## Lectures 4 \& 5: Alkanes Continued!

I. Stereochemistry of Open-Chain Alkanes
A. Representing alkanes in 3D
B. Conformational analysis

1. Ethane
2. Propane
3. Butane
II. Cycloalkanes
A. Properties
B. Nomenclature

C. Stereochemisty
D. Ring size and strain (cyclopropane, cylcobutane, cyclopentane)
E. Cyclohexane

## Conformational Energy of Ethane

The energy changes continuously as a function of the torsion angle. We represent this on a plot called the potential energy diagram .

The length of time that a molecule resides in one conformational minimum is determined by the barrier height ( $\square \mathrm{G}^{\neq}$).

Image removed due to copyright reasons.

Barrier to rotation $=\mathrm{E}_{\text {highest }}-\mathrm{E}_{\text {lowest }}=2.9 \mathrm{kcal} / \mathrm{mol}$

## Why is Staggered Form Lower in Energy?

One explanation for the lower energy of staggered ethane is that the staggered conformer is stabilized by hyperconjugation (stabilizing overlap between $\square$ сн and $\square^{*}$ сн orbitals that does not occur in the eclipsed conformer).


A second explanation for the lower energy of the staggered ethane conformer is that electronelectron repulsion between the $\mathrm{C}-\mathrm{H}$ bonds is occurring in the eclipsed conformer (same principles as VSEPR theory), which destabilizes it.

Please see the following articles for further information:
Weinhold, F. Nature 2001, 411, 539-541.
Bickelhaupt F. M.; Baerends, E. V. Angew. Chem. Int. Ed. 2003, 42, 4183-4188. (rebuttal)
Weinhold, F. Angew. Chem. Int. Ed. 2003, 42, 4188-4194. (re-rebuttal) and others . . .

## Conformational Energy of Butane

For ethane, each conformational minimum has an identical structure, and thus, the same energy (all the stable conformers are equally populated).

The situation is different for butane.


The conformational maxima and minima of butane have different energies!

## Conformational Analysis Summary

Torsional energy - higher energy associated with eclipsed conformation
Torsional strain - resistance to rotating to an eclipsed conformation (eclipsed ethane is torsionally strained by $3 \mathrm{kcal} / \mathrm{mol}$ )

Steric strain - repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow

Gauche - spatial relationship with a $60^{\circ}$ torsion (dihedral) angle
Anti - spatial relationship with a $180^{\circ}$ torsion angle
Interactions
H-H eclipsing (torsional strain) $\quad 1.0 \mathrm{kcal} / \mathrm{mol}$
H-Me eclipsing (mostly torsional strain) $\quad 1.4 \mathrm{kcal} / \mathrm{mol}$
$\mathrm{Me}-\mathrm{Me}$ eclipsing (steric and torsional strain) $\quad 2.6 \mathrm{kcal} / \mathrm{mol}$
Me-Me gauche interaction (steric strain) $\quad 0.9 \mathrm{kcal} / \mathrm{mol}$

## Naming Cycloalkanes

1. Find parent (ring or chain, depending on which is larger)
2. Label point of attachment of alkyl, halo, etc. as C1
3. Continue numbering so that the second substitutent is the lowest possible number
4. If 2 or more alkyl groups could potentially get the same number, use alphabetical order as a tie-breaker

## Ring Inversion (Flipping) of Cyclohexane



Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

## Atomic Motions Involved in Ring Inversion



Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

## Drawing Cyclohexane Chairs

Steps 1-3: Draw three pairs of parallel lines as shown

$$
\mid \rightarrow \underset{(1)}{ } \rightarrow \underset{(2)}{ }
$$

(3)
Steps 4-6: Draw equatorial bonds parallel to ring bonds in bold

$$
\underset{\substack{\text { (5) }}}{\sim}
$$

Steps 7,8: Draw axial bonds as vertical lines below and above ring.



- Interconverts equatorial and axial substituents.
- Energetic barrier = $10 \mathrm{kcal} / \mathrm{mol}$; occurs rapidly at room temperature.


| A-Values to Remember |  |
| :--- | :---: |
| -X | A-Value |
| $-\mathrm{CH}_{3}$ | 1.74 |
| $-\mathrm{CH}_{2} \mathrm{CH}_{3}$ | 1.8 |
| $\left.-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)_{2}$ | 2.1 |
| $-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}$ | 5.4 |
| -CN | 0.2 |
| -OH | 1.0 |
| -Cl | 0.5 |
| -Br | 0.6 |
| A-Value $=$ magnitude of |  |
| equatorial preference |  |

## Di-Substituted Cyclohexane: Which Conformer is Preferred?

1. Try to place all substituent equatorial.

2. If you can't, place the substituent with the largest $A$-value equatorial.

