3.4
The Shapes of Cycloalkanes: Planar or Nonplanar?
assumed cycloalkanes are planar polygons

distortion of bond angles from 109.5° gives angle strain to cycloalkanes with rings either smaller or larger than cyclopentane

Baeyer deserves credit for advancing the idea of angle strain as a destabilizing factor.

But Baeyer was incorrect in his belief that cycloalkanes were planar.
Types of Strain

• **Torsional strain**
  strain that results from eclipsed bonds

• **van der Waals strain (steric strain)**
  strain that results from atoms being too close together

• **angle strain**
  strain that results from distortion of bond angles from normal values
Measuring Strain in Cycloalkanes

Heats of combustion can be used to compare stabilities of isomers.

But cyclopropane, cyclobutane, etc. are not isomers.

All heats of combustion increase as the number of carbon atoms increase.
Measuring Strain in Cycloalkanes

Therefore, divide heats of combustion by number of carbons and compare heats of combustion on a "per CH₂ group" basis.
Heats of Combustion in Cycloalkanes

<table>
<thead>
<tr>
<th>Cycloalkane</th>
<th>kJ/mol</th>
<th>Per CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropane</td>
<td>2,091</td>
<td>697</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>2,721</td>
<td>681</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>3,291</td>
<td>658</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3,920</td>
<td>653</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>4,599</td>
<td>657</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>5,267</td>
<td>658</td>
</tr>
<tr>
<td>Cyclononane</td>
<td>5,933</td>
<td>659</td>
</tr>
<tr>
<td>Cyclodecane</td>
<td>6,587</td>
<td>659</td>
</tr>
</tbody>
</table>
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According to Baeyer, cyclopentane should have less angle strain than cyclohexane. The heat of combustion per CH₂ group is less for cyclohexane than for cyclopentane. Therefore, cyclohexane has less strain than cyclopentane.
Adolf von Baeyer (19th century)

assumed cycloalkanes are planar polygons

distortion of bond angles from 109.5° gives angle strain to cycloalkanes with rings either smaller or larger than cyclopentane

Baeyer deserves credit for advancing the idea of angle strain as a destabilizing factor.

But Baeyer was incorrect in his belief that cycloalkanes were planar.
3.5 Conformations of Cyclohexane

heat of combustion suggests that angle strain is unimportant in cyclohexane

tetrahedral bond angles require nonplanar geometries
Chair is the most stable conformation of cyclohexane.

All of the bonds are staggered and the bond angles at carbon are close to tetrahedral.
All of the bond angles are close to tetrahedral but close contact between flagpole hydrogens causes van der Waals strain in boat.

Boat conformation is less stable than the chair
Eclipsed bonds gives torsional strain to boat.

Boat conformation is less stable than the chair.
Skew boat is slightly more stable than boat.

Less van der Waals strain and less torsional strain in skew boat.
the chair conformation of cyclohexane is the most stable conformation and derivatives of cyclohexane almost always exist in the chair conformation
3.6
Axial and Equatorial Bonds in Cyclohexane
The 12 bonds to the ring can be divided into two sets of 6.
6 Bonds are axial

Axial bonds point "north and south"
The 12 bonds to the ring can be divided into two sets of 6.
6 Bonds are equatorial

Equatorial bonds lie along the equator
3.7
Conformational Inversion (Ring-Flipping) in Cyclohexane
Conformational Inversion

chair-chair interconversion (ring-flipping)

rapid process (activation energy = 45 kJ/mol)

all axial bonds become equatorial and vice versa
Half-chair

Skew boat


3.8
Conformational Analysis of Monosubstituted Cyclohexanes

most stable conformation is chair

substituent is more stable when equatorial
Chair chair interconversion occurs, but at any instant 95% of the molecules have their methyl group equatorial.

Axial methyl group is more crowded than an equatorial one.
Source of crowding is close approach to axial hydrogens on same side of ring.
Crowding is called a "1,3-diaxial repulsion" and is a type of van der Waals strain.
Crowding is less pronounced with a "small" substituent such as fluorine.

Size of substituent is related to its branching.
Crowding is more pronounced with a "bulky" substituent such as tert-butyl.

*tert*-Butyl is highly branched.
van der Waals strain due to 1,3-diaxial repulsions