Angle strain

- The strain induced in a molecule when bond angles are forced to deviate from the ideal 109° tetrahedral value (Adolf von Baeyer – 1885)

4.3 Stability of Cycloalkanes: Ring Strain

Stability of Cycloalkanes: Ring Strain

- Experimental data show that Baeyer’s theory is only partially correct
- Baeyer assumed all cycloalkanes to be flat
- Angle strain occurs only in small rings that have little flexibility

The three kinds of strain that contribute to the overall energy of a cycloalkane:

1. Angle strain – the strain due to expansion or compression of bond angles
2. Torsional strain – the strain due to eclipsing of bonds on neighboring atoms
3. Steric strain – the strain due to repulsive interactions when atoms approach each other too closely
4.4 Conformations of Cycloalkanes

Cyclopropane
- Most strained of all the rings
- Angle strain – caused by 60° C-C-C bond angles
- Torsional strain – caused by the eclipsed C-H bonds on neighboring carbon atoms
  a) Structure of cyclopropane showing the eclipsing of neighboring C-H bonds giving rise to torsional strain
  b) Newman projection along a C-C bond of cyclopropane

Conformations of Cycloalkanes
- Bent C-C bonds
  - Orbitals can’t point directly toward each other
  - Orbitals overlap at a slight angle
  - Bonds are weaker and more reactive than typical alkane bonds

- C-C bond:
  255 kJ/mol (61 kcal/mol) for cyclopropane
  355 kJ/mol (85 kcal/mol) for open-chain propane

Conformations of Cycloalkanes
Cyclobutane
- Total strain is nearly same as cyclopropane
  - Angle strain – less than cyclopropane
  - Torsional strain – more than cyclopropane because of larger number of ring hydrogens
- Not planar (not flat)
  - One carbon atom lies 25° above the plane of the other three
  - Newman projection along C1-C2 bond shows that neighboring C-H bonds are not quite eclipsed
Conformations of Cycloalkanes

Cyclopentane
- Less strain than cyclopropane or cyclobutane
- Planar cyclopentane exhibits:
  - Angle strain – very minimal
  - Torsional strain – large amount
- Cyclopentane twists to a nonplanar (puckered) conformation
  - C1, C2, C3 and C4 are nearly planar but C5 is out of the plane
- Balance between increased angle strain and a decreased torsional strain

Conformations of Cyclohexane

Substituted cyclohexanes
- Most common cycloalkanes
- Occur widely in nature
  - Steroids
  - Pharmaceutical agents

Cyclohexane
- Adopts chair conformation
  - No angle strain
    - All C-C bonds are 111.5°, close to the ideal 109°
  - No torsional strain
    - Neighboring C-H bonds are staggered
Conformations of Cyclohexane

Drawing chair conformation of cyclohexane

- Step 1 – draw parallel lines, slanted downward and slightly offset from each other
- Step 2 – place topmost carbon atom above and to the right of the plane of the other four, and connect the bonds
- Step 3 – place bottommost carbon atom below and to the left of the plane of the middle four, and connect the bonds

Note: Bonds to the bottommost carbon atom are parallel to the bonds to the topmost carbon.

Conformations of Cyclohexane

Chair conformation
- Angle strain – none
- Torsional strain – none

Twist-boat conformation
- About 23 kJ/mol (5.5 kcal/mol) higher in energy than chair
  - Angle strain – minimal
  - Torsional strain – large amount

Twist-boat cyclohexane (23 kJ/mol strain)

4.6 Axial and Equatorial Bonds in Cyclohexane

Chair conformation of cyclohexane
- Chemical behavior of many substituted cyclohexanes is influenced by conformation
- Simple carbohydrates (such as glucose) adopt a cyclohexane chair conformation which directly affects their chemistry

Cyclohexane (chair conformation)
Glucose (chair conformation)
Chair conformation of cyclohexane

- There are two kinds of positions for substituents on the cyclohexane ring
  - Axial positions – 6 axial positions perpendicular to ring and parallel to ring axis.
  - Equatorial positions – 6 equatorial positions are in rough plane of the ring around the equator

Axial and Equatorial Bonds in Cyclohexane

Chair conformation of cyclohexane

- Each carbon atom in cyclohexane has one axial and one equatorial hydrogen.
  - Each face of the ring has three axial and three equatorial hydrogens in an alternating pattern.

Axial and Equatorial Bonds in Cyclohexane

Chair conformation of cyclohexane

- Drawing axial and equatorial positions

Axial Bonds: The six axial bonds, one on each carbon, are parallel and alternate up-down.

Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

Completed cyclohexane
There is only one form of a monosubstituted cyclohexane.

Cyclohexane rings are conformationally mobile.

Different chair conformations readily interconvert exchanging axial and equatorial positions - called a ring-flip.

Ring-flip occurs by keeping the middle four carbon atoms in place while folding the two end carbons in opposite directions.

Axial substituent becomes an equatorial substituent after ring-flip and vice versa.

Energy barrier to ring-flip is about 45 kJ/mol (10.8 kcal/mol).

Draw 1,1-dimethylcyclohexane in a chair conformation, indicating which methyl group in your drawing is axial and which is equatorial.
4.7 Conformations of Monosubstituted Cyclohexanes

The two conformers of a monosubstituted cyclohexane are not equally stable
- Substituent is almost always more stable in equatorial position
- Percentages of two isomers calculated by equation based on the value of $K$

$$\Delta E = -RT \ln K$$

$\Delta E$ is the energy difference between isomers
$R$ is the gas constant [8.315 J/(K · mol)]
$T$ is the Kelvin temperature
$K$ is the equilibrium constant between isomers

Conformations of Monosubstituted Cyclohexanes

Plot of percentages of two isomers at equilibrium versus the energy difference between them using

$$\Delta E = -RT \ln K$$

Conformations of Monosubstituted Cyclohexanes

- Energy difference between axial and equatorial conformations is due to 7.6 kJ/mol of steric strain caused by **1,3-diaxial interactions**
- C1 methyl group too close to C3 and C5 axial hydrogens
Steric strain

- Origin of the steric strain between an axial methyl group and an axial hydrogen atom in methylcyclohexane is identical to the steric strain in gauche butane.

- Equatorial methylcyclohexane has no such interactions and is more stable.

**Conformations of Monosubstituted Cyclohexanes**

- 1,3-Diaxial steric strain
  - Depends on the nature and size of the substituent.
  - Steric strain increases paralleling increase of bulk of alkyl group.

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Conformations of Monosubstituted Cyclohexanes