Value

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351 / 354

OCTOBER 17th 2001 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.

The examination consists of Parts 1 - 8, each of which should be attempted. Note that some parts provide you with a choice of questions, *i.e*. answer 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered in the booklet provided. A periodic table with atomic numbers and atomic weights is located on the inside of this front cover.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 39 which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

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14 **PART 1 RELATIVE PROPERTIES**

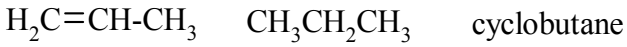
ANSWER ANY SEVEN (7) of questions 1-8.

Arrange the items in **questions 1-8** in **DECREASING ORDER** (*i.e.* greatest, most etc. **first**) with respect to the indicated property.

Use the following code to indicate your answers.

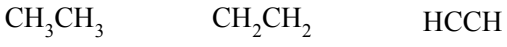
A.	**i > ii > iii**	D.	**ii > iii > i**
B.	**i > iii > ii**	E.	**iii > i > ii**
C.	**ii > i > iii**	AB.	**iii > ii > i**

1. The C-C-C bond angle in each of the following molecules:



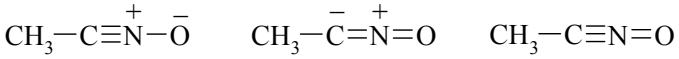
i **ii** **iii**

2. The strength of the **CH** bonds in each of the following :



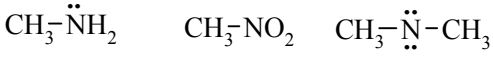
i **ii** **iii**

3. The relative importance of the following resonance contributors to CH_3CNO :



i **ii** **iii**

4. The formal charge on the **nitrogen** atom in each of the following molecules:



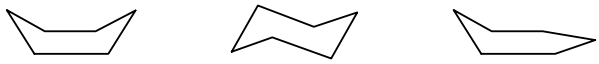
i **ii** **iii**

Value

Use the following code to indicate your answers.

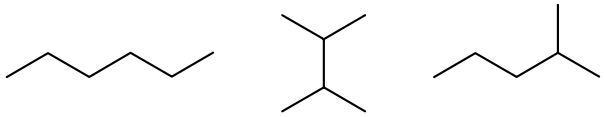
A.	**i > ii > iii**	D.	**ii > iii > i**
B.	**i > iii > ii**	E.	**iii > i > ii**
C.	**ii > i > iii**	AB.	**iii > ii > i**

5. The relative energies of the following conformations of cyclohexane :



i **ii** **iii**

6. The heat of combustion, ΔH_c^o for each of the following molecules: (least exothermic to most exothermic)



i **ii** **iii**

7. The number of constitutional isomers for the following molecular formulae:

C_3H_6O	C_3H_6	C_6H_{14}
i	**ii**	**iii**

8. The relative energies of the following orbitals of a **carbon** atom:

sp^3	sp^2	sp
i	**ii**	**iii**

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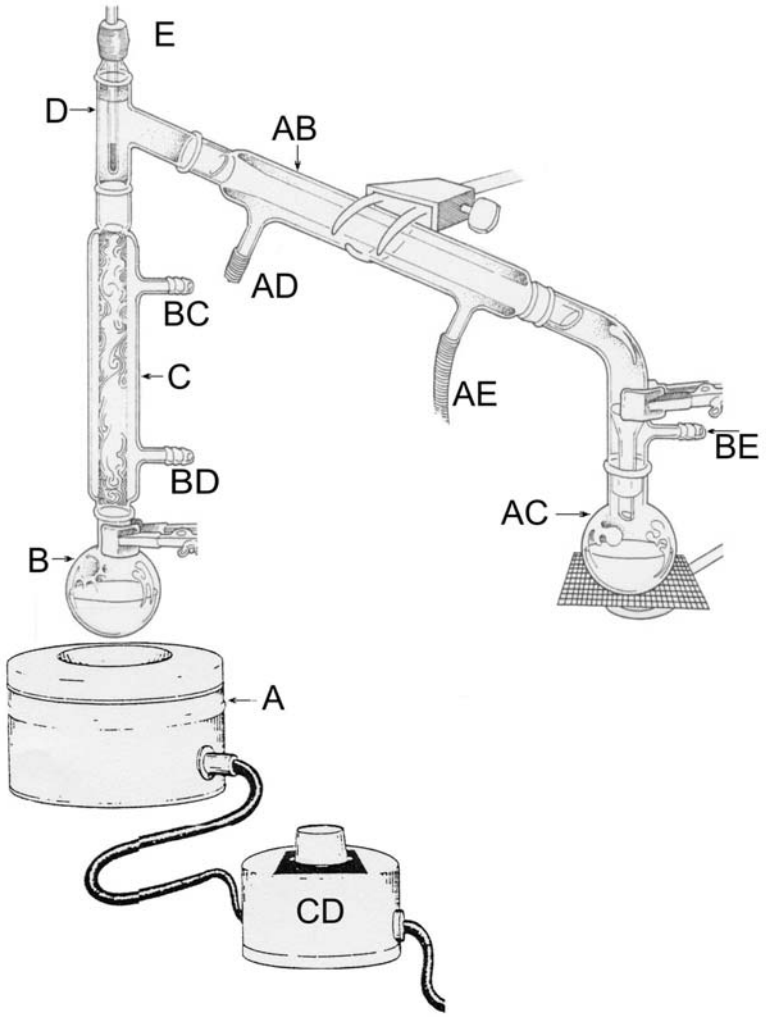
10 **PART 2: LABORATORY**

ANSWER ALL of the questions 9-18.

For **questions 9-18**, select the **letter label** on the diagram of the apparatus used in the DISTILLATION experiment that corresponds to the equipment / set-up indicated by the question number below.



9. Condenser
10. Fractionating column
11. Distilling flask
12. Receiver flask
13. Thermometer adaptor
14. Heating mantle
15. Heating controller
16. Water in
17. Water out
18. Distilling head

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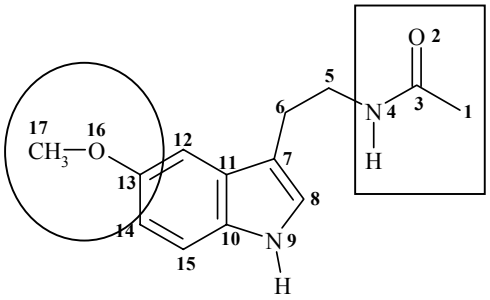
14 **PART 3: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 19 - 25.

For each of the **questions 19 - 25** about MELATONIN (shown below), select the answer from those provided. **In some cases more than one answer may be correct and for full marks all correct answers must be selected.**



MELATONIN

19. What is the oxidation state of **C3**?

A. +3 **B**. +2 **C**. 0 **D**. -2 **E**. -3

20. What is the oxidation state of **C17**?

A. +2 **B**. +1 **C**. 0 **D**. -1 **E**. -2

21. Which bond is the shortest **CC** bond ?

A. **C1−C3** **B**. **C5−C6** **C**. **C6−C7** **D**. **C7−C8** **E**. **C11-C12**

22. What is the functional group in the rectangular box ?

A. Carboxylic Acid **B**. Amine **C**. Amide **D**. Imine **E**. Nitro

23. What is the functional group in the circular box ?

A. Carboxylic Acid **B**. Ester **C**. Ether **D**. Alcohol **E**. Phenol

24. How many units of unsaturation are there in melatonin ?
(units of unsaturation is the same as the index of hydrogen deficiency or IHD)

A. 5**B**. 6 **C**. 7 **D**. 7.5 **E**. 8

25. Which of the following atoms in melatonin is **NOT** considered to be sp2 hybridised ?

A. **O2** **B**. **N4** **C**. **C5** **D**. **N9** **E**. **C11**

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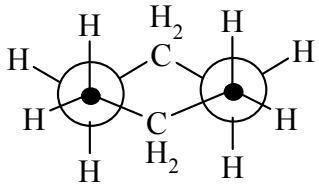
12 **PART 4: CONFORMATIONAL ANALYSIS**

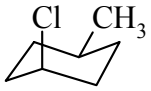
ANSWER ALL of the questions 26-31.

26. Which one of the following terms **best** describes the conformation of cyclohexane shown below ?



A axial
B boat
C chair
D equatorial
E twist boat

27. Which of the following terms **best** describes the position of the **methyl** group in the conformation of *cis*-1-chloro-4-methylcyclohexane shown below ?

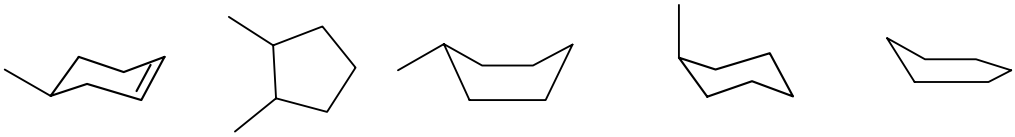


A anti
B axial
C chair
D equatorial
E gauche

28. Which term **best** describes the relationship between a pair of structures with the same molecular formulae that differ due to the presence of different functional groups or branching patterns ?

A: confidential **B**: constitutional **C**: configurational
D: conformational **E**: geometric **AB**: not isomers

29. Identify a **pair** of conformational isomers of methylcyclohexane ?



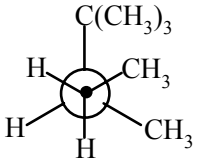
A **B** **C** **D** **E**

Value

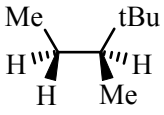
30. Which of the following is the **best** example of torsional strain ?

A: the strain of cyclobutane compared to butane
B: the alignment of the C-H bonds in cyclopropane
C: the 60^{o} bond angle in cyclopropane
D: the flagpole interaction in boat cyclohexane
E: the 1,3-diaxial interaction in 1,1-dimethylcyclohexane

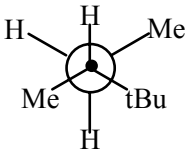
31. Which of the following represents the most stable conformation of 2,2,3-trimethylpentane ?



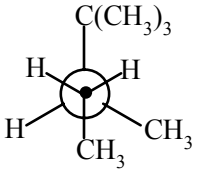
A



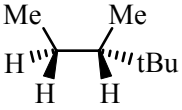
B



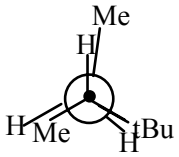
C



D



E



AB

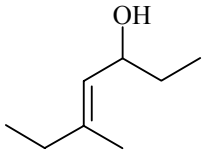
Value

14 **PART 5: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 32-39.

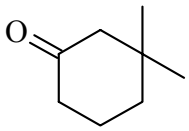
For each of questions 32 to 35, select the correct name for the compound shown:

32.



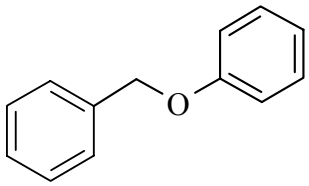
A. (E)-5-methyl-3-heptanal
B. (Z)-3-methyl-3-hepten-5-al
C. (E)-5-methyl-4-hepten-3-ol
D. (Z)-5-methyl-4-hepten-3-ol
E. (E)-5-methyl-3-heptanol

33.



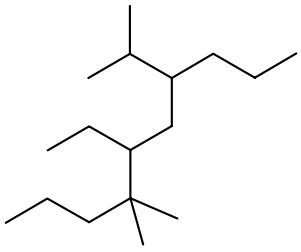
A. 5,5-dimethylcyclohexanol
B. 3,3-dimethylcyclohexanone
C. 1,1-dimethylcyclohexanone
D. 3,3-dimethylcyclohexanal
E. 3,3-dimethylcyclohexanol

34.



A. Dibenzyl ether
B. Benzyl phenyl ether
C. Benzyl phenyl ester
D. Diphenyl ether
E. Phenyl benzoate

35.

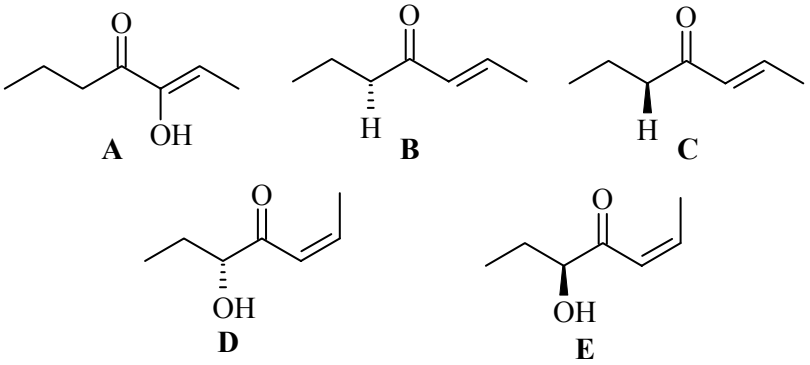


A. 4-isopropyl-3-(1-methyl-2-pentyl)octane
B. 5-ethyl-4,4-dimethyl-7-(1-methylethyl)decane
C. 6-ethyl-7,7-dimethyl-4-(1-methylethyl)decane
D. 5-ethyl-4,4,8-trimethyl-7-n-propylnonane
E. 2-ethyl-4-isopropyl-1,1-dimethyl-1,4-dipropylbutane

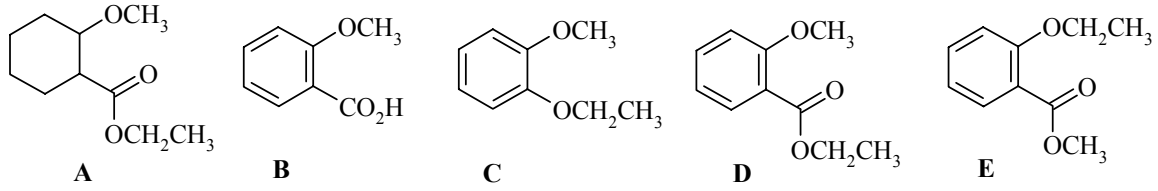
Value

For each of questions 36 to 39, select the correct structure for the name shown:

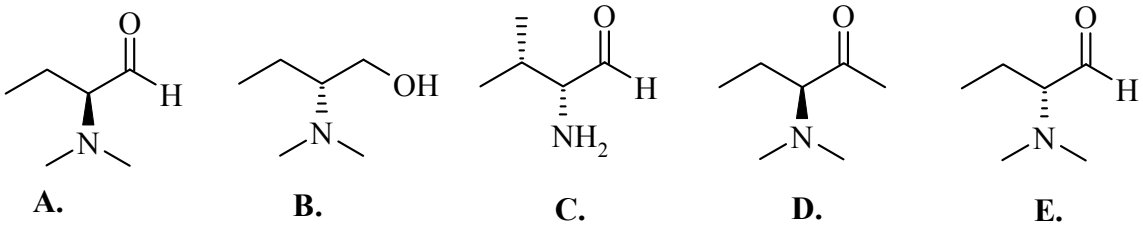
36. (2Z, 5S)-5-hydroxyhept-2-en-4-one:



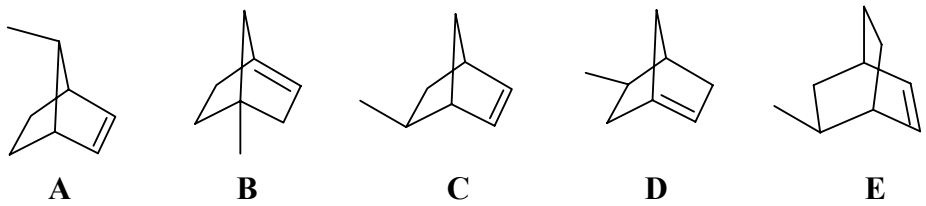
37. Ethyl 2-methoxybenzoate:



38. (S)-N,N-dimethyl-2-aminobutanal:



39. 5-methylbicyclo[2.2.1]hept-2-ene:



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12 **PART 6: STRUCTURE DETERMINATION**:

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

THE QUESTIONS IN THIS SECTION SHOULD ALL BE ANSWERED BASED ON THE FOLLOWING DATA:

An elemental analysis was performed on a sample taken from an unlabelled drum found buried in the ground in a former industrial area. The result indicated that the sample contained 83.24% C and 16.76% H by weight. The sample was further analysed. Fractional distillation gave **the only** 3 isomeric hydrocarbons of that molecular formula. The boiling points of the isomers were 9^{o}C, 28^{o}C and 36^{o}C.

(a) Use the combustion analysis data to determine the empirical formula.

(b) Draw the 3 isomers.

(c) Provide the IUPAC name of for the 3 compounds from part (b)

(d) For the 3 isomers above, match them to their boiling points. Explain your choice.

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12 **PART 7: MECHANISM**

Write your answer in the booklet provided.

Draw a mechanism sequence using double headed (*i.e.* electron pair) curly arrows that represents the single reaction sequence described verbally by the following points in which an alkyl halide, 2-phenyl-2-propyl bromide, is hydrolysed in water to give an alcohol, 2-phenyl-2-propanol.

Step 1. Loss of a leaving group from the 2-phenyl-2-propyl bromide creating a bromide ion and a resonance stabilised carbocation.

Step 2. Attack of a molecule of water (as a nucleophile) on this electrophilic carbon leading to the formation of a new CO sigma bond and giving an oxonium ion.

Step 3. An acid - base reaction in which a water molecule removes a proton from the oxonium ion producing the alcohol, 2-phenyl-2-propanol and a hydronium ion.

Draw the **four** other *major* resonance contributors of the structure of the carbocation produced in step 1.

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12 **PART 8: THERMODYNAMICS**

Write your answer in the booklet provided. Show your working as PARTIAL marks will be given.

1,2-Dimethylcyclopropane exists as two isomers, *cis*- and *trans*- . The heat of formation, ΔH_f of isomer **I** is +46.45 kcal/mol and the heat of combustion, ΔH_c of isomer **II** is -804.5 kcal/mol. Given that the heats of combustion for graphite, ΔH_c C (graphite) = -94.05 kcal/mol and for hydrogen, ΔH_c H_2 (gas) = -57.8 kcal/mol, calculate the heat of combustion, ΔH_c for the isomer **I** and the heat of formation, ΔH_f of isomer **II**.

Identify which of the isomers **I** and **II** is *cis*- and which is *trans*-.

Based on the data, identify the more stable isomer and explain this based on the conformational features of the structures.

****THE END****