II.13 Spectroscopy and Structure Elucidation

Civil Services 2016–2026: **86** parts, **880** marks · IFoS 2016–2025: **101** parts, **700** marks

Syllabus. Principle and applications in structure elucidation: (i) Rotational: diatomic molecules; isotopic substitution and rotational constants. (ii) Vibrational: diatomic molecules, linear triatomic molecules, specific frequencies of functional groups in polyatomic molecules. (iii) Electronic: singlet and triplet states; n→π* and π→π* transitions; application to conjugated double bonds and conjugated carbonyls, Woodward-Fieser rules; charge transfer spectra. (iv) Nuclear magnetic resonance (^{1}H NMR): basic principle; chemical shift and spin-spin interaction and coupling constants. (v) Mass spectrometry: parent peak, base peak, metastable peak, McLafferty rearrangement.

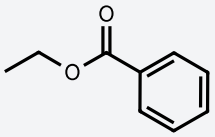
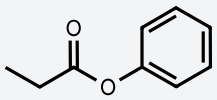
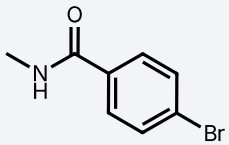
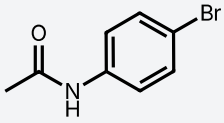
Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	55	55	55	80	90	85	90	105	95	100	70
IFoS	60	55	45	80	75	50	85	80	90	80	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

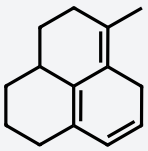
2026

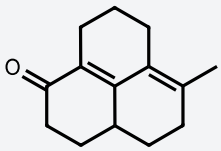
CSE 2026 · Q5(d) IR of esters and amides; Woodward–Fieser calculations [10 marks]

(i) How can the following pairs of compounds be distinguished based on the vibrational frequencies of their ⟩C=O and ⟩N–H bonds?


and


and


(ii) Using the Woodward–Fieser rules, calculate the λ_{max} values of the following compounds:


compound 1


compound 2

CSE 2026 · Q5(e) NMR of ethene and ethyne; benzyl to tropylium cation [10 marks]

(i) Explain and compare the chemical shifts of hydrogens in ^{1}H NMR spectra of ethene and ethyne.

(ii) Write the mechanism of rearrangement of benzyl cation to tropylium cation in mass spectrometry.

CSE 2026 · Q8(a) Rotational constant; vibrational order; chelated C=O and OH [15 marks]

(i) Calculate the rotational constant of a diatomic molecule if the moment of inertia is 13.97×10^{-47} kg m^2. (Given: Planck's constant $h = 6.626 \times 10^{-34}$ Js and velocity of light $c = 2.998 \times 10^8$ ms^{-1})

(ii) Arrange the following molecules in increasing order of vibrational frequency (cm^{-1}): HF, HI, NO, CO

(iii) Explain the specific vibrational frequencies (⟩C=O and –OH) in pentane-2,4-dione and 2-hydroxypropiophenone.

CSE 2026 · Q8(b) ^{1}H NMR: furfural, arenes, ethanol, nitroacetophenones [15 marks]

(i) Discuss the spin-spin interactions and coupling constants in ^{1}H NMR spectrum of furfuraldehyde.

(ii) Distinguish between (A) anthracene and phenanthrene, and (B) pure ethanol and ethanol in presence of trace amount of acidic impurity, based on ^{1}H NMR spectra.

(iii) How can you differentiate between 2-nitroacetophenone and 3-nitroacetophenone based on approximate

chemical shifts and spin-spin interactions? (Consider only ortho-coupling)

CSE 2026 · Q8(c) UV of enones; charge-transfer complexes; mass spectra [20 marks]

(i) Explain the effect of conjugation on λ_{max} and intensity due to n-π^* and π-π^* transitions in 3-buten-2-one compared to acetone.
(ii) Explain the formation of charge-transfer complex between (A) picric acid and anthracene, and (B) tetracyanoethylene and aniline, using electronic spectroscopy.
(iii) Identify the molecular ion peak(s) and peaks due to McLafferty rearrangement in the mass spectrum of ethyl 4-chlorobenzoate.
(iv) Write the structures of ions at m/z 108, 93, 78, 77 and 65 in the mass spectrum of anisole.

2025

CSE 2025 · Q5(d) Rotational spectroscopy [10 marks]

(i) Which of the following molecules is/are active to rotational spectroscopy and why? 5
CH_4, H_2O, NH_3, BCl_3, XeF_4

(ii) The spacing between lines in the microwave spectrum of CO decreases by substituting ^{12}C by ^{13}C. Why? 5

CSE 2025 · Q5(e) NMR at two field strengths; mass spectrum of a ketone [10 marks]

(i) In a 100 MHz NMR instrument, a particular set of protons absorbs at δ = 3·0 with J = 4·5 Hz. Find the chemical shift (in Hz) and the coupling constant J in a 500 MHz instrument for the same set of protons. 5

(ii) The mass spectrum of n-butyl phenyl ketone ($C_6H_5COCH_2CH_2CH_2CH_3$) shows peaks at m/z 162, 120, 105 and 85. Predict the fragmentation pattern. 5

CSE 2025 · Q6(b) Three numericals [15 marks]

(i) Calculate the frequency of radiation required for a transition of J = 4 to J = 5 in the rotational spectrum of HCl. The rotation constant B = 10·6 cm^{-1}. 5

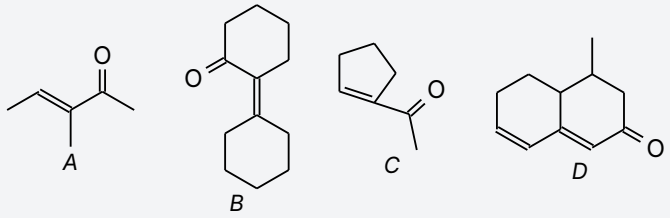
(ii) The fundamental vibrational frequency of HCl is 2990 cm^{-1}. Calculate the fundamental vibrational frequency of DCl assuming the same bond strength. 5

(iii) The molecular formula of a compound is C_3H_3N. The IR absorption frequencies are 1650 cm^{-1}, 2250 cm^{-1} and 3100 cm^{-1}. Assign a structure for the compound. 5

CSE 2025 · Q7(a) Two UV bands of acetone; λmax by the Woodward–Fieser rules [15 marks]

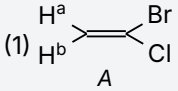
(i) Acetone shows a weak absorption at 280 nm and a strong absorption at 190 nm in the UV spectrum. Account for the observation. 5

(ii) Using Woodward-Fieser rules, calculate λ_{max} for the following compounds: 10

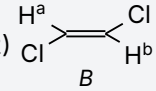


CSE 2025 · Q8(a) Coupling constants of the lettered protons; Chemical shifts of H^a and H^b; Number of ^1H NMR signals [15 marks]

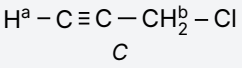
(i) Estimate the expected splitting (coupling constant J in Hz) for the lettered protons in the ^1H NMR spectrum of the following compounds:

(1) 

A

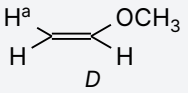
(2) 

B

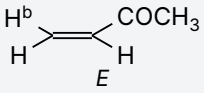
(3) 

C

(ii) Compare the chemical shifts of the labelled protons H^a and H^b in the ^1H NMR spectrum of the following compounds and justify your answer: 10

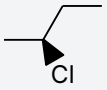


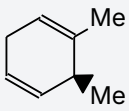
D



E

(iii) Count the number of peaks observed in the ^1H NMR spectrum of the following compounds. Justify your answer: 5

(1) 

(2) 

CSE 2025 · Q8(b) Structure of the halogenated ester; C_6H_{12} alkenes with peaks at m/z 42 and 56 [15 marks]

(i) A halogenated ester shows M^+ peak at m/z 166 (10%) and $M + 2$ peak at m/z 168 (9·8%) in mass spectrum. ^1H NMR spectrum of this compound shows two triplets and a singlet at δ 2·9, 3·6 and 3·8 ppm, respectively in the intensity ratio 1:1:1·5. Deduce the structure of the compound. Justify your answer. 10

(ii) Two isomeric alkenes with same molecular formula C_6H_{12} show strong peaks at m/z 42 and 56 in the mass spectrum. Propose fragmentation pattern for both the peaks. 5

CSE 2025 · Q8(c) Characteristic fragment ions; Structure of $C_4H_5NO_2$ [20 marks]

(i) (1) Phthalic acid diethyl ester shows a characteristic peak at m/z 149 in the mass spectrum. Account for the observance of this peak by fragmentation pattern.
(2) The mass spectrum of ethylbenzene shows a characteristic peak at m/z 91 while *n*-propylbenzene shows strong peak at m/z 92. Explain with the help of fragmentation pattern. 10

(ii) An unknown organic compound with molecular formula $C_4H_5NO_2$ displays a band at 2250 cm^{-1} and a strong band at 1740 cm^{-1} in the IR spectrum. The compound shows only two signals in 3:2 ratio in the ^1H NMR spectrum. Find out the structure of the compound. Justify your answer. 10

IFoS 2025 · Q5(d) Proton NMR of dry ethanol [5 marks]

Write the ^1H NMR spectral data of pure ethanol in anhydrous $CDCl_3$ indicating approximate chemical shift values of each signal and their spin multiplicity and integration.

IFoS 2025 · Q5(e) Mass fragmentation of acetic anhydride [5 marks]

A compound having molecular formula $C_4H_6O_3$ gives the following mass fragments. Deduce the fragmentation pattern to identify the mass peaks and the base peak.
m/z = 102, 60, 43, 42, 15.

IFoS 2025 · Q5(f) Structure from combined spectra [15 marks]

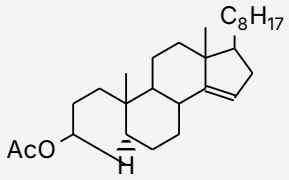
An organic compound with molecular formula $C_{10}H_{12}O_2$ exhibits the following spectral data:
IR (cm^{-1}): 3100, 2944, 2856, 1690, 1100 cm^{-1}
^1H NMR ($CDCl_3$): δ 7.80 (2H, d, J = 8 Hz), 6.80 (2H, d, J = 8 Hz), 4.10 (2H, q, J = 7.2 Hz), 2.4 (3H, s), 1.25 (3H, t, J = 7.2 Hz)
Mass: m/z 164, 121, 43, 15.
Derive the structure of the compound and assign all the data.

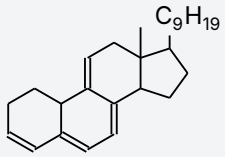
IFoS 2025 · Q6(b) Two ester NMR patterns; A symmetric malonate ester [10 marks]

(i) Write approximate ^1H NMR chemical shift values and multiplicity of each signal to differentiate between ethyl acetate and methyl propionate. 5
(ii) A compound having molecular formula $C_{11}H_{20}O_4$ gives the following ^1H NMR data. Identify the compound and assign the protons. 5
^1H NMR ($CDCl_3$, 300 MHz): δ 4.18 (q), 1.92 (t), 1.24 (q), 0.82 (t) ppm.

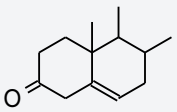
IFoS 2025 · Q7(b) Checking the conjugated chromophore; Conjugated and non-conjugated ketones [10 marks]

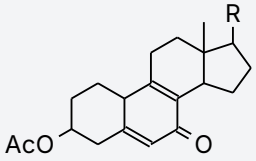
(i) Calculate the ultraviolet absorption maxima of substituted dienes using Woodward-Fieser rules: 5

(I) 

(II) 

(ii) Deduce the λ_{max} values in given α-β-unsaturated carbonyl compounds using Woodward-Fieser rules: 5

(I) 

(II) 

IFoS 2025 · Q8(a) CO rotational constant and bond length; Isotopic change in rotational constant [15 marks]

(i) Deduce the rotational constant and C – O bond length in carbon monoxide when the first line in the rotational spectrum has a frequency of 3·8424 cm^{-1}.
Given: Avogadro number = 6.022×10^{23}
$h = 6.625 \times 10^{-27}$ cm^2 g/s; $c = 3 \times 10^{10}$ cm/s 10
(ii) Calculate the change in the rotational constant, when hydrogen is replaced by deuterium in the hydrogen molecule. 5

IFoS 2025 · Q8(b) Isotope exchange and zero-point energy; Hot-band population in iodine [20 marks]

(i) Calculate the change in energy for a given reaction:

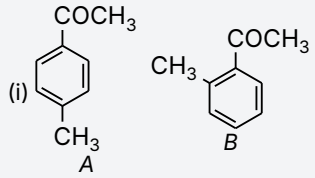
$$HCl + D_2 \longrightarrow DCl + HD$$

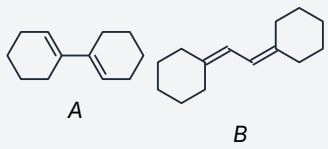
Given the frequencies of vibration of the molecules at v = 0, HCl = 2885 cm^{-1}, D_2 = 2990 cm^{-1}, DCl = 1990 cm^{-1} and HD = 3627 cm^{-1}, $h = 6.625 \times 10^{-34}$ m^2 kg/s, $c = 3 \times 10^8$ m/s. 10
(ii) What will be the intensity of the hot band $v = 1 \rightarrow v = 2$ relative to the fundamental $v = 0 \rightarrow v = 1$ in Iodine molecule at temperature 300 K?
Given: Equilibrium vibration frequency of Iodine molecule = 215 cm^{-1}
Anharmonicity constant x_e = 0.003.
$c = 3 \times 10^8$ m/s; $h = 6.625 \times 10^{-34}$ m^2 kg/s 10

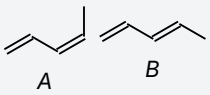
2024

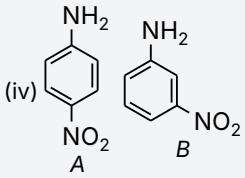
CSE 2024 · Q5(d) Higher λmax in each pair [10 marks]

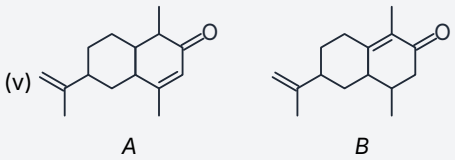
In UV spectra of the following pairs, which compound will have higher λ_{max}?

(i) 

(ii) 

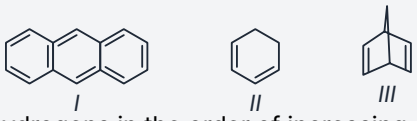
(iii) 

(iv) 

(v) 

CSE 2024 · Q5(e) Number of ^{1}H NMR signals and order of chemical shift [10 marks]

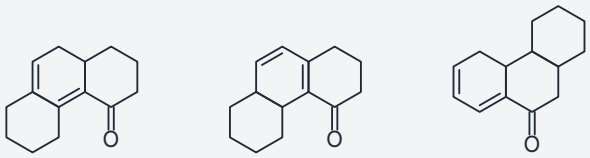
In ^{1}H NMR spectrum of the following compounds, how many signals will be observed?



In each case, label and arrange the hydrogens in the order of increasing chemical shift.

CSE 2024 · Q7(a) λmax of three dienones by Woodward–Fieser rules [15 marks]

Calculate the value of λ_{max} in the following compounds using Woodward-Fieser rules:



CSE 2024 · Q7(c) Two isomeric esters $C_{10}H_{12}O_2$; Fragment ions m/z 58 and m/z 92 [20 marks]

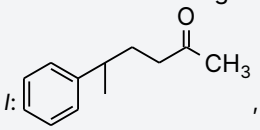
(i) Given below are the NMR spectral characteristics of two isomeric compounds with molecular formula $C_{10}H_{12}O_2$:

(1) ^{1}H NMR: δ 2.0 (3H, s), 2.93 (2H, t), 4.3 (2H, t), 7.3 (5H, s)

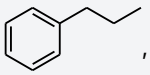
(2) ^{1}H NMR: δ 1.23 (3H, t), 3.72 (2H, s), 4.13 (2H, q), 7.3 (5H, s)

Both of these compounds exhibit a peculiar peak in IR spectra at 1730 cm^{-1}. Deduce the structures of these two compounds. [10]

(ii) In the mass spectra of compounds *I* and *II*, prominent peaks at *m/z* 58 and *m/z* 92 are observed, respectively. Write the structures of the fragment ions and discuss their formation:

I: 

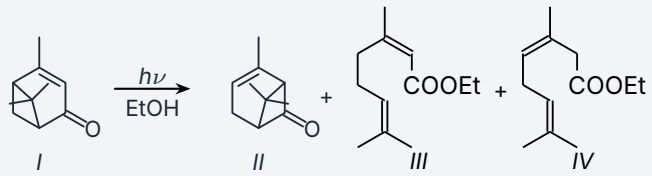
, *m/z* 58

II:  , *m/z* 92

[10]

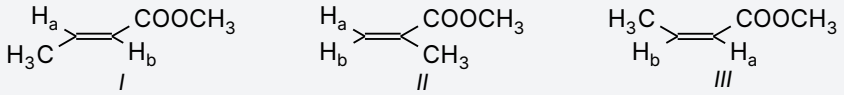
CSE 2024 · Q8(a) Assignment of four C=O stretching bands [15 marks]

Ethanolic solution of compound *I* on irradiation leads to the formation of compounds *II*, *III* and *IV*. The resulting reaction mixture exhibits bands at 1787, 1740, 1715 and 1685 cm^{-1} for $\nu_{C=O}$. Assign these C=O stretching frequencies to the corresponding compounds giving reasons:



CSE 2024 · Q8(b)(ii) Order of J(Ha–Hb) [5 marks]

(ii) Arrange the following compounds in the order of increasing coupling constant values ($J_{H_a-H_b}$):



[5]

CSE 2024 · Q8(c) Two alkenes from 2-chloro-2,3-dimethylbutane; Fragmentation of diethyl ether; Bond length of HCl from its moment of inertia [20 marks]

(i) 2-Chloro-2,3-dimethyl butane on dehydrohalogenation can lead to the formation of two products. Explain how the two can be distinguished using ^{1}H NMR and IR spectral data. [10]

(ii) The mass spectral data of diethyl ether is as under:
m/z 74, *m/z* 59, *m/z* 45, *m/z* 31, *m/z* 29
Explain the fragmentation pattern. [5]

(iii) Using the following data, calculate the bond length of HCl:
$I = 2.70 \times 10^{-47}$ kg m^2
1 a.m.u. $= 1.661 \times 10^{-27}$ kg [5]

IFoS 2024 · Q5(b) Zero-point vibrational energy [5 marks]

What is the energy of the lowest vibrational level of the simple harmonic oscillator? Justify your answer.

IFoS 2024 · Q5(f) IR comparison of two secondary amides [5 marks]

Distinguish between acetanilide and N-methyl benzamide on the basis of IR spectroscopy.

IFoS 2024 · Q5(g) Chlorine and bromine isotope patterns [5 marks]

How can you identify the presence of (i) chlorine, (ii) bromine and (iii) both chlorine and bromine atoms in the molecule based on the percentage intensity of isotope peaks relative to the intensity of molecular ion peak?

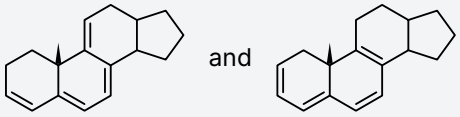
IFoS 2024 · Q5(h) Spin labels for macromolecules [5 marks]

Define spin labels. Write the name and structure of the most commonly used spin label for macromolecules' structure investigation.

IFoS 2024 · Q7(b) UV bands of a ketone and an enone; Woodward–Fieser estimates for two tetraenes [15 marks]

(i) Give and compare the approximate values of λ_{max} and ε of 3-pentanone and 3-penten-2-one due to π-π^* and n-π^* transitions. 10

(ii) Predict λ_{max} of the following molecules based on Woodward-Fieser rules: 5



IFoS 2024 · Q7(c) Identification of an amino ester [15 marks]

Identify the structure of a compound having molecular formula $C_6H_{13}NO_2$ and displaying the following spectral data:

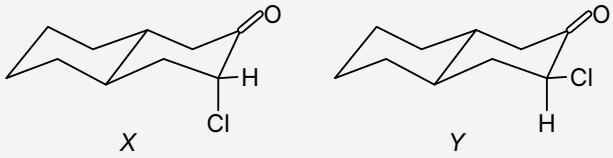
IR: ν_{max} 2981 cm^{-1} and 1736 cm^{-1}

^1H NMR: δ 1.31 (t, 3H), 2.42 (s, 6H), 3.20 (s, 2H), 4.18 (q, 2H)

Explain the mass spectral fragmentation of the identified compound for m/z 131, 116, 103, 86 and 84 peaks.

IFoS 2024 · Q8(a) Axial versus equatorial alpha chlorine; IR-active vibrations [10 marks]

(i) How can you distinguish the following compounds on the basis of IR spectroscopy? 5



(ii) State which of the following molecules are infrared active: 5

CH_3OH, CH_3NH_2, CO_2, CH_4, CO

IFoS 2024 · Q8(b) Mass spectra of benzyl alcohol and anisole [10 marks]

Differentiate between benzyl alcohol and anisole on the basis of mass spectral fragmentation.

IFoS 2024 · Q8(c) NMR distinction of two isomer pairs; Structure from an aldol-condensation spectrum [20 marks]

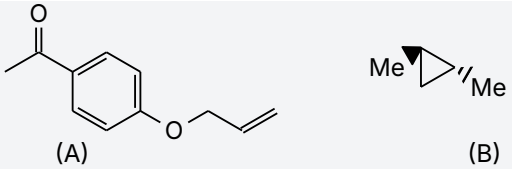
(i) Distinguish between (1) ethyl acetate and methyl propionate and (2) 2-nitroacetophenone and 4-nitroacetophenone with reference to number of signals, approximate chemical shift values and spin-spin couplings (multiplicity) in their ^1H NMR spectra. 10

(ii) Deduce the structure of the compound obtained by condensation of benzaldehyde and acetone in the presence of a base based on the following ^1H NMR spectral data: 10

δ 2.31 (s, 3H), 6.73 (d, 1H, J = 16 Hz), 7.32–7.40 (m, 5H), 7.52 (d, 1H, J = 16 Hz)

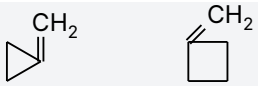
2023

CSE 2023 · Q5(a) Number of ^1H NMR signals in (A) and (B) [10 marks]



How many signals would you expect in the ^1H NMR spectrum of above compounds? Mark these protons.

CSE 2023 · Q5(b) C=C stretch of methylenecyclopropane and methylenecyclobutane [10 marks]



Compare the C=C stretching vibrations in the above compounds and give a suitable explanation for your answer.

CSE 2023 · Q6(a) Energy change of HCl + D_2 → DCl + HD; C=O bands of butyric acid, its ethyl ester and its anhydride [15 marks]

(i) The frequencies of vibration of the following molecules in their $v = 0$ states are HCl : 2885 cm^{-1}; D_2 : 2990 cm^{-1}; DCl : 1990 cm^{-1} and HD : 3627 cm^{-1}. Calculate the energy change of the following reaction: $HCl + D_2 \longrightarrow DCl + HD$

Determine whether energy is liberated or absorbed.

[Given: $h = 6.626 \times 10^{-34}$ J s; $c = 2.998 \times 10^{8}$ m s^{-1}; $N_A = 6.022 \times 10^{23}$ mol^{-1}] *10*

(ii) The IR spectra of butyric acid and ethyl butyrate show sharp strong singlet absorption at 1725 cm^{-1} and 1740 cm^{-1}, respectively. By contrast, the IR spectrum of butyric anhydride shows a broad, sharp doublet at 1750 cm^{-1} and 1825 cm^{-1}. Why are these so different? *5*

CSE 2023 · Q6(c) Structure of $C_{16}H_{25}NO$ from IR and ^1H NMR; Order of chemical shift of the lettered protons [20 marks]

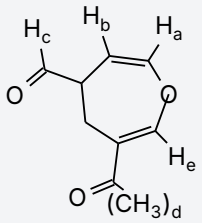
(i) An organic compound having molecular formula $C_{16}H_{25}NO$ gave following IR and ^1H NMR data:

IR (cm^{-1}) = 1690

^1H NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, J = 7 Hz, 6H), 1.29 (d, J = 7 Hz, 6H), 2.40 (q, J = 7 Hz, 4H), 2.55 (t, J = 7 Hz, 2H), 2.65 (t, J = 7 Hz, 2H), 3.12 (septet, 1H), 7.21 (d, J = 8 Hz, 2H), 7.81 (d, J = 8 Hz, 2H)

Determine the structure of the compound. *10*

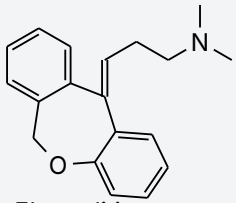
(ii)



Assign and arrange the lettered protons in the increasing order of their chemical shift value in ^1H NMR spectrum. *10*

CSE 2023 · Q8(a) Doxepin: site of ionisation, m/z 58 ion and metastable ion; Ketone $C_7H_{12}O$ with λmax = 249 nm [15 marks]

(i) For the following compound:



(i) Identify the site of initial ionization under EI conditions.

(ii) Draw the structure of ion having m/z = 58 value.

(iii) Calculate the m/z value of metastable ion formed during the formation of above ion. *10*

(ii) Draw the structural formula of a ketone with MF $C_7H_{12}O$ that absorbs in the UV with λ_{max} = 249 nm. *5*

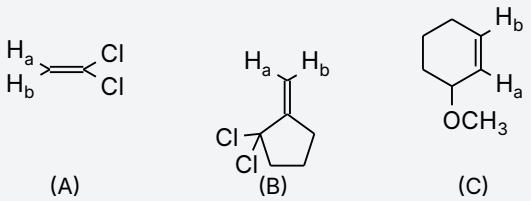
CSE 2023 · Q8(b) Microwave activity; rotational constants of CO; Expected J(Ha–Hb) in three alkenes [15 marks]

(i) (A) H_2, HCl, BrF, CH_4 and H_2O

Which of the above molecule(s) will show a microwave rotational spectrum? Justify your answer.

(B) The first rotational absorption of $^{12}C^{16}O$ was observed at 3.84235 cm^{-1} while that of $^{13}C^{16}O$ was observed at 3.67337 cm^{-1}. Find their rotational constants. *10*

(ii)



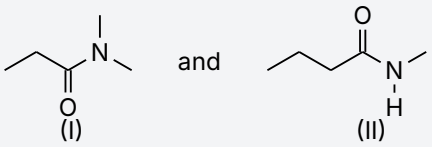
(A) (B) (C)

Estimate the expected splitting (J in Hz) for the lettered protons in the above compounds: *5*

CSE 2023 · Q8(c) Keto and enol percentages of acetylacetone from integration; Two isomeric amides $C_5H_{11}NO$ by mass spectrometry; Fundamental vibrations of CO_2 and their IR activity [20 marks]

(i) In the ^1H NMR spectrum of acetyl acetone the height of the integration curve at methylene ($-CH_2$) signal was found to be 10 mm and that of methine (=CH) signal was 22 mm. Calculate the percentage of keto and enol form in the sample. *10*

(ii)



(I) (II)

How could the above pair of isomeric compounds be differentiated by mass spectrometry? *5*

(iii) How many fundamental vibrational frequencies would be expected to be observed in the IR spectrum of CO_2? Sketch them. Identify the IR-active vibrations with justification. *5*

IFoS 2023 · Q5(d) Woodward–Fieser calculation and a name error [5 marks]

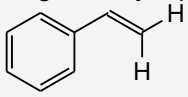
Calculate λ_{max} values of 2-methoxy-pent-3-en-2-one (A) and 3-methoxy-2-methyl-but-2-enal (B).

IFoS 2023 · Q5(e) Distinguishing ortho and para xylene [5 marks]

Differentiate between o-xylene and p-xylene using IR spectroscopy.

IFoS 2023 · Q5(f) Chemical and magnetic equivalence in styrene [5 marks]

Identify the chemically equivalent protons and magnetically equivalent protons in the following compound:



IFoS 2023 · Q5(g) Parent ion from a metastable peak [5 marks]

From the data given below, calculate the mass of the parent peak (P) whose daughter peak is 65.

MS (m/z): 106, P, 65, 46·42, 29, 15

IFoS 2023 · Q6(c) Two C3H6O carbonyl compounds [5 marks]

Two compounds having molecular formula C_3H_6O react separately with 2,4-dinitrophenyl hydrazine to give blood red precipitates. Using IR spectroscopy, how would you ascertain the functional group(s) present in the

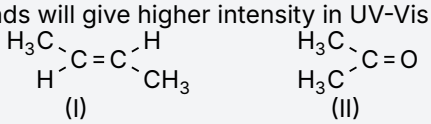
compounds?

IFoS 2023 · Q6(d) Meaning of a coupling constant [5 marks]

What is coupling constant in ^{1}H NMR spectroscopy? How does external magnetic field affect coupling constant values? For two vicinal protons, do we observe same or different coupling constant values and why?

IFoS 2023 · Q6(e) Intensity of alkene and ketone UV absorption [5 marks]

Which of the following two compounds will give higher intensity in UV-Vis spectra and why?



(I) (II)

IFoS 2023 · Q6(f) Isotopic substitution in rotational spectra [5 marks]

Write the effect of isotopic substitution on the rotational spectrum of a diatomic molecule.

IFoS 2023 · Q7(e) Two unsaturated ester isomers [5 marks]

A compound having molecular formula $C_5H_8O_2$ may be either ethyl acrylate or vinyl propionate. How would you identify the correct compound using IR spectroscopy?

IFoS 2023 · Q7(g) Chemical-shift separation in Hz [5 marks]

A compound gives two signals at δ 4·3 ppm and δ 5·7 ppm. If the spectrum is recorded in a 400 MHz NMR machine, write their chemical shift difference in Hz (hertz).

IFoS 2023 · Q7(h) Hydration of phenylacetylene [5 marks]

A compound with molecular formula C_8H_6 gives a product (C_8H_8O) upon treatment with dil. sulphuric acid in the presence of mercurous sulphate. Write approximate ^{1}H NMR chemical shifts and multiplicity of the protons in the product.

IFoS 2023 · Q8(b) A C9H12 alkylbenzene mass spectrum [5 marks]

A compound having molecular formula C_9H_{12} gives the following MS (m/z) data:
m/z 120, 92, 91, 77 and 51
Write the mass fragmentation of the compound to elucidate the structure of the fragment having mass m/z 92.

IFoS 2023 · Q8(c) Benzene radical anion [5 marks]

Answer the following, when benzene is treated with an alkali metal in THF as solvent:
(i) The spectroscopy to be used to identify the product.
(ii) The structure of the product.
(iii) Total spin of the product.
(iv) The number of lines observed.
(v) The intensity distribution of the lines.

IFoS 2023 · Q8(e) Identification of glutaric anhydride [15 marks]

A compound with molecular formula $C_5H_6O_3$ gives the following data:
MS (m/z) 114, 76, 73, 60, 55
IR (cm^{-1}) 2981, 1850, 1758, 1250
^{1}H-NMR ($CDCl_3$) δ 2·43 (t, 4H), 1·96 (pent., 2H)
^{13}C-NMR ($CDCl_3$) δ 177, 33, 19·6
Assign the structure to the compound.

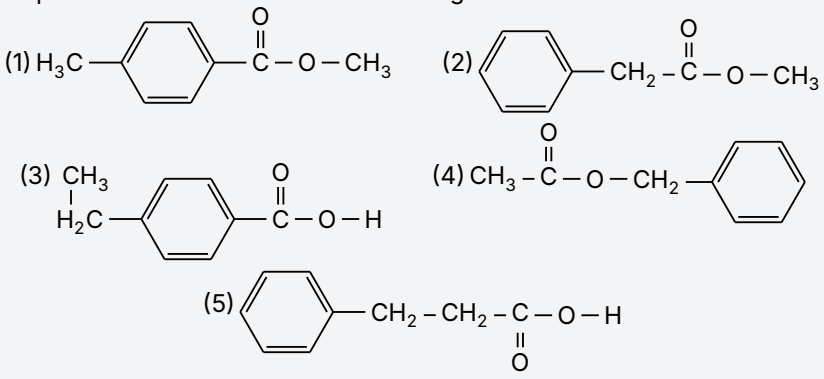
2022

CSE 2022 · Q5(d) N–H stretching of amines in IR; alcohols in PMR [10 marks]

(i) How will you distinguish between NH stretching absorption of a primary amine and a secondary amine by using IR spectroscopy?
(ii) How will you distinguish among primary, secondary and tertiary alcohols on the basis of PMR spectroscopy?

CSE 2022 · Q5(e) Matching three sets of IR and NMR data with five structures [10 marks]

Given below are the IR and NMR spectral characteristics of three compounds:
(i) IR: 1750 cm^{-1}; NMR: δ 2·0 (s, 3H), 5·1 (s, 2H) and 7·3 (s, 5H)
(ii) IR: 1740 cm^{-1}; NMR: δ 3·5 (s, 3H), 3·6 (s, 2H) and 7·4 (s, 5H)
(iii) IR: 3200–2800 (various bands) and 1700 cm^{-1}; NMR: δ 2·75 (t, 2H), 2·95 (t, 2H), 7·4 (s, 5H) and 12·0 (s, 1H)
Match each of these spectral data with one of the following structures:



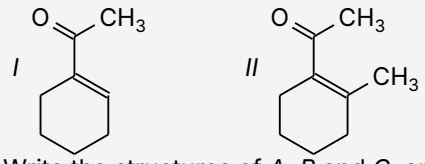
CSE 2022 · Q7(c) Compound A (M = 102) and its cleavage products B and C; Three isomeric carbonyl compounds $C_5H_{10}O$ [20 marks]

(i) A compound (*A*) containing C, H and O has molecular weight 102 and displays two signals in the ^{1}H NMR spectrum at δ 1·1 (d) and 3·55 (septet) in the integral ratio of 6 : 1. Treatment of *A* with 1 mole of HI gives rise to *B* and *C*. In the IR spectrum, *B* gives a strong absorption band at 3330 cm^{-1}, whereas its ^{1}H NMR spectrum shows signals at δ 1·05 (d, 6H), 3·6 (septet, 1H) and 4·4 (s, 1H, disappeared with D_2O). The ^{1}H NMR spectrum of *C* gives signals at δ 1·9 (d, 6H) and 4·25 (septet, 1H). Reaction of *A* with excess of HI gives only *C*. Identify *A*, *B* and *C*. Write all the reactions involved.
(ii) Three isomeric compounds having MF $C_5H_{10}O$ give positive 2,4-DNP test and display the following NMR spectral characteristics. Identify the compounds. Among them, one isomeric compound on treatment with KOH (concentrated) gives two products. Write their structures also:

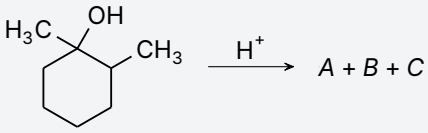
(1) A triplet at δ 1·05 and a quartet at δ 2·47 (2) Two singlets (3) A doublet at δ 1·0, a singlet at δ 2·1 and a septet at δ 2·2

CSE 2022 · Q8(a) Carbonyl stretching frequency of two acetylcyclohexenes; Dehydration of 1,2-dimethylcyclohexanol; telling the alkenes apart by IR [15 marks]

(i) Among the following compounds *I* and *II*, which has more carbonyl stretching frequency in IR spectra? Explain:

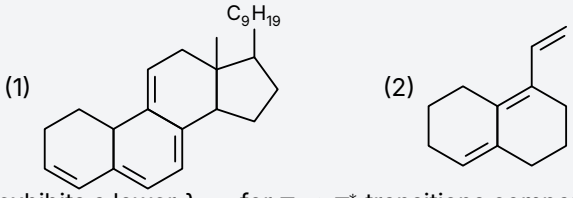


(ii) Complete the following reaction. Write the structures of *A*, *B* and *C*, and explain how IR spectroscopy is helpful to distinguish among them:



CSE 2022 · Q8(b) λmax of two polyenes by Woodward–Fieser rules; λmax of 1,3-butadiene and 1,3,5-hexatriene [15 marks]

(i) Calculate the λ_{max} values of the following compounds:



(ii) Explain why 1,3-butadiene exhibits a lower λ_{max} for $\pi \rightarrow \pi^*$ transitions compared to that of 1,3,5-hexatriene.

CSE 2022 · Q8(c) McLafferty rearrangement; fragmentation of butyl butyrate; C_2H_2BrCl with J = 16 Hz; two dienones from UV data [20 marks]

(i) What is McLafferty rearrangement? Discuss the mass spectral fragmentation of butyl butyrate with the following given data of ions:

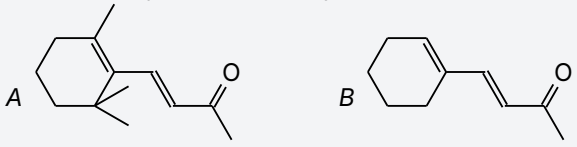
m/z 101, *m/z* 73, *m/z* 71 and *m/z* 56

Write the structures of fragment ions.

(ii) (1) A compound with MF C_2H_2BrCl exhibits two doublets (J = 16 Hz) in its PMR spectrum. Suggest a suitable structure along with other possible structures.

(2) How can the structures of *A* and *B* be decided based on their UV spectral data?

[λ_{max} = 296 nm (ε_{max} = 10700) and λ_{max} = 281 nm (ε_{max} = 20800)]



IFoS 2022 · Q5(d) CO bond length from rotational spacing [5 marks]

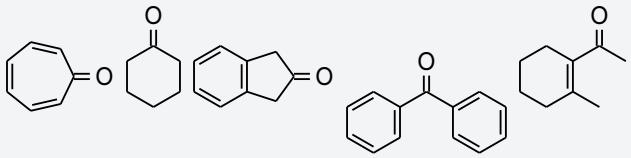
When rotational spectra of CO molecule are studied, a series of equidistant lines at a gap of 3·84 cm^{-1} is observed. Calculate the bond length of CO.

IFoS 2022 · Q5(e) Isotope shift of C–H stretching [5 marks]

C—H stretching frequency of an alkane is found at 2900 cm^{-1}. What will be the change in stretching frequency, if deuterium replaces hydrogen? Calculate $\bar{\nu}$.

IFoS 2022 · Q5(f) Relative carbonyl stretching frequencies [5 marks]

Arrange the following carbonyl compounds in order of increasing C—O stretching frequencies (cm^{-1}):

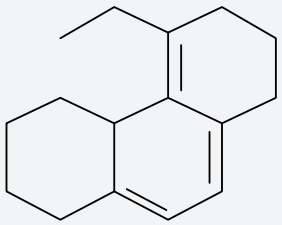


I II III IV V

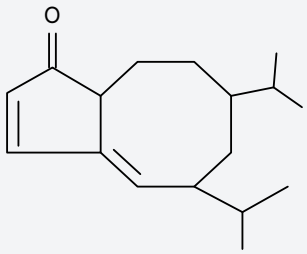
IFoS 2022 · Q7(a) Woodward–Fieser calculations [10 marks]

Calculate λ_{max} for the following compounds using Woodward-Fieser rules:

(i)



(ii)



IFoS 2022 · Q7(b) Tautomers and chromophores [5 marks]

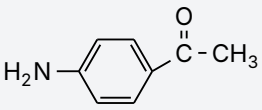
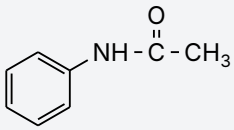
Draw tautomers of but-3-en-2-one and identify auxochromic and chromophoric groups in both forms.

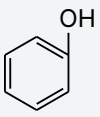
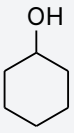
IFoS 2022 · Q7(c) ESR of pyrazine [5 marks]

Predict ESR peaks for pyrazine. Represent their intensity ratio also.

IFoS 2022 · Q7(d) Infrared distinctions [10 marks]

How do IR spectra help to distinguish the following pairs of compounds?

(i)  and 

(ii)  and 

IFoS 2022 · Q8(a) N–H identification in hexamethylenediamine [5 marks]

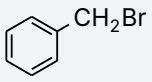
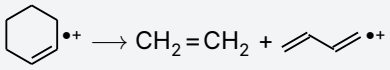
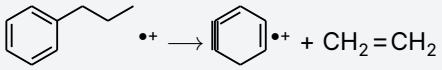
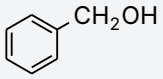
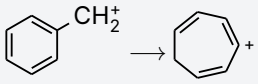
HMDA is a starting material of polymer Nylon-6. How can we prove the presence of N—H bond in HMDA through PMR spectroscopy?

IFoS 2022 · Q8(b) Aromatic proton coupling constants [5 marks]

Do *ortho*-, *meta*- and *para*-hydrogens of monosubstituted benzene show spin-spin coupling? Predict the approximate values of their coupling constants.

IFoS 2022 · Q8(c) Matching mass-spectral behaviour [10 marks]

Match the following columns:

	Column—A		*Column—B*
(A)	Scrambling	I.	
(B)	M-18 peak	II.	
(C)	M and M+2 peak (1 : 1)	III.	
(D)	Retro-Diels-Alder	IV.	
(E)	McLafferty rearrangement	V.	

IFoS 2022 · Q8(d) Diphenyl ether and its mass fragments [10 marks]

Phenol reacts with bromobenzene in the presence of catalytic amount of copper and gives compound *A*, which is a sweet smelling liquid. In mass spectral analysis of *A*, prominent peaks are observed at *m*/*z* = 170, 141 and 71. Predict the structure of *A* and also represent its fragmentation pattern.

IFoS 2022 · Q8(e) A fragrant aromatic aldehyde [10 marks]

An organic compound *A* having molecular formula $C_8H_8O_3$ burns with sooty flame. It is fragrant solid with the following spectroscopic data. Predict its structure:
UV: λ 275 nm, 292 nm, 295 nm
IR: 3250, 3060, 2950, 2840, 2760, 2720, 1700, 1600, 1580, 1500, 1250, 1050 cm^{-1}
NMR: *δ* 5·75 (s); *δ* 7·1 (*d*), 8 Hz; *δ* 7·1 (*dd*), 2 Hz, 8 Hz; *δ* 8·05 (s); *δ* 9·80 (s)
Mass (*m*/*z*): 152, 151, 123, 137, 109, 89

2021

CSE 2021 · Q5(a) Five ^{1}H NMR signals of pentane-2,4-dione [10 marks]

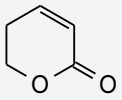
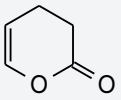
2,4-Pentadione exhibits five signal in ^{1}H NMR spectrum. Account for the observation. Also write the approximate chemical shift.

CSE 2021 · Q5(e) McLafferty rearrangement in pentan-2-one; base peak of pentan-3-one [10 marks]

2-Pentanone and 3-Pentanone are structural isomers. Only one of the isomers exhibits McLafferty rearrangement. Identify and show the McLafferty fragmentation for this isomer. Also propose base peak for the other isomer, which does not exhibit the McLafferty rearrangement.

CSE 2021 · Q6(a) Product of acetone with dilute sodium hydroxide from its spectra; Higher carbonyl stretching frequency in two pairs [20 marks]

(i) IR : 1620 cm^{-1} and 1695 cm^{-1}
^1H NMR : δ 1·9 (s, 3H), 2·1 (s, 6H), 6·15 (s, 1H)
The molecule obtained on treatment of acetone with dilute sodium hydroxide exhibits the above spectral data. Propose the structure of this molecule.

(ii) I.  and  II. $CH_3-CO-O-C_2H_5$ and $C_6H_5-CO-O-C_2H_5$
Identify the compound in each of the above pairs, that can be expected to exhibit carbonyl stretching signal at higher frequency.

CSE 2021 · Q7(c) Structure of a phenol $C_{10}H_{14}O$ from IR, mass and NMR data [15 marks]

A molecule with molecular formula $C_{10}H_{14}O$ exhibits a broad band at 3464 cm^{-1} in IR spectrum. Its mass spectrum exhibits base peak at m/z 135 and the ^1H NMR spectrum exhibits the following signals :
δ 1·3 (d, 6H); 2·4 (s, 3H), 3·4 (m, 1H), 4·6 (s, D_2O exchangeable), 6·6 (s, 1H), 6·8 (d, 1H) and 7·1 (d, 1H). Deduce the structure.

CSE 2021 · Q8(b) $C_9H_{18}O$ with a single ^1H NMR line; Two UV bands of acetone [15 marks]

(i) A molecule with molecular formula $C_9H_{18}O$ exhibits only one signal at δ 1·2 ppm in ^1H NMR spectrum. This also exhibits a strong absorption at 1710 cm^{-1} in IR spectrum. Propose structure for this molecule.

(ii) The UV spectrum of acetone exhibits two signals of different intensities, one at λ_{max} 280 nm and the other at λ_{max} 190 nm. Assign corresponding electronic transitions to the observed signals.

CSE 2021 · Q8(c) ^1H NMR spectrum of methyl propenoate; Two carbonyl bands of chloroacetone [15 marks]

(i) Predict the number of signals, nature of the signals (s/d/t/m) and approximate chemical shifts in ^1H NMR spectrum of methyl propenoate.

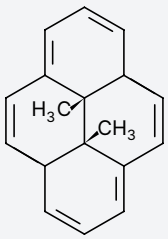
(ii) Acetone exhibits only one carbonyl stretching frequency in IR spectrum whereas chloroacetone exhibits two at 1725 and 1745 cm^{-1}. Explain why.

IFoS 2021 · Q1(h) Hyperfine lines of an isotopic radical [5 marks]

How many lines are possible in the ESR spectrum of $^{13}\dot{C}F_2H$?

IFoS 2021 · Q3(a)(ii) Strongly shielded internal methyl groups [5 marks]

(ii) Give reason why methyl groups are observed at −4·2 δ ppm in the PMR spectrum of the following compound: 5



IFoS 2021 · Q3(c)(i) ESR resonance field [5 marks]

(i) ESR is observed for hydrogen atom with an instrument operating at 9·5 GHz. If G value for electron in hydrogen atom is 2·0026, what is the magnetic field applied? (μ_B = 9·274 × 10^{-24} J T^{-1}) 5

IFoS 2021 · Q5(e) Azobenzene and hydrazobenzene [5 marks]

Suggest a suitable explanation by using UV-visible spectroscopy for the following statement:

Azobenzene is a deep orange-red compound while hydrazobenzene is colourless.

IFoS 2021 · Q8(a) Methylcyclohexenes by mass spectrometry; Hydroxy-methoxyacetophenone assignment [10 marks]

(i) Using mass spectroscopy, how will you distinguish between 3-Methylcyclohexene and 4-Methylcyclohexene? 5

(ii) An unknown organic compound with molecular formula $C_9H_{10}O_3$ shows the following spectral data:

IR (ν_{max}, cm^{-1}): 3400 and 1680

PMR (δ, ppm): 7.8 (1 H, d, J = 8 cps), 7.0 (1 H, d, J = 8 cps), 6.5 (1 H, s), 5.8 (1 H, s, D_2O exchangeable), 3.9 (3 H, s), 2.3 (3 H, s)

Identify the structure of the compound and write the reduction product of the compound with Zn–Hg | HCl. 5

IFoS 2021 · Q8(b) Identification of an aromatic diester [10 marks]

An unknown organic compound with MF $C_{12}H_{14}O_4$ gave the following spectral data:

UV (λ_{max}, nm): 225 and 265

IR (ν_{max}, cm^{-1}): 2900, 2800, 1720, 1030 and 860

PMR: δ 1.48 (6 H, t, J = 7 cps), 4.4 (4 H, q, J = 7 cps) and 8.1 (4 H, s)

Mass (m/z): 222, 194, 177 (base peak), and 149.

On the basis of the above spectral data, deduce the structure of the compound.

IFoS 2021 · Q8(c)(i) Oxidative coupling of acetic anhydride [5 marks]

(i) Acetic anhydride when refluxed with potassium permanganate, gives compound A, $C_4H_4O_3$. The IR spectrum of A shows bands at 1860 cm^{-1} and 1785 cm^{-1}. What is A? Suggest reactive intermediate formed in its formation and give its hydrolysis product. 5

IFoS 2021 · Q8(e) IR distinctions between functional groups [5 marks]

How would you distinguish between the following pairs of organic compounds by IR spectroscopy?

(i) $H_3C-CO-C_6H_4-OCH_3$ (para) and $H_3C-CO-C_6H_4-NO_2$ (para)

(ii) $CH_3-CH_2-CO-Cl$ and $Cl-CH_2-CH_2-OCH_3$

2020

CSE 2020 · Q5(d) Aromatic out-of-plane C–H wagging and adjacent hydrogens [10 marks]

Arrange the following compounds in increasing order of out of plane C—H wagging vibrations, as shown, and give a suitable explanation to justify your answer:

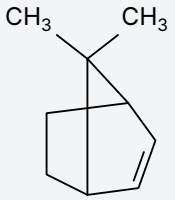
(*A*) 1,3-$R_2C_6H_4$, the H between the two R shown (*B*) 1,2-$R_2C_6H_4$, the four ring H shown

(*C*) 1,3-$R_2C_6H_4$, the three adjacent H shown (*D*) benzene, all six H shown

CSE 2020 · Q5(e) Methyl groups of 7,7-dimethylnorbornene: anisotropy of C=C [10 marks]

Consider the two methyl groups labelled as Ⓐ and Ⓑ in the following compound, and answer the given questions:

Ⓑ Ⓐ



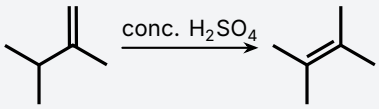
(i) Which methyl group would exhibit a higher chemical shift in ^{1}H NMR spectrum?
(ii) Offer a suitable explanation to justify your choice of methyl group.
(iii) Predict the approximate chemical shift values for both the methyl groups.

CSE 2020 · Q7(a) C=O stretching wavenumber from the force constant; IR of C_5H_{10} [15 marks]

(i) Calculate C = O stretching frequency, K = 12.3×10^5 dyne/cm.
(ii) A compound has molecular formula C_5H_{10}, showing absorption at 1380 cm^{-1}. Identify the structure of the compound.

CSE 2020 · Q7(c) Metastable ions in toluene; IR monitoring of an alkene isomerisation [20 marks]

(i) What are metastable ions and how are they formed? The mass spectrum of toluene shows strong molecular ion peak at m/z 91 and its fragment at m/z 65. Calculate the value for metastable ion peak.
(ii) Identify how vibrational spectroscopy might be used to monitor the progress of the following reaction:

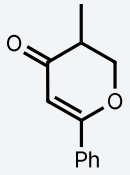


CSE 2020 · Q8(a) NMR shift in Hz and ppm; UV bands of 3-buten-2-one [15 marks]

(i) Dichloromethane has a chemical shift of 532 Hz from TMS (tetramethylsilane) on a 100 MHz spectrometer. What will be the chemical shift in ppm? What would the chemical shift be in ppm and Hz on a 600 MHz spectrometer?
(ii) 3-Buten-2-one gives two peaks in its ultraviolet spectrum at 213 nm (ε = 7100) and 320 nm (ε = 27). What type of transition is responsible for each absorbance? Account for the difference in molar absorptivity for the two absorptions.

CSE 2020 · Q8(c) Bullatenone: correcting a structure from IR, NMR and MS [20 marks]

An organic compound *X* was erroneously assigned the following structure:



X

The spectral data of the organic compound are given below. On the basis of the spectral data, justify why *X* is definitely a wrong structure and write the correct structure compatible with the spectral data:

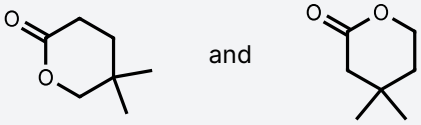
IR (cm^{-1}): 1705, 1604
^{1}H NMR: δ_H (ppm) 1.43 (s, 6H), 5.82 (s, 1H), 7.35 (*m*, 3H), 7.68 (*m*, 2H)
MS: m/z 188 (10%) (high resolution confirms $C_{12}H_{12}O_2$), 105 (20%), 102 (100%), 77 (20%)

IFoS 2020 · Q5(e) C_4H_6O isomers with λmax 187 and 280 nm [5 marks]

Write all the isomers possible with the molecular formula C_4H_6O whose UV spectra exhibit a high intensity peak at λ_{max} = 187 nm and a very low intensity peak at λ_{max} = 280 nm.

IFoS 2020 · Q5(f) Distinguishing two dimethyl δ-valerolactones by ^{1}H NMR [5 marks]

How would you use ^{1}H NMR spectroscopy to distinguish between the following compounds?



IFoS 2020 · Q5(g) Why mass spectra use a 70 eV beam; why fragmentation occurs [5 marks]

Why are majority of mass spectra run with a 70 eV beam? Also explain why does fragmentation occur in mass spectrometry.

IFoS 2020 · Q5(h) ESR hyperfine patterns: one ^{14}N with two H; three equivalent ^{14}N [5 marks]

Draw the ESR hyperfine structure of radicals containing (a) one ^{14}N and having two equivalent protons, and (b) having three equivalent ^{14}N nuclei.

IFoS 2020 · Q6(b) Benzyl acetate from IR, NMR and MS [10 marks]

An unknown organic compound gave the following spectral data:
(i) IR (ν_{max}, cm^{-1}) : 1743, 1229, 751, 698
(ii) ^{1}H NMR (δ, ppm) : 2·06 (s, 3H), 5·08 (s, 2H) and 7·33 (m, 5H)
(iii) Mass [m/z (relative intensity %)] : 150 (34·1), 151 (3·5), 152 (0·32), 108 (100), 91 (50), 79 (26), 77 (13·6), 43 (40·3)

Identify the unknown organic compound and explain all observed spectral data.

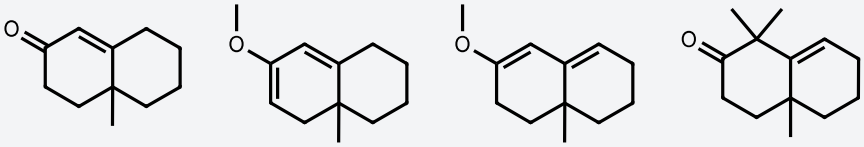
IFoS 2020 · Q6(c) Moment of inertia and bond length of CO from B [5 marks]

Calculate the value of I and r of CO.

$$B = 1{\cdot}92118\ cm^{-1}$$

IFoS 2020 · Q6(e) Following an octalone to dimethyl octalone conversion by UV and IR [5 marks]

Enone *A* is a versatile starting material, and can be converted into compounds *B*, *C* or *D*.



A *B* *C* *D*

(i) Show how one could easily differentiate between the structures using UV spectroscopy.
(ii) Define explicitly how IR spectroscopy can be used to follow the conversion of *A* to *D*.

IFoS 2020 · Q7(c) Three $C_5H_{11}Br$ isomers identified from IR of their NaOH products [10 marks]

Three bottles on the stockroom shelf marked $C_5H_{11}Br$ have their labels fallen off. Having only IR machine at your disposal, you first treat a sample of the contents in each bottle with NaOH in aqueous ethanol, and then you determine the IR spectrum of each product or product mixture. Here are the results:
(i) $C_5H_{11}Br$ isomer in bottle A on treatment with NaOH in aqueous ethanol : IR bands at 1660, 2850 – 3020 and 3350 cm^{-1}.
(ii) $C_5H_{11}Br$ isomer in bottle B on treatment with NaOH in aqueous ethanol : IR bands at 1670 and 2850 – 3020 cm^{-1}.
(iii) $C_5H_{11}Br$ isomer in bottle C on treatment with NaOH in aqueous ethanol : IR bands at 2850 – 3020 cm^{-1}.
(1) What does the data tell you about each product or product mixture?

(2) Suggest possible structures for the contents of each bottle.

IFoS 2020 · Q7(e) Absorption of IR versus UV radiation [5 marks]

What is the main difference in absorption of infrared and UV radiation by a molecule?

IFoS 2020 · Q8(b) ESR of the ·CD_3 radical [5 marks]

ESR of $CD_3^{\bullet}$ radical:

CD_3 one odd $e^{\ominus}$, S = 1/2 and I = 1. Then

(i) calculate number of lines.
(ii) draw spike lines.
(iii) calculate intensity pattern.
(iv) draw spectrum.

IFoS 2020 · Q8(c) C_7H_5OBr from IR, NMR and MS: 3-bromobenzaldehyde [10 marks]

A compound with molecular formula C_7H_5OBr gave the following data:
(i) IR (ν_{max}, cm^{-1}) : 1700, 1192, 786, 707, 672, 647 and 642.
(ii) ^1H NMR (δ, ppm) : 10·00 (s – 1H), 8·2 (d – 1H), 7·8 (d – 1H), 7·7 (dd – 1H), 7·3 (d – 1H)
(iii) Mass [m/z] : 184 – 186, 183 – 185, 155 – 157, 74 – 77.
Assign the structure of the compound explaining the observed spectral data.

IFoS 2020 · Q8(e) Methyl shifts of acetonitrile and chloromethane [5 marks]

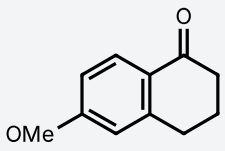
Assigning the chemical shift value of methyl protons of acetonitrile and chloromethane in ^1H NMR spectrum, offer a suitable explanation for the difference.

2019

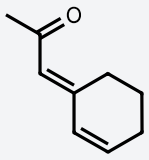
CSE 2019 · Q5(d) λmax by Woodward–Fieser and Scott rules [10 marks]

Predict λ_{max} for the following molecules:

(i)

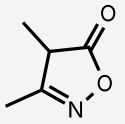


(ii)

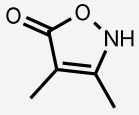


CSE 2019 · Q5(e) IR spectra of two isoxazolone tautomers [10 marks]

How will you distinguish the two using IR-spectroscopy?



I



II

CSE 2019 · Q6(a) Structure of C_7H_9N from UV, IR and NMR: p-toluidine [15 marks]

On the basis of the given spectroscopic data, deduce the structure of C_7H_9N:

UV	: λ_{max} = 290 nm (in ethanol)
IR ($\bar{\nu}$)	: 3440 cm^{-1}, 3360 cm^{-1}, 3025 cm^{-1}, 2920 cm^{-1}, 1625 cm^{-1}, 1380 cm^{-1}, 810 cm^{-1}
^1H-NMR (ppm)	: $\delta_{2.16}$, s, 3H; $\delta_{3.24}$, s, 2H; $\delta_{6.37}$, d, 2H (J = 8.0 Hz); $\delta_{6.79}$, d, 2H (J = 8.0 Hz)

CSE 2019 · Q7(a) Structure of $C_8H_4O_3$ from IR, NMR and mass spectrum: phthalic anhydride [15 marks]

An organic compound with molecular formula $C_8H_4O_3$ exhibited the following spectroscopic data:
IR (cm^{-1}) : 1830, 1760, 1120
^{1}H-NMR : $\delta_{8.049}$, 2H, *s*; $\delta_{7.635}$, 2H, *s*
Mass : *m*/*z* = 148, 104, 76, 50
Deduce the structure of the compound and justify the formation of the above fragment ions.

CSE 2019 · Q8(a) Structure of $C_7H_5Cl_3O$ from its NMR spectrum [15 marks]

An organic compound having molecular formula $C_7H_5Cl_3O$ exhibited the following ^{1}H-NMR data (ppm):
$\delta_{3.9}$, *s*; $\delta_{6.8}$, *d* (*J* = 8.0 Hz); $\delta_{7.3}$, *d* (*J* = 8.0 Hz)
Deduce the structure of the compound.

CSE 2019 · Q8(b) ^{1}H NMR of the three bromochloroethylenes [15 marks]

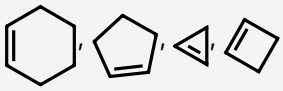
How will you distinguish various isomers of bromochloroethylene on the basis of ^{1}H-NMR spectroscopy?

IFoS 2019 · Q5(e) Anisotropic effect in aromatic protons [5 marks]

What is anisotropic effect? Explain this effect in aromatic protons.

IFoS 2019 · Q5(f) C=C stretching of cycloalkenes and ring strain [5 marks]

Arrange the following cycloalkenes in order of their wave numbers' increasing manner and explain the importance of strain:



IFoS 2019 · Q6(a) Structures from UV/IR/NMR data; an iodoform-positive C_8H_8O [10 marks]

(i) An unknown organic compound gave the following spectral data:
UV : 280 nm, ε_{max} = 20
IR : 1698 cm^{-1}
PMR (δ, ppm) : 3·4 (s, 3H), 6·6 (2H, d, *J* = 8 Hz), 7·5 (2H, d, *J* = 8 Hz) and 9·5 (1H, s)
Find the structure and explain the data. 5

(ii) A compound with molecular formula C_8H_8O gave positive iodoform test and gave the following data:
IR (ν_{max}, cm^{-1}) : 1685
NMR (δ, ppm) : 2·1 (s, 3H), 7·1–7·3 (m, 5H)
Mass (Rel. Abu. %) : *m*/*z* 120, 105, 77 and 51
Find the structure and give its mass fragmentation. 5

IFoS 2019 · Q6(d) Microwave-active molecules; DCl and HCl spectra differ [10 marks]

(i) Which of the following molecules will show microwave rotational spectrum? Identify it and justify your answer:

H_2, HCl, NO, N_2, CO, Cl_2

5

(ii) "DCl and HCl show different spectra." Give reason. 5

IFoS 2019 · Q7(a) Vibrational frequency and wavenumber of $H^{35}Cl$ from the force constant [10 marks]

^{1}H ^{35}Cl has a force constant value of 483·1 N m^{-1}. Calculate the fundamental frequency and wave number.

IFoS 2019 · Q7(b) Vibrational modes of H_2O and their IR activity [10 marks]

Diagrammatically show different modes of vibration of H_2O molecules. Justify whether these are infrared-active or not.

IFoS 2019 · Q7(d) 2-Pentanone versus 3-pentanone by MS; fragmentation of 4-heptanone [10 marks]

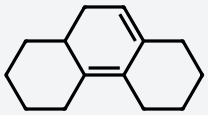
(i) How will you distinguish 2-pentanone from 3-pentanone by mass spectroscopy? 5

(ii) Discuss the mass spectral fragmentation of 4-heptanone. 5

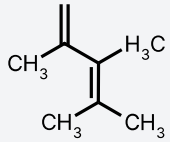
IFoS 2019 · Q8(c) Electronic transitions; λmax of three dienes by Woodward–Fieser [10 marks]

What are different types of electronic transitions possible when an organic compound is exposed to UV-visible radiation? Explain and calculate the λ_{max} values of the following compounds in nm:

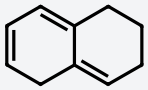
(i)



(ii)



(iii)



IFoS 2019 · Q8(d) Metastable peaks and isotopic peaks of halogens and sulphur [10 marks]

Discuss the following with suitable examples and give their importance in mass spectrometry:

(i) Metal stable peaks

(ii) Isotopic peaks of halogens and sulphur

2018

CSE 2018 · Q4(b) Two C_7H_{14} cycloalkanes from their base peaks [10 marks]

The mass spectra of two different cycloalkanes both show a molecular ion peak at m/z = 98. One spectrum shows a base peak at m/z = 69 and the other shows a base peak at m/z = 83. Identify the two cycloalkanes.

CSE 2018 · Q4(d) Structure of $C_5H_{10}O$ from UV, IR, NMR and mass spectra [15 marks]

An organic compound (MF $C_5H_{10}O$) exhibits the following spectral characteristics :

UV (λ_{max} : 280 nm)

IR ν_{max} : 1715 cm^{-1}

^1H NMR (δ, ppm) : 0.90 (3*H*, *t*), 1.60 (2*H*, *m*), 2.20 (3*H*, *s*), 2.40 (2*H*, *t*)

Mass (*m*/*z*) : 86, 71, 58, 43 (100%)

Deduce the structure of the compound and explain the principal ions observed in the mass spectrum.

CSE 2018 · Q5(d) Chemical shift is independent of the spectrometer frequency [10 marks]

A signal has been reported to occur at 120 Hz downfield from TMS in an NMR spectrometer with a 60 MHz operating frequency.

(i) What is its chemical shift?

(ii) What would its chemical shift be in an instrument operating at 100 MHz?

(iii) How many hertz downfield from TMS would the signal be in a 100 MHz spectrometer?

CSE 2018 · Q8(d) UV and Woodward–Fieser rules: β-ionone and its ring analogue [10 marks]

How do the UV spectral data λ_{max} 296 nm, ε_{max} 10700 and λ_{max} 281 nm, ε_{max} 20800 help in deciding between structures *X* and *Y*?



X *Y*

CSE 2018 · Q8(e) Charge-transfer spectra of donor–acceptor complexes [10 marks]

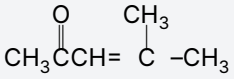
Explain charge-transfer spectra by taking a suitable donor-acceptor type complex.

IFoS 2018 · Q5(d) Structure of A (C, H, O) from ^{1}H NMR and dehydration [5 marks]

Compound *A* consisting of carbon, hydrogen and oxygen shows in ^{1}H-NMR (100 MHz) a singlet (9H) in the upfield region, another singlet (2H) in downfield compared to the previous protons and a third broad singlet (1H) that appears in the most downfield region. *A* on heating with H_2SO_4 produces *B*, which again on catalytic hydrogenation produces 2-methylbutane. Write the structures of *A* and *B*, and account for the ^{1}H-NMR.

IFoS 2018 · Q5(e) Two UV bands of mesityl oxide [5 marks]

4-Methyl-3-penten-2-one has two absorption bands in its UV spectrum—one at 236 nm and one at 314 nm.



(i) Why are there two absorption bands?

(ii) Which band shows the greater absorbance?

IFoS 2018 · Q5(f) Two C_7H_{14} cycloalkanes from base peaks at m/z 69 and 83 [5 marks]

The mass spectra of two different cycloalkanes both show a molecular ion peak at *m*/*z* = 98. One spectrum shows a base peak at *m*/*z* = 69 and the other shows a base peak at *m*/*z* = 83. Identify the cycloalkanes.

IFoS 2018 · Q6(b) m/z 91 of ethylbenzene versus m/z 92 of n-propylbenzene [10 marks]

Ethylbenzene shows a characteristic peak at *m*/*z* = 91, while *n*-propylbenzene shows strong peak at *m*/*z* = 92. Explain with the help of fragmentation pattern.

IFoS 2018 · Q6(d) O–H stretch of ethanol in CS_2 versus neat [5 marks]

Which will show an oxygen-hydrogen stretch at a greater wave number—ethanol dissolved in carbon disulfide or an undiluted sample of ethanol? Justify your answer briefly.

IFoS 2018 · Q8(a) Ring-opening of 2,2-dimethylcyclopropanone by methoxide: spectral proof [15 marks]

2,2-Dimethylcyclopropanone undergoes ring-opening when attacked by methoxide ion. The product (b.p. 101 °C) has the following spectral properties:

IR : 1740 cm^{-1} (s), 1160 cm^{-1} (no absorption near 1600 cm^{-1} or 3100 cm^{-1})
^{1}H-NMR : δ 3·6 (3H, singlet), δ 1·2 (9H, singlet)
UV : Transparent above 200 nm
Mass : *m*/*z* 116, 85, 59, 31

Deduce the structure of the product and assign the spectral data. From the mechanism, an alternative

product might have arisen. What is it?

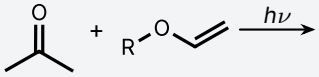
2017

CSE 2017 · Q5(e) IR distinction of two pairs of compounds [10 marks]

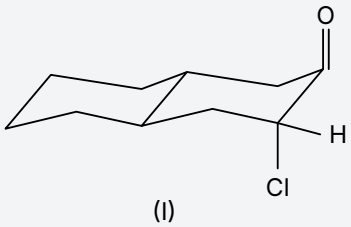
How can you distinguish between the following pairs of compounds by using IR spectroscopy?
(i) Salicylic acid and p-Hydroxy benzoic acid
(ii) Propionaldehyde and Acetone

CSE 2017 · Q7(a) Paternò–Büchi reaction; NMR of bromopropanes; IR of α-chloro ketones [15 marks]

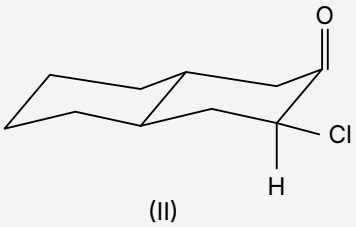
(i) Write the intermediates and possible products in the following photochemical reaction.



(ii) How many ^{1}H NMR signals do you expect for 1-bromopropane and 2-bromopropane? Give their splitting pattern.
(iii) How will you distinguish the following compounds by IR spectroscopy? Which will absorb more wave number in cm^{-1}, and why?



(I)



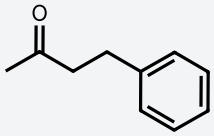
(II)

CSE 2017 · Q7(c) UV spectra of cis- and trans-stilbene [10 marks]

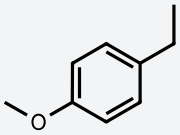
How can you distinguish between *cis* and *trans* isomers of stilbenes from UV spectral study? Explain.

CSE 2017 · Q8(b) Mass spectra of 4-phenylbutan-2-one and 4-ethylanisole [10 marks]

Predict the M^+ peaks and mass spectral fragmentation for the following compounds.



and



CSE 2017 · Q8(d) Structure of $C_9H_{10}O_2$ from UV, IR and NMR [10 marks]

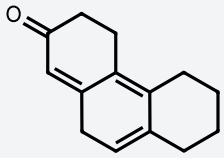
An unknown organic compound having molecular formula $C_9H_{10}O_2$ exhibited the following spectral data:
UV : 270 nm; IR : 1680 cm^{-1}
^{1}H NMR : δ 7.6 (2H, d, J = 8 Hz), 6.9 (2H, d, J = 8 Hz), 3.9 (3H, s), 2.0 (3H, s).
Deduce the structure of the compound.

IFoS 2017 · Q5(a) McLafferty rearrangement [5 marks]

Illustrate 'McLafferty Rearrangement' with a suitable example.

IFoS 2017 · Q5(b) λmax of a tricyclic dienone by Woodward–Fieser rules [5 marks]

Calculate λ_{max} of the given compound (A) by the use of Woodward-Fieser rule.



(A)

IFoS 2017 · Q5(d) Which molecules show a microwave rotational spectrum? [5 marks]

Which of the following will show a microwave rotational spectrum and why?

H_2, HCl, CH_4, H_2O and CH_3Cl

IFoS 2017 · Q5(e) Moment of inertia of CO from line spacing [5 marks]

The rotational spectrum of CO shows a series of lines placed 3·84235 cm^{-1} apart. Calculate the moment of inertia of C=O bond. [h = 6·626 × 10^{-27} erg sec.]

IFoS 2017 · Q5(f) Fundamental vibrational modes of CO_2 [5 marks]

Show all the possible fundamental modes of vibration of CO_2 molecule.

IFoS 2017 · Q5(g) ESR spectrum of the methyl radical [5 marks]

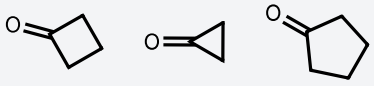
Explain the E.S.R. spectrum of the methyl radical.

IFoS 2017 · Q5(h) Chemical shift from a 1058 Hz signal at 200 MHz [5 marks]

In ^1H NMR spectrum of a compound at 200 MHz, a signal at 1058 Hz was observed. Calculate the chemical shift (δ) for this proton.

IFoS 2017 · Q6(a) ν(C=O) of cyclopropanone, cyclobutanone, cyclopentanone; silicones [10 marks]

(i) Arrange ν_{max} (C=O) of the given compounds in decreasing order and give suitable explanation of your answer.



(A) (B) (C)

5

(ii) What are silicones? Mention some of its uses. 5

IFoS 2017 · Q7(b) Bathochromic shift with conjugation; azo coupling with β-naphthol [10 marks]

(i) 'In electronic spectra a bathochromic shift is often associated with increasing conjugation' — Explain. 5

(ii) Aniline on treatment with sodium nitrite and HCl in cold generates a product (X) which on treatment with β-naphthol gives (Y). Provide the structures of X and Y. Name the concerned reaction. 5

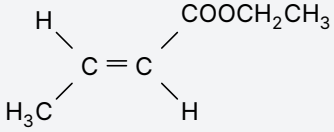
2016

CSE 2016 · Q6(e) IR spectra of cis- and trans-cyclohexane-1,3-diol [10 marks]

How can *cis* and *trans*-1,3-cyclohexane diol be distinguished using IR spectra?

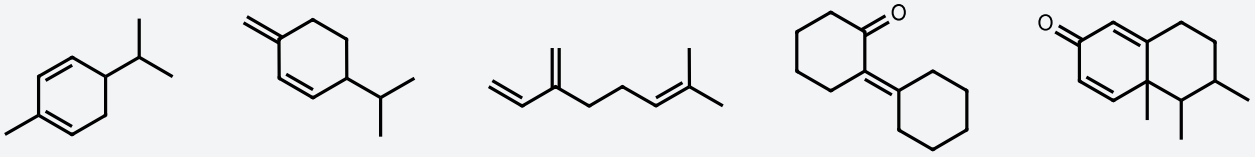
CSE 2016 · Q7(d) ^{1}H NMR of ethyl (E)-but-2-enoate [10 marks]

Assign the observed chemical shift values of 1.22, 1.88, 4.13, 5.81 and 6.95 for the following compound:



CSE 2016 · Q8(a) Woodward–Fieser rules: which structure absorbs at 229 nm [15 marks]

Which of the following structures has λ_{max} 229 nm? Give the calculations of each:



(i) *(ii)* *(iii)* *(iv)* *(v)*

CSE 2016 · Q8(b) Mass spectrum: the M-1 peak of pentanal [10 marks]

Identify the compound, which can give $M^+ - 1$ peak among the following. Discuss its fragmentation pattern with *m/e* values:

(i) $CH_3CH_2CH_2CH_2CHO$ (ii) $CH_3CHOHCH_2CH_2CH_3$ (iii) $CH_3CH_2COCH_2CH_3$ (iv) $CH_3COOCH_2CH_2CH_3$

CSE 2016 · Q8(c) Equivalent protons and number of ^{1}H NMR signals [10 marks]

Draw structures, label equivalent protons and indicate the number of signals in each of the following:

(i) Mesitylene (ii) *p*-ethylbenzene (iii) Isopropylbenzene

IFoS 2016 · Q5(e) Chemical shift at 60 MHz and 100 MHz [5 marks]

A compound contains two types of protons which exhibit signals at 139·2 Hz and 430·2 Hz downfield from TMS in a spectrometer operating at 60 MHz. What will be their relative position when measured on a 100 MHz instrument ?

IFoS 2016 · Q5(f) λmax of CH_3Cl, CH_3Br, CH_3I: n→σ* [5 marks]

Explain the following variations in λ_{max} (in nm) of CH_3Cl (173), CH_3Br (204), CH_3I (258).

IFoS 2016 · Q5(g) Bathochromic shift with increasing conjugation [5 marks]

Why is a bathochromic shift observed with increasing conjugation in electronic spectra ? Explain.

IFoS 2016 · Q5(h) McLafferty rearrangement: butyrophenone, m/z 120 and 105 [5 marks]

What is McLafferty rearrangement in Mass Spectrometry ? Mass spectrum of 1-phenyl butanone exhibits m/z (mass by charge) 105 as a base peak and m/z 120 as one of the major peaks. Explain.

IFoS 2016 · Q7(a) $C_6H_{10}O$ from UV, IR and ^1H NMR: mesityl oxide [20 marks]

An organic liquid with molecular formula $C_6H_{10}O$ gave the following spectral data :

UV : ν_{max} 230 nm (ε 12600), 329 nm (ε 41)
IR : ν_{max} 2950–2860 (m), 1695 (s), 1620 (m), 1460 (m) cm^{-1}
NMR : δ 1.9 (s, 3H), 2.1 (s, 6H), 6.15 (s, 1H)

Write the possible structure of compound with suitable justification. Predict its ^{13}C-NMR spectrum.

IFoS 2016 · Q7(b) ^1H NMR of p-xylene and ethylbenzene [10 marks]

How can the NMR spectrum distinguish between the isomers — p-xylene and ethyl benzene ? Justify your answer.

IFoS 2016 · Q7(c) ESR spectra of three aromatic radicals [10 marks]

Give the ESR spectra of Naphthalene negative ion, Anthracene negative ion and Triphenyl methyl radical.