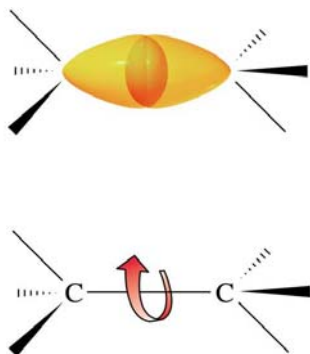## 2.10 Conformations of Alkanes:
### rotation about carbon-carbon bonds

For any $\sigma$–bond:

Overlap of end-on overlapping orbitals is not diminished by rotation about the internuclear axis
⇨ rotation about a single bond does NOT break the bond
⇨ the energy barrier to rotation is quite small

**At room temperature:**
**single bonds rotate freely!**

Fig.2.3

(1)

## Conformations

= different 3D arrangements of the atoms within the molecule **due to rotation around single bonds**

• different conformations = **rotational isomers**
**conformational isomers**
**"conformers"**

**For ethane:**

Rotate about C-C bond

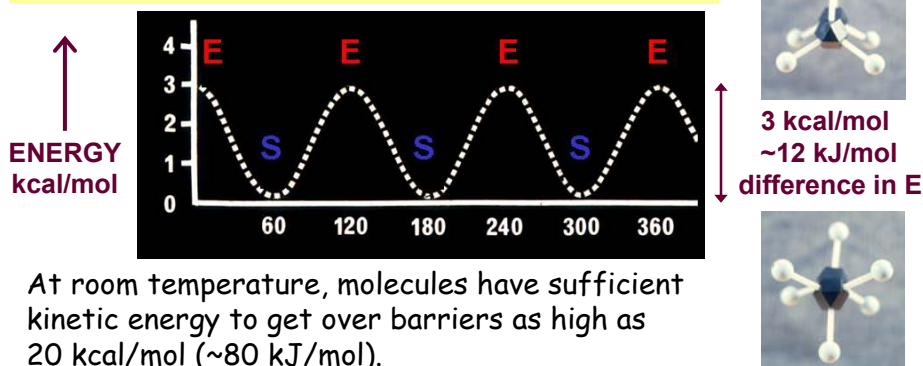keep rotating
(total of 60° from eclipsed)

**ECLIPSED**
all C-H bonds lined up:
• bonding e⁻s repel each other
• produces "torsional strain"

maximum energy conformation

**STAGGERED**
bonding electrons as far apart as possible

lowest E conformation

(2)

**ENERGY
kcal/mol**

**3 kcal/mol
~12 kJ/mol
difference in E**

At room temperature, molecules have sufficient
kinetic energy to get over barriers as high as
20 kcal/mol (~80 kJ/mol).

⇨ at R.T., have constant rotation around C-C bonds
(and all other single bonds) → conformational flexibility

However: molecules spend most of their time in the more
stable (energetically favorable) *staggered* conformations.

(3)

---

**Newman projections: looking down a C-C bond...**



If we look
this way
down the
C-C bond...
...we'll see ⇨

**Perspective
drawing**
of staggered
conformation
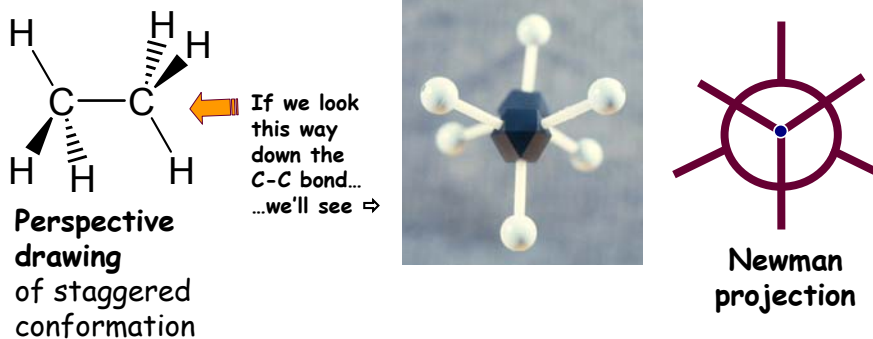
**Newman
projection**

**A Newman projection:** a view of a molecule down the axis
of a carbon-carbon bond

→ **the carbon in the front = the point where the 3 bonds intersect**
→ **the carbon in the back = a circle**
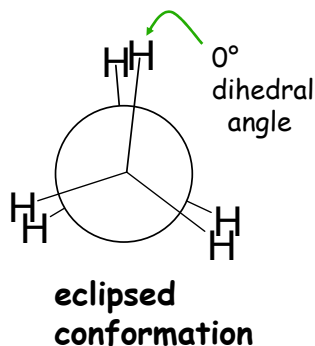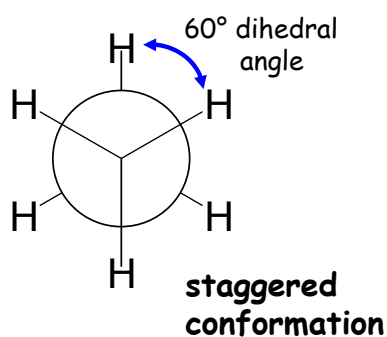
Helps visualize interactions within the molecule...

(4)

Visualize **spatial relationship between atoms bonded to adjacent carbon atoms**
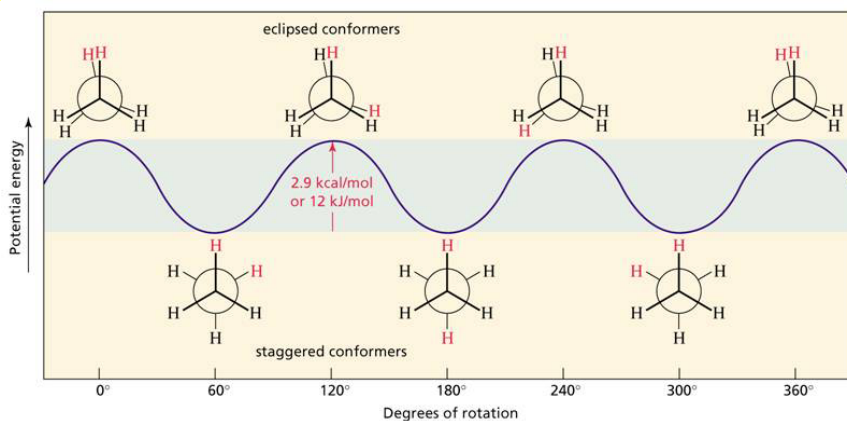→ get feeling for torsional strain in different conformers
→ predict which conformation most molecules will adopt!

**Dihedral angle** ($\theta$) = angle between groups on adjacent carbon atoms as viewed in the Newman projection formula.
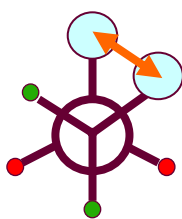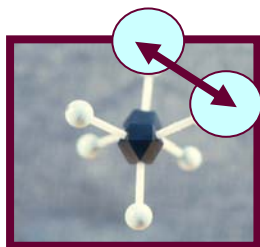


60° dihedral angle

**staggered conformation**

0° dihedral angle

**eclipsed conformation**

(5)

## Different Conformations of Ethane



eclipsed conformers

2.9 kcal/mol or 12 kJ/mol

staggered conformers

Potential energy

0°    60°    120°    180°    240°    300°    360°

Degrees of rotation

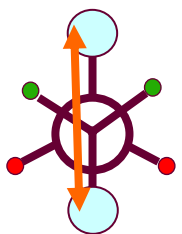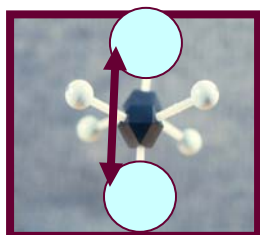• A staggered conformer is more stable than an eclipsed conformer
• Torsional strain: repulsion between pairs of bonding electrons

(6)

**60° dihedral angle**
   between these two positions

Interaction between them
   = a **"gauche" interaction**
→ introduces **"steric strain"**
   *repulsion of electron clouds*
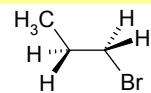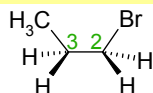   *of these groups*

**180° dihedral angle**
   between these positions

Interaction between them
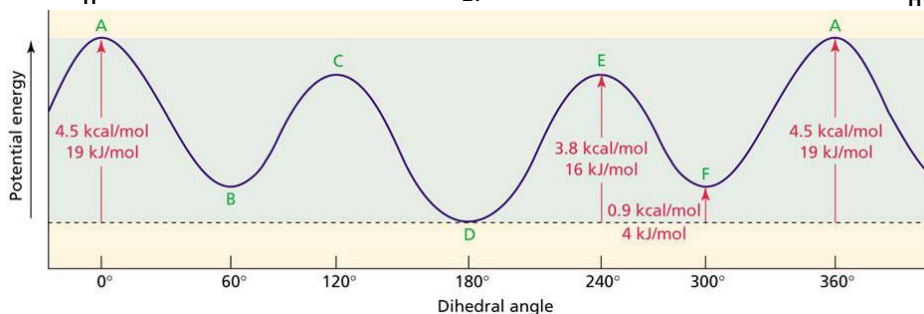= an **"anti" interaction**

→ **very little steric strain**

(7)

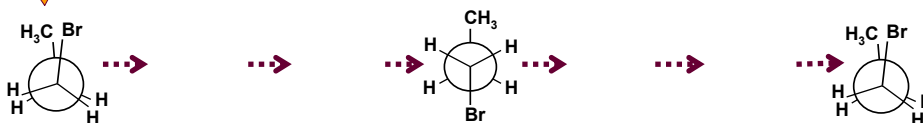Perspective view of
an eclipsed conformer

$H_3C$    Br
H""''32""''H
H    H

$H_3C$    H
H    H
H    Br

Perspective view of
a staggered conformer
(the *anti* conformer)

Newman
projection
down C2-C3

$H_3C$ Br
H   H
   H

$CH_3$
H   H
H   H
   Br

$H_3C$ Br
H   H
   H

A    C    E    A

Potential energy

4.5 kcal/mol
19 kJ/mol

3.8 kcal/mol
16 kJ/mol

4.5 kcal/mol
19 kJ/mol

B    D    F

0.9 kcal/mol
4 kJ/mol

0°    60°    120°    180°    240°    300°    360°

Dihedral angle

**Bruice Fig.2.5** – for butane's conformations, looking down C2-C3 bond
→ $CH_3$-Br steric repulsions not exactly same as $CH_3$-$CH_3$, but same general trend

## 2.11  Cycloalkanes:  Ring Strain

• Angle strain results when bond angles deviate from the ideal 109.5° bond angle

→ destabilization due to decrease in efficiency of orbital overlap
→ $\sigma$-bonds *should* be straight,  not bent like a banana !

more stable          less stable
stronger…            weaker…

good overlap         poor overlap
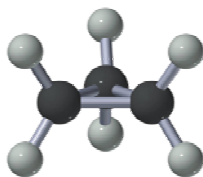strong bond          weak bond
(a)                  (b)

banana bonds

(9)

## Conformations of Cycloalkanes:  $C_nH_{2n}$

MOST STABLE CONFORMATIONS = puckered, in order to minimize
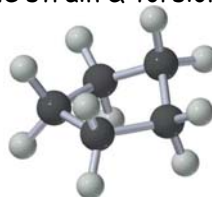angle strain & torsional strain

**cyclopropane**
*Cannot pucker*
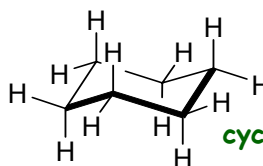*Cannot avoid angle strain*
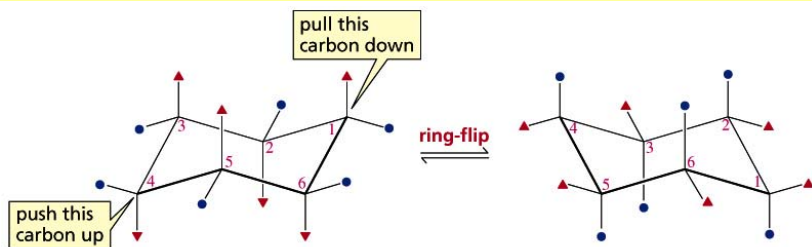→ *Highly reactive !*

**cyclobutane**

**cyclopentane**

banana bonds

H H H H H H H H H H H H H H H H H H H
**cyclohexane**

(10)

## "Ring Flipping" in Cyclohexane: chair-chair interconversion

pull this carbon down
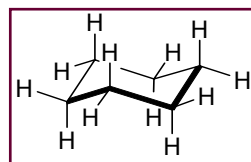


ring-flip

push this carbon up

"axial"
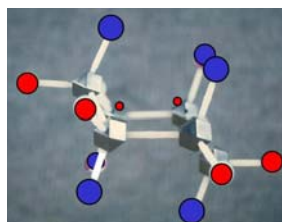
"equatorial"

"axial"

(11)

## CYCLOHEXANE:   the chair conformation

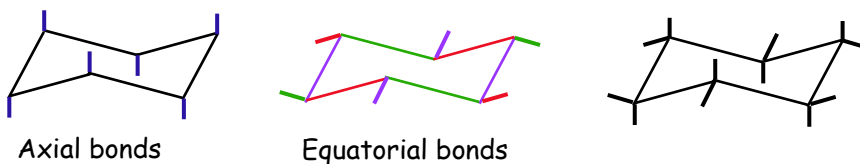1st: Draw parallel lines



2nd: Connect the lines with lop-sided shallow "V"s
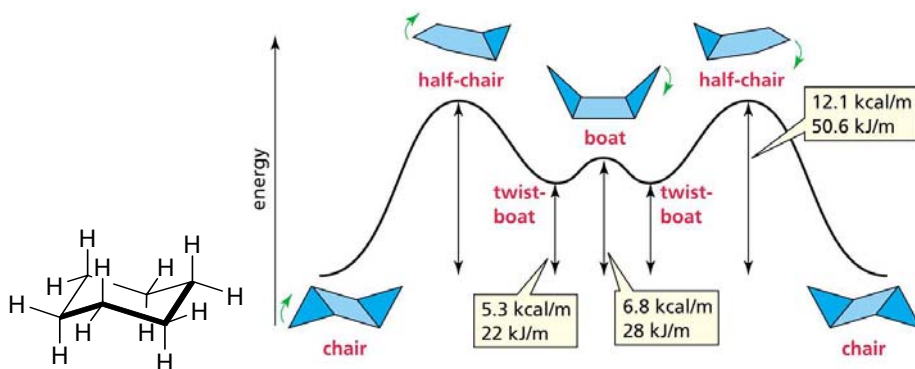(or…make parallel lines to outline seat, then connect to head & toe)

3rd:  Add axial & equatorial bonds:  1 of each on each carbon
(axial point straight up/down; equatorial off to the sides…)

Axial bonds          Equatorial bonds

(12)

energy

half-chair    boat    half-chair

12.1 kcal/m
50.6 kJ/m

twist-boat    twist-boat

5.3 kcal/m
22 kJ/m

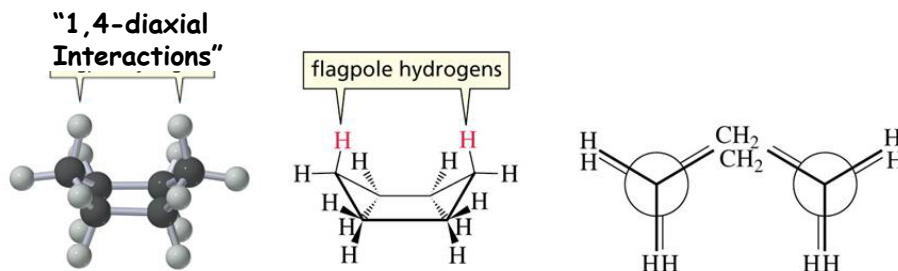6.8 kcal/m
28 kJ/m

chair    chair

(13)

**Torsional and steric strain in cyclohexane:**    Bruice
Fig.2.9

Why is the **BOAT conformation** so unstable?
1.)  lots of eclipsed bonds (torsional strain)
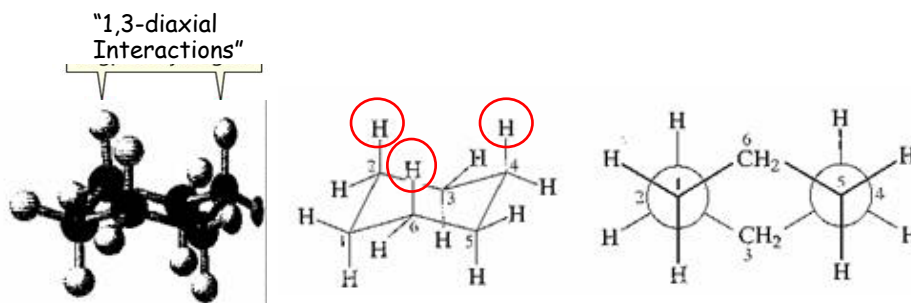2.) 1,4-diaxial interactions (H-H steric strain)

**"1,4-diaxial
Interactions"**



flagpole hydrogens

(14)

Why is the **CHAIR conformation** so stable?
  1.) no eclipsed bonds (minimal torsional strain)
  2.) no major steric interactions:
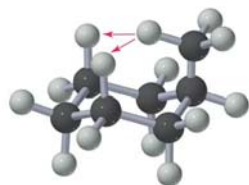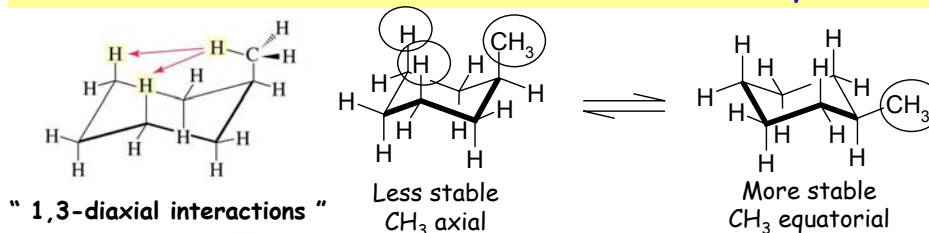        H-R gauche interactions = very minor
        H-H "1,3-diaxial interactions" = very minor

Bruice
Fig.2.7

"1,3-diaxial
Interactions"

(15)

## 2.13 Substituted cyclohexanes
**increased steric interactions: 2 chair confo's not necessarily same E**

" 1,3-diaxial interactions "

Less stable
CH$_3$ axial

More stable
CH$_3$ equatorial

BULKIER SUBSTITUENTS PREFER
TO SIT IN EQUATORIAL POSITIONS
 because of fewer steric interactions

⇨ Less strain → increased stability
⇨ in a sample:  most of the molecules will adopt
            the most stable conformation
⇨ can predict most likely way molecules will look!
⇨ useful for predicting reactivity later…
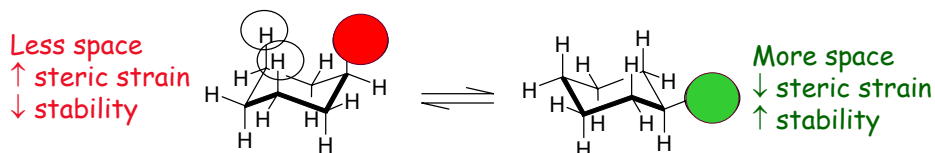
(16)

## Larger substituents prefer equatorial positions

Less space
↑ steric strain
↓ stability



More space
↓ steric strain
↑ stability

| Table 2.10 | Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C | | | | |
|---|---|---|---|---|---|
| Substituent | Axial $\xrightleftharpoons{K_{eq}}$ Equatorial | | Substituent | Axial $\xrightleftharpoons{K_{eq}}$ Equatorial | |
| H | 1 | | CN | 1.4 | |
| $CH_3$ | 18 | | F | 1.5 | |
| $CH_3CH_2$ | 21 | | Cl | 2.4 | |
| $CH_3\overset{CH_3}{\underset{}{CH}}$ | 35 | | Br | 2.2 | |
| | | | I | 2.2 | |
| $CH_3\overset{CH_3}{\underset{CH_3}{C}}$ | 4800 | | HO | 5.4 | |

$K_{eq} = \dfrac{[R\ equatorial]}{[R\ axial]}$

larger $K_{eq}$
⇨ eq. preferred

Good way to get
a feeling for
"steric bulk"

(17)

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## ASSIGNED READINGS

### BEFORE NEXT LECTURE:

**Read:**          rest of Ch.2

**Practice:**     drawing cyclohexane & ring flipping

(18)