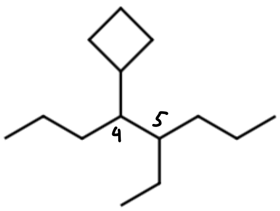
1. Name each of the following compounds using IUPAC (systematic) names. (10 points)

a. 

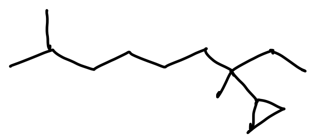
b. 

4-cyclobutyl-5-ethyloctane

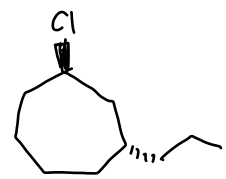
6-methyl bicyclo [3.1.1] heptane

2. Draw structures for the following compounds. (10 points)

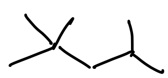
a. 2,7-dimethyl-7-cyclopropylnonane



b. *trans*-1-chloro-3-propylcycloheptane



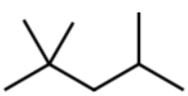
3. Which hydrocarbon has the higher boiling point, octane or 2,2,4-trimethylpentane? Explain why in terms of intermolecular forces. (10 points)

 vs  } less surface area - lower bp

higher bp since
the less branched hydrocarbon has greater London dispersion forces!

4. Which molecule A or B below gives off more heat during combustion - burning in oxygen – which is the same as asking which has the greatest value for heat of combustion ($\Delta H_{comb.}$)? Explain. Can the value of $\Delta H_{comb.}$ for molecule C be reasonably compared to A or B? (20 points)

The observed trend is that more highly branched hydrocarbons are more stable



A

more branched is more stable

B

less branched is less stable!

C

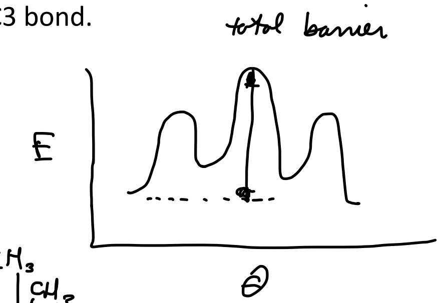
} this compound has a different molecular formula - would yield a different number products during combustion.

Both A & B have same formula so ΔH_{comb} comparison is valid!

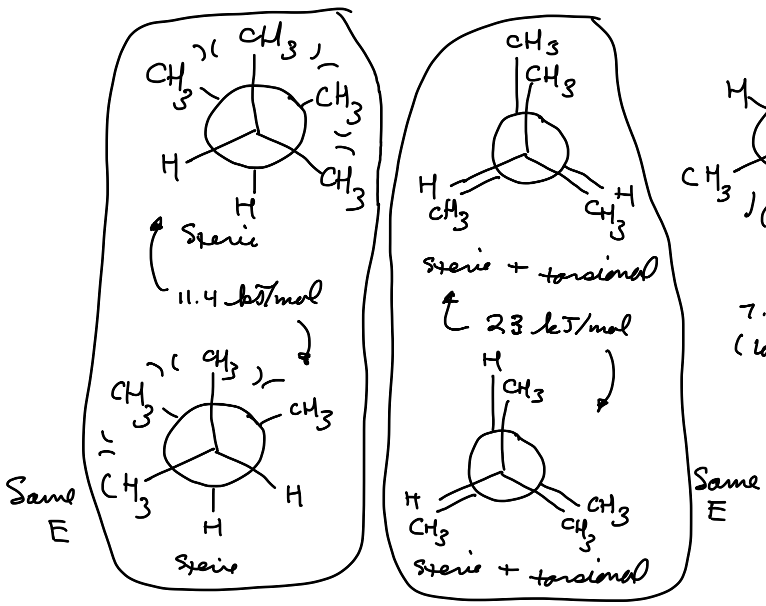
$C_8H_{18} + \frac{25}{2} O_2 \longrightarrow 8 CO_2 + 9 H_2O$ + heat

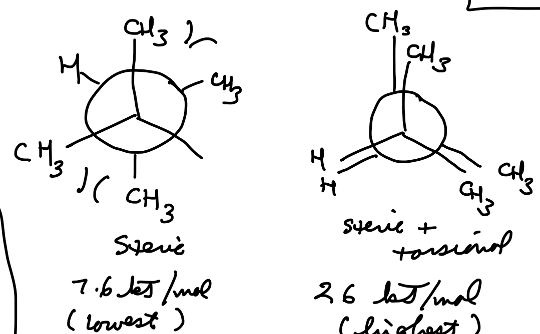
5. Using Newman projections, show all six (6) *conformations* of 2,3-dimethylbutane, $CH_3CH(CH_3)CH(CH_3)_2$, as viewed down the C2-C3 bond. (15 points)

   a. For each conformation, indicate what type of strain is present - *torsional*, *steric*, or *angle* strain.
   b. Indicate the *least stable* and the *most stable* conformations. If any of the conformations have the same energy, then show which ones do.
   c. Use the data below to *estimate* the total barrier to rotation about the C2-C3 bond.



H-H eclipsed	4 kJ/mol
H-CH_3 eclipsed	6 kJ/mol
CH_3-CH_3 gauche	3.8 kJ/mol
CH_3-CH_3 eclipsed	11 kJ/mol



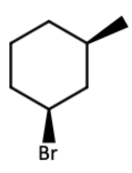


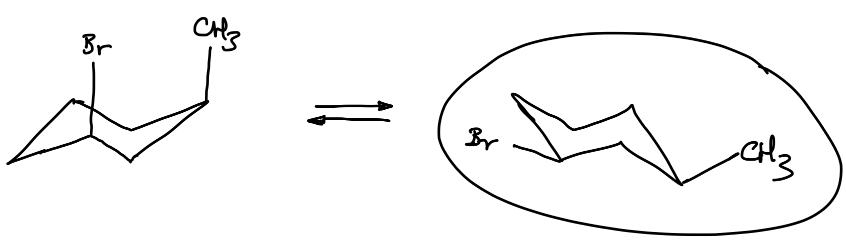
Total barrier to rotation is the difference between least and most stable conformations, So

26 kJ/mol − 7.6 kJ/mol

= 18.4 kJ/mol

6. For the compound shown below, draw both chairs and indicate which one is more stable. (Remember, you get *style* points for well-drawn chairs) (10 points)





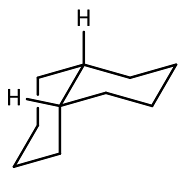
more stable

7. Consider the structures of *cis*-decalin and *trans*-decalin: (10 points)

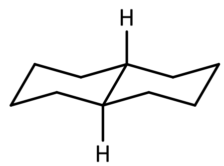
a. Which of these compounds would you expect to be more stable?

b. The less stable isomer has 10.2 kJ/mol strain compared to the more stable isomer. Provide an explanation for the likely cause of this strain.

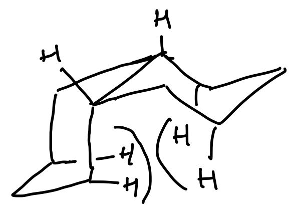
more stable



cis-decalin

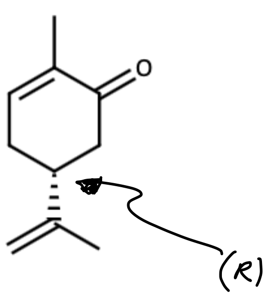


trans-decalin

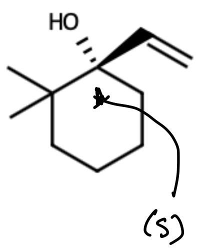


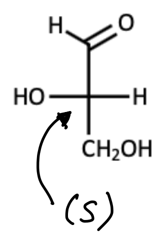
↑ this isomer has 1,3-diaxial interactions that introduce steric strain

8. Assign the *configurations* of each stereocenter in the following compounds using the appropriate notation. (15 points)

a. 

carvone

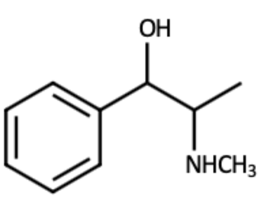
b. 

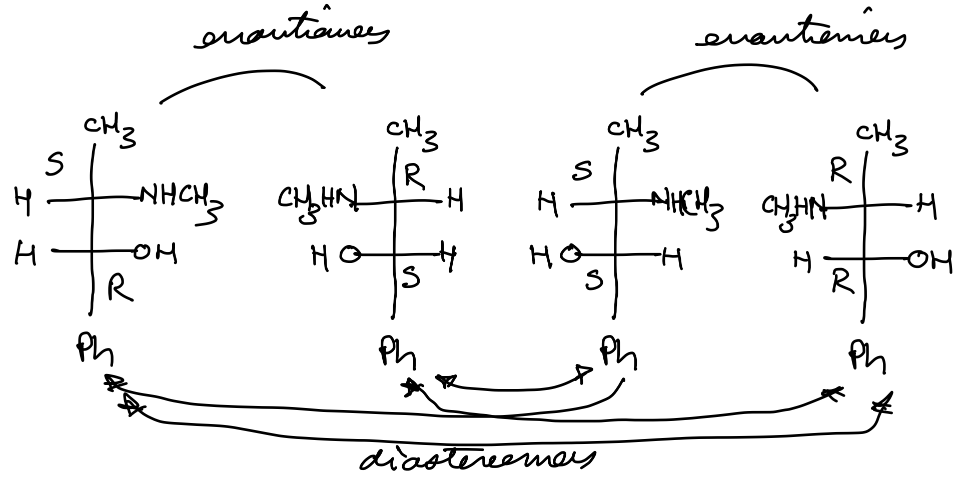
c. 

glyceraldehyde

9. Show *all* of the stereoisomers for the compound shown below) using *Fischer projections*. Label each asymmetric carbon with the corresponding *configuration*. Indicate the relationship between each pair of isomers as *enantiomers* or *diastereomers*. If one of the isomers is a *meso* compound, then circle and label it. (20 points)

no meso compounds!





10. Indicate whether the following statements are *absolutely* true or false. (12 points)

a. All *enantiomers* are optically active. true

b. (2*R*,3*R*)-pentane-2,3-diol is the *enantiomer* of (2*S*,3*R*)-pentane-2,3-diol. false

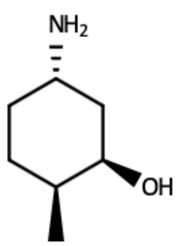
c. If a molecule has a sigma plane of symmetry (σ) then it is achiral. true

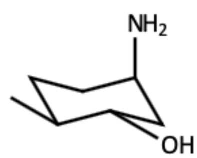
d. All *meso* compounds are optically active. false

e. *trans*-1,3-dimethylcycloheptane is chiral. true

f. If a molecule with one asymmetric carbon has a positive (+) *specific rotation* ([α]) then the absolute configuration must be (*R*). false

11. What is the relationship between the following two structures? Are they *enantiomers*, *diastereomers*, *constitutional isomers*, or *identical*? (5 points)





diastereomers

12. In Spring 2018, the CHEM 12B class performed a classical resolution of racemic α-methylbenzylamine (shown below). The class combined their final products and obtained the following data during the determination of the optical rotation. (20 points)

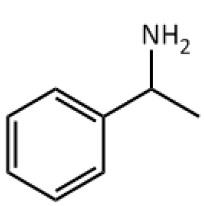
α = -38.2° degrees (this is the *observed rotation*)

$[\alpha] = \frac{-38.2}{(0.94)(1.00)} = -40.6°$

Given that the literature value of the specific rotation for the (*S*) enantiomer of this compound is $[\alpha]$ = -40.3°, the density of the liquid amine is 0.94 g/mL (either enantiomer), the path length (*l*) of the polarimeter cell was 1.00 dm, and, The *specific rotation* is defined as: $[\alpha] = \frac{\alpha}{c \cdot l}$

a. calculate the optical purity (o.p.) of the resolved amine (which is also the same as %ee).

b. show the (S) enantiomer using the appropriate notation.



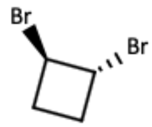
optical purity $= \frac{-40.6}{-40.3} \times 100$

$= 100.74 = 100\% = \%ee$

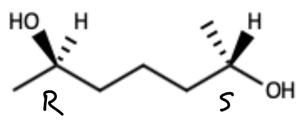
So essentially pure (S)

2 sig. figs

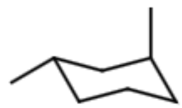
13. Indicate whether each compound below is *chiral* or *achiral*. If the compound is *achiral* indicate why – identify what type of symmetry it has (hint: another possible reason for being achiral has to do with dynamic equilibrium) (20 points)

a. 

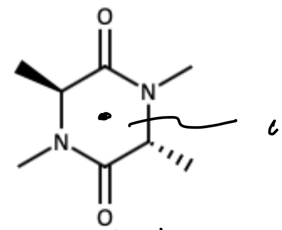
chiral

b. 

achiral
– meso compound has σ (or i) depending on conformation

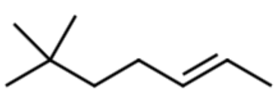
c. 

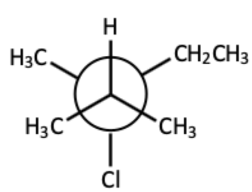
chiral

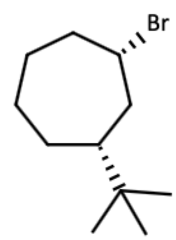
d. 

achiral
– has a point of reflection (inversion) (i)

14. Provide names for the following molecules. (15 points)

a. 

b. 

c. 

a. trans - 6,6 - dimethyl hept-2-ene

b. (R) - 3 - chloro - 2,3 - dimethyl pentane

c. cis - 1 - bromo - 3 - t - butyl cycloheptane
or
(1S,3R) - 1 - bromo - 3 - (1,1 - dimethylethyl) cycloheptane

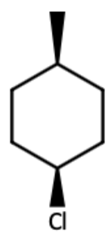
15. Consider the molecule shown below and answer the following: (40 points)

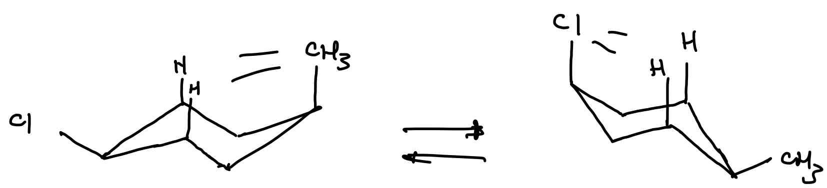
a. Provide an IUPAC name for the structure
b. Show both chair conformations
c. Estimate ΔG for the equilibrium between the two chairs – use data below.
d. Calculate the equilibrium constant (K_{eq}), at 25°C.

(Note: be clear about the sign of ΔG which depends on which of the two chairs you draw first, then calculate the corresponding K_{eq}) (Given: $K_{eq} = e^{-\Delta G/RT}$, R = 8.314 J/mol K, K = C + 273.15)

SUBSTITUENT	1,3-DIAXIAL INTERACTIONS (KJ/MOL)
$-Cl$	2.0
$-OH$	4.2
$-CH_3$	7.6
$-CH_2CH_3$	8.0
$-CH(CH_3)_2$	9.2
$-C(CH_3)_3$	22.8

a. cis-1-chloro-4-methylcyclohexane





7.6 kJ/mol strain

2.0 kJ/mol strain

T = 25°C = 298K

$\Delta G = (2.0 - 7.6)$ kJ/mol

$= -5.6$ kJ/mol $= -5600$ J/mol

$K_{eq} = e^{-(-5600 \text{ J/mol})/(8.314 \text{ J/mol}\cdot\text{K})(298\text{K})}$

$= 9.6$ if $\Delta G = \ominus$

or

$= 0.10$ if $\Delta G = \oplus$