

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 351

OCTOBER 20th 1999

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. 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 appended to the end of the exam.

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**.

14 PART 1 RELATIVE PROPERTIES

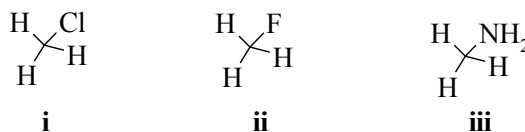
ANSWER ANY SEVEN (7) of Questions 1-8.

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

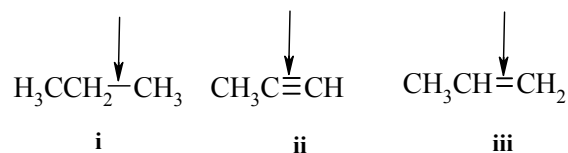
Use the following code to indicate your answers.

- | | | | |
|----|--------------|-----|--------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

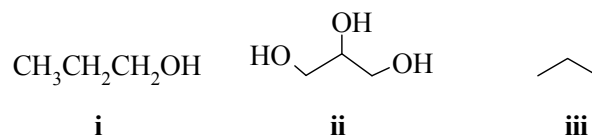
1. The size of the molecular dipole of the following molecules:



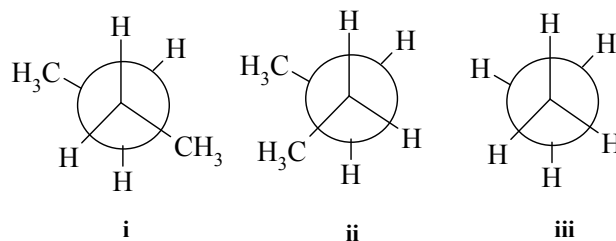
2. The length of the indicated bonds in each of the following



3. The solubility of each of the following molecules in hexane:



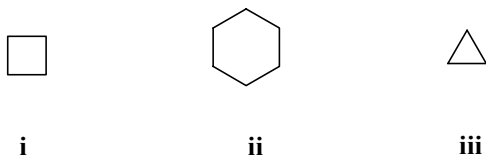
4. The amount of torsional strain in each of the following conformations:



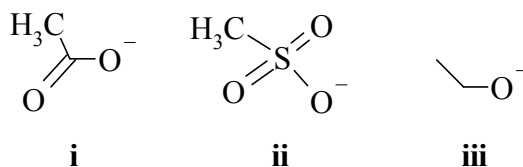
Use the following code to indicate your answers.

- | | | | |
|----|--------------|-----|--------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

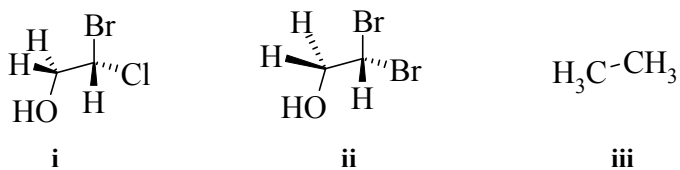
5. The heat of combustion, ΔH_c° , per methylene ($-\text{CH}_2-$) for each of the following molecules: (most endothermic to most exothermic)



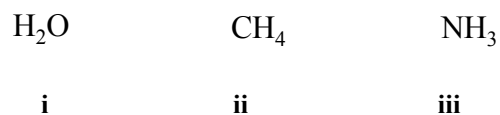
6. The relative stability of the following anions:



7. The number of staggered conformations of different energies that are possible for the following molecules:



8. The H-X-H bond angle in each of the following molecules:



10 PART 2: LABORATORY**ANSWER ALL of the questions 9-18.**

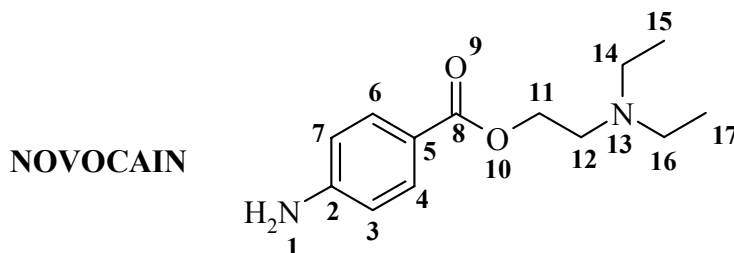
For questions 9-18, decide whether the whole statement is true or false. If it is TRUE, blacken A. If it is FALSE, then blacken B. (1 mark / question)

9. When recording the melting point of a solid it is important to correct to the sea level value for literature comparisons.
10. When measuring a melting point it is important to heat vigorously to ensure that the sample melts in as short a time as possible.
11. Sublimation is the process by which a vapour passes straight to the solid phase.
12. A Buchner funnel can be used to carry out an extraction like that in the caffeine experiment.
13. During distillation, the fractionating column should be cooled by a gentle flow of water.
14. The vapour above a mixture of miscible liquids will have the same composition as the mixture of liquids.
15. The partition or distribution coefficient is given by the ratio of the concentrations of a solute dissolved in two immiscible solvents.
16. A higher than expected melting point would just indicate a slightly impure sample.
17. In paper chromatography the paper is the stationary phase and the mobile phase is a solvent mixture.
18. In chromatography, the R_f value is defined as (distance travelled by solvent front) / (distance travelled by sample).

14 PART 3: MOLECULAR PROPERTIES

ANSWER ALL of the questions 19 - 25.

For each of the questions 19 - 25 about the painkiller NOVOCAIN (below), select the answer from those provided. In some case more than one answer may be correct.

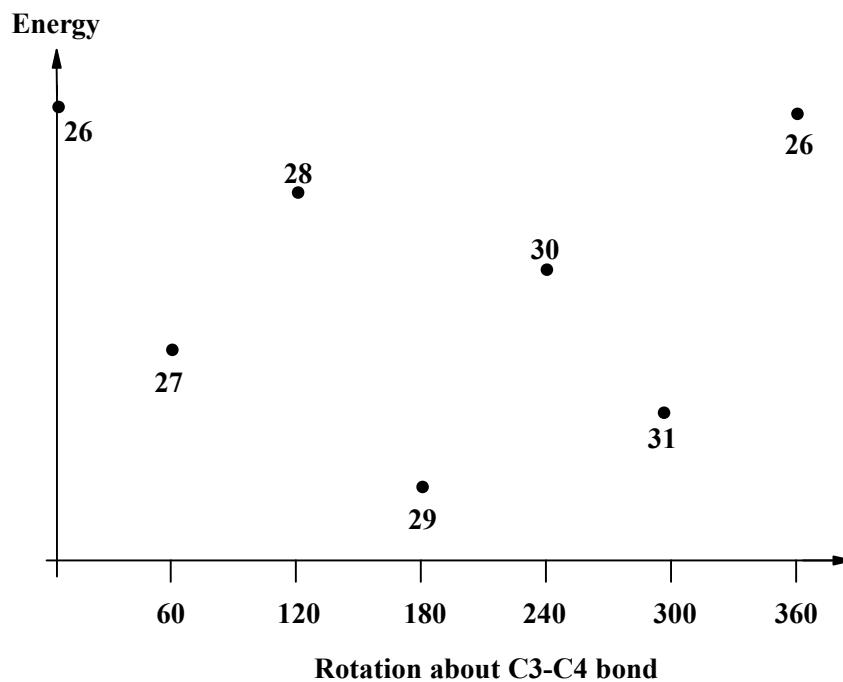
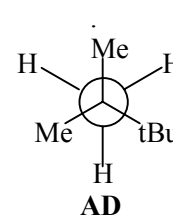
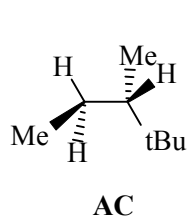
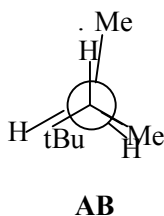
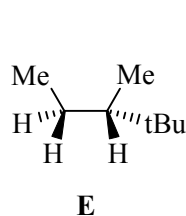
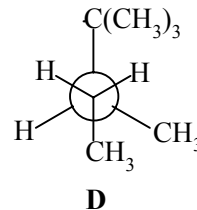
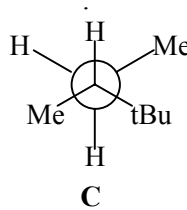
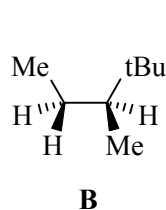
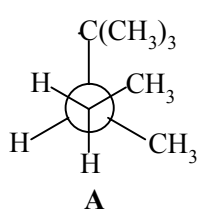


19. What is the oxidation level of **C8** ?
- A. +3 B. +2 C. 0 D. -2 E. -3
20. What is the oxidation level of **C12** ?
- A. +2 B. +1 C. 0 D. -1 E. -2
21. Which carbon(s) is (are) sp^3 hybridised ?:
- A. C4 B. C5 C. C8 D. C11 E. C15
22. What is the hybridisation of **O9** ?
- A. sp B. sp^2 C. sp^3 D. sp^4 E. $1s^2 2s^2 2p^4$
23. What is the hybridisation of **O10** ?
- A. sp B. sp^2 C. sp^3 D. sp^4 E. $1s^2 2s^2 2p^4$
24. Which of the following functional groups are found in Novocain ?
- A. amide B. amine C. nitro D. ether E. ester
25. Which carbon atom is located in a position *para* to the amino substituted carbon ?
- A. 3 B. 4 C. 5 D. 6 E. 7

15 PART 4: CONFORMATIONAL ANALYSIS**ANSWER ANY FIVE (5) of the questions 26-31.**

The diagram shown below gives the relative energies of conformations of 2,2,3-trimethylpentane due to rotation about the C3-C4 bond.

For each of **questions 26 to 31** indicated by the numbers in the diagram, select the structure from the list provided below the diagram that corresponds to the conformation indicated

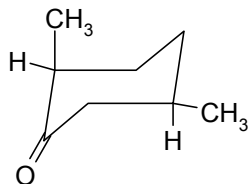
**Possible Selections for Qu 26-31**

14 PART 5: NOMENCLATURE

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

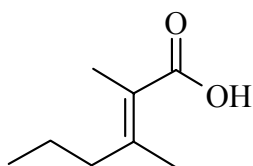
For each of questions 32 to 35, select the correct name for the compound shown:

32.



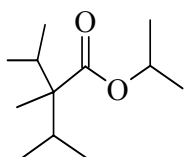
- A. *trans*-2,5-dimethoxycyclohexanone
 B. *cis*-3,6-dimethylcyclohexanone
 C. *cis*-2,5-dimethylcyclohexanone
 D. *trans*-2,5-dimethylcyclohexanone
 E. *cis*-2,5-dimethoxycyclohexanone

33.



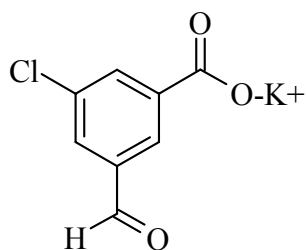
- A. (*Z*)-2,3-dimethyl-2-hexenoic acid
 B. 2,3-dimethyl (*E*)-2-hexenoate
 C. (*Z*)-2,3-dimethyl-2-hexenal
 D. (*E*)-2,3-dimethyl-2-hexenoic acid anhydride
 E. (*E*)-2,3-dimethyl-2-hexenoic acid

34.



- A. isobutyl 2,3-dimethylbutanoate
 B. 3,3,0-triisopropyl propanoate
 C. isopropyl 2,2-diisopropylpropanoate
 D. isopropyl 2-isopropyl-2,3-dimethylbutanoate
 E. isopropyl isopentylisopropylformic acid

35.

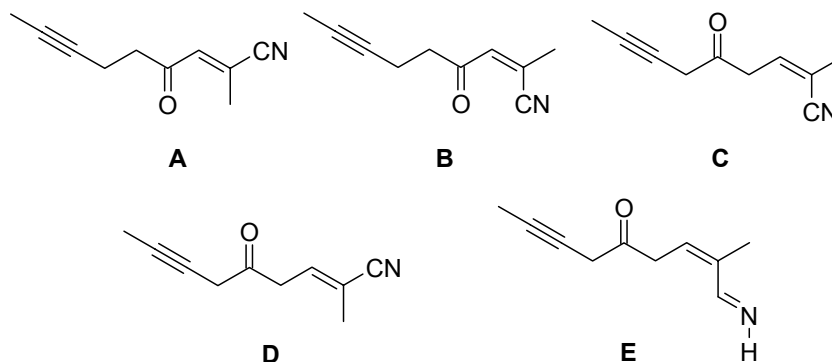


- A. sodium 5-chloro-3-formylbenzoate
 B. sodium 5-chloro-3-formylbenzoic acid
 C. potassium 3-chloro-5-formylbenzoate
 D. 5-chloro-3-formylbenzoate of potassium
 E. potassium 5-chloro-3-formylbenzoate

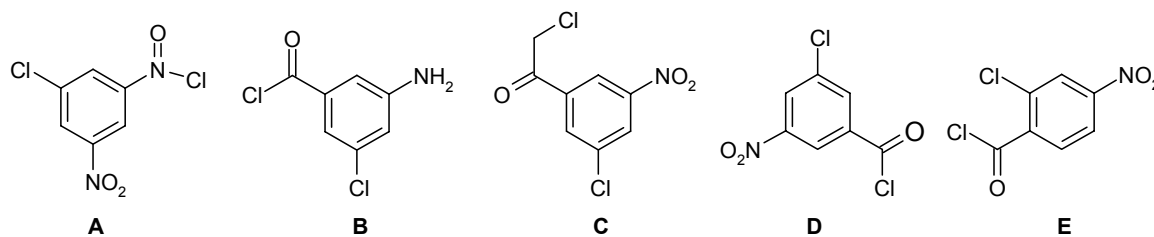
Value

For each of questions 36 to 41, select the correct structure for the name shown:

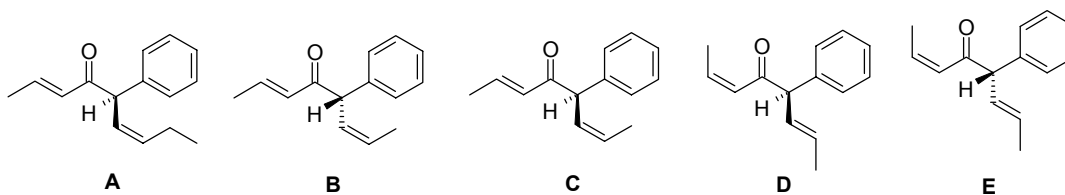
36. (2Z)-2-methyl-5-oxonon-2-en-7-ynenitrile



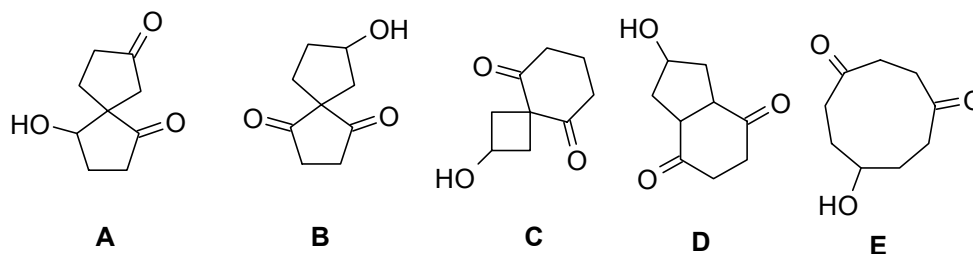
37. 3-chloro-5-nitrobenzoyl chloride:



38. (2E,6Z,5R)-5-phenyl-2,6-octadien-4-one:



39. 7-hydroxyspiro[4.4]nona-1,4-dione:



Value11 PART 6: STRUCTURE DETERMINATION:

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

All the questions in this section should be answered based on the following data:

A combustion analysis was performed on a sample taken from a drum found in a landfill site. The result indicated that the sample contained 40.67% C, 8.53% H, and 23.82% N. The sample was further analysed and found to be a mixture of isomers with a molecular weight = 59.07 g/mol.

Use the combustion analysis data to determine the empirical formula.

Draw a pair of geometrical isomers and provide the IUPAC name of them.

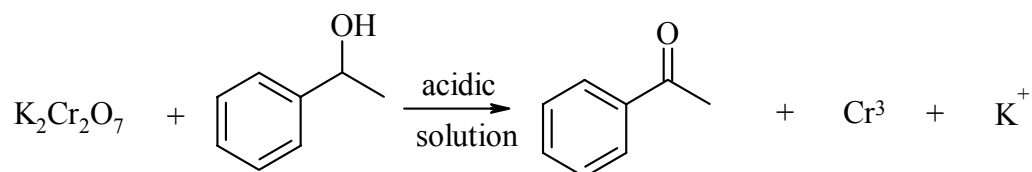
Draw a pair of constitutional isomers and provide the IUPAC name of them.

For the four isomers above, draw diagrams to indicate any resonance contributors and label them as major or minor. If there are no resonance contributors possible for a particular structure, indicate why.

Value11 PART 7: REDOX REACTIONS

Write your answer in the booklet provided.

You are getting prepared to perform the following unbalanced reaction:



- Balance the equation and show how you arrived at your answer.
- How many grams of $\text{K}_2\text{Cr}_2\text{O}_7$ are required to convert 10g of 1-phenylethanol to 1-phenylethanone?
- Is the phenylethanol oxidized or reduced to form 1-phenylethanone? Illustrate your answer by showing how the oxidation number(s) change on the carbonyl carbon atoms.

Value11 PART 8: THERMODYNAMICS

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

There are four possible isomeric 1-tert-butyl-3-methylcyclohexanes in which the cyclohexane is in a chair conformation. The calculated heats of formation, ΔH_f° , of these four structures are listed below.

Draw the four possible structures

Match the heats of formation, ΔH_f° , values to the appropriate structures

Justify your choice.

Using the available data, calculate **EITHER**:

- i) the heat of combustion, ΔH_c° , of the most stable structure, **OR**,
- ii) the equilibrium constant, K , for the interconversion of the two *cis* forms at 25°C.

DATA:

kcal/mol	kJ/mol
ΔH_f° (1) = -38.16	ΔH_f° (1) = -159.66
ΔH_f° (2) = -40.53	ΔH_f° (2) = -169.58
ΔH_f° (3) = -44.41	ΔH_f° (3) = -185.81
ΔH_f° (4) = -46.84	ΔH_f° (4) = -195.98
ΔH_c° (H ₂ , gas) = -68.0	ΔH_c° (H ₂ , gas) = -284.51
ΔH_c° (C, graphite) = -94.0	ΔH_c° (C, graphite) = -393.3
R = 1.987 cal/molK	R = 8.314 J/molK

****THE END****