Chapter 7 Additional Problems

1. Explain the following observations: Treatment of 4-methylcyclopentene with OsO₄ and H₂O₂ gives two diastereomeric meso compounds, while treatment of 4-methylcyclohexene with OsO₄ and H₂O₂ gives two diastereomeric racemic compounds.

b. The cyclic amine 1-chloro-2,2-dimethylaziridine can be resolved into enantiomers, but the acyclic amine chloroisopropylmethylamine (and other acyclic amines bearing three different substituents on nitrogen) cannot.

![1-chloro-2,2-dimethylaziridine](image1)

![chloroisopropylmethylamine](image2)

c. Treatment of styrene (Ph-CH=CH₂) with osmium tetroxide gives racemic 1-phenylethane-1,2-diol (Ph-CHOH-CH₂OH), but treatment of styrene with osmium tetroxide in the presence of a ligand (a compound that binds to a metal) derived from dihydroquinine gives optically active 1-phenylethane-1,2-diol.

![dihydroquinine](image3)
2. When three different carbon atoms of cyclohexane bear substituents, the conformer with two groups in the equatorial positions is usually the more stable. Draw the more stable chair conformation for each of the following compounds.

a. \textit{cis}-4-ethyl-\textit{trans}-3-methylcyclohexanol
b. \textit{cis}-2-bromo-\textit{cis}-3-methylcyclohexanecarboxylic acid
c. \textit{trans}-3-bromo-\textit{trans}-4-chloro-1-methylcyclohexane
d. \textit{trans}-4-methyl-\textit{cis}-1,3-cyclohexanediol
3. Draw a structure for each of the following compounds, then draw the conformer that you expect to be most stable.
   a. spiro[3.5]nonane   b. trans-bicyclo[3.3.0]octane
   c. spiro[2.4]heptane   d. trans-2,2-dibromobicyclo[4.4.0]decane
   e. 2-methylspiro[3.3]heptane   f. bicyclo[4.3.1]decane
4. Organophosphorus derivatives of inositol are important constituents of certain phospholipids, the major class of membrane building blocks in all living cells. Inositol is named 1,2,3,4,5,6-hexahydroxycyclohexane, and it can exist in different isomeric forms depending on whether the OH group attached to each carbon atom is up or down relative to the plane of the ring. Draw the most stable isomer of inositol in its most stable conformation.

5. Draw the two chair conformers of cis-1,4-di-tert-butylcyclohexane. Neither of these is the preferred conformation. Instead, the twist-boat conformer has the lowest energy. Draw the two possible twist-boat structures. Identify the more stable one and explain why this conformation is expected to predominate.
Problems 6-8 involve perhydroanthracenes.

6. Perhydroanthracene can be formed by the hydrogenation of anthracene.

![Anthracene and Perhydroanthracene Reactions](attachment:image.png)

There are 5 diastereomers of perhydroanthracene, which are shown below.

![Diastereomers of Perhydroanthracene](attachment:image.png)

The following six molecular models correspond to the stable conformers of these five diastereomers. Note: one of these diastereomers can adopt two different conformations, both of which are shown. Use RasMol to view and rotate the models.

Model A. http://eee.uci.edu/03f/40300/pha.pdb What diastereomer does this model correspond to? _______
Model B. http://eee.uci.edu/03f/40300/phb.pdb What diastereomer does this model correspond to? _______
Model C. http://eee.uci.edu/03f/40300/phc.pdb What diastereomer does this model correspond to? _______
Model D. http://eee.uci.edu/03f/40300/phd.pdb What diastereomer does this model correspond to? _______
Model E. http://eee.uci.edu/03f/40300/phe.pdb What diastereomer does this model correspond to? _______
Model F. http://eee.uci.edu/03f/40300/phf.pdb What diastereomer does this model correspond to? _______

In which of these models are all of the cyclohexane rings in chair conformations? _____________________
In which of these models is at least one of the cyclohexane rings in a boat (twist-boat) conformation? _____________________
7. As we have discussed in class, it's important to be able to make conformationally realistic drawings of structures containing cyclohexane rings. Draw the carbon skeletons of models A-F. Do not draw the hydrogens or the C-H bonds; just draw the C-C bonds.

A.               B.               

C.               D.               

E.               F.               

8. Which diastereomer is unstrained? ________

How many 1,3-diaxial interactions are present in the ct diastereomer? ________ Estimate how much higher in energy (enthalpy) it is than the unstrained one. ________

How many 1,3-diaxial interactions are present in the cac diastereomer? ________ Estimate how much higher in energy (enthalpy) it is than the unstrained one. ________

Estimate how much higher in energy (enthalpy) the tat diastereomer is than the unstrained one. ________

Explain why the two conformers of the remaining diastereomer are of roughly comparable energy. Hint: They are both very strained, but in different ways.________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________

Two of the five diastereomers can be resolved into enantiomers. Which are they? _______________ (Hint: all conformers of each diastereomer can interconvert rapidly.)