

## Lectures 4 & 5: Alkanes Continued!

### I. Stereochemistry of Open-Chain Alkanes

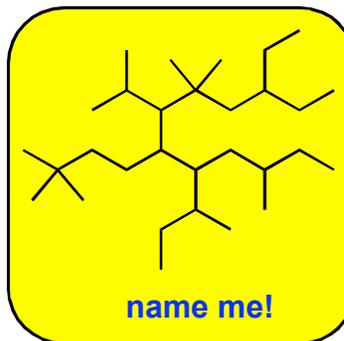
#### A. Representing alkanes in 3D

#### B. Conformational analysis

1. Ethane
2. Propane
3. Butane

### II. Cycloalkanes

- A. Properties
- B. Nomenclature
- C. Stereochemistry
- D. Ring size and strain (cyclopropane, cyclobutane, 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.

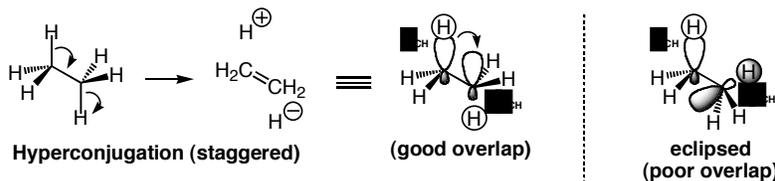
The length of time that a molecule resides in one conformational minimum is determined by the barrier height ( $\Delta G^\ddagger$ ).

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

## 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  $\sigma_{\text{C-H}}$  and  $\sigma^*_{\text{C-H}}$  orbitals that does not occur in the eclipsed conformer).



A second explanation for the lower energy of the staggered ethane conformer is that **electron-electron repulsion** between the C-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)

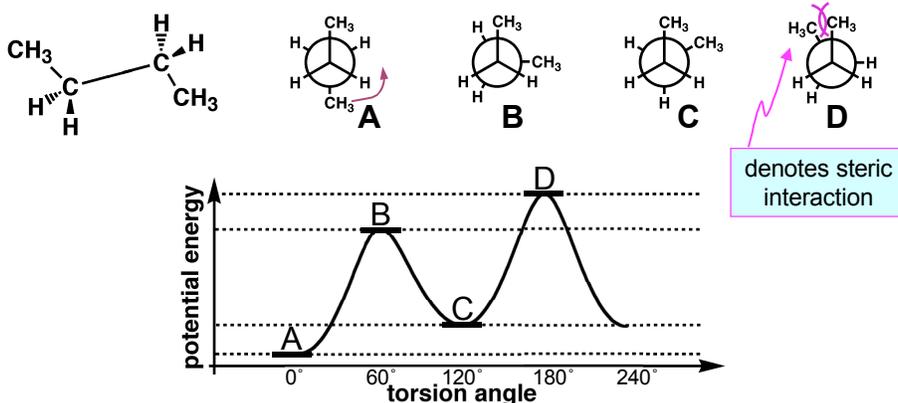
Weinhold, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 4188-4194. (re-rebuttal)

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!

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## 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 kcal/mol)

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

**Gauche** - spatial relationship with a 60° torsion (dihedral) angle

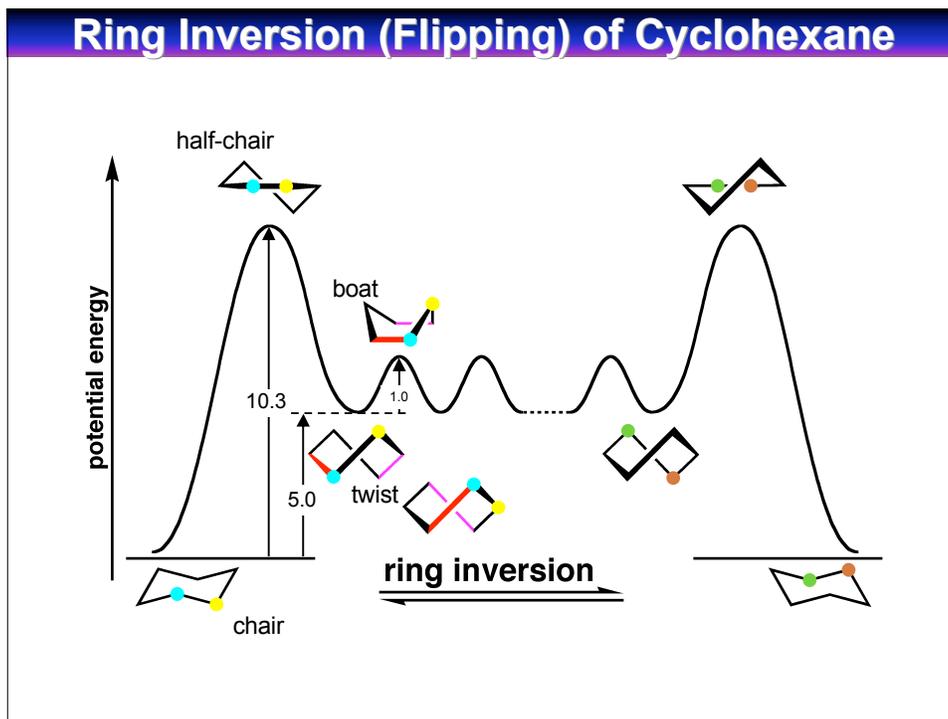
**Anti** - spatial relationship with a 180° torsion angle

### **Interactions**

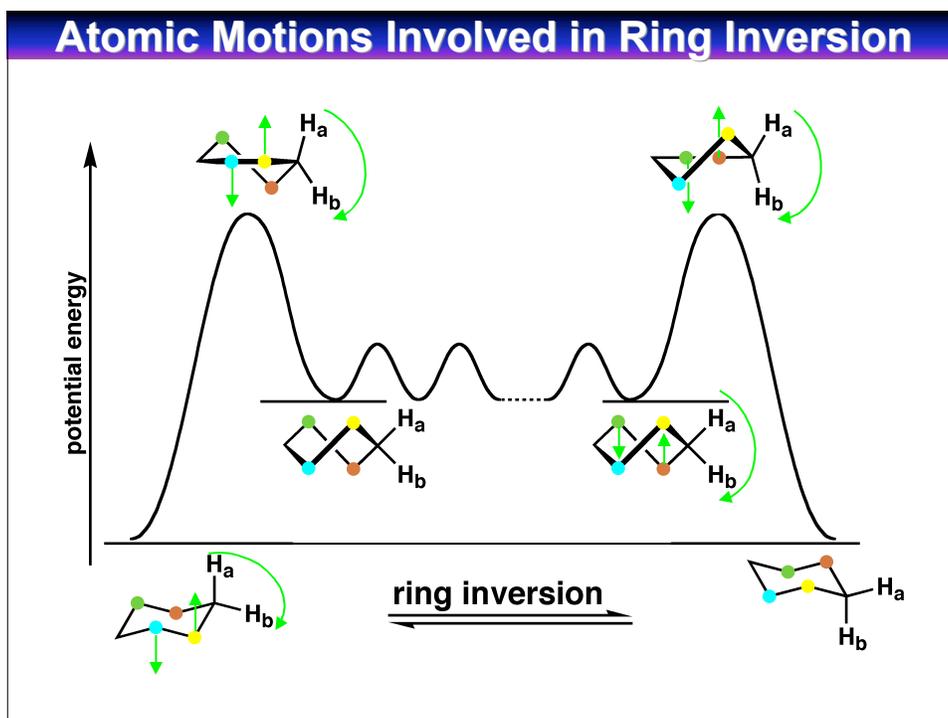
H-H eclipsing (torsional strain)	1.0 kcal/mol
H-Me eclipsing (mostly torsional strain)	1.4 kcal/mol
Me-Me eclipsing (steric and torsional strain)	2.6 kcal/mol
Me-Me gauche interaction (steric strain)	0.9 kcal/mol

## 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 substituent 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



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