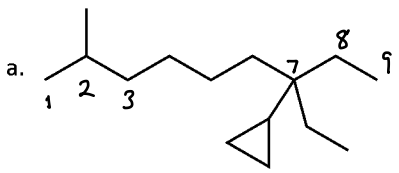
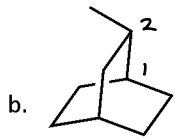
1. Name each of the following compounds using IUPAC (systematic) names. (10 points)

a.



7-cyclopropyl-7-ethyl-2-methylnonane

b.

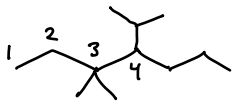


← 25, but not required

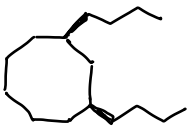
2-methylbicyclo[2.2.2]octane

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

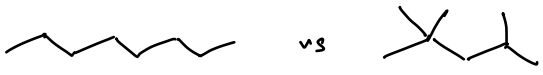
a. 3,3-dimethyl-4-(1-methylethyl)heptane



b. *cis*-1,3-dibutylcyclooctane



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

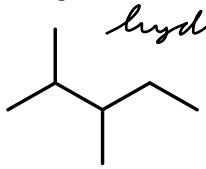


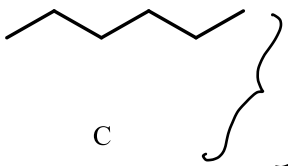
} less surface area - lower bp

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. Why can't 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 10 points





this compound has a different molecular formula so it would a different number of products from combustion and can't be compared to the others

less branched is less stable!

more branched is more stable

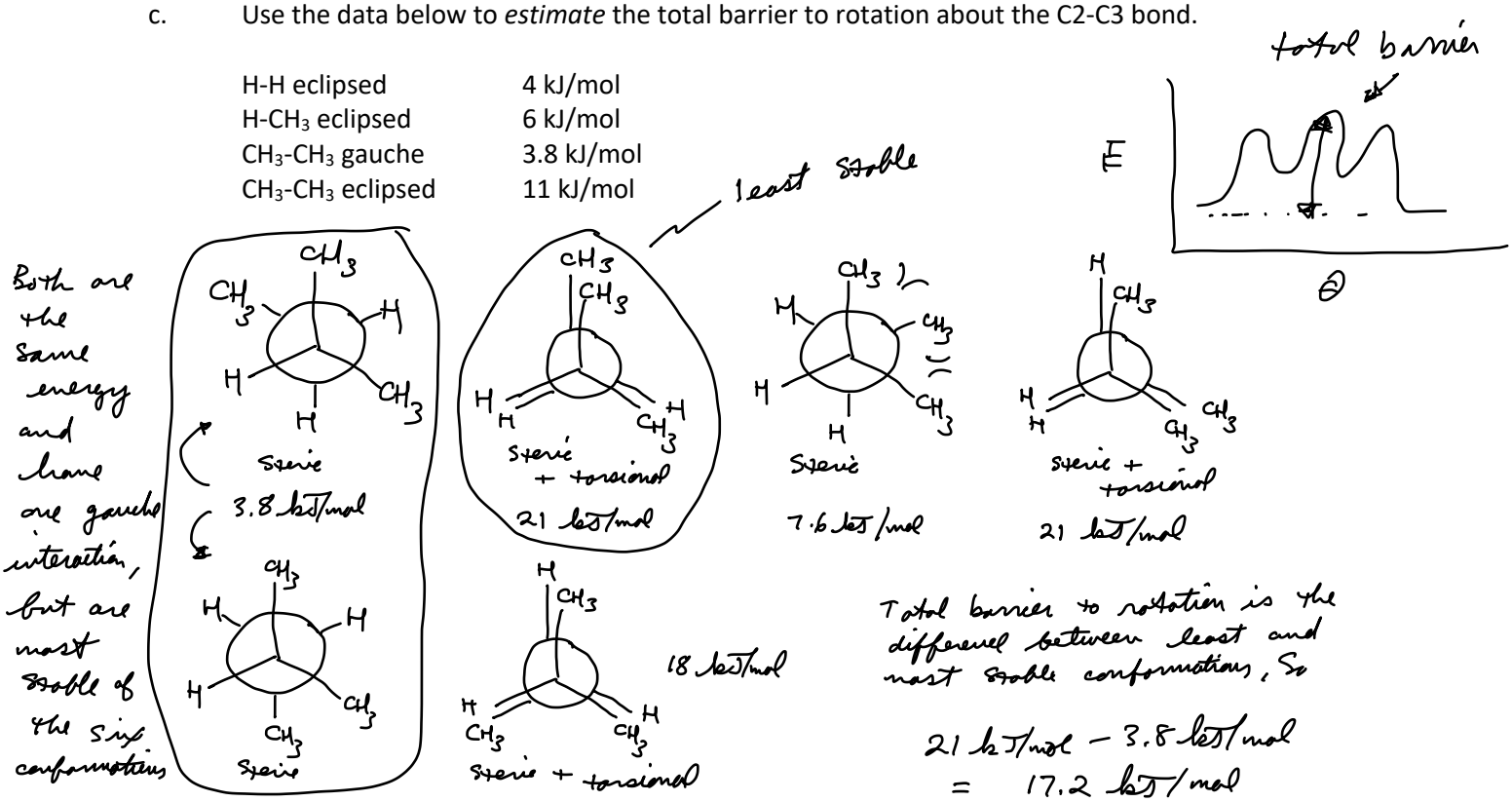
Both A & B have same formula so ΔH_{comb} comparison is valid!

$C_7H_{16} + 11\,O_2 \rightarrow 7\,CO_2 + 8\,H_2O$ + heat

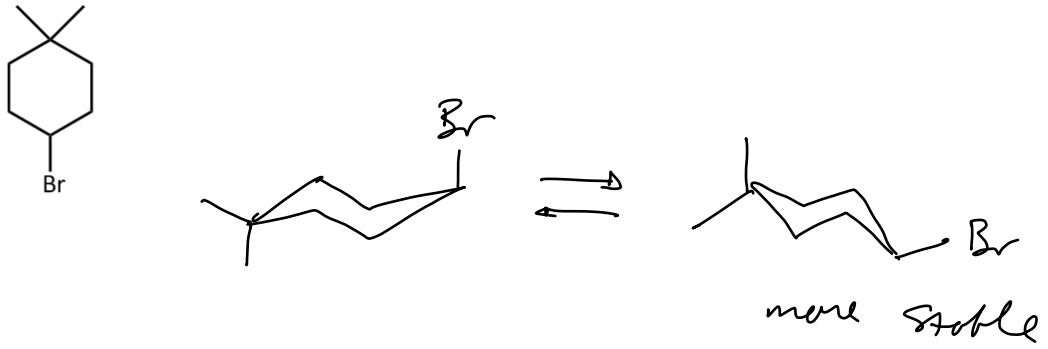
5. Using Newman projections, show all six (6) *conformations* of 2-methylbutane, $CH_3CH(CH_3)CH_2CH_3$, as viewed down the C2-C3 bond. (15 points)

   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

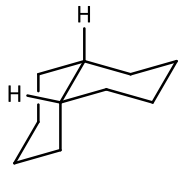


6. For the compound shown below, draw both chairs and indicate which one is more stable. (Remember, you get *style* points for well-drawn chairs) (10 points)

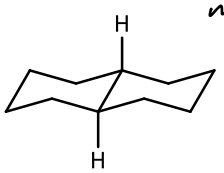


7. Consider the structures of *cis*-decalin and *trans*-decalin: (10 points)

   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.

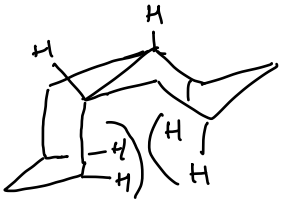


cis-decalin



trans-decalin

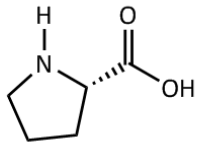
more stable



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)

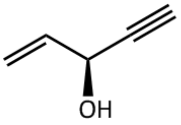
a.



proline
(an amino acid)

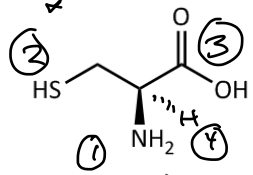
(S)

b.



(S)

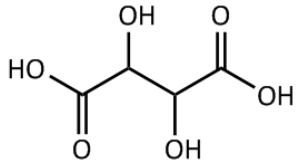
c. note sulfur is higher priority than oxygen

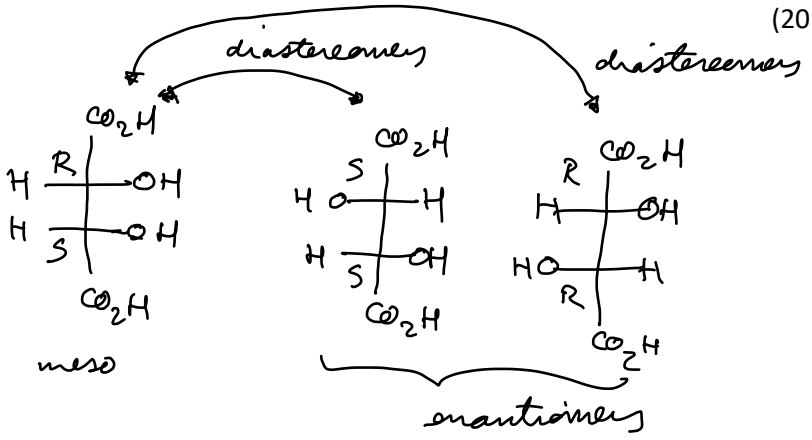


cysteine
(another amino acid)

(R)

9. Show *all* of the stereoisomers for tartaric acid (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)





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

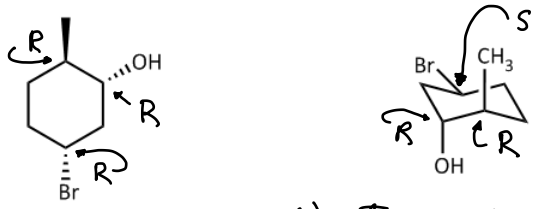
c. If a molecule has a sigma plane of symmetry (σ) then it is achiral. true

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

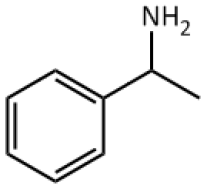
12. In Spring 2017, the CHEM 12B class performed a classical resolution of racemic α-methylbenzylamine (shown below). The class combined their final products and obtained the following data during the determination of the optical rotation. (20 points)

α = -37.4° degrees (this is the *observed rotation*)

Given that the literature value of the specific rotation for the (*S*) enantiomer of this compound is [α] = -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: $[\alpha] = \frac{\alpha}{c \cdot l}$

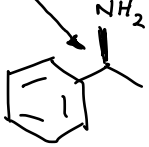
a. calculate the optical purity (o.p.) of the resolved amine (which is also the same as %ee).

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



(S)

$[\alpha]_{lit} = -40.3°$ pure sample



Experimental

$[\alpha]_{exp} = \frac{\alpha}{c \cdot l} = \frac{-37.4°}{(0.94)(1.00)} = -39.8°$

optical purity = $\frac{[\alpha]_{exp}}{[\alpha]_{lit}} \times 100 = \frac{-39.8}{-40.3} \times 100 = 98.72$

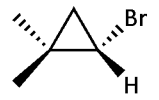
= 99% ee

c = is concentration in mg/mL

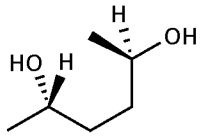
for pure liquids

c = d (density) (Note: using d = 0.945 gives a better answer)

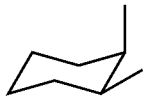
13. Indicate whether each compound below is *chiral* or *achiral*. If the compound is *achiral* indicate why – identify what type of symmetry it has (hint: another possible reason for being achiral has to do with dynamic equilibrium) (20 points)

a. 

chiral

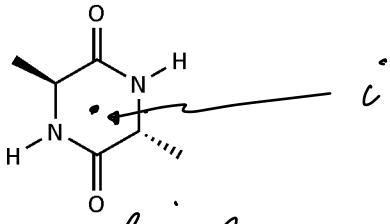
b. 

chiral

c. 
achiral

c. can be viewed from above, to see a σ-plane, however none of the conformations truly have this symmetry!

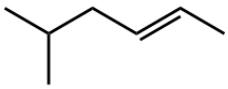
→ this conformation is in dynamic equilibrium w/ the enantiomeric chair

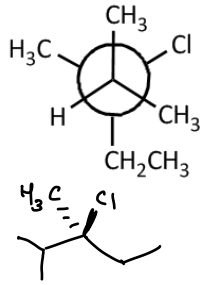
d. 

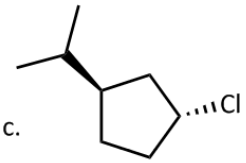
achiral

this compound has a point of inversion (i) – this make the structure achiral

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

a. 

b. 

c. 

a. trans - 5 - methyl hex-2-ene

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

c. trans - 1 - chloro - 3 - isopropyl cyclopentane
or
(1R, 3R) - " "

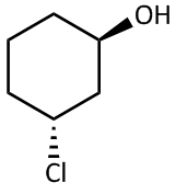
15. Consider the molecule shown below and answer the following: (40 points)

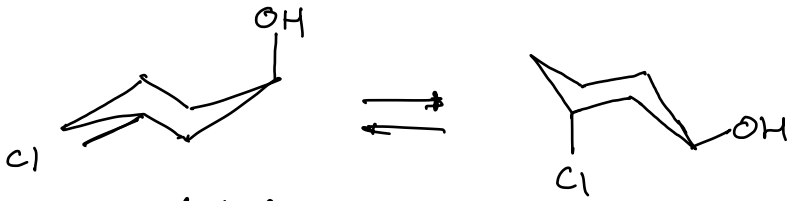
a. Provide an IUPAC name for the structure
b. Show both chair conformations
c. Estimate ΔG for the equilibrium between the two chairs – use data below.
d. Calculate the equilibrium constant (K_{eq}), at 25°C.

(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. (1R,3R)-3-chlorocyclohexanol





4.2 kJ/mol strain

2.0 kJ/mol strain

$T = 25°C = 298K$

$\Delta G = (2.0 - 4.2)$ kJ/mol

$= -2.2$ kJ/mol $= -2200$ J/mol

$-(-2200 \text{ J/mol})/(8.314 \text{ J/mol·K})(298\text{K})$

$K_{eq} = e$

$= 2.4$ if $\Delta G = \ominus$

$= 0.42$ if $\Delta G = \oplus$