

Instructions to candidates

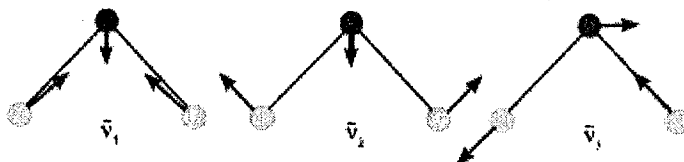
Duration: Three (03) hours

Number of questions: Six (06)

Answer all questions

Mark allocation: 400

1. a. Assume that the following are the normal vibration modes of water molecule: The arrows represent the direction of the motion of atom during the vibration.



Apply the symmetry operations of water molecule, which belongs to the C_{2v} point group for these vibration modes, and identify the corresponding irreducible representations.

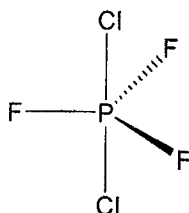
(30 Marks)

- b. Determine the symmetry point group for the following molecules and ions. The decision tree for the identifying a molecular point group is given at the end of the paper.

- i. NH_3
- ii. I_3^- (linear)
- iii. H_2B-BH_2 (BH_2 planes are twisted 90°)
- iv. SF_6

(20 Marks)

2. The following question refer to the trigonal bipyramidal molecule, PF_3Cl_2 , shown below.

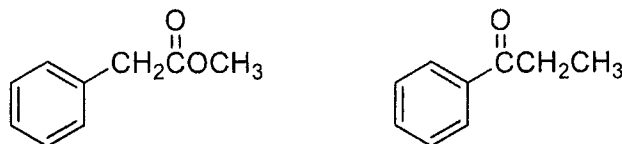


- a. Copy this molecule as it is to your answer booklet and diagrammatically show all symmetry elements and list all associated symmetry operations. Marks will be deducted for listing of incorrect symmetry operations. (15 Marks)
- b. Determine the point group of the molecule. The decision tree for the identifying a molecular point group is given at the end of the paper. (10 Marks)
- c. What is the order of the point group that this molecule belongs to? Character tables are given at the end of the paper. (5 Marks)
- d. How many symmetry classes are present in this point group? (5 Marks)

- e. Which irreducible representation is the totally symmetric representation? (5 Marks)
- f. List the Mulliken symbols of the irreducible representations do the following atomic orbitals belong:
- Pz
 - S
 - d_{xz}
 - d_z^2
- (10 Marks)
- g. Determine the direct product of the following representation and list the corresponding Mulliken symbol for the resulted product
- $A_2' \times A_2''$
 - $E' \times A_1''$
- (5 Marks)
- h. Determine and indicate the corresponding reducible representation (Γ) for each symmetry operation belongs to PF_3Cl_2 molecule? (20 Marks)
- i. List the translational, rotational and vibrational molecular modes of this molecule (15 Marks)

3.

- a. Explain how FTIR spectroscopy could be used to distinguish between the following two compounds. Be as specific as possible (20 Marks)

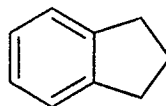


- b. Explain how 1H -NMR spectroscopy could be used to distinguish between the two compounds in problem 3a. Be as specific as possible (20 Marks)
- c. Predict the relative chemical shift positions of α and β hydrogen (i.e. which hydrogen is more downfield/upfield) of the following two compound and briefly explain your answer.



(20 Marks)

- d. How many peaks would appear in the ^{13}C -NMR spectrum of the following compound? Give the approximate positions of these peaks. Provide a brief explanation for your answer.

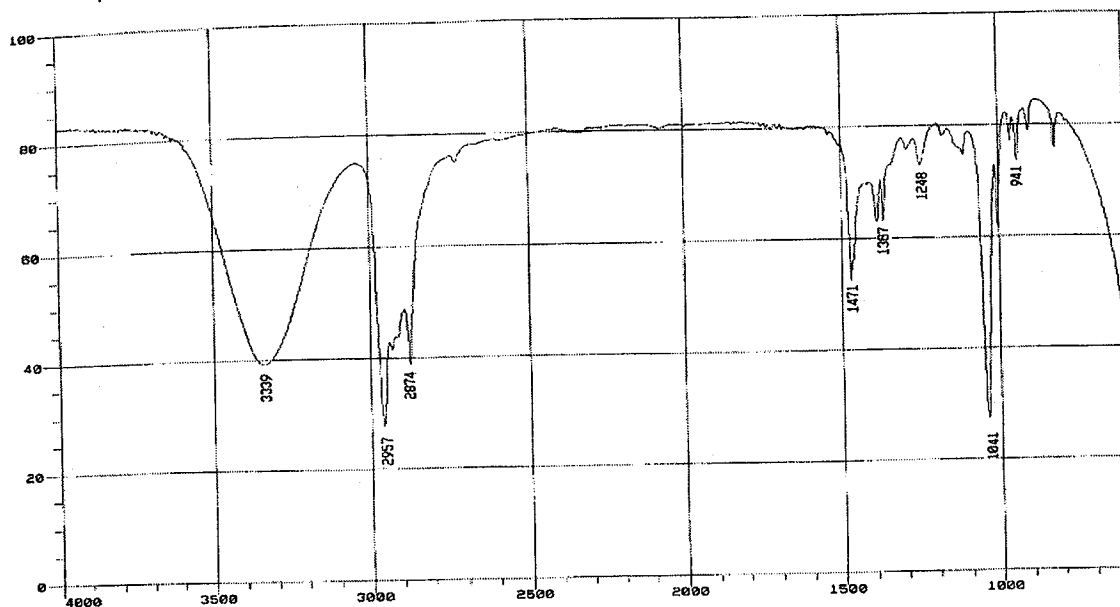


(10 Marks)

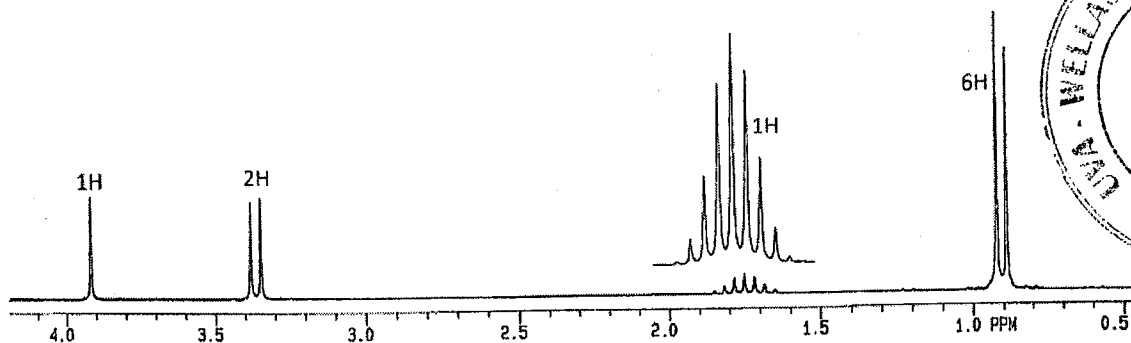
4. you are given a molecular formula, FTIR and $^1\text{H-NMR}$ spectra. Using this information, your task is to determine the structure of the compound.

Molecular formula: $\text{C}_4\text{H}_{10}\text{O}$

IR spectrum



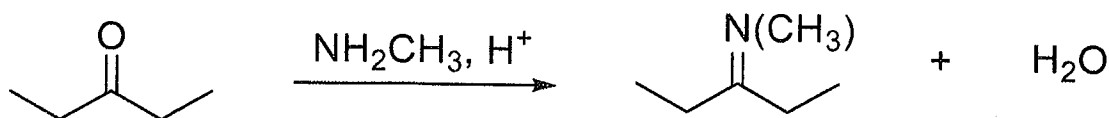
$^1\text{H-NMR}$ spectrum



- Determine the degree of unsaturation to limit the number of possible structures. (10 Marks)
- Look at the IR absorption bands at wavenumbers above 1500 cm^{-1} to determine what functional groups are likely in the compound. Remember that these functional groups must be consistent with the degree of unsaturation and the $^1\text{H-NMR}$ spectrum. (20 Marks)
- Determine the structure of the compound. The peak positions and the splitting of NMR signals will help you to determine the structure. If you can't figure out the entire structure at once, it helps to come up with fragments of the molecule that you can stick together into larger and larger groups until you have the entire structure. (30 Marks)

5.

- a. Show all the steps of the mechanism for the reaction shown below using curved arrows to represent movement of electron pairs. Remember: the only reagents you may use are those provided below.

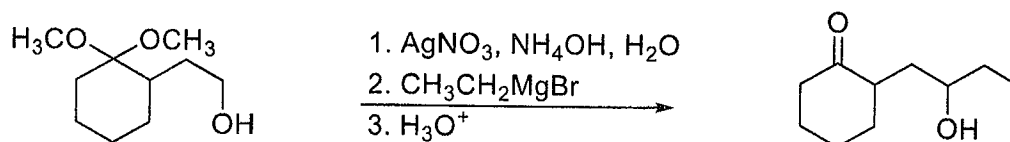


(30 Marks)

- b. Explain why the monitoring the pH of a reaction involving an amine in the formation of an imine is required. (20 Marks)
- c. Sterically, aldehydes react faster than ketones because they only have one alkyl group attached to the carbonyl carbon, making the carbonyl less sterically hindered. What is the other reason that aldehydes react faster than ketones? (20 Marks)

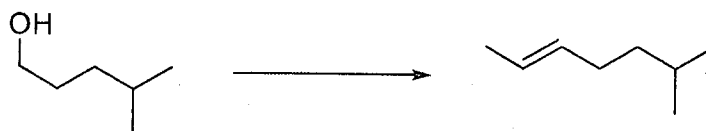
6.

- a. The following sequence does not form the desired product as shown when tried in the organic laboratory. Explain why. (10 Marks)



- b. The following conversions will require more than one but less than four steps of reagents to arrive at the final product. Write the appropriate reagents in their appropriate orders. Partial credit may be given for approaches without reagents, if intermediate structures are shown. (20 Marks)

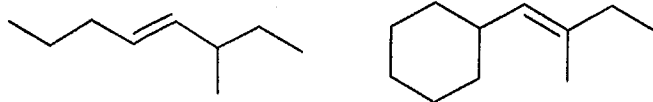
i.



ii.



- c. Determine the possible options if using a Wittig reagent to construct the following molecules. (20 Marks)



d. Determine if each of the reactions shown is oxidations, reductions or neither. (10 Marks)

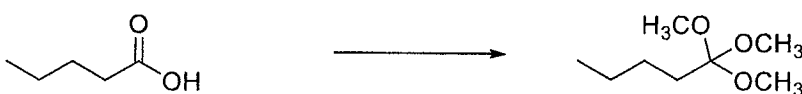
i.

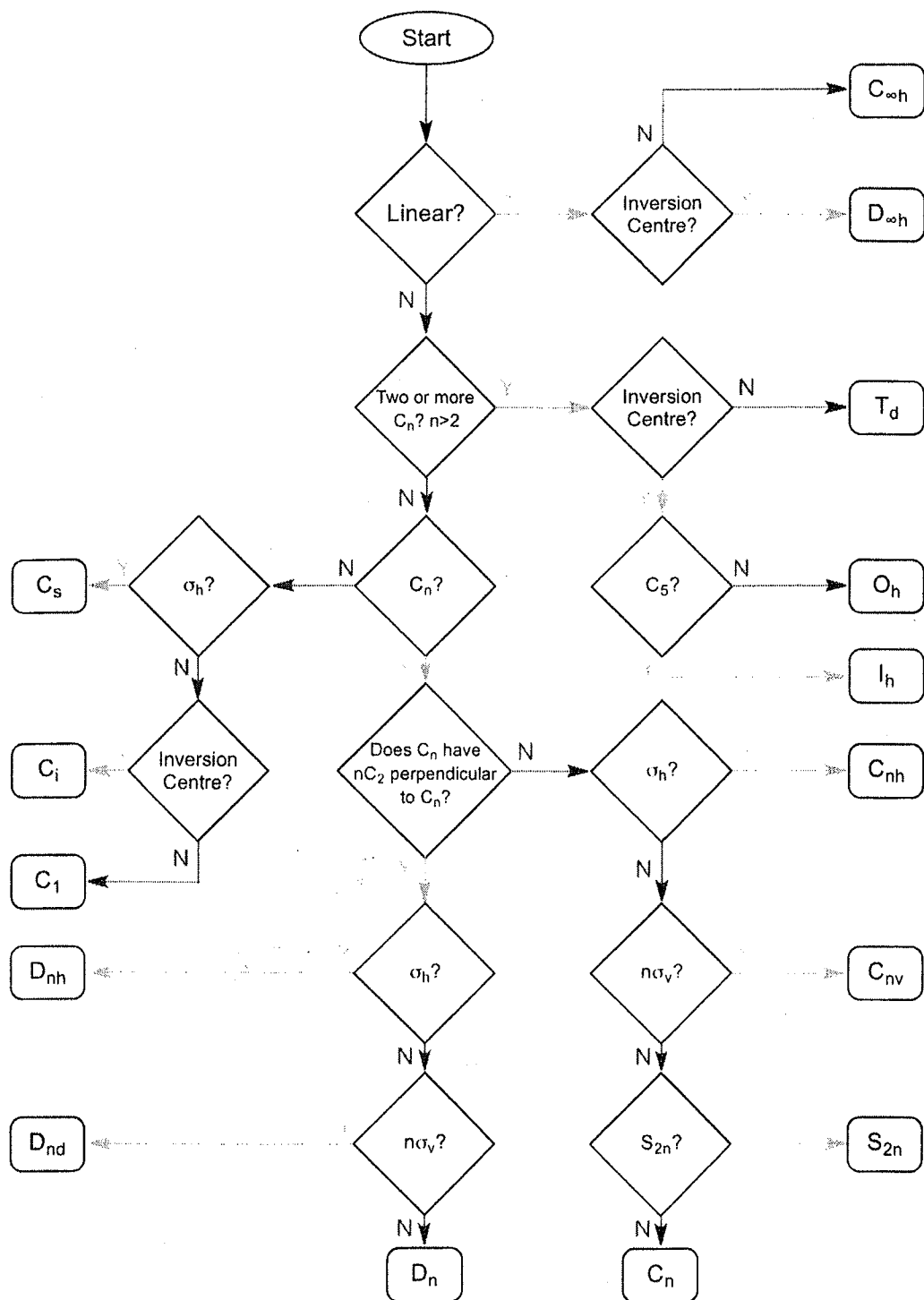


ii.



iii.





The decision tree for identifying a molecular point group

$C_{3v} (3m)$	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy)(zx, yz)$

$T_d (43m)$	E	$8C_1$	$3C_2$	$6S_4$	$6\sigma_4$	$b = 24$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$	
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$	
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z) (xy, yz, zx)	

$D_{2h} (6m2)$	E	$2C_2$	$3C_2$	σ_h	$2S_6$	$3\sigma_v$	$b = 12$	
A_1'	1	1	1	1	1	1	$x^2 + y^2, z^2$	
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y) $(x^2 - y^2, xy)$	
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y) (zx, yz)	

$O_h (m3m)$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_6$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$b = 48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, yz, zx)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

