This question paper contains **8** printed pages]

AI—12—2017

FACULTY OF SCIENCE

M.Sc. (Second Year) (Third Semester) EXAMINATION

MARCH/APRIL, 2017

(CBCS Pattern)

CHEMISTRY

Paper (CH-531)

(Advanced Spectroscopic Methods)

(Thursday, 20-4-2017) **Time : 2.00 p.m. to 5.00 p.m.**

Time—Three Hours *Maximum Marks*—75

N.B. :— (*i*) *All* questions are compulsory.

(*ii*) Figures to the right indicate full marks.

(*iii*) Multiple choice questions (MCQs) should be attempted only once on page number three of answer-book with complete answer.

1. Attempt any *three* of the following : 15

(*a*) Explain how mass spectroscopy is useful to detect halogens in organic compounds.

(*b*) Acetophenone, phenol and benzoic acid can be distinguished by the characteristic bands in their IR-Spectra.

(*c*) Calculate the number of fundamental modes of vibration in C_2F_2 and BCl_4^-.

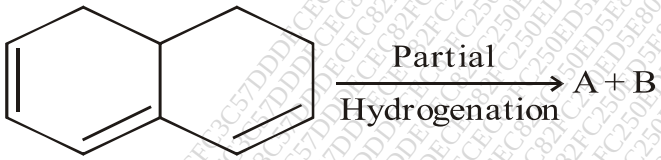
(*d*) In UV spectrum of crotonaldehyde band due to $\pi \rightarrow \pi^*$ in petroleum ether appears at λ_{max} 214 nm but the same band in ethanol appears at 220 nm.

(*e*) Enumerate in brief basic principles of ^{13}C-NMR spectroscopy.

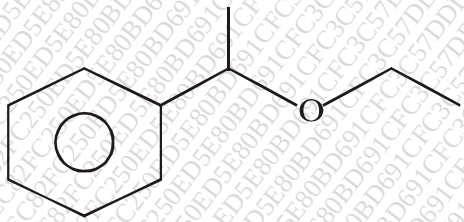
P.T.O.

2. Attempt any *three* of the following : 15

(*a*) Partial hydrogenation of triene shown below results into two compounds A and B, having molecular formula $C_{10}H_{14}$ compound. A shows absorption maximum at 235 nm and B shows at 275 nm. Assign the structures of the A and B compounds.

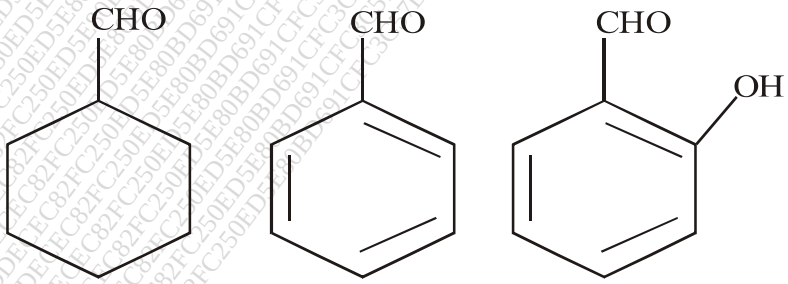


(*b*) Explain the genesis of the ions for the following :



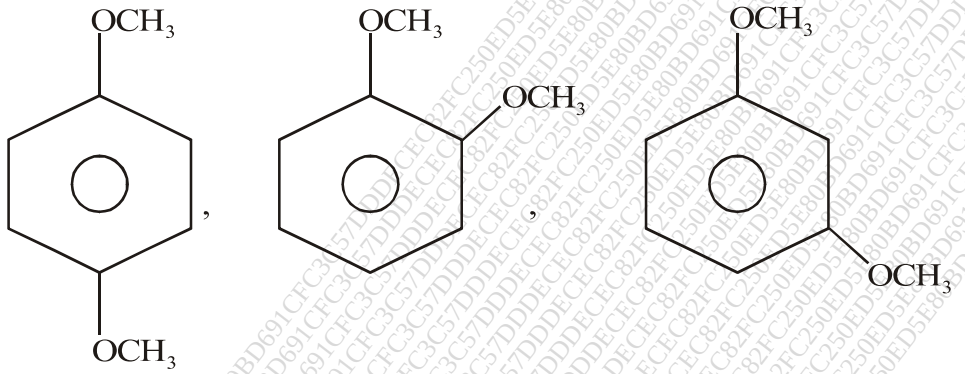
150, 135, 106, 105, 79, 77.

(*c*) The following aldehydes exhibits $\diagdown$C=O stretching bands at 1666 cm^{-1}, 1700 cm^{-1} and 1730 cm^{-1}. Assign to the proper aldehyde giving justification :



(*d*) What will be force constant for the band in N_2, if fundamental vibrational frequency is 7×10^{13} s^{-1} (Given : N = 14·007).

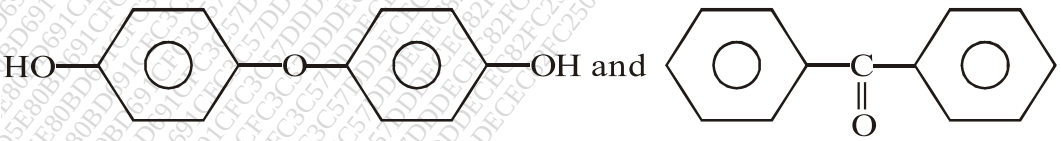
(*e*) How will you differentiate among the three following compounds with the help of ^{13}C NMR spectroscopy :



3. Solve the following :

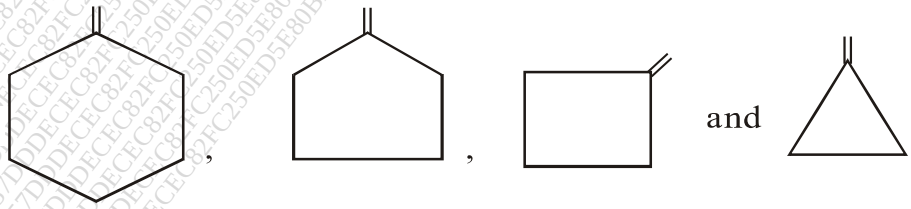
(*a*) Distinguish between the following pair by using the indicated spectral data methods : 7

(*i*)



[IR]

(*ii*)

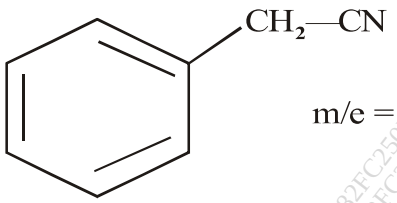


[IR]

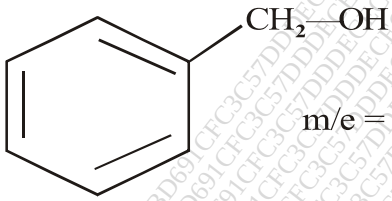
P.T.O.

Or

Explain the genesis of the ions : 7

(*i*) 

m/e = 117, 91, 90, 77, 65

(*ii*) 

m/e = 108, 107, 106, 105, 77, 79

(*b*) A compound with MF $C_{10}H_{12}O$ displays the following spectral data : 8

IR : 1690, 1600, 1580, 1490, 770, 690 cm^{-1}

PMR : δ_{PPM} : 1.3 (*d*, 6H),

5.3 (Septet, 1H)

7.3 – 7.7 (m, 5H)

^{13}C NMR (δ_{PPM}) :

22(*q*)

68(*d*)

128(*d*)

129(*d*)

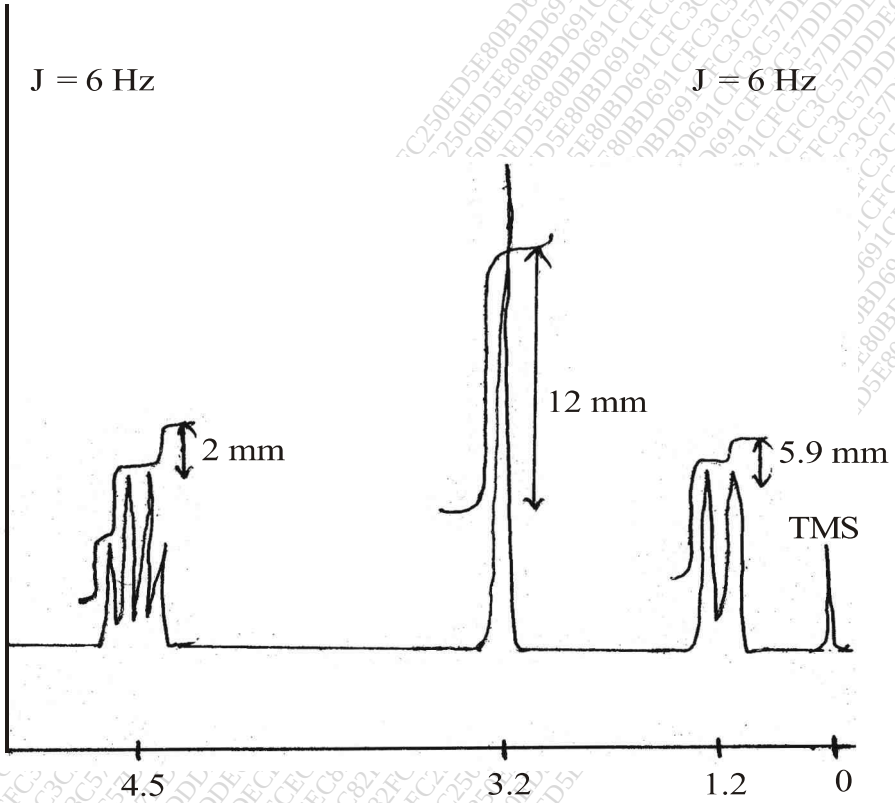
131(*s*)

135(*d*)

175(*s*)

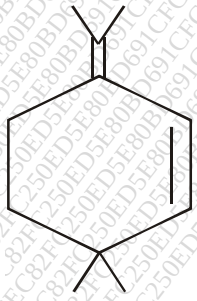
Or

A compound $C_4H_{10}O_2$ shows the following NMR spectrum. Deduce its structure : 8

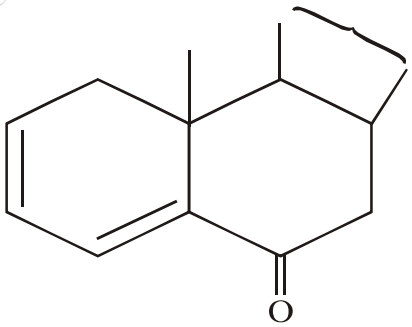


4. Solve the following :

(*a*) Using the Woodward-Fieser rules predict λ_{max} of the following compounds : 7



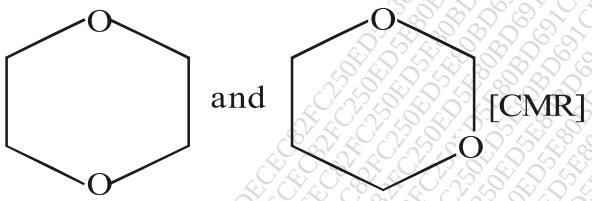
and

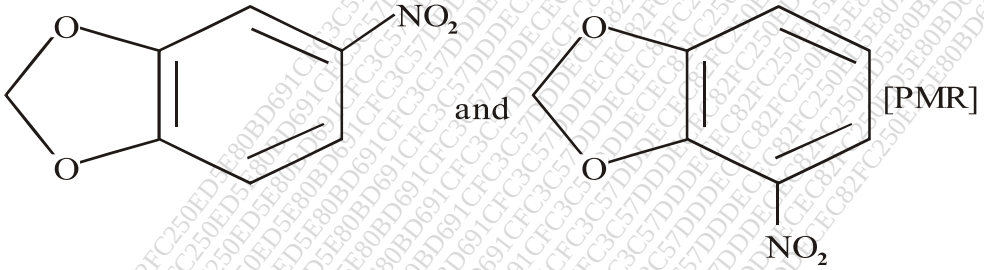


P.T.O.

Or

Distinguish between the following pairs by using the indicated spectral method : 7





(*b*) Deduce the structure of the following compound using given spectral data and justify your answer : 8

Molecular formula: $C_8H_{10}O$

UV λ_{max} : 250, 260, 265

($\in$ 230, 270, 230)

IR : 3360 (broad), 1610, 1550 cm^{-1}

PMR : 1.6 δ (br s, 3.8 mm)

2.8 δ(+J = 7 Hz, 8 mm)

3.9 δ(+J = 7 Hz, 7.9 mm)

7.2 δ(S, 20 mm).

Or

Assign the structure to the compound with MF $C_{11}H_{14}O_3$ which displays following data : 8

UV : 225 nm ($\in_{max}$ 9000)

IR : 3200-2800 (broad), 1690, 1510, 830 cm^{-1}

PMR(δ, PPM) $\delta_{1.95}$ (m, 12 mm, J = 6 Hz)

$\delta_{2.22}$ (*t*, 12 mm, J = 6 Hz), $\delta_{3.2}$(*t*, 12 mm, J = 6 Hz)

$\delta_{3.78}$ (*s*, 18 mm), $\delta_{7.05}$(*d*, 12 mm, J = 8 Hz)

$\delta_{6.75}$ (*d*, 12 mm, J = 8 Hz).

$\delta_{12.5}$ (*s*, 6 mm exchangeable with D_2O

Justify spectral data.

5. (A) Select the *correct* answer from the following Multiple Choice Questions and rewrite complete answer : 5

(*i*) Base peak in mass spectrum is obtained due to :

(*a*) less stable ion

(*b*) most stable ion

(*c*) meta stable ion

(*d*) none of the above.

(*ii*) In the NMR spectrum of a compound, one proton signal is seen at 12 δ, it must be due to :

(*a*) alcoholic —OH

(*b*) —COOH

(*c*) Phenol

(*d*) Aldehyde

(*iii*) Which one of the following is the correct basic value of λ_{max} for homoannular diene ?

(*a*) 214 nm

(*b*) 217 nm

(*c*) 253 nm

(*d*) 215 nm

(*iv*) Quadruple splitting observed in :

(*a*) K_3 $[Fe(CN)_6]$

(*b*) $K_2[Fe(CN)_5NO].2H_2O$

(*c*) Na_2 $[Fe(CN)_5NO]$

(*d*) All of the above

P.T.O.

(*v*) In IR spectrum, due to the presence of strong hydrogen bonding, the absorption band shifts to :

(*a*) higher wave number

(*b*) lower wave number

(*c*) Both the above

(*d*) no effect

(B) Write short notes on any *two* : 10

(*a*) Deshielding due to hydrogen bonding

(*b*) Electronic effect on absorption frequency of carbonyl.

(*c*) MacLafferty rearrangement.