

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 σ bond remains intact.
- The different spatial arrangements produced by rotation about single bonds are called *conformations*.



Newman Projections

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



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 C-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.



Staggered and Eclipsed Conformations





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 Cyclic Molecules

- 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.





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





- 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.





- 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.





- 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.



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.





t

correct

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



- 2. The axial bonds should point in the same direction as the "V" to which they are connected.

incorrect



correct

4. The bottom three carbons are assumed to lie toward the viewer.





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.





- 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 1,3diaxial interactions.
- Steric strain from 1,3-diaxial interactions generally increases as the size of the substituent increases.





- In general, the more stable chair conformer is the one where more of the larger substituents are placed in the equatorial position.
 - TABLE 3.1Relative 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)
-CI	67.4	32.6	0.6
-0CH ₃	73.4	26.6	0.55
-CH ₃	94.6	5.4	1.8
$-C_6H_5$	99.4	0.6	3.0
$-C(CH_3)_3$	99.96	0.04	3.0

• 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.



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



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• In general, the more stable conformer is the one with more substituents in the equatorial position.

