III Semester M.Sc. Examination, January 2019
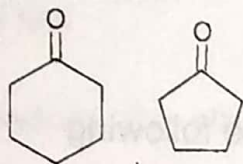
(CBCS)

CHEMISTRY

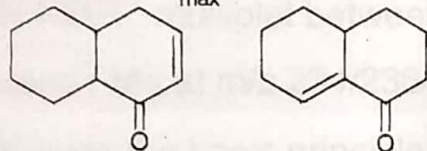**303 : OC : Organic Spectroscopy**

Time : 3 Hours

Max. Marks : 70

Instruction : Answer question no. **1** and **any five** of the following.

1. Answer **any ten** of the following : (10×2=20)

   a) Which of the following has higher stretching frequency for carbonyl group ? Give reason.

   b) Calculate λ_{max} value for the following compounds using Woodward-Fiser rules.

   c) Write briefly the solvent effect on n → Π* transition in UV spectroscopy.

   d) Differentiate chemically equivalent and magnetically equivalent protons taking suitable example.

   e) Integration is used in the interpretation of PMR but not for ^{13}CMR. Why ?

   f) What are deuterium exchange reactions ? Mention their importance.

   g) Write the structure of an organic compound (MF : $C_3H_4Cl_2O$) that shows a singlet in its PMR spectrum.

   h) How do you differentiate between Cis– and trans-protons in an olefin by ^1H– NMR ?

   i) How do you distinguish acetanilide and N-methyl benzamide by ^{13}C NMR ?

   j) State nitrogen rule and give its importance in mass spectrometry.

   k) Deduce the structure of the compound from following spectral data :

   Mol. formula : $C_{10}H_{12}O_2$

   IR : 1780, 2985, 1600 cm^{-1}

   ^1H NMR = 1.2 (d,6H), 3.8(septet, 1H) and 7.8 (s, 5H).

   l) EI-MS are recorded only in rarified gaseous state. Explain.

2. a) A compound with M.F $C_6H_{10}O$ gave the following spectral data. uv : λ_{max} : 237 ($\varepsilon = 11700$) and 310 ($\varepsilon = 57$) IR : 3020, 2980, 1680 (vs) and 1460 cm^{-1}. Deduce the structure of the compound.

b) How do you distinguish between intramolecular and intermolecular hydrogen bonding using IR spectroscopy ?

c) Explain the factors affecting group frequencies in IR spectroscopy. (4+3+3=10)

3. a) Discuss anisotropic effects prevalent in ^1H NMR for

   i) Alkenes

   ii) Alkynes.

b) Write a note on chemical shift reagents :

c) Give an example each for compounds which exhibit the following spin-systems according to Pople's nomenclature. (4+3+3=10)

   i) AX,

   ii) AM_2,

   iii) AB and

   iv) A_3X_2.

4. a) Write briefly about off resonance decoupled ^{13}C NMR spectrum.

b) Account on Nuclear Overhauser effect.

c) Discuss ^{19}F NMR spectroscopy.

(3+4+3=10)

5. a) Explain the mechanism of McLafferty rearrangement taking suitable example.

b) Deduce the structure of an organic compound with mol.wt, 150 shows the following spectral data :

UV : λ_{max} 276 nm ; IR : 3030-2979, 1695, 1692 cm^{-1}

^1H NMR = 2.1(s, 3H), 3.85(s, 3H), 7.2(d, 2H) and 7.65(d, 2H)

c) Write briefly about FAB method of ionisation and give its advantages over other methods of ionisation.

(4+3+3=10)

6. a) Write the comparison between IR and Raman.

   b) Comment on the ^1H NMR spectra of completely pure and slightly impure ethanol sample.

   c) Give an account on vicinal coupling and geminal coupling. **(3+3+4=10)**

7. a) Write note on COSY.

   b) Sketch proton coupled, proton decoupled and off-resonance decoupled ^{13}C NMR of 4-methyl acetophenone.

   c) Illustrate the genesis and applications of isotope ion peaks in interpretation of MS. **(3+3+4=10)**

8. a) Deduce the structure of an organic compound containing halogen which has following spectral data :

   ^1H NMR : multiplet between 7-7.5

   Mass : M+ at m/z 234/236/238. Other fragment ion peaks at m/z 155/157.

   b) Discuss the basic principle of mass spectrometry.

   c) Deduce the structure of unknown compound (MF : C_4H_7N) which has following spectral data :

   IR : 2941, 2275, 1460 cm^{-1}

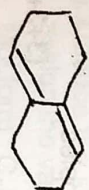 ^1H NMR = 1.33(d, 6H, J = 6.5 Hz), 2.72(m, 1H, J = 6.5 Hz). **(3+3+4=10)**

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III Semester M.Sc. Examination, January 2018

(CBCS)

CHEMISTRY

303 – OC : Organic Spectroscopy

Time : 3 Hours

Max. Marks : 70

Instruction : Answer Question No. 1 and any five of the remaining questions.

1. Answer **any ten** of the following :

   (2×10=20)

   a) How are the following pairs of structural isomers distinguished by uv-vis spectra ?

   A

   and

   B

   b) What are Fermi resonance bands ? Give examples.

   c) Reason why nitro-compounds show two bands of equal intensity at 1550 and 1350 cm⁻¹.

   d) Differentiate spin-spin relaxation from spin-lattice relaxation process.

   e) Mention the most common internal standards used to record ¹HNMR spectra of

   i) aqueous and   ii) organic solutions.

   f) Write the Karplus equation and draw the Karplus curve. Give its importance.

   g) Sketch the GDNP spectrum of the methyl radical.

   h) Highlight the basic criterion for a molecule to exhibit NOE.

   i) Give the nuclear magnetic spin quantum numbers (I) for :

   i) ²H;   ii) ¹⁵N;   iii) ²⁹Si and   iv) ³¹P

   j) What are metastable ions ? How are they recognized in a mass spectrum ?

   k) Draw the block diagram for a FAB-MS instrument.

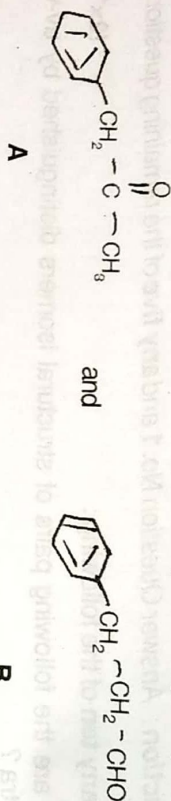   l) State and explain the nitrogen rule.

2. a) Outline the Woodward-Fieser rules to predict the λ_{max} of α, β-unsaturated carbonyl compounds.

   b) Citing examples, illustrate the usefulness of IR spectroscopy to distinguish :

   i) Inter-and intra-molecular H-bonding.

   ii) Keto-enol tautomerization.

   (5+5=10)

3. a) Write an account of solvent effects on the position of uv-bands of α, β-unsaturated carbonyl compounds.

   b) How are the following pairs of compounds distinguished by IR spectra ?

   A

   and

   B

   c) Highlight the complementarity of IR-and Raman spectroscopies.

   (3+3+4=10)

4. a) Illustrate the criteria of a reference compound which may be used as an internal standard to record NMR spectra.

   b) State and explain the first order splitting rules of ^{1}H NMR.

   c) With the help of a diagram, indicate the anisotropic effects in aromatic hydrocarbons.

   (3+3+4=10)

5. a) Give any two methods to distinguish first and second-order ^{1}H NMR spectra.

   b) Citing suitable examples, distinguish chemically and magnetically-equivalent protons.

   c) How are the following compounds distinguished by ^{1}H NMR ?

   COOCH$_3$ and   CH$_3$COO
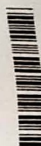
   i) Methyl pirolate   ii) tert-Butylacetate.
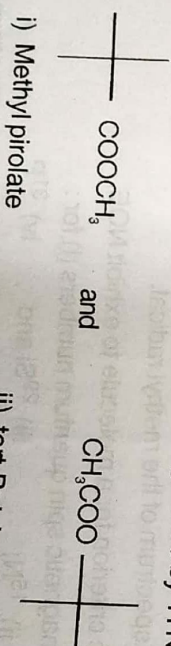
   (3+4+3=10)

6. a) Discuss any two methods for the simplification of complex ^{1}H NMR spectra.

   b) Ethyl benzene gave the following ^{1}H NMR data :

   δ : 7.27 (s, 5H), 2.71(q, 2H) and 1.35(t, 3H) ppm. Sketch the ^{1}H-^{1}H cosy of ethyl benzene.

   c) Write a note on DEPT.

   (3+4+3=10)

7. a) Outline the quasi-equilibrium theory for fragmentation of organic molecules.

b) How is the isotope abundance method useful in determining the molecular-ion peak ?

c) Deduce the structure of an organic compound from the following data and assign the values :

Mol.form. C_9H_8O

uv λ_{max} : 244, 292 nm.

IR : 2901, 2803, 1708, 1072 and 744 cm^{-1}

^{1}HNMR : δ : 7.28(m, 4H) and 3.57(s, 4H) ppm.

^{13}CNMR : δ : 214.5, 137.8, 124.7 and 43.8 ppm.

MS m/e : 132(M$^+$), 104(base peak), 78, 77 and 28.

(3+3+4=10)

8. a) Deduce the structure of an organic compound from the following data and assign the values :

Mol.form : $C_6H_{10}O_2$

uv : λ_{max} : 200 nm.

IR : 3052, 2980, 2876, 1722, 1652 and 1184 cm^{-1}.

^{1}HNMR :   δ : 7.25 – 6.36 (m, 1H, J = 16.25 Hz)

5.84 (m, 1H, J = 16.25 Hz)

3.82(q, 2H, J = 7Hz)

1.82 – 1.49(d/d, 3H) and

1.11(t, 3H, J = 7 Hz) ppm.

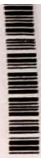^{13}CNMR : δ : 167.1, 144.3, 122.6, 60.9, 18.4 and 14.5 ppm.

MS $\dfrac{m}{e}$: 114(M$^+$), 99, 69(base peak) and 41.

b) Write short notes on :

i) ^{19}F-NMR.

ii) HRMS and its usefulness.

(6+4=10)

III Semester M.Sc. Examination, December 2015

(CBCS)
CHEMISTRY
303-OC – Organic Spectroscopy

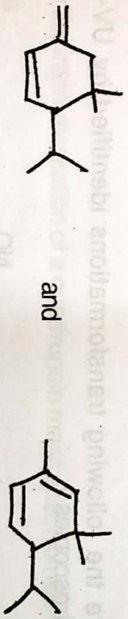Time : 3 Hours

Max. Marks : 70

Instruction : Answer question no. 1 and any five of the remaining questions.

1. Answer **any ten** of the following :

(2×10 = 20)

a) With the help of a neat diagram, indicate the allowed electronic transitions in organic molecules.

b) Citing suitable examples, illustrate 'Mass Effect'.

c) Predict the λ_{max} for the following compounds :

and

d) Mention the relaxation method in pulsed ^{13}C FT – NMR. How is the method exploited to obtain CMR spectra ?

e) How are first order ^1HNMR spectra distinguished from higher order spectra ?

f) Write the 'J' values which distinguish cis – and trans – geometrical isomers.

g) Give two criteria for an organic molecule to exhibit NOE.

h) Predict the approximate chemical shift values of the labelled carbon in the following transformation :
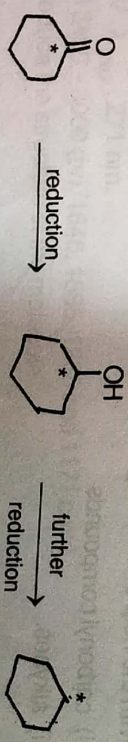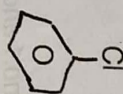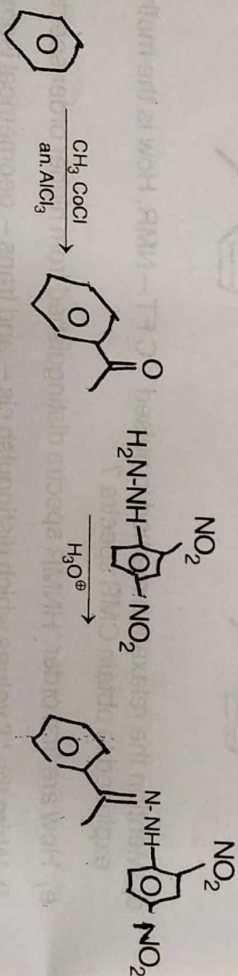
i) Primary amines show ill-resolved peaks for the NH_2 protons in their ^1HNMR spectra. Why ?

j) Define 'nitogen rule'.

k) Sketch the profile of the molecular ion peaks for :

Br   and   Cl
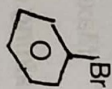
l) Formulate the most prominent fragmentation pattern for the EI – MS of aniline.

2. a) Discuss the Woodward-Fieser rules to predict the λ_{max} of α, β - unsaturated carbonyl compounds.

b) How is IR useful to determine keto-enol tautomerisation ? Explain with suitable example.

c) How are the following transformations identified by UV-visible and IR spectroscopies ?

$$\xrightarrow[\text{an. AlCl}_3]{CH_3\,CoCl}$$

$$H_2N-NH-\!\!\bigcirc\!\!-NO_2 \xrightarrow{H_3O^\oplus}$$
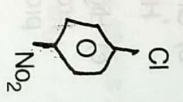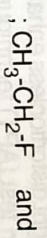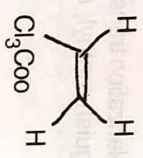

$$\xrightarrow{}$$ N-NH-\!\!\bigcirc\!\!-NO_2

3. a) State and explain the first order splitting rules of ^1HNMR.

b) With the help of neat diagrams, illustrate the anisotropic effects prevalent in

   i) carbonyl compounds

   ii) alkynes.   (4+3+3=10)

c) Write the spin – systems for the following compounds according to Pople's notation :

$Cl_2CH-CHO$;

(i)

Cl_3Coo

(ii)

; CH_3-CH_2-F

(iii)

and

(iv)

(3+3+4=10)

4. a) Discuss any two methods for the simplification of complex ^1HNMR spectra.

b) With suitable example, write an account of CIDNP.

c) How is dynamic NMR useful to determine the formation of carbocations as reactive intermediates ?

(4+3+3=10)

5. a) Outline the instrumentation of a quadrupole mass spectrometer.

b) Discuss :

i) Stevenson- Audier rule

ii) α - Cleavage in mass spectral fragmentations.

c) Highlight the formation and importance of diffused peaks in EI – MS.

(4+4+2=10)

6. a) Draw the MO diagram for methyl vinyl ketone and indicate the allowed transition.

b) A compound has molecular formula $C_8H_8O_2$ and gave the following UV and IR data :

UV λ_{max} : 271 nm.

IR 3400 – 3000 (br), 1646, 1585, 1286 and 1171 cm^{-1}.

Deduce the structure of the molecule.

c) Discuss the complimentarity of IR and Raman spectroscopies.

(3+3+4=10)

7. a) Write the Karplus equation. Draw the Karplus curve and highlight its importance.

   b) Give an account of the double-irradiation technique for simplification of the ^{1}HNMR spectra of acidified ethyl alcohol.

   c) Highlight distortionless enhancement polarization transfer (DEPT) and attached proton test (APT) techniques to distinguish methyl, methylene and methine protons.

   (3+3+4=1

8. a) Illustrate ^{1}H – ^{1}H COSY with an example.

   b) How is HR-MS useful to determine the exact molecular formulae of organic compounds ?

   c) Deduce the structure of an organic compound with molecular formula $C_{11}H_{13}$ NO and assign the values.

   UV: λ_{max} 398 nm

   IR : 2915, 2861, 2742, 1679, 1601, 1472 and 823 cm^{-1}

   ^{1}HNMR : δ : 9.62(d, 1H), 7.55 (m, 2H, J = 8Hz)

       7.53 (d, 1H, τ = 12Hz)

       6.84 (d, 2H, τ = 8Hz)

       6.22 (m,/1H, τ = 12Hz) and

       2.86 (s, 6H)

   ^{13}CNMR : δ : 193.6 (d), 152.6 (d), 151.4 (s),

       128.5 (d), 121.3 (s), 111.8 (d),and 40.3 (q).

   MS $\dfrac{m}{e}$ (rel. intensity) : 175 (16), 174 (100), 173 (39)

       146 (36), 131 (18), 121 (47)

       103 (16) and 77 (17)

   (3+3+4=10)

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III Semester M.Sc. Examination, December 2016
(CBCS)
CHEMISTRY
303 – OC : Organic Spectroscopy

Time : 3 Hours

Max. Marks : 70

Instruction : *Answer question No. 1 and any five of the remaining questions.*

1. Answer **any ten** of the following : (2×10=20)

a) What are different types of transitions involved in UV-Vis spectroscopy ? Arrange them as per their decreasing order of energy level.

b) Using UV-Vis spectroscopy how you will distinguish the cis-and trans-stilbenes ?

c) Give the range of finger print and function group regions in IR spectrum. Mention its significance for the interpretation of a spectrum.

d) Why esters of O-chlorobenzoic acid show two > c = 0 stretching frequencies in its IR spectrum ?

e) In the PMR of cyclohexane the vicinal coupling constant 'J' between diaxial protons in larger than the diequatorial protons. Why ?

f) What information will you get from HETCOR spectrum of a compound ?

g) Which relaxation process is responsible for NMR phenomenon and why ?

h) Why the chemical shift range in CMR is very wide as compared to PMR spectroscopy ?

i) Write the structure of a base-ion peak at m/z 56 observed in the mass spectrum of 1-hexanol.

j) How can you use the information of ortho effect to explain the formation of ion at m/z 149 in the ester of phthalic acid ?

k) Why IR absorption due to carbonyl stretching occurs at higher frequency than c-c double bond ?

l) Sketch the off-resonance decoupled CMR of the following compound and assign the chemical shift values :

$$CH_3 - C \equiv C - CH_2 - CO\,NH_2$$

2. a) Explain the woodward-Fieser rules to predict the λ max of conjugated dienes using suitable examples.

   b) How will you distinguish the following pairs of compounds using IR spectroscopy ?

   i) Anthranilic acid and 4-amino benzoic acid

   ii) Hexan-2, 4-dione and hexane – 2, 5 – dione.

   c) Write a note on complementarity of IR and Raman spectroscopy.   (3+4+3=

3. a) What is magnetic anisotropy in NMR ? Explain using benzene as an example.

   b) What is deuterium exchange technique in PMR spectroscopy ? Explain its applications with appropriate examples.

   c) The following monoterpenoid, α -pinene has three methyl groups in different environments, as revealed by their chemical shift values at δ 0.85, 1.27 and 1.63. Assign the values and justify your answer.

(3+4+3=10

4. a) Explain the HETCOR technique used in 2D NMR. Mention its applications with suitable examples.

   b) Discuss the NOE phenomenon with the help of suitable example. Using this technique how will you distinguish the E-and Z-citral.

   $(Me_2C = CH - CH_2CH_2C(Me) = CH - CHO)$.

   c) How the number and position of CMR signals can help in the identification of the four isometric alcohols with the mol. formula $C_4H_{10}O$?   (3+3+4=10)

5. a) How will you differentiate 3-methyl-and 4-methyl-cyclohexenes by mass-spectral fragmentation pattern ?

   b) Explain the differences observed in the EI and CI mass spectra of n-butyl propenoate.

   c) An organic compound with the molecular formula C_7H_5OCl showed the following spectral data :

   $IR(cm^{-1})$: 3070, 1730, 1595 and 830

   ^1HNMR (δ, ppm) : 9.0 (s, 1H), 7.6 (d, 2H) and 8.2(d, 2H)

   Mass (m/z : 140 (M$^+$), 142 (M$^+$ + 2).

   Deduce the structure of compound and assign the values.   (3+3+4=10)

6. a) Explain with suitable examples, effect of the following factors on the IR absorption frequency of carbonyl group :

    i) Conjugation

    ii) Bond angle.

b) Discuss the effect polarity of solvents on the UV-Vis absorption of α, β-unsaturated carbonyl compounds.

c) Deduce the structure of an organic compound having molecular formula $C_{10}H_{13}O_2N$ with help of following spectral data : Assign the values :

    IR (CM^{-1}) : 3400, 3200, 1500, 830

    ^{1}HNMR (δ, ppm) : 7.9 (bs, 1H), 4.0 (9, 2H, J = 8Hz), 2.1 (s,34), 1.3 (f, 3H, J = 8Hz), 6.8 (d, 2H) and 7.5(d, 2H)

    ^{13}C NMR (δ, ppm) : 15(q), 24(q), 64(f), 115 (d), 123(s), 157(s) and 171(s) .

                                       (3+3+4=10)

7. a) What is the mass of the 'McLafferfy ion' from the following compounds :

    i) Butanal

    ii) Heptanal

    iii) 2-Octanone

    iv) 2-pentanone.

b) With suitable example, discuss 2D-homonuclear correlation experiment for ^{1}H NMR. Explain the importance of 'cross peaks' and diagonal peaks.
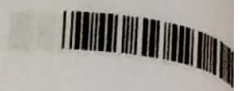
c) Deduce the structure of an organic compound having molecular formula $C_8H_{11}N$ with the help of following spectral data :

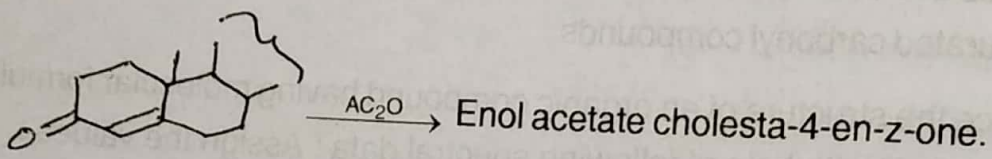   IR(cm^{-1}) : 3400 (s), 3040, 2880, 1400, 1500, 1600, 700(s), 750(s).

    ^{1}HNMR (δ, ppm) : 6.5-7.5(m, 5H), 3.3(s, 1H), 3.1 (quartet, 2H) and 1.2 (f, 3H)

    Ms (m/z) : 106 (Base peak).

                                       (4+3+3=10)

8. a) Explain the CIDNP technique in NMR spectroscopy. Discuss its application using appropriate examples.

b) Discuss any two methods for the simplification of complex spectra ^{1}H NMR spectroscopy.

c) Cholesta-4-en-3-one gives and enol acetate which has λ max at 238 nm. Suggest the structure for the enol acetate.

 $\xrightarrow{AC_2O}$ Enol acetate cholesta-4-en-z-one.

(3+4+3=10