Marks are indicated against each section.

Section-A

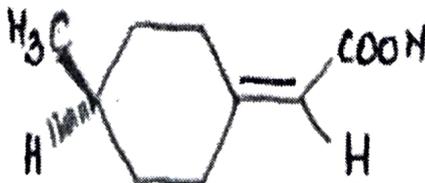
1. Answer all questions. 5×3=15

(a) Designate the absolute configuration of the following compounds :

(i)

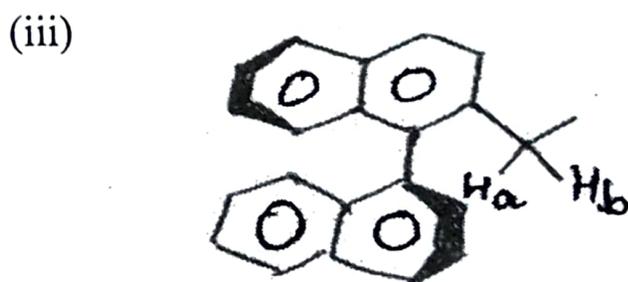
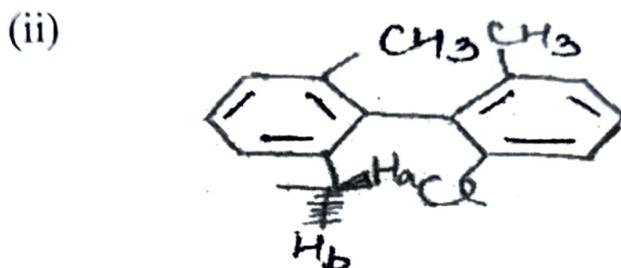


(ii)



(b) Write a concise note on the chirality of amines.

- (c) Write the relation between H_a/H_b atoms and assigned the configuration of the compounds.



- (d) Draw the preferred conformation of cis-2-methylcyclohexanol and give suitable reason.
- (e) What is optical purity ? Explain it with suitable example.

Section-B

Note: Answer all questions of the following : $4 \times 5 = 20$

2. (a) Write the structure of meso tartaric acid in Newman projection and translate it into Fischer Projection, Sawhorse and Wedge Dash representations.

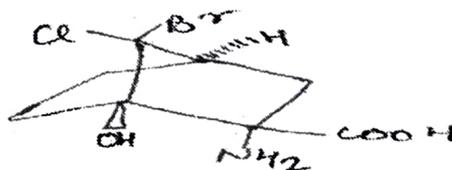
Or

- (b) What do you mean by stereogenic carbon? Illustrate the chirality in compounds lacking stereogenic carbon atoms with at least one example?
3. (a) Assign absolute configuration of each chiral centres of the compounds (i & ii) and helical descriptors (P/M) of the compounds (iii & iv):

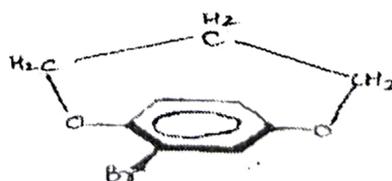
(i)



(ii)



(iii)



(iv)



Or

(b) Intermolecular overcrowding leads to molecular dissymmetry and give rise to optical activity explain.

4. (a) Draw all possible conformation of the following and comment on their relative stabilities.

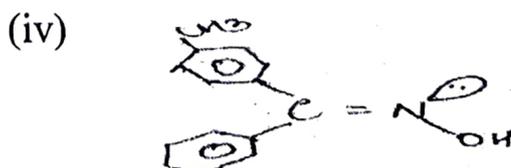
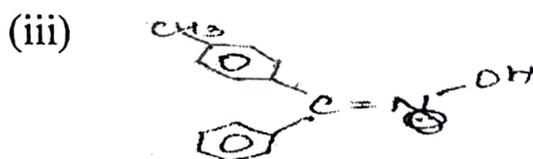
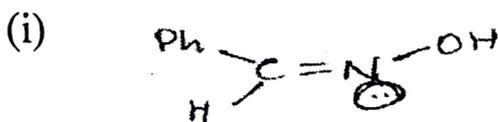
(i) Cyclohexane-1,2-diol

(ii) 2-Iodocyclohexanone

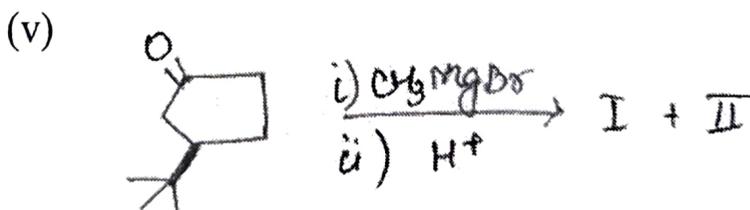
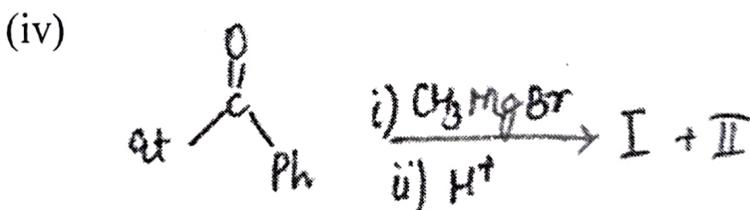
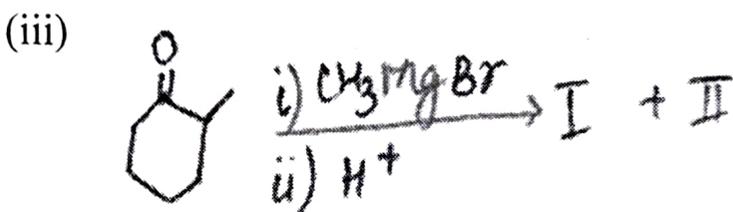
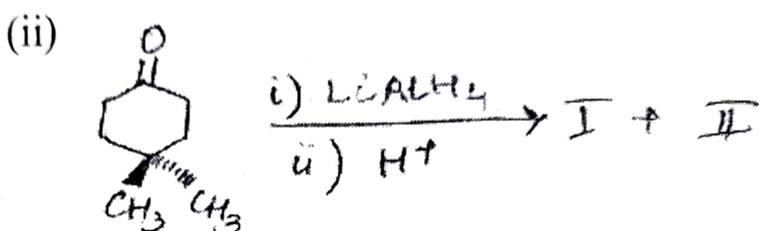
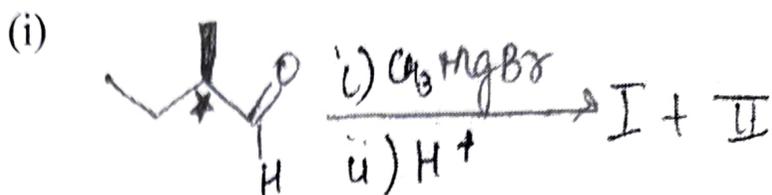
Or

(b) (i) What is is-trans isomerism of compounds containing (C=N). Explain it with suitable examples.

(ii) Write the nomenclature of the following compounds :



5. (a) Identify the faces between compounds, I & II of each pairs and also write the product I & II:



Or

- (b) What are regioselective reactions? Explain it by using examples.

Section-C

Note: Answer any two questions of the following : $2 \times 20 = 40$

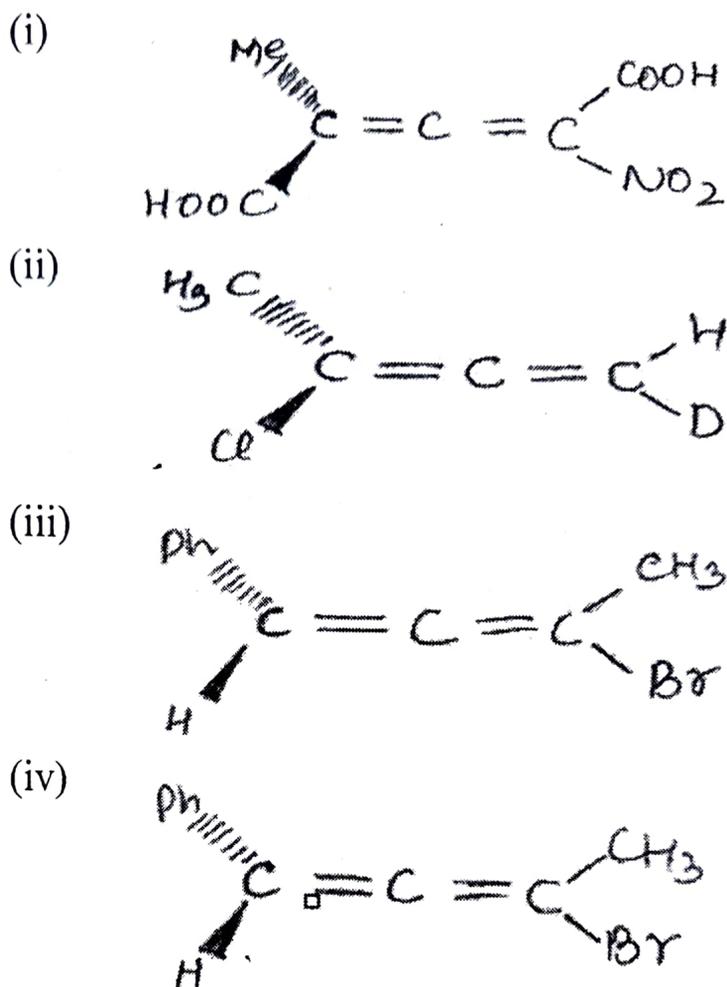
6. Define atropisomerism with its conditions. Explain atropisomerism of biphenyls on the following points.

(a) Conditions of biphenyl atropisomers to be resolvable.

(b) Procedure adopted to specify absolute configuration of suitably substituted biphenyls.

7. (a) Account for the cause of resolvability in suitable allene derivatives, write explanatory notes on structure and optical activity of allenes.

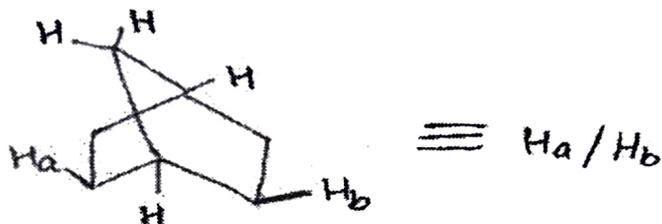
(b) Assign absolute configuration of following allenes using elongated tetrahedral approach:



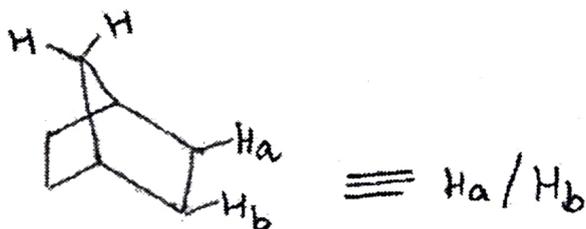
8. (a) Discuss the configurational and conformational aspects of disubstituted cyclohexane derivatives
- (b) What are Chiral reagents ? Explain it by using suitable examples.
9. (a) How can you determine the configuration of Aldoximes & Ketoximes. Give proper explanation with suitable examples.

- (b) How E and Z systems are suitable to specify the configuration of oximes. Give suitable explanation with examples.
- (c) Write the relation between the following given atom of molecules.

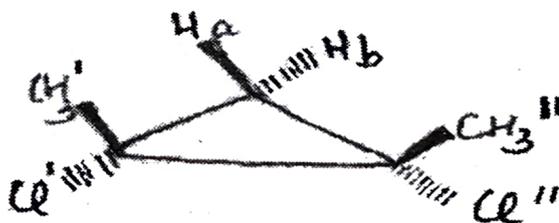
(i)



(ii)



(iii)



(iv)



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