

## Structure and Stereochemistry of Alkanes

**Reading:** Wade chapter 3, sections 3-10- 3-16

**Study Problems:** 3-43, 3-44, 3-45, 3-46

### **Key Concepts and Skills:**

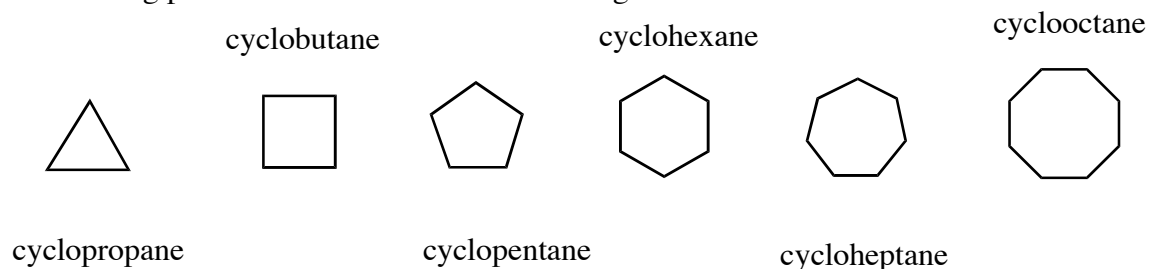
- Compare the energies of cycloalkanes, and explain ring strain
- Identify and draw cis and trans stereoisomers of cycloalkanes.
- Draw accurate cyclohexane conformations, and predict the most stable conformations of substituted cyclohexanes

### **Lecture Topics:**

#### **I. Cycloalkanes, structure and nomenclature**

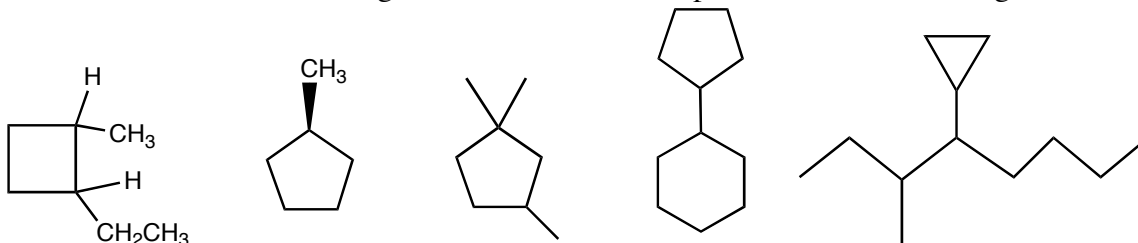
**Cycloalkanes** are alkanes that contain rings of carbon atoms.

Cycloalkanes are non-polar, inert compounds just like alkanes, and their boiling points and melting points increase with molecular weight.

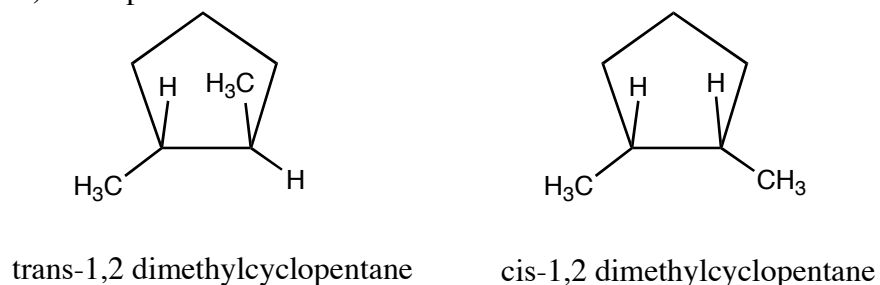


### **Nomenclature**

Follows same rules as for straight-chain alkanes. Examples: name the following



Similar to alkenes, there is no free rotation about the ring carbon-carbon bonds of cycloalkanes. Thus, cis-trans isomerism is observed. (note: cis-trans isomers do not interconvert!) Example:



Draw out: cis-1 methyl-3-propyl cyclobutane and trans-1-methyl-3-propyl cyclobutane.

### Ring Strain

The most common cycloalkanes are 5 and 6-membered rings. Why?

Remember that the ideal bond angle for  $sp^3$ -hybridized carbons is  $109.5^\circ$ .

If a cycloalkane requires bond angles other than  $109.5^\circ$ , the orbitals of its C-C bond cannot achieve optimum overlap. This phenomenon is termed **angle strain**.

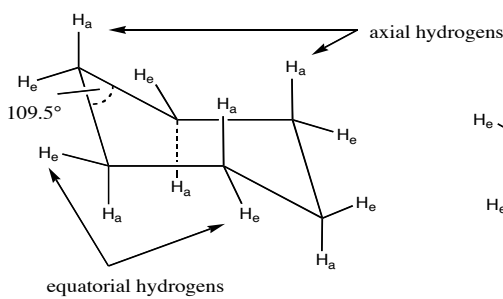
Example: cyclobutane necessarily has bond angles close to  $90^\circ$ , and thus it has a significant degree of angle strain.

In addition, **torsional strain** due to eclipsing interactions in cyclobutane (similar to what we encountered in conformational analysis of straight-chain alkanes) are also significant.

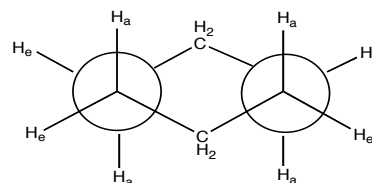
**Ring strain** results from the combined contributions of angle strain and torsional strain.

Ring strain can be assessed from the heats of combustion of various cycloalkanes: compounds with extra (higher) energy because of ring strain release more energy during combustion. Upon normalization of each combustion value for the number of carbons in each ring, values of ring strain can be compared between the cycloalkanes.

- Cyclopropane** has a very large ring strain value, due largely to the high degree of angle strain ( $60^\circ$  vs.  $109.5^\circ$ ). Because of the poor overlap of the  $sp^3$  orbitals for the C-C bonds, the sigma bonds of the ring are referred to as “bent bonds”  
Because of the planarity of cyclopropane, torsional strain is also significant due to the eclipsing interactions of C-H bonds (3 kcal/mol each).
- Cyclobutane** reduces torsional strain by assuming a slightly folded structure in which the bond angles are  $88^\circ$ . C-H bonds in the folded structure are not completely eclipsed.
- Cyclopentane** is also not a planar molecule; it assumes a puckered conformation also to reduce eclipsing interactions. Bond angles are  $\sim 108^\circ$ . Such a pucker undulates through the ring from carbon to carbon, providing relief of torsional strain.
- Cyclohexane** rings are very commonly encountered in chemistry (in steroids, carbohydrates, etc) and will be studied intensively. Cyclohexane has no ring strain, having no angle strain and no torsional strain in its most stable conformation. **Staggered conformations and  $109^\circ$  bond angles are observed in the chair form of cyclohexane!**

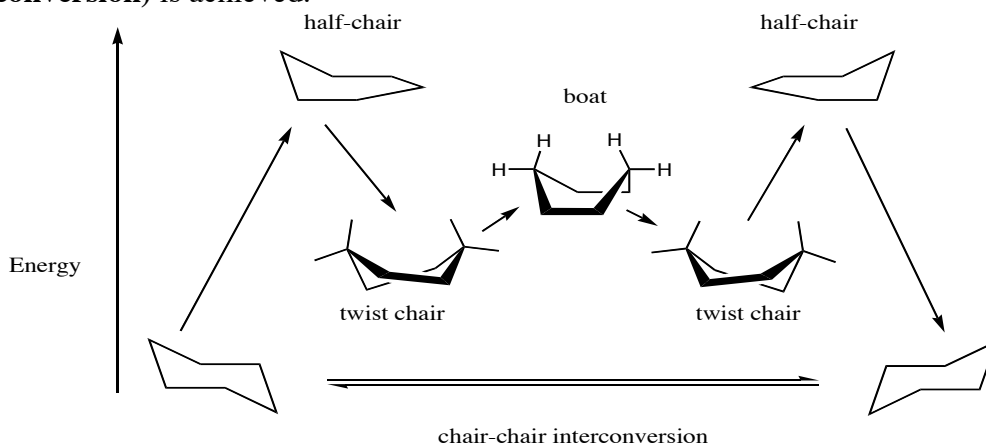


Chair conformation of cyclohexane



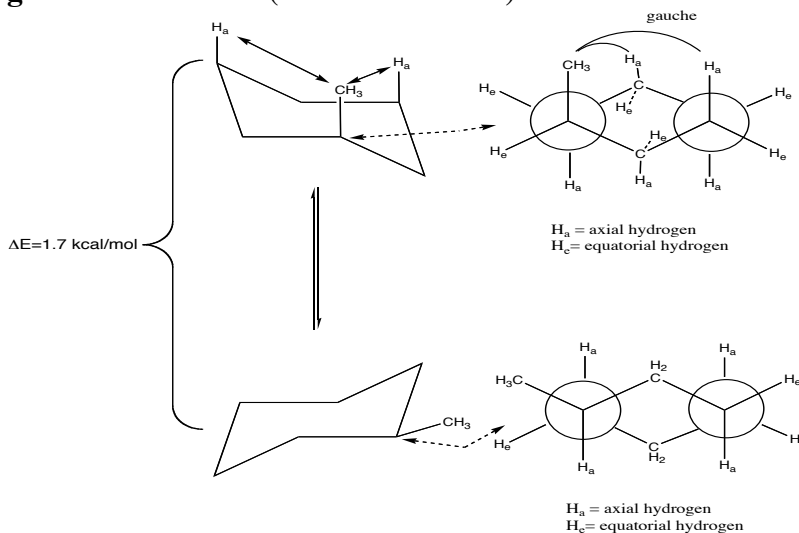
$H_a$  = axial hydrogen  
 $H_e$  = equatorial hydrogen

Several other cyclohexane conformers exist, all of which are higher in energy than the chair. The **boat conformation** is 6.9 kcal/mol higher in energy than the chair (due to **flagpole** interactions of axial hydrogens and extensive eclipsing interactions); the **twist boat** is 5.5 kcal/mol higher in energy than the chair; the **half-chair** is 10 kcal/mol higher in energy than the chair (due to both angle strain and torsional strain). Note: all of these conformations are encountered when a **ring flip** of the chair form (or **chair-chair interconversion**) is achieved.



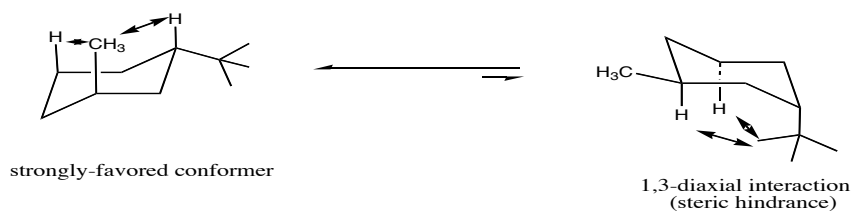
### Conformations of substituted cyclohexanes

A substituent on a cyclohexane ring can occupy either an axial or an equatorial position. By ring-flip, there are two possible conformations of methyl cyclohexane, one with an axial  $\text{CH}_3$  and one with an equatorial  $\text{CH}_3$ . The conformer with the axial  $\text{CH}_3$  is 17 kcal/mol higher in energy than the conformer with the equatorial  $\text{CH}_3$ . The reason is that there are two **gauche** interactions (0.9 kcal/mol each) in the axial conformer.



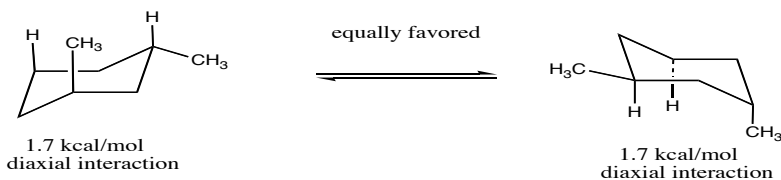
This example illustrates the importance of **1,3-diaxial interactions** for axial alkyl groups or other substituents on a cyclohexane ring. These interactions are a form of **steric hindrance** and tend to disfavor the axial conformer and favor the equatorial conformer, (where no 1,3 diaxial interactions are present) which is thus in energy. The energy difference between axial and equatorial conformers depends on the size of the substituent, and the energy difference is greater for larger groups. See table 3-6 in Wade,

and compare the axial/equatorial energy difference for a *t*-butyl group (5.4 kcal/mol) vs that of a methyl group (1.7 kcal/mol). *Regardless of other groups present on a cyclohexane ring, tert-butyl groups usually occupy an equatorial position.*

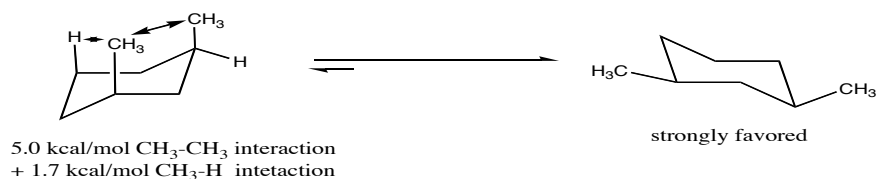


Compare:

trans-1,3-dimethyl cyclohexane



cis-1,3-dimethyl cyclohexane



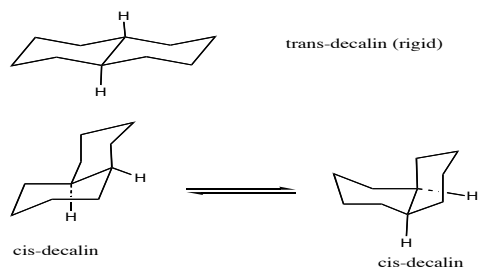
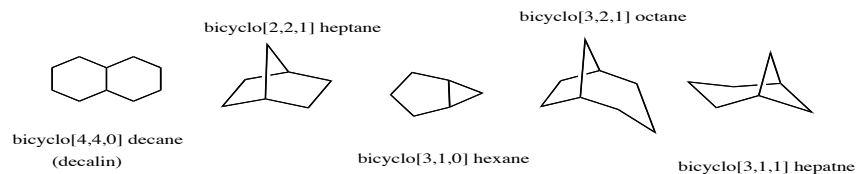
We can compare substituents on a cyclohexane ring in a 1,3-relationship; for trans-1,3-dimethylcyclohexane, either conformer has a 1,3-diaxial interaction for an axial methyl group, and both conformers are of equal energy; for cis-1,3-dimethylcyclohexane, one conformer has both methyl groups axial and is strongly disfavored (higher in energy) for steric reasons; the other conformer has both methyl groups equatorial, and thus is the lowest energy structure for the 1,3-dimethylcyclohexanes. As a result, the trans isomer is 1.7 kcal/mol higher in energy than the cis isomer. *Note: the cis and the trans isomer do not interconvert!*

### •Bicyclic molecules

**Fused ring systems** share two adjacent carbon atoms and the bond between them.

**Bridged ring systems** share two non-adjacent carbon atoms and one or more carbon atoms between them; **spirocyclic ring systems**, in which two ring systems share only one carbon atoms, are rare in nature. The nomenclature of these compounds is straightforward

**Decalin** is the most common example of a fused ring system and has both cis and trans forms. Trans-decalin, which cannot undergo a ring flip, is quite rigid; cis-decalin is quite flexible, in contrast.



Additional Problems for practice:

1. Draw the two chair conformations of cis and trans-1-chloro-2-methylcyclohexane. In each case, which is more stable? By how much (use table 3-6 in text)
2. Which isomer is more stable, cis or trans decalin? Explain your answer in terms of the steric interactions of the two molecules.
3. Draw the following disubstituted cyclohexanes and label the substituents as axial or equatorial. The substituents can be any alkyl group of your choosing. Remember to include the ring-flip structure as well.
  - (a) 1,3 trans disubstituted
  - (b) 1,3-cis disubstituted
  - (c) 1,5-cis disubstituted
  - (d) 1,4-cis disubstituted
  - (e) 1,5-trans disubstituted
  - (f) 1,6-trans disubstituted