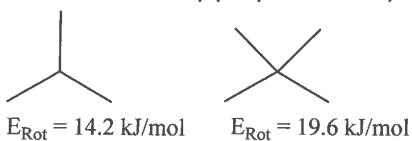


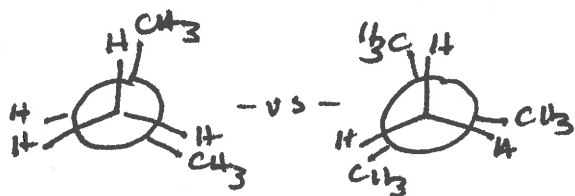
1. The barrier to rotation around the C-C bonds for 2-methylpropane and 2,2-dimethylpropane are shown below.



a. Why does the potential energy of a molecule increase as rotating around a bond? Be specific about sources of destabilization that result from rotating about a bond.

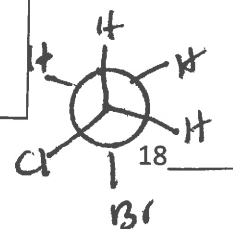
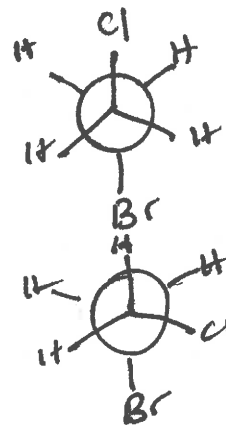
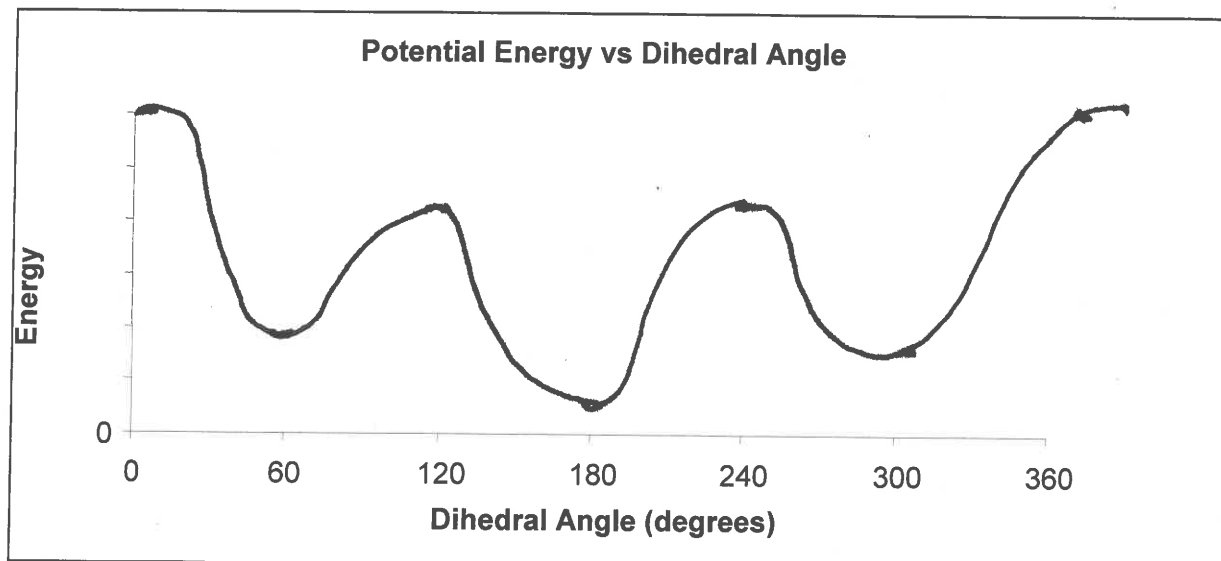
Rotation between conformations requires passing through eclipsed conformations resulting in torsional strain (due to repulsion between bonds). Also, stabilizing orbital interactions are disrupted. Bonds lengthen in response to the strain, increasing the overall energy. 6

b. Why is the barrier to rotation around a C-C bond in 2,2-dimethylpropane over 5 kJ/mol greater than that for 2-methylpropane? Your explanation should discuss specific structural differences between these compounds. 4

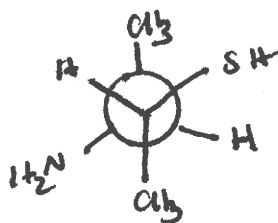
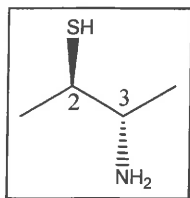


In 2,2-dimethylpropane there is an additional  $\text{CH}_3 \cdot \text{H}$  eclipsing interaction that increases the steric strain in the eclipsed conformation. 4

2. Plot the potential energy versus dihedral angle for one complete rotation around the C-C bond in 1-bromo-2-chloroethane. Assume the  $0^\circ$  dihedral angle conformation is the Cl•Br eclipsed conformation.

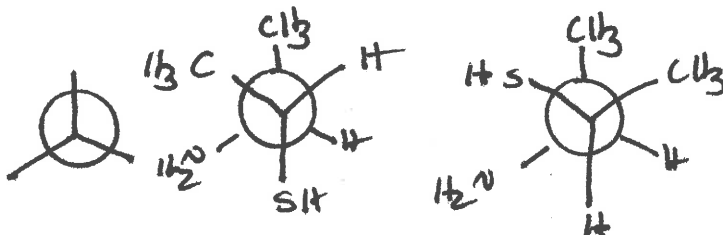


3. a. Draw a Newman projection for the following molecule looking down the C(2)-C(3) bond showing the conformation depicted in the structure below.



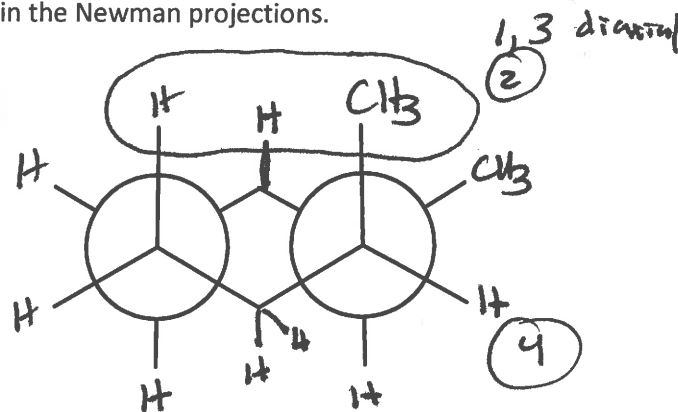
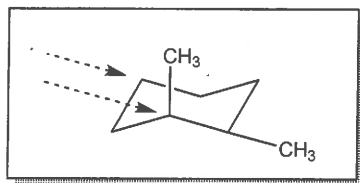
(4)

b. Draw a second Newman projection looking down the same bond as above that shows a CH<sub>3</sub>-CH<sub>3</sub> gauche conformation.



(4)

4. Complete the Newman projection template provided for the chair conformation shown for 1,2-dimethylcyclohexane. The arrows indicate the bond axes that one should be looking down in the Newman projections.



b. Does the structure in the box represent the cis or the trans isomer?

cis (2)

c. Circle the atoms involved in the methyl 1,3-diaxial interactions shown in the completed Newman projection.

d. How would we describe the relationship between the two methyl groups in this conformation?

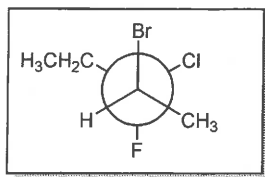
gauche (2)

e. Do the methyl groups in this conformation interact in any way with each other that might result in increased strain in the conformation? Explain your response.

(4)

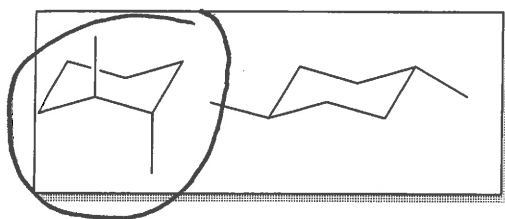
The CH<sub>3</sub>-CH<sub>3</sub> gauche interaction will introduce about 3.8 kJ/mol of steric strain into the conformation

5. The following questions refer to the Newman projection in the box.



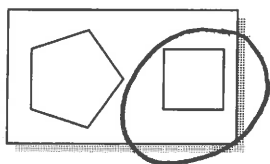
- a. What is the dihedral angle between Br and Cl? 60°
- b. Which pair of halogens are in an anti orientation? Br and F
- c. What is the dihedral angle between the methyl and ethyl groups? 180°
- d. Which pair of halogen atoms are in a geminal relationship? F and Cl

6. Circle the conformation in the box that incurs the greatest steric strain and specify the most important source of the strain. 8



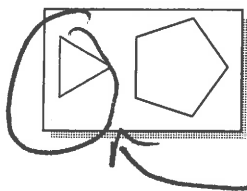
The conformation selected has two axial methyl groups each introducing  $\sim 7.8$  kJ/mol of steric strain

7. Circle the compound in the box that suffers from greater strain in its most stable conformation. What source(s) of strain are most significant for this compound? 4



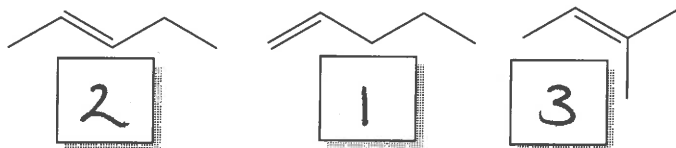
Overall greater ring strain from both angle strain and some torsional strain

8. Circle the compound in the box below that suffers from greater torsional strain in its most stable conformation. 2

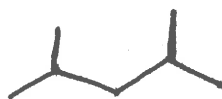
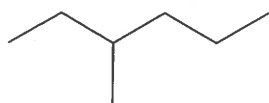


all C-H bonds are eclipsed

9. Organize the following isomeric alkenes in order of increasing  $|\Delta H_f|$ , where 1 = least exothermic enthalpy of formation. 3

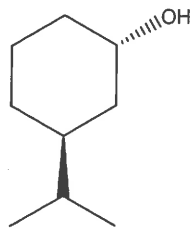


10. Draw a structure for any isomer of the alkane below that is expected to have a lower (i.e. less exothermic) enthalpy of combustion. 3



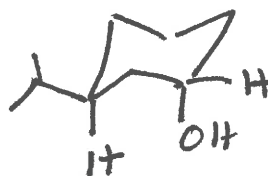
and many more

11. a. Draw the most stable chair conformation for the following compound. Pay careful attention to the absolute stereochemistry of the structure.



**Axial Steric Strain Energy**

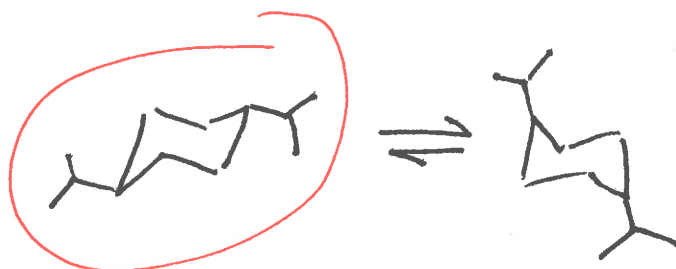
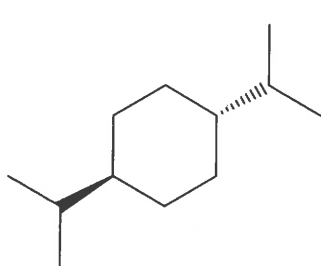
OH	2.5 kJ/mol
i-Pr	9.2 kJ/mol



4

b. Draw both chair conformations for the isomer of 1,4-diisopropylcyclohexane shown below. Circle the more stable conformation.

8



c. Which isomer of 1,4-diisopropylcyclohexane is expected to have a higher heat of combustion? **The cis isomer or the trans isomer?** Clearly explain your choice, including the connection between heat of combustion and the enthalpy (thermodynamic stability) of a compound. (Note that you analyzed one of the isomers in the previous part of the question.) 6

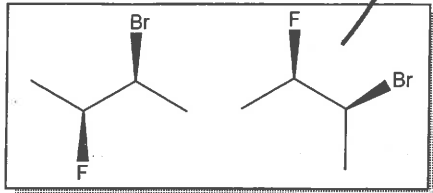
The cis isomer should have a higher heat of combustion because it is less stable.

In the cis isomer's most stable conformation an i-Pr group is in an axial configuration

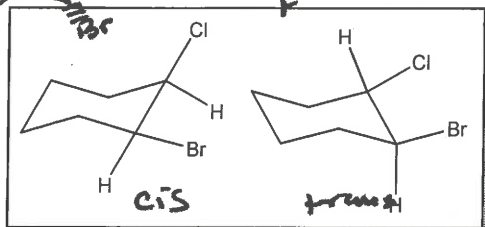


The trans isomer places both i-Pr groups in equatorial configurations

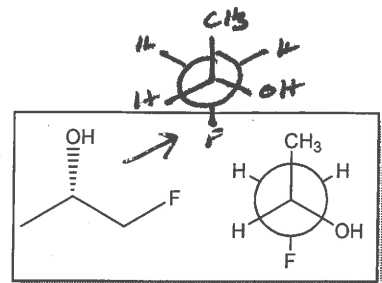
12. State the stereochemical relationship between the pairs of structures in each box. The structures can be related as being enantiomers, diastereomers, or identical.



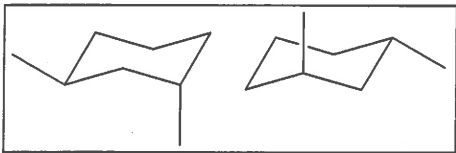
~~enantiomers~~  
diastereomers



diastereomers

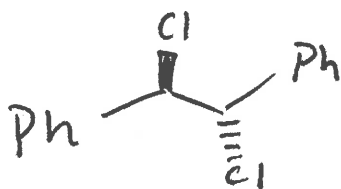
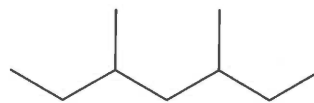
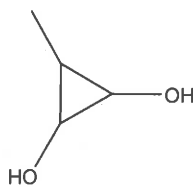
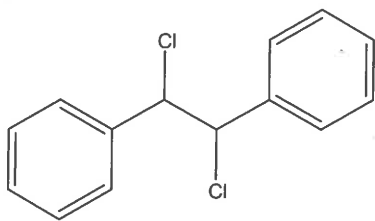


identical

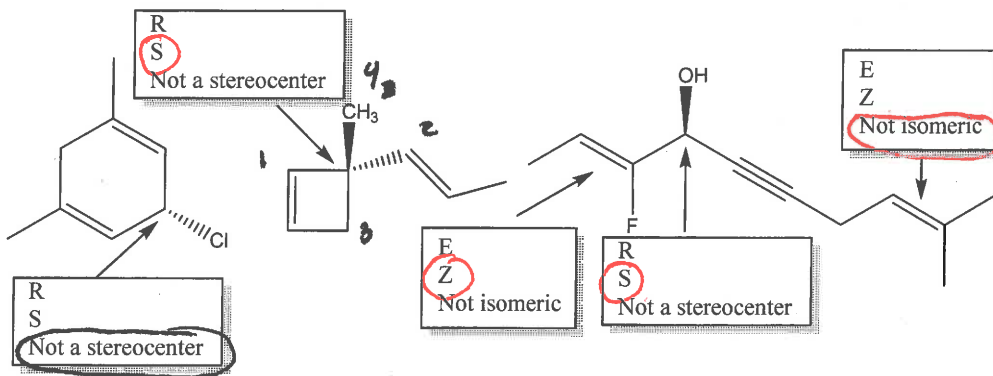


Identical

13. Each of the following compounds has at least one meso isomer. Draw a meso structure for each of the compounds using dash-wedge notation at stereocenters.

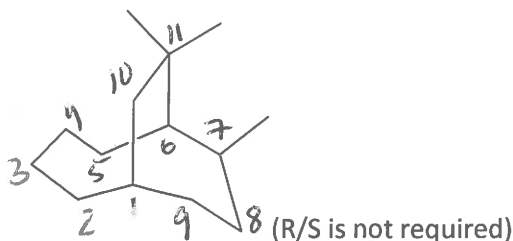


14. Choose the correct stereochemical designator for each of the centers/bonds indicated in the structures below.



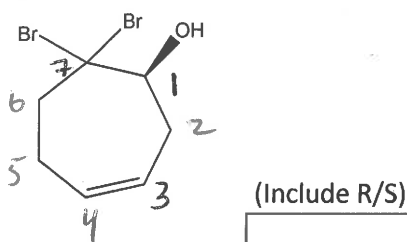
15. Assign IUPAC names to the following compounds. Include the R/S designator as part of the name for the compound in part b.

a.



7, 11, 11-trimethyl bicyclo[4.3.2]undecane

b.



(1S)-7,7-dibromocyclohept-3-enol

16. A chemist attempting to synthesize (+)-menthol produced a product that contained a small amount of the (-)-enantiomer as well. To determine the optical purity, the chemist dissolved 2.50 g of the product in enough ethanol to make 25.00 mL of solution. The observed rotation of the solution was  $9.75^\circ$  when measured in a 20.0 cm polarimeter cell. Given the literature specific rotation of (+)-menthol is  $[\alpha]_D = +50.0^\circ$ , calculate the percent (-)-menthol in the product mixture.

$$[\alpha_{\text{mix}}] = \frac{\alpha_{\text{obs}}}{c \cdot l}$$

$$\frac{9.75^\circ}{0.100 \text{ g/mL} \cdot 2.00 \text{ dm}}$$

$$48.75^\circ$$

$$c = \frac{2.50 \text{ g}}{25.0 \text{ mL}} = 0.100 \text{ g/mL}$$

$$l = 20.0 \text{ cm} \cdot \frac{1 \text{ dm}}{10 \text{ cm}} = 2.00 \text{ dm}$$

$$\frac{[\alpha_{\text{mix}}]}{[\alpha_{\text{pure}}]} = \frac{C_+ - C_-}{100}$$

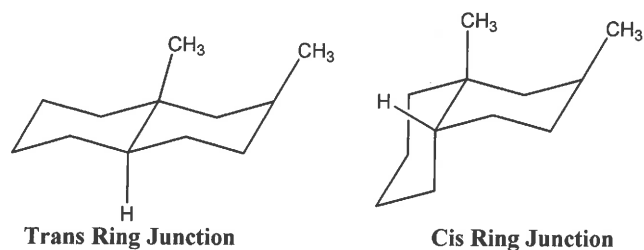
$$C_+ = 100 - C_-$$

$$\frac{[\alpha_{\text{mix}}]}{[\alpha_{\text{pure}}]} = \frac{100 - 2C_-}{100}$$

$$\frac{48.75^\circ}{50.0^\circ} \cdot 100 = 100 - 2C_-$$

1,25%

Chair conformations for two isomers of 1,3-dimethyldecalin are shown below. One isomer has a trans ring junction while the other is cis.



a. Both conformations shown are highly strained. Specifically identify sources of strain.

Both isomers suffer from 1,3 diaxial ~~strain~~ <sup>interactions</sup>  
 (in the conformations shown)

between the two methyl groups.

The cis isomer suffers from additional strain from 1,3-diaxial interactions between the bonds in the rings

b. The isomer with the cis ring junction is expected to be more stable. Clearly explain why this is so.

The <sup>cis</sup> isomer can flip both chair placing both CH<sub>3</sub> groups in equatorial configurations. <sup>(relative to the ring)</sup>

The trans isomer is incapable of "ring flipping." All that's possible is to place right ring in a twist boat conformation.

