

### STUDY GUIDE FOR CHAPTER 3

1. Projections.
  - A. *Newman* projections.
  - B. *Sawhorse* projections.
  - C. *Wedge-and-dash* representations.
2. Structure and conformational analysis of simple alkanes.
  - A. Methane – tetrahedral geometry, bond angles, bond lengths.
  - B. Ethane – C – C single,  $\sigma$ -bond. Free rotation allowed by the symmetry of the  $\sigma$ -bond – leads to generation of conformations. Learn VERY WELL how to represent molecules via *Newman* projections (we will use them many times). Two distinct conformations for ethane – *eclipsed* and *staggered*. What are the values of the dihedral angle? Which conformation is higher in energy and by how much? What is the **increment** (i.e. the share) per single pair of eclipsing C – H bonds – about 1 kcal/mol. Remember this value. The molecule, upon  $60^\circ$  changes of the dihedral angle passes from eclipsed to staggered to eclipsed and so on. Learn to draw and understand the potential energy vs. dihedral angle diagrams. Each two consecutive staggered conformations are separated by a higher in energy eclipsed conformation. Therefore, upon rotation, there will be a certain amount of resistance (strain) associated with the transition to an eclipsed conformation – *torsional strain*. The energy required to overcome this resistance (strain) is the *torsional energy* (about 3 kcal/mol in ethane).
  - C. Propane – same analysis, but this time one C – H bond is replaced by a C – CH<sub>3</sub> bond. The eclipsed conformation is even higher in energy – about 3.3 kcal/mol, which gives for the eclipsed interaction of C – H and C – CH<sub>3</sub> a value of 1.3 kcal/mol. Draw the potential energy – dihedral angle diagram.
  - D. Butane – two different C – C bonds. Of interest is the rotation around the central, C<sub>2</sub> – C<sub>3</sub> bond. Four distinct conformations – *totally eclipsed* (dihedral angle between the two C-CH<sub>3</sub> bonds is  $0^\circ$ ), *gauche* ( $60^\circ$ ), *eclipsed* ( $120^\circ$ ) and *anti* ( $180^\circ$ ). Draw the potential energy – dihedral angle for an entire  $360^\circ$  rotation. What are the relative energies of the 4 conformations? Why is the *gauche* higher in energy than the *anti* – because of *steric hindrance* (*van der Waals strain*), which is the interaction of two bulky groups in a close spatial arrangement. Its cost, in the case of the *gauche* conformation of butane is about 0.8 kcal/mol. It is only a fraction of the steric hindrance in the totally eclipsed conformation, which is some 6.1 kcal/mol higher in energy than the *anti*. In the totally eclipsed conformation the energy rise is a combination of *torsional strain* + *steric hindrance*. These two types of strain together comprise the so-called *steric strain*. Its value for butane is 6.1 kcal/mol. Taken into account the fact that three eclipsing bonds contribute a total of about 3 kcal/mol, it follows that the steric hindrance is worth another 3 kcal/mol.
  - E. Higher alkanes – an all-*anti* conformation is the lowest in energy, but in reality partially *anti* and partially *gauche*.

**REMEMBER:** We are talking about energies of the size 3 to 5 kcal/mol. This is low enough so that molecules possess enough energy and the rotations around bonds continue to occur. It just means that some conformations are **preferred** (and thus in higher percentage in the mixture), but are not exclusive, i.e. at any given time butane is a mixture of *anti*, *gauche*, *eclipsed*, *totally eclipsed* and those in-between. But the preferred are *anti* (most) and *gauche*.
3. Structure and conformational analysis of cycloalkanes.
  - A. *Cis-Trans* Isomerism – in a simplified picture, the cycle can be considered as a plain, with an “up” and “down” face. If there are two substituents, and they point towards the same face, then *cis*-isomer; if they point towards opposite faces, *trans*-isomer. Examples.

- B. Stabilities of cycloalkanes – ring strain. All cycloalkanes consist of  $sp^3$ -hybridized carbons ONLY, which implies bond angles of  $109.5^\circ$ . But a closer inspection of cycloalkanes leads to the conclusion that the actual angles, especially in the small cycles (rings) are very far from this value:  $60^\circ$  in cyclopropane,  $90^\circ$  in cyclobutane. This forced contraction of the angles imposes a different type of strain on such systems – *angle strain*. Draw cyclopropane and then draw the hybrid orbitals responsible for the C – C bonds. See for yourself that the angle deviation is significant. On top of the *angle strain*, these systems will have significant *torsional strain* – from the eclipse of C – H bonds (Draw a Newman projection along any of the C – C bonds in cyclopropane or cyclobutane to see the eclipse). Together, the *angle + torsional* strain compound the so-called *ring strain*. How do we measure ring strain – through the heats of combustion. Think of it this way: If you have more energy stored in a particular material, and you burn it, then more heat would be evolved. The ring strain is exactly the extra energy that the molecule might possess, which would be released upon burning. The only thing that should not be forgotten: The evolved energy has to be divided by the number of C – C bonds in the ring, or as people call it, the evolved energy has to be normalized per bond. Then it needs to be compared to the value per bond in a system that has zero ring strain, for which purpose the most convenient would be an open-chain system, since it has, by its very nature, zero ring strain. This performed, it comes out that cyclopropane has the highest ring strain per bond, followed by cyclobutane, cyclopentane and cyclohexane, the latter having zero ring strain. With further increase of the ring size the values tend to vary somewhat irregularly, but in general they change very little from that for cyclohexane. In other words, ring larger than cyclohexane do not really exhibit any substantial increase of the ring strain, regardless of the expected larger and larger deviation from the tetrahedral angle, if those rings were planar. This inconsistency, and the overall trend in the heats of combustion is accounted for by the fact that, with the exception of cyclopropane, all other ring systems are nonplanar.
- C. Cyclopropane – largest ring strain, due to very unfavorable angle strain + large torsional strain. Because of this high ring strain, cyclopropane is chemically different from the other cycloalkanes; it is considerably more reactive, tending to undergo ring-opening reactions. Its molecular structure is effectively described by the so-called *bent* or *banana bonds model*.
- D. Cyclobutane – also unfavorable angle strain, but avoids partially the torsional strain by a slight folding, further contracting the bond angles to  $88^\circ$ .
- E. Cyclopentane – very small angle strain (slight deviation from the ideal  $109.5^\circ$ ) and avoids torsional strain by assuming an “envelope” conformation, which undulates, i.e. the ring carbons undergo successive “up” and “down” motions so that the ring “flap” moves around the ring. Check the Newman projection.
4. Conformational Analysis of Cyclohexane – zero ring strain, by assuming a puckered conformation, in which all angles are  $109.5$  and there are no eclipsing bonds (i.e. torsional strain). It is the so-called *chair* conformation. The *boat* conformation also has  $109.5$  angles, but is higher in energy because of torsional strain, also interference of the “*flagpole*” hydrogens. How does the boat avoid this strain – by assuming a *twist-boat* conformation. The highest in energy is the *half-chair* conformation. Draw the conformational energy diagram of cyclohexane. Make sure you see the advantage of the *chair* vs. *boat* conformation, or the *twist-boat* vs. *boat* conformation.

The complete energy diagram describes the transition from chair, through half-chair, to twist boat, which, through a boat, is converted to the other twist boat, the latter, via the other half-chair, eventually goes to the other chair. This process is continuous, known as the chair-chair interconversion.

If you take a closer look at the chair you will see that there are two types of hydrogens. Through the center of the chair passes a vertical axis of symmetry. Six of the hydrogen atoms, one per carbon, have their bonds parallel to this axis – *axial* hydrogens. The other six (one per carbon) are called *equatorial*. An important issue eventually becomes how to draw

these bonds (and hydrogens) “up” and “down”. Here is an easy way: It is not difficult to see that the axial C–H bonds point either up or down, and they alter, i.e. up, down, up, etc. It is more difficult with the equatorial. But remember this: If the axial bond at a particular carbon is UP, then the equatorial bond at the same carbon has to be DOWN. Remember and practice this, as it will be very important when it comes to writing various disubstituted *cis*- or *trans*-isomers. Learn to properly draw chairs and boats; you will find it very useful in the future.

5. Substituted Cyclohexanes.

- A. Monosubstituted cyclohexanes – the substituent could be axial or equatorial. Which is more stable and why – the chair with substituent in equatorial position, since this avoids TWO unfavourable gauche interactions of the substituent with methylene groups from the ring. If the substituent is methyl, then according to our earlier analysis of butane, such gauche interaction is associated with about 0.8 kcal/mol energy rise. For two interactions it would be 1.6 kcal/mol.
- B. Disubstituted cyclohexanes – there are several possibilities:
- a) Cis-1,2-disubstituted – one axial and one equatorial group;
  - b) Trans-1,2-disubstituted – two axial OR two equatorial. Which is more stable and why?
  - c) Cis-1,3-disubstituted – two axial OR two equatorial groups. Which is more stable and why?
  - d) Trans-1,3-disubstituted – one axial and one equatorial;
  - e) Cis-1,4-disubstituted – one axial and one equatorial;
  - f) Trans-1,4-disubstituted – two axial or two equatorial groups. Which is more stable and why?

Consider the case of differently -sized substituents. The bulkier always is preferably equatorial!!

Two additional points of attention here: 1) Learn to draw and recognize the *cis*- and *trans*-isomers in a “flat” (i.e. two-dimensional) drawing, in which they are represented by solid or dashed wedges. 2) Consider the case of very bulky groups in axial positions – how can this change the entire conformation of the system, in order for the bulky group to avoid the unfavorable interactions.

6. Bicyclic Systems – they can be *fused*, *bridged* and *spirocyclic*. Nomenclature. *Cis*- and *trans*-decalin.

- A. Spirocyclic – two rings share a single carbon atom.
- B. Fused – two rings share two adjacent carbon atoms.
- C. Bridged – two rings share two non-adjacent carbon atoms.

7. Heterocyclic Systems – if there is a non-carbon atom present in the ring, then it is a heterocyclic compound. They could involve O, S, N or other *heteroatoms* (i.e. atoms different from carbon).