CHM 1321B
Mid Term 1 version b

1) Give brief explanations or definitions for the following. Use structures when possible (**4 Points**).

a) enantiomer

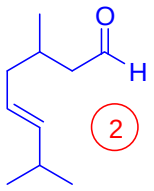
Compound that can exist as non superimposable mirror images (2)

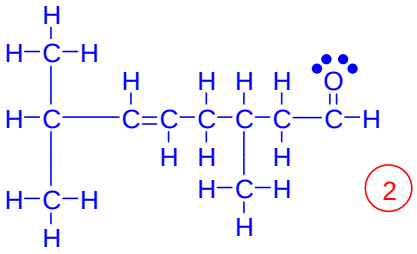
b) electronegativity

Ability of an atom to attract electrons (2)

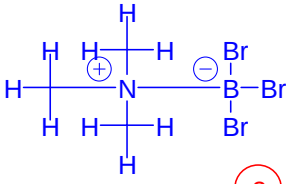
2) Draw the following as Lewis and line structures: (**12 points**)

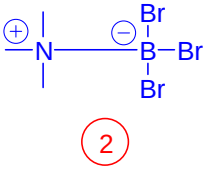
a) $(CH_3)_2CHCHCHCH_2CHCH_3CH_2CHO$



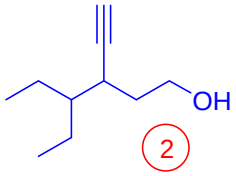


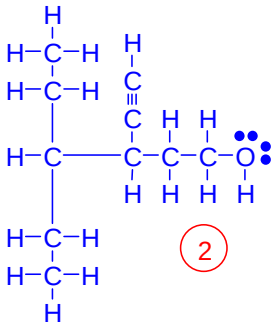
b) $(H_3C)_3NBBr_3$





c) $CH_3CH_2CH(CH_2CH_3)CH(CCH)CH_2CH_2OH$

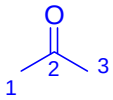




3) For the following compound:

$CH_3C(O)CH_3$

a) What is the hybridization of all carbons and of the oxygen? (**4 points**)



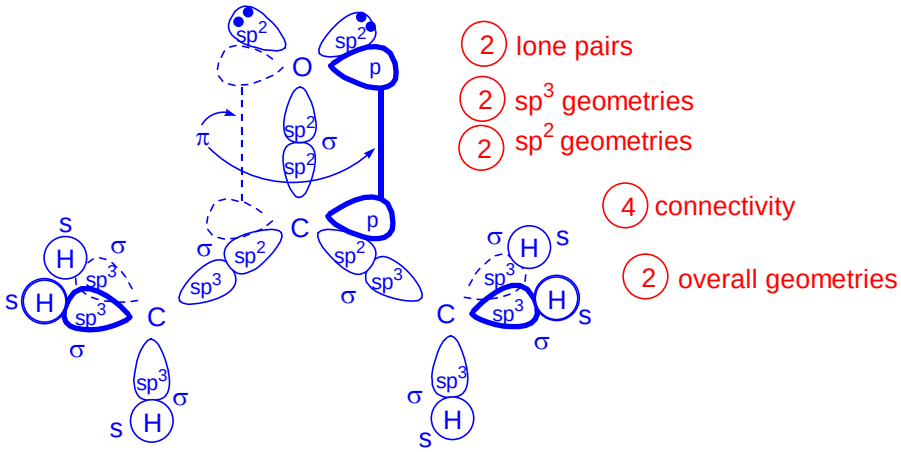
C(1) = sp^3 (1)

C(2) = sp^2 (1)

C(3) = sp^3 (1)

O = sp^2 (1)

b) Show the structure of the molecule using the LCAO method. (**12 points**)

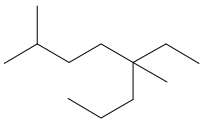


c) Label all the atomic orbitals used and the bonds formed in part b. (**6 points**)

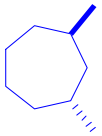
d) What is the geometry of the carbons and the oxygen? (**4 points**)

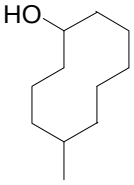
C(1) = tetrahedral (1)
C(2) = trigonal (1)
C(3) = tetrahedral (1)
O = trigonal (1)

4) Give IUPAC names or structures for the following: (**6 points**)

a) 

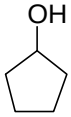
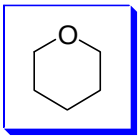
5-Ethyl-2,5-dimethyloctane (2)

b) trans-1,3-dimethylcycloheptane  (2)

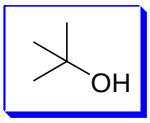
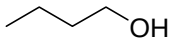
c) 

5-Methyl-cyclodecanol (2)

5) For each of the following pairs, indicate which has the lowest melting point. Briefly justify your choice in each case. (**9 points**)

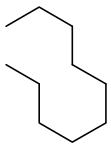
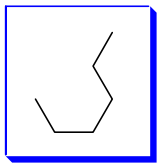
a)  and  (1)

First structure can hydrogen bond with itself in addition to having van der Waals interactions.
Second structure capable of dipole-dipole and van der Waals only.
Hydrogen bonds are stronger than dipole interactions so the first structure will experience stronger intermolecular forces and have a higher melting point.
Therefore the second structure has the lowest melting point (2)

b)  and  1

Both structures can hydrogen bond and have van der Waals interactions.
First structure is branched and so the molecules will pack together less well.
This will reduce the intermolecular forces and therefore the first structure has the lowest melting point

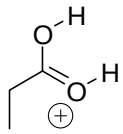
2

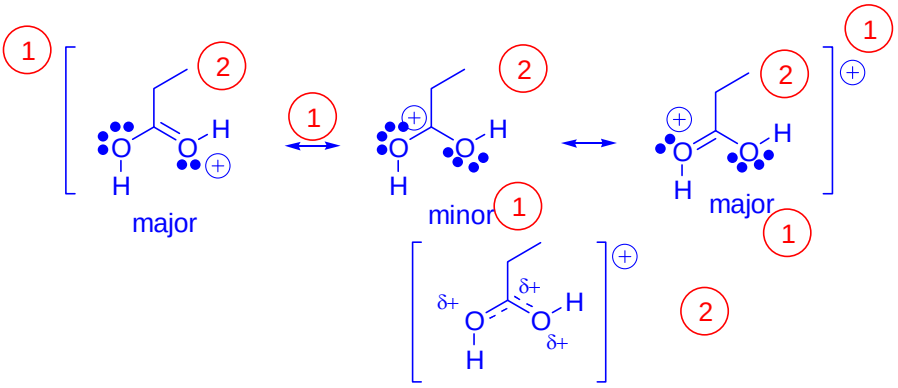
c)  and  1

Both structures have van der Waals interactions only.
First structure is larger and will experience more van der Waals contacts than the second structure
This will reduce the intermolecular forces on the second structure and therefore it has the lowest melting point

2

6) Draw the important resonance forms for the following. Identify the major and minor forms and show the resonance hybrid structure. (**13 points**)

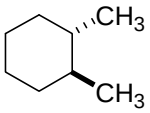




1 1 2 1 1 2 2 1 1 2

7) Draw two different chair conformers for the following structures. For each pair, indicate which form is the most stable and *justify* your choice.

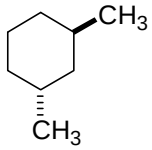
a) (**6 points**)

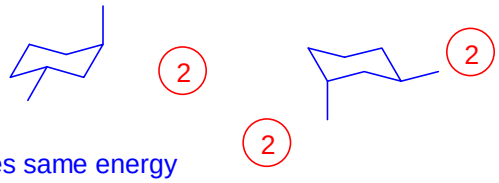


2 2

most stable
both methyl groups equatorial 2

b) (**6 points**)

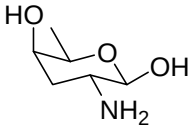


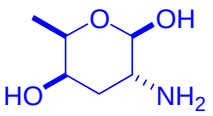


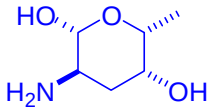
2 2 2

structures same energy
each structure has one methyl group equatorial
and one methyl group axial

c) Draw the following compound as a simple line structure (not a chair). (**4 points**)

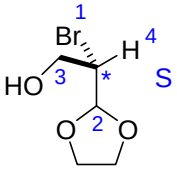


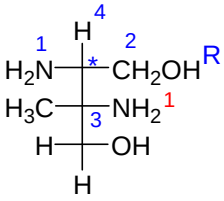


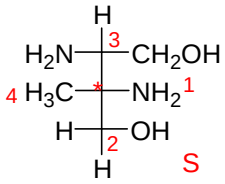
or


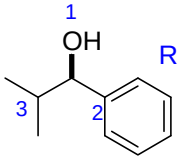
4

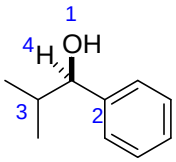
8) For the following compounds
   a) show the stereogenic centre(s) by labeling them with a star (*)(**4 points**)
   b) determine the priorities of the substituents on each stereogenic centre. For compounds with more than one centre, make sure you clearly indicate which priorities refer to which centre. (re-drawing the structure helps) (**8 points**)
   c) Determine the configuration of each stereocentre (**4 points**)

(i)


(ii)




(iii)


R (H is priority 4 and is in back)


9) The specific rotation of (R)-glucopyranose is +40.0° in $CHCl_3$. A sample of glucopyranose in $CHCl_3$ (*c* = 1.0) gives a rotation of -10.0° when measured in a 5 cm cell. What is the ratio of (R) to (S) glucopyranose in the sample (**6 points**)?

$$[\alpha] \text{ of sample} = \frac{\alpha}{l \bullet c}$$ (1)

$$= \frac{-10^{o}}{(1.0) \bullet \frac{5}{10}}$$

$$= -20^{o}$$ (1)

$$\text{optical purity} = \frac{|-20^{o}|}{+40^{o}} \times 100\ \%$$ (1)

$$= 50\ \%$$

(minus sign of sample rotation indicates (S) isomer predominates because (R) isomer has a +ve sign)

$$\text{ee} = \text{optical purity} = \frac{|d - l|}{d + l} \times 100\ \%$$ (1)

$$0.5 = \frac{|d - l|}{d + l}$$

total amount of d + l in solution must = 100 %, therefore let d + l = 100, this means d = 100 - l

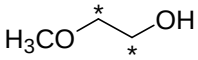
$$0.5 = \frac{100 - 2l}{100}$$ (1)

l = 25

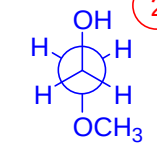
d = 75

The (S) isomer accounts for 75 % of the solution (sign is -ve) and the (R) isomer accounts for 25 % of the solution. The ratio of (R) to (S) is therefore 1 : 3 (1)

10) For the following compound:



a) Draw the Newman projection of the bond indicated (*) in the most stable conformation and name the conformer. (**4 Points)**

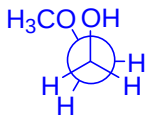


2 Newman properly drawn

1 Lowest energy conformer

anti staggered 1

b) Draw the Newman projection of the <u>least</u> stable conformer and name the conformer. **(4 Points)**

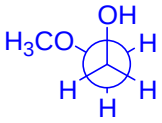


2 Newman properly drawn

1 Highest energy conformer

eclipsed 1

c) Draw the Newman projection of the <u>second most</u> stable conformer and name the conformer. (**4 Points)**

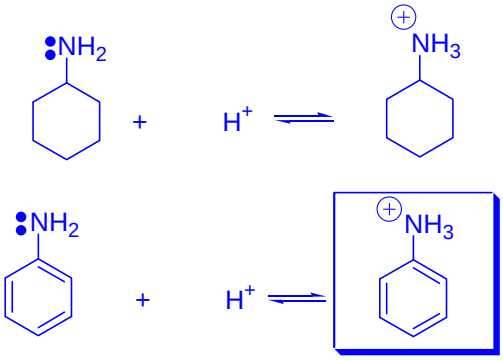


2 Newman properly drawn

1 Second Lowest energy conformer

gauche staggered 1

Bonus: Which of the following amines is the strongest base? You must justify your answer to get the marks. (**2 Points**)



This base is stabilized by resonance. It is therefore lower in energy that the base shown in the first equation. This makes it a weaker base.