

CHEM 321 Organic Chemistry I - Professor Kathleen Kilway

"Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 5 - 2, 5, 7, 9, 10, 14, 17, 18, 19, 20, 22, 26, 28, 33, 35, 36, 37, 38, 41, 45, 46.

CHAPTER 5: RINGS

Section 5.1

I. Preview

Section 5.2

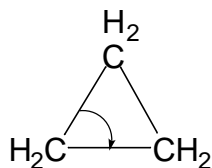
II. Rings and Strain

A- Two Types of Strain

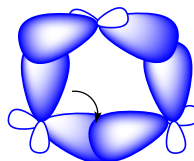
- 1- **Angle Strain** - The increase in energy caused by the deviation of an angle from the ideal demanded by the hybridization (See Figures 5.2 - 5.4 on pages 192 and 193).
- 2- **Torsional Strain** - The destabilization induced in a molecule through eclipsed bonds (See Figure 5.5 on page 193).

B- Cycloalkanes

- 1- 3-Membered ring, cyclopropane.
 - a- Internuclear angle 60° , inter-orbital angle 104° .
 - b- The strain induced by the reduction of the ideal tetrahedral angle of 109.5° to 60° is great.
 - c- Planarity causes other strain problems (See Figure 5.6 on page 194).



internuclear angle = 60°



interorbital angle = 104°

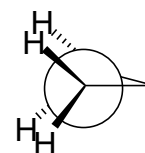


Figure 1

- d- The effects of high strain (angle - difficult to estimate- plus torsional - 6 kcal/mol) in cyclopropane show up in a number of ways.
- e- The strain overall destabilizes cyclopropane by about 25 kcal/mol.
- 2- 4-Membered ring, cyclobutane.
 - a- Angle strain less of a problem, 90° smaller deviation from 109.5° .
 - b- Puckering relieves torsional strain, increases angle strain in cyclobutane.
 - c- Angle at which ring puckers, 34° (See Figure 5.9 on page 195).
 - d- The interconversion between puckered structures costs 1.4 kcal/mol.
- 3- 5-Membered ring, cyclopentane.
 - a- Planar cyclopentane.
 - i- Five pairs of eclipsed hydrogens (at a cost of 10 kcal/mol).

- ii- Internal angle of 108° , angle strain small.
- b- Two forms of nonplanar cyclopentane (See Figure 5.11 on page 196). Neither form is static.
 - i- Twist.
 - ii- Envelope.

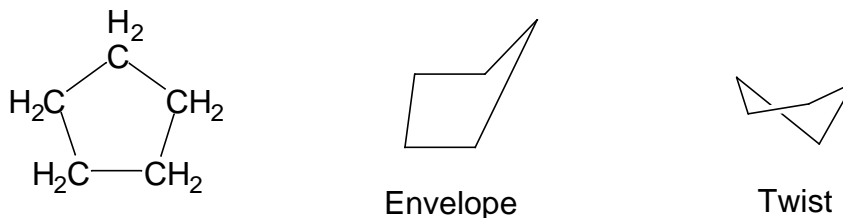


Figure 2

- 4- 6-Membered ring, cyclohexane.
 - a- Distortion from planarity relieves both angle and torsional (12 kcal/mol) stress.
 - b- The "chair" form is the energy minimum cyclohexane (See Figure 5.12 on page 196).

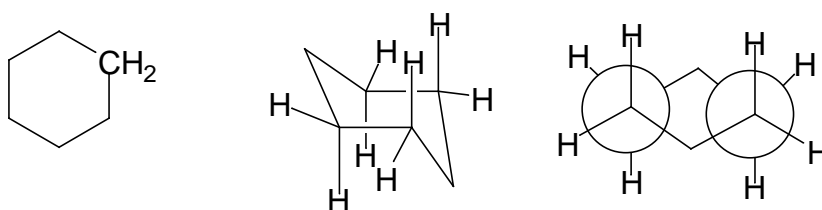


Figure 3

- c- Larger rings will have nonplanar forms, but nothing comparable to cyclohexane's energy minimum.
- d- Types of hydrogens.
 - i- **Axial hydrogens** - The set of six, straight up and down hydrogens in chair cyclohexane.
 - ii- **Equatorial hydrogens** - The set of six hydrogens, also "up and down", but more or less in the plane of the ring in chair cyclohexane.

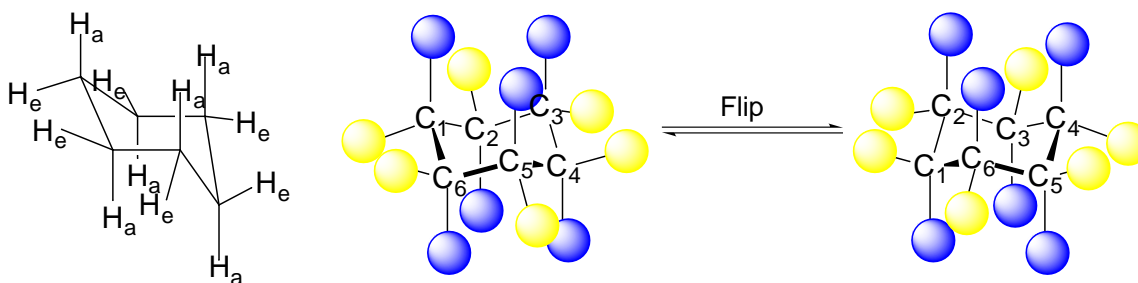


Figure 4

- iii- Axial hydrogens are interconverted with the set of equatorial hydrogens through ring "flipping" of the chair.
- iv- See Figure 5.15 on page 197 for an example.

Section 5.3

III. Quantitative Evaluation of Strain Energy

A- Heats of Formation

- 1- A negative ΔH_f° for a compound means that its formation from its constituent elements would be exothermic - heat is liberated.
- 2- A positive ΔH_f° means that the constituent elements are more stable than the compound and its formation would be endothermic - energy would have to be applied.
- 3- See Figure 5.18 on page 199 and Table 5.1.
- 4- The heat of formation decreases (becomes more exothermic/ CH_2 unit) until you reach cyclohexane.

B- Strain Analyzed by Heats of Combustion

- 1- The higher the ΔH_c° , the less stable the compound (See Figure 5.22 on page 202 and Table 5.2).
- 2- Subtraction of 157.5 kcal/mol, the ΔH_c of a strain-free methylene group, gives the strain energy per CH_2 and therefore, the strain energy for the ring compound.
- 3- The heat of combustion per CH_2 unit decreases until cyclohexane.

Section 5.4

IV. Stereochemistry of Cyclohexane: Conformational Analysis

A- Conformational Analysis

- 1- The determination of the minimum energy form of a molecule through analysis of steric interactions. Example: Cyclohexane. (See Figure 5.23 on page 204).
 - a- Kinetic measurements allow an evaluation of the energies involved.
 - b- Transition states are energy mountains (full-boat, half-chair).
 - c- Note: Small energy differences between two molecules in equilibrium result in a very large excess of the more stable isomer.

B- Van der Waals Strain

- 1- When two atoms are too close together, the energy of the system increases. This increase is called van der Waals strain.

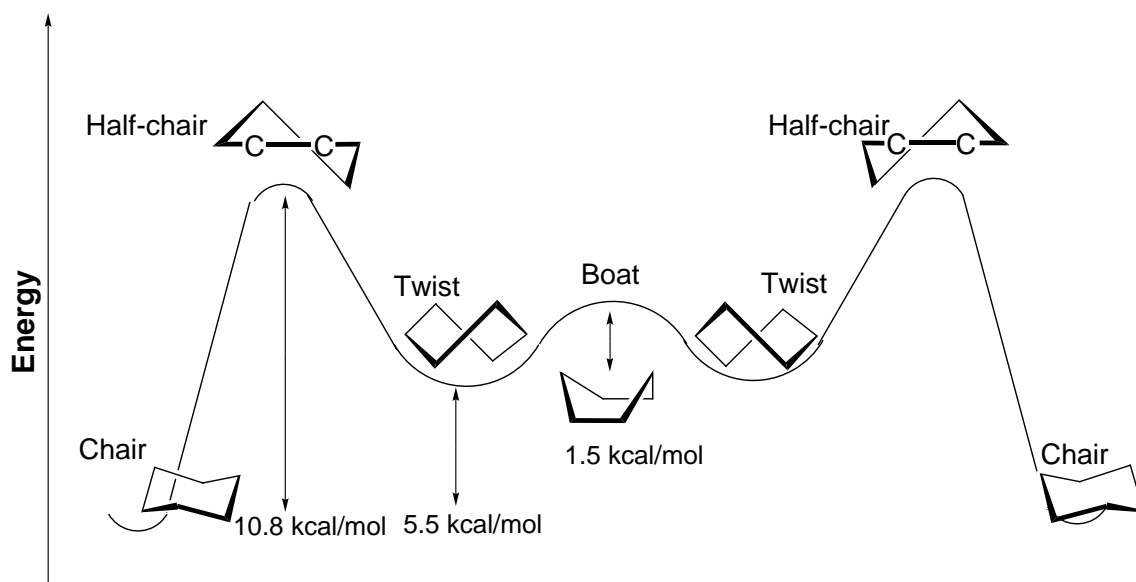


Figure 5

Section 5.5

V. Monosubstituted Cyclohexanes

A- All cycloalkanes except cyclopropane distort from planarity so as to minimize strain.

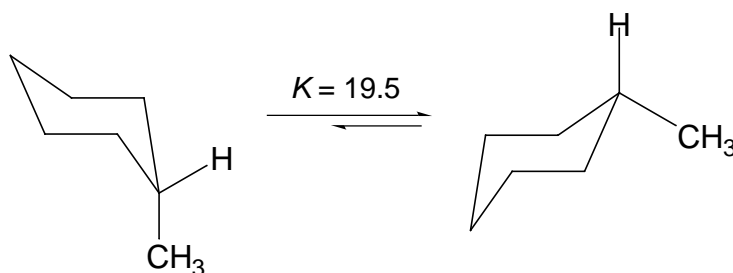


Figure 6

- 1- Gauche vs. Anti conformations, energy differences.
- 2- Calculation, percentage of isomers (methyl groups-- equatorial vs. axial).
- 3- Calculation, percentage of isomers (larger groups--equatorial vs. axial).

B- The amount of strain can be measured in a variety of ways, including measurements of heats of combustion or heats of formation.

C- Put larger(est) groups in the equatorial positions.

- 1- See Figure 5.30 on page 208.

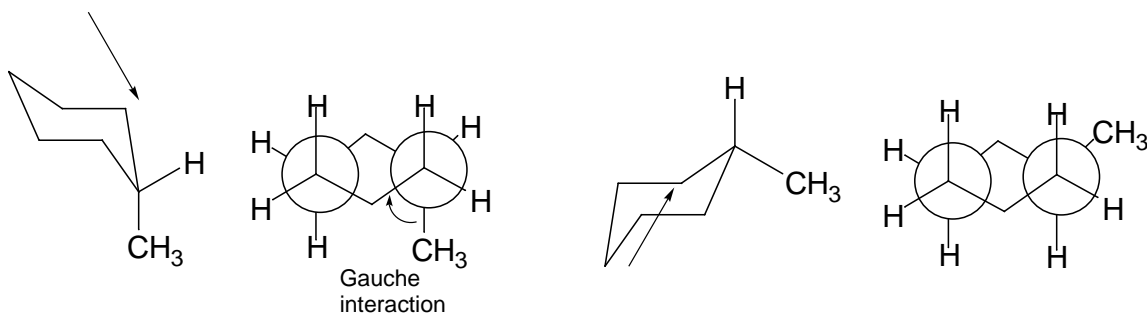


Figure 7

Section 5.6

VI. Disubstituted Ring Compounds

A- 1,1-Disubstituted Cyclohexanes

1- 1,1-Dimethylcyclohexane.

- a- Achiral.
- b- One methyl group axial and the other is equatorial.
- c- Ring flip does not alter structure. Axial methyl group becomes equatorial and equatorial methyl group becomes axial ($K=1$).
- d- See Figure 8 and Figure 5.34 on page 211 for an illustration.

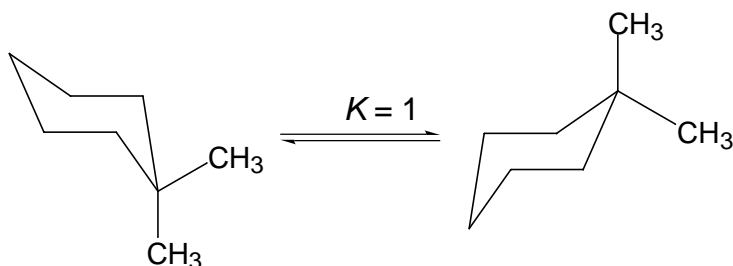


Figure 8

2- 1-Isopropyl-1-methylcyclohexane.

- a- Achiral.
- b- Ring flip changes structure:
 - i- One with isopropyl group axial and methyl group equatorial.
 - ii- The other with isopropyl group equatorial and methyl group axial.
 - iii- K does not equal zero. The structure with the larger isopropyl group in the equatorial position is more stable.
- c- Two isomers.
- d- See Figure 5.35 on page 211 for an illustration.

B- 1,2-Disubstituted Cyclohexanes

1- *Cis*-1,2-dimethylcyclohexane.

- a- Achiral.
- b- One methyl group is axial and the other is equatorial (See Figure 5.38 on page 213).
- c- Ring flip does not alter structure. Axial methyl group becomes equatorial and equatorial methyl group becomes axial ($K=1$).

- d- The two conformational isomers are enantiomers.
 e- Total of two stereoisomers of *cis*-1,2-dimethylcyclohexane.
 f- See Figure 9 and Figure 5.39 on page 213 for an illustration.

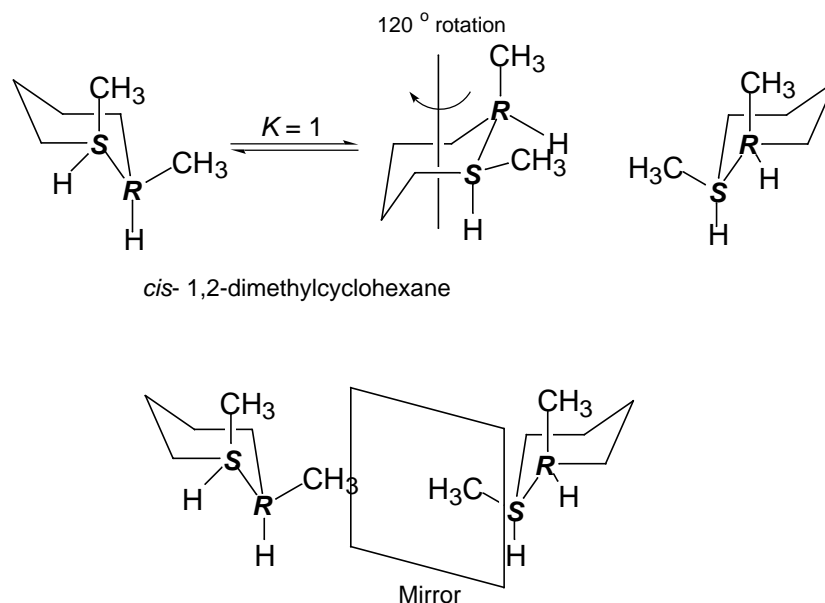


Figure 9

- 2- *Trans*-1,2-dimethylcyclohexane.
- a- Ac
 - b-
 - c- Chiral.
 - d- Either both methyl groups axial or both equatorial.
 - e- Ring flip alters structure from diaxial to diequatorial form.
 - i- The structure with both methyl groups in equatorial position is more stable.
 - ii- The two structures are called conformational diastereomers.
 - iii- See Figure 5.40 on page 214.
 - d- Each of the two diastereomers also has an enantiomer, nonsuperimposable mirror image.
 - e- Total of four stereoisomers of *trans*-1,2-dimethylcyclohexane, A, B, C, and D. B comes from the ring flip of A and likewise D from C. The all equatorial isomers are more stable because there are no gauche interactions. A-B, A-C, B-D, C-D are diastereomers. While, A-D and B-C are enantiomers.

Note: The *cis* and *trans* refer to the sidedness of a molecule and do not depend strictly on the angles between the groups. In a *cis* disubstituted cyclopropane, the dihedral angle between the *cis* groups is 0°, whereas it is 60° in the disubstituted cyclohexanes. The methyl groups are referred to as *cis* in either case. In *trans*-1,2-dimethylcyclopropane, the dihedral angle between the methyl groups is 120°, whereas in the six-membered ring it is 60°.

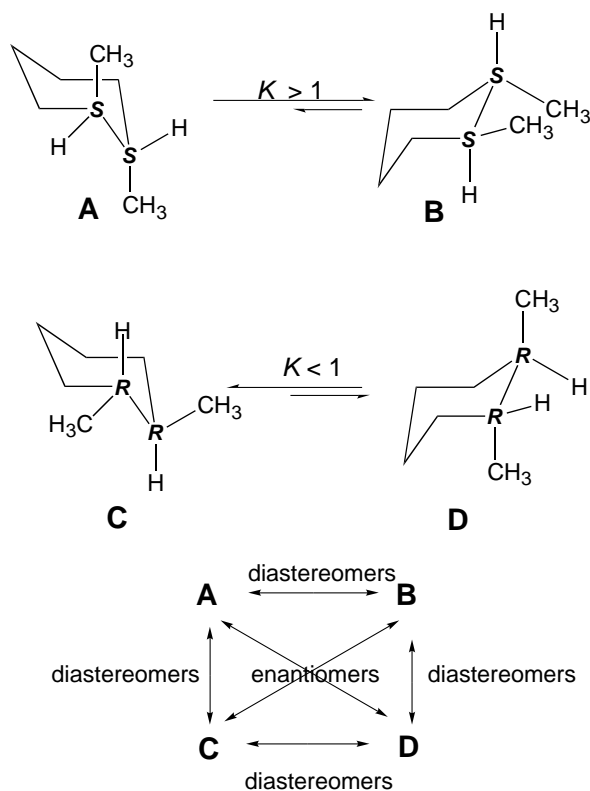


Figure 10

- 3- *Cis*-1-isopropyl-2-methylcyclohexane.
 - a- Ring flip alters structure (See Figure 5.42 on page 215).
 - i- Structures are conformational diastereomers.
 - b- Total of four possible stereoisomers (See Figure 5.43 on page 216).
- 4- *Trans*-1-isopropyl-2-methylcyclohexane.
 - a- Total of four possible stereoisomers (See Figure 5.46 on page 217).

Section 5.7

VII. Bicyclic Compounds

A- Modes of Attachment (See Figure 5.47 on page 218)

- 1- Spiro - Two rings that share a single carbon.
- 2- Fused - Two rings that share two carbons.
- 3- Bridged - Two rings that share more than two atoms.

B- Bridgehead positions

- 1- The bridgehead positions are shared by the rings in a bicyclic molecule.

C- Naming protocol for a typical bicyclic compound

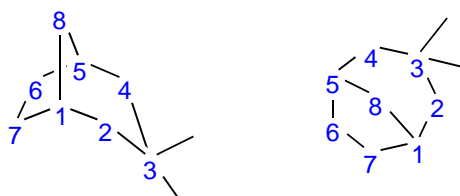


Figure 11

- 1- Count from one bridgehead around the longest bridge to the other bridgehead (1, 2, 3, 4, 5).
- 2- Next, count around the second longest bridge (6, 7).
- 3- Last, number the shortest bridge (8). This compound is a 3,3-dimethylbicyclooctane.
- 4- See Figure 5.58 on page 222 for another example.

Section 5.8

VIII. Polycyclic Systems

- 1- More rings can be fused and attaching to give you cholesterol, cubane, etc.
- 2- See Figure 5.63 on page 224 for examples.