



PRABHAT KUMAR COLLEGE, CONTAI

M.A. 4TH Semester Examinations 2021
(Under CBCS pattern)

Subject : Chemistry

PAPER/COURSE – CHEM: 401

Advanced Spectroscopy-II

FULL MARKS : 50

TIME : 02 Hrs.

Candidates are required to give their answers in their own words as far as practicable.

The figures in the right-hand margin indicate full marks.

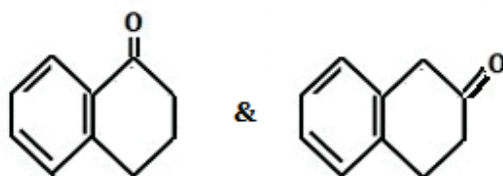
Attempt any Four (04) of the following:

4 x 10

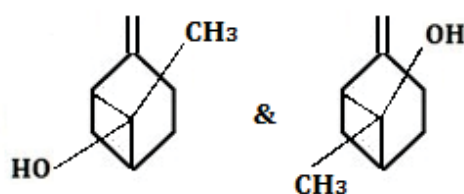
- a] What do you mean by metastable ion? (3)
b] Write down the important features of parent ion peaks. (7)
- a] What is molecular ion or parent ion? (2¹/₂)
b] Show the fragmentation pattern of the following molecules in mass spectrum. (7¹/₂)
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CH}_3$
 - $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3) - \text{CH}_3$
- a] Calculate the chemical shift in ppm (δ) for a proton that has resonance at 126 Hz downfield from TMS on spectrophotometer that operates at 60 MHz. (2¹/₂)
b] How will you differentiate the following pairs by NMR spectrum? (7¹/₂)
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(ii)



(iii) Cis-stilbene and trans-stilbene

4. a] Do all the bonds in a molecular ion undergo fission? (2)
b] What is McLafferty rearrangement? Give an example. (2)
c] Predict the structure of the compound whose peaks in the mass spectrum have m/e values 86, 71, 58 and 43 (100%). (3)
d] A hydrocarbon with molecular formula C_7H_{12} (M^+ m/e 96) shows large peaks at m/e 54 and due to $M-15$. What structure can be assigned to the compound? (3)
5. a] A compound with molecular formula, $C_6H_{12}O_2$ shows four signals: (i) singlet 1.1 δ (6H), (ii) singlet 2.1 δ (3H), (iii) singlet 2.6 δ (2H), and (iv) singlet 3.9 δ (1H). Propose a structure consistent with the given data. (3)
b] An organic compound with molecular weight 108 is not acidic in nature but can be easily oxidized to a crystalline compound (melting point $122^\circ C$). it gives the following spectral data:
UV: λ_{max} 255 $m\mu$, ϵ_{max} 202
IR: 3402 (s, b) 3065 (w), 2288 (m), 1499 (w), and 1455 cm^{-1} (m)
NMR: 2.74 τ (singlet, 24.5 squares), 5.4 τ (singlet, 9.5 squares), and 6.10 τ (singlet, 4.8 squares). (5)
c] What is spin-spin relaxation? (2)



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6. a] Define coupling constant. (2)
- b] What do you say about the induced magnetic fields in multiple bond systems? (2)
- c] What are the full forms of HMQC and DEPT? (1)
- d] A compound with molecular formula $C_9H_5NO_4$ shows the following bands in its infrared spectrum.
3000-2500 (b), 2225 (m), 1715 (s), 1605, 1518 (s), 1344 (s) and $900-700\text{ cm}^{-1}$ (s).
In NMR spectrum two bands are formed as (i) -1.1τ (singlet, 5.3 squares) and (ii) unsymmetrical pattern $2.6-2.75\tau$ (21.1 squares). Determine the structural formula of the compound. (5)
7. a] What is spin-spin coupling? (2)
- b] What is NMR shift reagent? (2)
- c] Which reference compound is used for NMR in D_2O ? Write its structure. (2)
- d] Give examples of two NMR active and two NMR inactive nuclei and explain why? (2)
- e] Mention some important characteristics of solvents used in NMR? (2)
8. a] Predict the structure of the organic compound which exhibits m/e peaks at 15, 43, 57, 91, 105 and 148 in mass spectrum. (3)
- b] How will you distinguish between the isomeric alcohols with molecular formula, $C_4H_{10}O$ by mass spectrometry? (3)
- c] What is precessional frequency? (2)
- d] Why is it necessary for a nucleus to behave as a tiny magnet to be studied by NMR spectroscopy? (2)