## Chemistry 2500

Chapter 3
Conformations by Rotations

## Rotations About Single Bonds

- It is important to understand that under normal conditions, STP, molecules are in constant motion and that atoms move relative to each other - rotation about single bonds.
- Rotation about a C-C bond does not change the overlap between the orbitals therefore the $\sigma$ bond remains intact.
- The different spatial arrangements produced by rotation about single bonds are called conformations.
rotations about single bonds are allowed

rotations about single bonds are allowed

a conformation of ethane

a different conformation of ethane

another conformation of ethane


## Newman Projections

- Newman Projections are used to clearly show the arrangement around a single bond.

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bond is viewed along its axis
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of the C-C bond of ethane

The atom closest to viewer is depicted at the point where the three bonds connect.


The atom furthest from viewer is depicted as a circle. The bonds to this atom connect to the outside of the circle.


Combine these depictions to obtain the Newman projection of the $\mathrm{C}-\mathrm{C}$ bond of ethane.
note that bonds touch the outside of the circle

## Staggered and Eclipsed Conformations

- Different conformations have different energies. Rotation about a particular bond is described by its torsion or dihedral angle.
- When the bonds of the front carbon atom align (or eclipse) with those of the back carbon atom, they form what is called a eclipsed conformation.
- Repulsion between the adjacent bonds create torsion strain, raising the energy of the conformation.
- Further rotation about the $\mathrm{C}-\mathrm{C}$ bond moves the atoms and bonds farther apart, reducing the torsion strain and lower the its energy.
- The torsional strain is at a minimum in a staggered conformation when the groups in front and back are as far apart as possible.


## Staggered and Eclipsed Conformations

- The greater the torsion angle, the less torsional strain.

torsion angle

eclipsed conformation:
greatest torsional strain $\rightarrow$ high energy

$-\mathrm{C}-\mathrm{C}-\mathrm{H}$ torsion angle $=0^{\circ}$
bonds on adjacent C atoms closest
$\rightarrow$ greatest repulsion between C-H bonds (greatest torsional strain)
|| rotate C-C bond


## staggered conformation: least torsional strain

 $\rightarrow$ low energy$\mathrm{H}-\mathrm{C}-\mathrm{C}-\mathrm{H}$ torsion


## Staggered and Eclipsed Conformations

eclipsed conformations: greatest torsional strain


## Steric Strain

- Steric strain is defined as a repulsive force between the electron clouds of atoms that are close to each other but not directly bonded.



## Steric Strain

- The bigger the group (i.e. the bigger the electron cloud), the more steric strain the molecule will experience.



## Strain in Cycilc Nolecules

- Cyclic molecules are often depicted as simple polygons, neglecting their true 3-dimentional structure.
- Angle strain arises from bond angles that do not permit maximum orbital overlap between atoms of a molecule.


## square <br> hexagon


cyclobutane
oxetane

cyclohexane

piperidine

## 3-Membered Rings

- 3-membered rings possess the most strain, experiencing angle, steric, and torsional strain.
- Despite their inherent strain, 3-membered rings do occur in nature.


maximum overlap between sp ${ }^{3}$ orbitals



## 4-Membered Rings

- 4-membered rings have non-planar conformations, which reduces the amount of inherent strain within the molecule.
- With less angle, torsion, and steric strain, 4-membered rings are inherently more stable than 3-membered rings.
planar

torsional strain: all C-H bonds completely eclipsed
butterfly



C-H bonds slightly less eclipsed reducing torsional strain

$\stackrel{\text { inversion }}{\rightleftharpoons}$


## 5-Membered Rings

- The most stable conformation for 5-membered rings is the envelope conformation.
- With even less strain, 5 -membered rings are inherently more stable than 4 - and 3-membered rings and are frequently found in nature.
planar

envelope



## torsional strain from 10

totally eclipsed C-H bonds
$108^{\circ} \approx 109^{\circ}$ little angle strain

## 6-Membered Rings

- Cyclohexane is the only ring under 14 carbon atoms that is relatively free from strain.
- The chair conformation is by far the most common conformation for 6 -membered rings.


Each of the bonds in a chair is parallel to one other bond; viewing the Newman projection of one bond will also show the projection of the parallel bond.

## 6-Membered Rings - Chair Conformations

- It is imperative that you learn how to properly draw chair conformations - refer to section 3.5.1 of your text.

Avoiding common errors

1. There should be no horizontal or vertical lines in the ring structure.

2. The equatorial bonds should be parallel to the ring bonds.

incorrect

correct

incorrect

correct
3. The axial bonds should point in the same direction as the " $V$ " to which they are connected.

incorrect

correct

incorrect



Practising drawing chairs is the best way to learn the proper perspective.

## 6-Membered Rings - Chair Conformations

- There are 2 different chair conformations that interconvert through a process called a ring flip or chair flip.
- For cyclohexane, both conformers resulting from the ring flip have the same energy.
side bonds slant to the right


axial hydrogens rotate to equatorial positions

equatorial hydrogens rotate to axial positions


## Substituted 6-Membered Rings

- When a substituent is added to a 6 -membered ring, the 2 conformers do NOT have the same energy.
- Substituents found in the axial position are less favorable due to $1,3-$ diaxial interactions.
- Steric strain from 1,3-diaxial interactions generally increases as the size of the substituent increases.

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methyl is equatorial-there is
no steric strain
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axial methyl experiences two 1,3-diaxial interactions with hydrogens



## Substituted 6-Membered Rings

- In general, the more stable chair conformer is the one where more of the larger substituents are placed in the equatorial position.


## TABLE 3.1 Relative Populations of Equatorial and Axial Conformations in Some Monosubstituted Cyclohexanes at 298 K

The A-value is the difference in free energy between the higher energy conformation (axial) and the lower energy conformation (equatorial).

| Substituent | \% Equatorial | \% Axial | A-Value (kcal/mol) |
| :--- | :---: | :---: | :---: |
| -Cl | 67.4 | 32.6 | 0.6 |
| $-\mathrm{OCH}_{3}$ | 73.4 | 26.6 | 0.55 |
| $-\mathrm{CH}_{3}$ | 94.6 | 5.4 | 1.8 |
| $-\mathrm{C}_{6} \mathrm{H}_{5}$ | 99.4 | 0.6 | 3.0 |
| $-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}$ | 99.96 | 0.04 | 3.0 |

## Disubstituted 6-Membered Rings

- When more than one substituent attached to a 6 -membered ring, the position of the substituents need to be analyzed in order to determine the most stable conformer.
methyl groups on same face of ring (top)


At each ring position, one substituent is closer to the top and the other is closer to the bottom. Adding hydrogens can help to keep track.
methyl groups occupy positions closest to top face

bottom face

bottom face

Once correct positions for groups have been established, the molecule can be re-drawn without hydrogens.

## Disubstituted 6-Membered Rings

- When more than one substituent attached to a 6 -membered ring, the position of the substituents need to be analyzed in order to determine the most stable conformer.

two 1,3-diaxial interactions
ring inversion

> each substituent that is axial becomes equatorial each substituent that is equatorial becomes axial

## Disubstituted 6-Membered Rings

- Keep in mind that dashes/wedges are completely independent of whether the group is axial or equatorial.



## Disubstituted 6-Membered Rings

- Keep in mind that dashes/wedges are completely independent of whether the group is axial or equatorial.

Adding labels to the ring atoms is a good way to locate substituents on related structures. The starting point and direction do not matter


## Disubstituted 6-Membered Rings

- In general, the more stable conformer is the one with more substituents in the equatorial position.
two 1,3-diaxial interactions

ring inversion


[^0]
[^0]:    two 1,3-diaxial interactions

