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PG (NEW) CBCS

M.Sc. Semester-IV Examination, 2020

CHEMISTRY

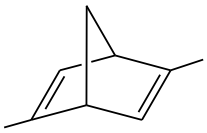
PAPER: CEM 401

ADVANCED APECTROSCOPY-II

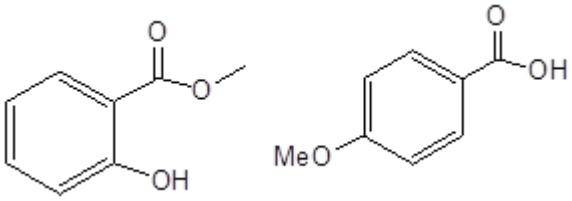
Full Marks: 40 **Time: 2 Hours**

Answer any one question from the following (within 250 words): 40X1=40

1. (a) Identify the number of ^{1}H NMR peaks observed in the following structure.



(b) Which of the following compounds will show a base peak at m/z 120 in its EI mass spectrum.



(c)What is chemical shift in NMR spectroscopy?

2. (a) Find the structure of an organic compound with M.F. $C_{\square}H_{\square}O_{\square}$ with the help of NMR data given below 13-C NMR

□ 128 d, □ 60 t, □ 132 t, □ 35 q, □ 170 s,

(b)What do you mean by ORD?

(c)What is the principle of Massbauer spectroscopy?

3. (a) Mention some important characteristics of solvent used in NMR.

(b) What is circular dichroism (CD)?

(c) What is spin-spin splitting in NMR spectra?

4. (a) What is Doppler effect?

(b) Calculate Doppler shift in Mossbauer experiment, where $\nu_{Source} = 3.84 \times 10^{18}$ Hz and relative velocity of source and observer is 2.2 mms^{-1}.

5. (a) Aromatic protons are more deshielded than ethylinic protons, although both the types of protons are attached to sp^2 hybridized carbon atom?

(b) How will you distinguish cis- and trans-stilbene by means of NMR spectroscopy?

6. (a) An aromatic compound (molecular mass = 135) gives the following signals in its PMR spectrum.

(i) Singlet (2.09δ), 3H (ii) A distorted singlet (3.09δ), H

(iii) A multiplet (7.7δ), 3H (iv) A multiplet (7.75δ), 2H

Predict the structure of the compound.

(b) A compound exhibits the following spectral data -

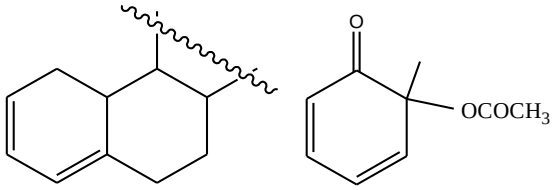
IR: (v) 1685 cm-1; 1H NMR: □□7.84 (d, J = 8 Hz, 2H), 7.60 (d. J = 8 Hz, 2H), 3.65 (t, J = 7 Hz, 2H), 3.18 (t, J = 7 Hz, 2H), 2.25 (pentet, J = 7 Hz, 2H) ppm; 13C NMR: □ 28, 36, 45, 128, 130, 133, 137, 197 ppm; EI MS m/z: 200, 198 (1 : 1). 185, 183 (1 : 1)

Identify the compound.

7. (a) Elucidate the structure of the compound having the following spectral data,

1H NMR: □□□□□□□br s, 1H), 5.5 □br s, 1H), 4.2 (q,2H), 2.0 (s,3H),1.1 (t,3H).

(b) Calculate the λ_{max} value of the given compounds using Woodward-Fieser rule .



8. (a) The pmr spectrum of a mixture of methyl iodide and tert-butyl bromide shows two signals at 2.20 δ and 1.8 δ with relative integrals of 5:1. What is the mole percent of each compound in the mixture?

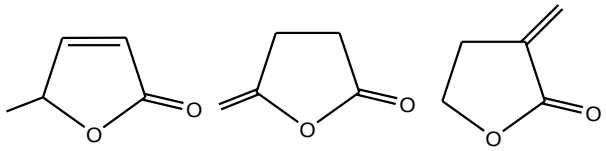
(b) Why is TMS used as a reference compound in NMR spectroscopy?

9. (a) The MB-spectrum of $K_4[Fe(CN)_6]$ consist of one line, where as that of $K_3[Fe(CN)_6]$ consist of two lines. Draw these spectra qualitatively and account for their appearance.

(b) Compare MB-spectrum of $K_4[Fe(CN)_6]$ vs.$[Fe(CN)_5NH_3]^{3-}$ and explain it.

(3)

10. What are factors effecting chemical shift in NMR spectroscopy? Indicate the order of stretching frequency in IR spectra of the following compounds with suitable reason.



11. Reaction of styrene ($PhCH=CH_2$) with HBr gives a mixture of regioisomers A (major) and B (minor). The ^1H NMR spectrum of the mixture shows four signals. Amongst others, at 5.17, 3.53, 3.15 and 2.00 ppm with relative integration of 2: 1: 1:6, respectively. Calculate the molar ratio of A and B. What is homoaromaticity?

12. Illustrate how the energy difference between nuclear spin states of a proton nuclei depend on the applied magnetic field strength and hence compare the same between ^1H and ^{13}C nuclear spin states under a particular radiofrequency spectrometer. Predict further which nuclei will exhibit maximum resonance intensity.

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