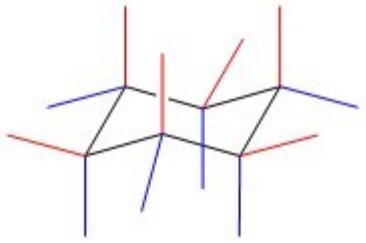
Chem 2210-02 Organic Chemistry

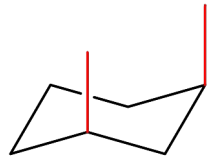
Exam 1

October 13, 2017

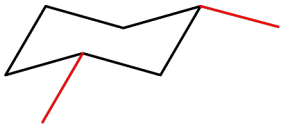
1. (a) Draw the two chair conformations of *cis*-1,3-dimethylcyclohexane, and label all the positions as axial or equatorial.(2%)



UP DOWN

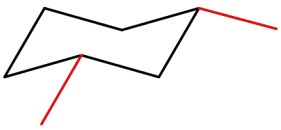


(A)

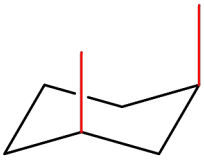


(B)

(b) Label the higher-energy conformation and the lower-energy conformation.(2%)



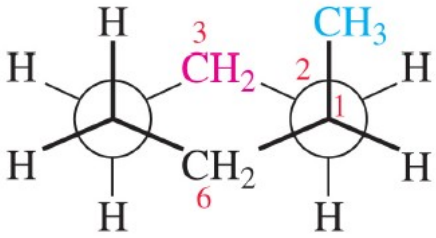
lower-energy conformation



higher-energy conformation

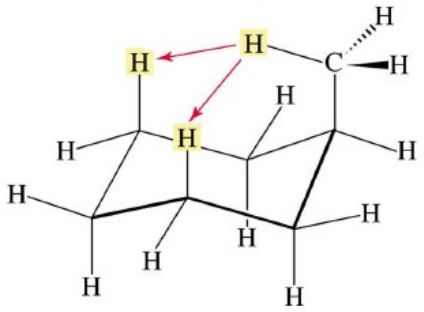
(c) The energy difference in these two conformations has been measured as about 5.4 kcal/mol. How much of this energy difference is due to the torsional energy of gauche relationships? (4%)

0.87 x 4 = 3.48 kcal/mole

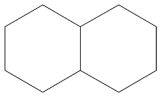


(d) How much energy is due to the additional steric strain of the 1,3-diaxial interaction? (4%)

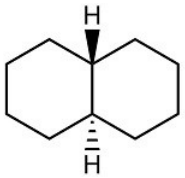
5.4-3.48=1.92 kcal/mole



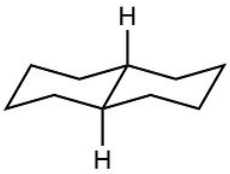
2. Draw the most stable conformation for each of *cis*- and *trans*-decalin. Use what you know about the conformational energies of substituted cyclohexanes predict which is the more stable isomer. How much energy difference between these two molecules? Give detail information. (9%)

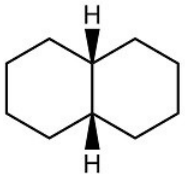


decalin

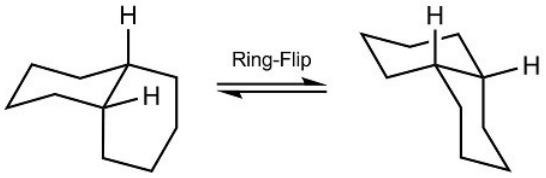


trans-Decalin



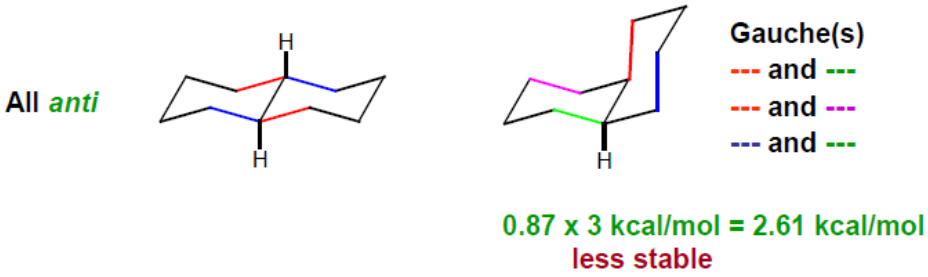


cis-Decalin



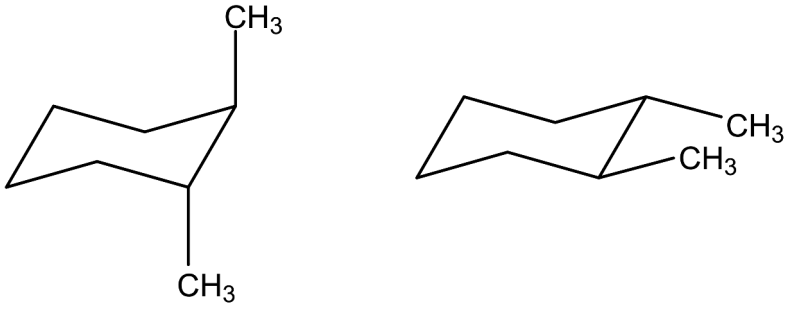
Trans-decalin is more stable

Energy difference : 3 gauche, 3x0.87=2.61 kcal/mole



3. Calculate the energy difference between the two chair conformations of *trans*-1,2-dimethylcyclohexane. (4%) (Note: gauche interaction between two methyl groups on cyclohexane is 0.87 kcal/mol)

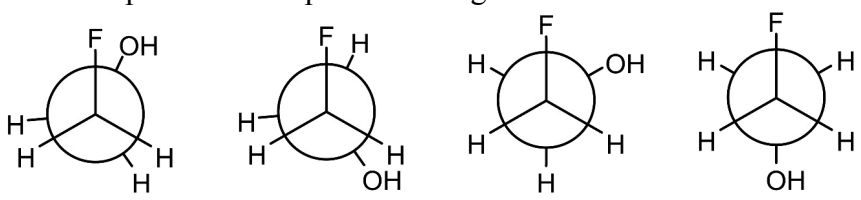
4 gache – 1 gache = 3 x 0.87=2.61 kcal/mole



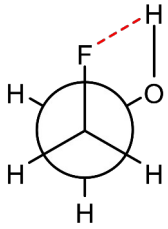
4. Use Newman projection to draw totally eclipsed, eclipsed, gauche, and *anti* conformations for 2-fluoroethanol. Which conformer is the most stable one? Why? (12%)

$HO-CH_2-CH_2-F$

Total eclipsed　　eclipsed　　gauche　　anti

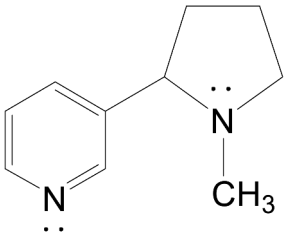


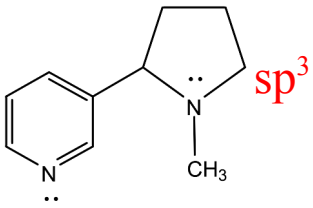
Stable



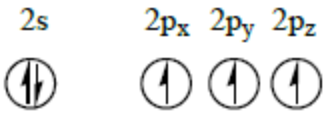
分子內氫鍵 (**Intramolecular Hydrogen Bond**)

5. In which orbitals are the lone pairs in nicotine?(4%)





sp^3



sp^2

Hybridization SP^n

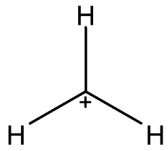
n = 3 – empty orbital(s) – p bonds

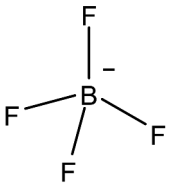
N: n= 3 – 0 – 1 = 2　sp^2

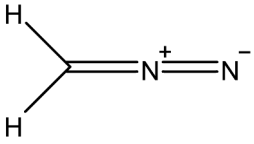
N: n= 3 – 0 – 0 = 3　sp^3

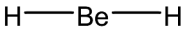
6. Predict bond angles for each of the following molecules, and hybridization of atoms in boldface. (24%)

(a) $\mathbf{CH_3^+}$　　(b) $\mathbf{BF_4^-}$　　(c) $\mathbf{H_2C{=}N{=}N}$　　(d) $\mathbf{BeH_2}$









120° 109.5° 120, 180 180

sp^2 sp^3 sp^2, sp , sp^2 sp

7. List the following acids in an order of decreasing acidity, and give a brief explanation for your arrangement. (6%)

CH_2CH_2OH CH_3CH_2OH CH_3CHOH CH_2CH_2OH
F F Cl

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3 > 1 > 4 > 2 Inductive effect

8. (a) Rank the following species from strongest base to weakest base, and give a brief explanation for your arrangement. (6%)

CH_3NH_2 $CH_3\bar{N}H$ CH_3OH CH_3O^- $CH_3C(=O)O^-$

$CH_3\bar{N}H > CH_3\bar{O} > CH_3NH_2 > CH_3C(=O)\bar{O} > CH_3OH$

1. Electronegativity $O^- > N^-$
2. The Brønsted-Lowry Acid Base Theory

   Conjugate Acid : CH_3COOH > $CH_3NH_3^+$

   Therefore for the basicity : CH_3NH_2 > CH_3COO^-

(b) Rank the following species from strongest acid to weakest acid, and give a brief explanation for your arrangement (6%)

CH_3CH_2OH $CH_3CH_2NH_2$ CH_3CH_2SH $CH_3CH_2CH_3$

$CH_3CH_2SH > CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3$

1. S 的原子大小 > O 原子大小，可以讓負電比較安定(delocaliz)
2. 電負度 O > N，故 O 可以讓電子比較安定，因此較酸
3. 直鏈的烷類沒有電負度大的原子可以穩定負電，因此酸性很低

9. List the following compounds in an order of decreasing boiling point and give a brief explanation. (5%)

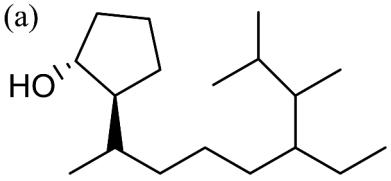
$CH_3CH_2CH_2CH_2CH_3$　　$CH_3CH_2CH_2CH_2OH$　　$CH_3CH_2CH_2CH_2Cl$　　$CH_3CH_2CH_2CH_2CH_2OH$

$CH_3CH_2CH_2CH_2CH_2OH > CH_3CH_2CH_2CH_2OH > CH_3CH_2CH_2CH_2Cl > CH_3CH_2CH_2CH_2CH_3$

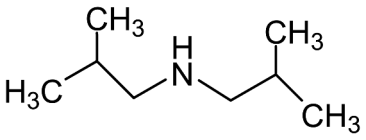
1. 碳鏈較長，鏈與鏈之間有較大的凡德瓦作用力
2. OH 相較 Cl 可以產生氫鍵，沸點較高
3. Cl（dipole-dipole interaction）相較直鏈烷類（London Dispersion Force），有較大的極性

10. Give IUPAC name for each of the following molecules. (12%)

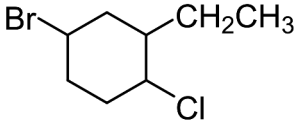
(a)



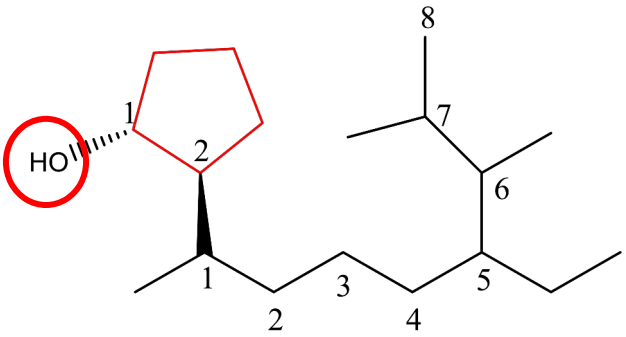
(b)



(c)

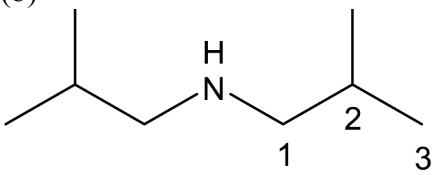


(a)



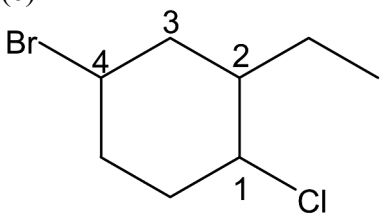
trans-2-(5-ethyl-1,6,7-trimethyloctyl)cyclopentanol

(b)



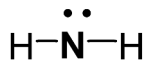
***N,N*-Bis(2-methylpropyl)amine**

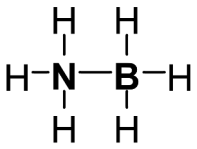
(c)



4-bromo-3-chloro-2-ethylcyclohexane

11. Give each labeled atom the appropriate formal charge. (6%)

(a) 

(b) 

Formal charge = the number of valence electrons –
(the number of nonbonding electrons +
1/2 number of bonding electrons)

(a) 5 – (2 + 4x1/2) = **+1**

(b) N: 5 – (0 + 8x1/2) = **+1**

B: 3 – (0 + 8x1/2) = **-1**