Handout #4, 5.12 Spring 2003, 2/14/02
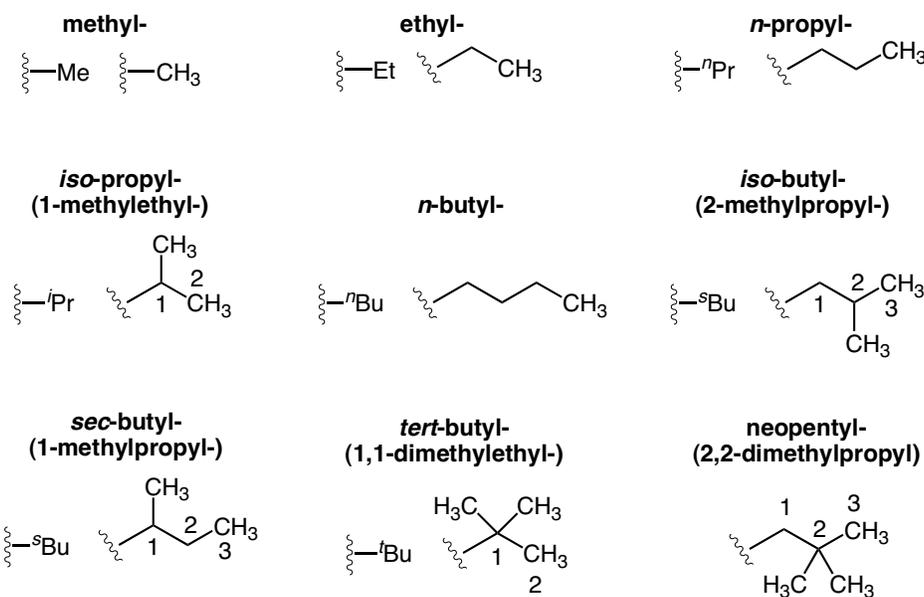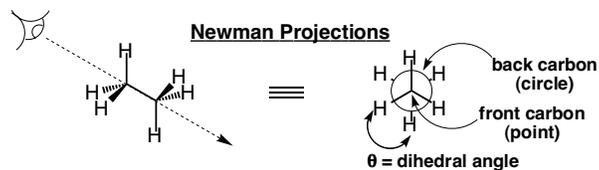## Alkanes: Nomenclature and Conformational Analysis

Formula (C_nH_{2n+2})	Name n-Alkane	Substituent	Name n-Alkyl	# Constitutional Isomers
CH_4	methane	$-CH_3$ (**–Me**)	methyl	1
C_2H_6	ethane	$-C_2H_5$ (**–Et**)	ethyl	1
C_3H_8	propane	$-C_3H_7$ (**–^{n}Pr**)	propyl	1
C_4H_{10}	butane	$-C_4H_9$ (**–^{n}Bu**)	butyl	2
C_5H_{12}	pentane	$-C_5H_{11}$	pentyl	3
C_6H_{14}	hexane	$-C_6H_{13}$	hexyl	5
C_7H_{16}	heptane	$-C_7H_{15}$	heptyl	9
C_8H_{18}	octane	$-C_8H_{17}$	octyl	18
C_9H_{20}	nonane	$-C_9H_{19}$	nonyl	etc.
$C_{10}H_{22}$	decane	$-C_{10}H_{21}$	decyl	
$C_{11}H_{24}$	undecane	$-C_{11}H_{23}$	undecyl	
$C_{12}H_{26}$	dodecane	$-C_{12}H_{25}$	dodecyl	
$C_{13}H_{28}$	tridecane	$-C_{13}H_{27}$	tridecyl	
$C_{14}H_{30}$	tetradecane	$-C_{14}H_{29}$	tetradecyl	
$C_{15}H_{32}$	pentadecane	$-C_{15}H_{31}$	pentadecyl	

Constitutional Isomers
(Be able to recognize these common fragments.)

methyl-

ethyl-

n-propyl-

***iso*-propyl-**
(1-methylethyl-)

n-butyl-

***iso*-butyl-**
(2-methylpropyl-)

***sec*-butyl-**
(1-methylpropyl-)

***tert*-butyl-**
(1,1-dimethylethyl-)

neopentyl-
(2,2-dimethylpropyl)

Conformational Analysis: The Fundamentals

Newman Projections

back carbon (circle)

front carbon (point)

θ = dihedral angle
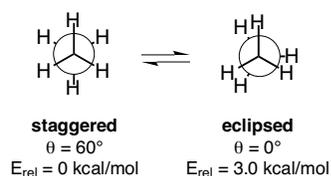
Barrier to Rotation: torsional energy; energy required to twist a bond into a specific conformation;
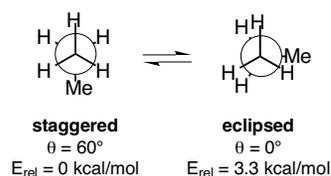Barrier to Rotation = E_{rel} (highest energy conformer) – E_{rel} (lowest energy conformer)

Ethane

staggered	**eclipsed**
θ = 60°	θ = 0°
E_{rel} = 0 kcal/mol	E_{rel} = 3.0 kcal/mol

Barrier to Rotation = 3.0 – 0 = 3.0 kcal/mol

➤ H/H-eclipsing = 1.0 kcal/mol

Propane

staggered	**eclipsed**
θ = 60°	θ = 0°
E_{rel} = 0 kcal/mol	E_{rel} = 3.3 kcal/mol

Barrier to Rotation = 3.3 – 0 = 3.3 kcal/mol

➤ H/Me-eclipsing = 1.3 kcal/mol

Butane

fully eclipsed	**gauche**	**eclipsed**	**anti**
(eclipsed)	(staggered)	(eclipsed)	(staggered)
$\theta_{Me/Me}$ = 0°	$\theta_{Me/Me}$ = 60°	$\theta_{Me/Me}$ = 120°	$\theta_{Me/Me}$ = 180°
E_{rel} = 6.0 kcal/mol	E_{rel} = 0.9 kcal/mol	E_{rel} = 3.6 kcal/mol	E_{rel} = 0 kcal/mol
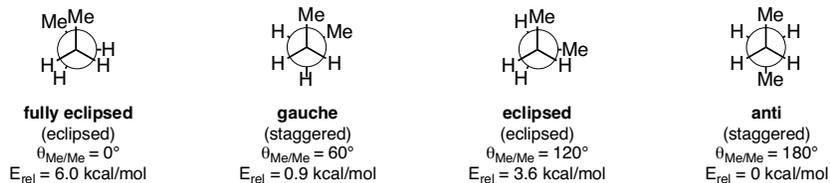
Barrier to Rotation = 6.0 – 0 = 6.0 kcal/mol

➤ Me/Me-eclipsing = 4.0 kcal/mol*

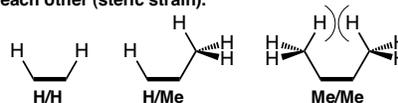➤ Gauche Butane Interaction (gbi) = 0.9 kcal/mol

Numbers to Remember

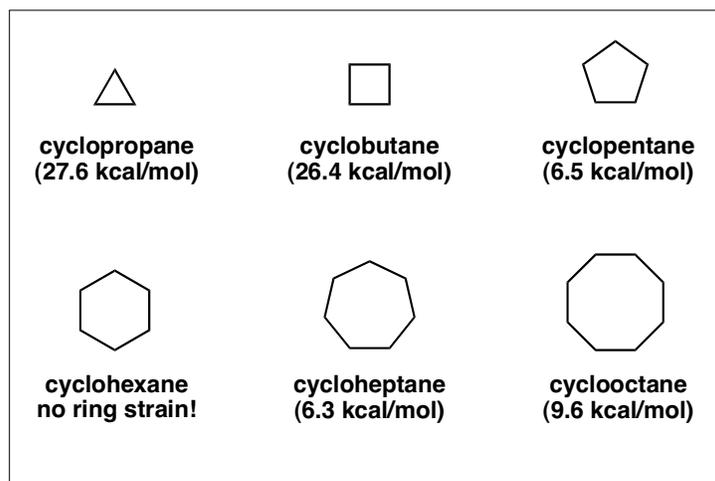H/H-eclipsing = 1.0 kcal/mol

H/Me-eclipsing = 1.3 kcal/mol

Me/Me-eclipsing = 4.0 kcal/mol*

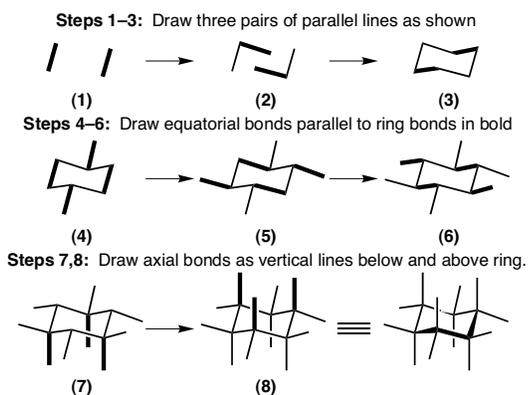Gauche Butane (gbi) = 0.9 kcal/mol

* In Wade, a Me/Me-eclipsing interaction is said to be worth 3.0 kcal/mol. Either value will be acceptable in this class, but most other sources assign the value of 4.0 kcal/mol. A Me/Me-eclipsing interaction is significantly higher than an H/H- or H/Me-eclipsing interaction because the hydrogens on the two methyl groups can actually bump into each other (steric strain).
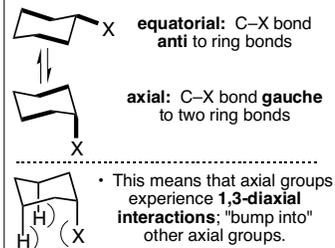

H/H   **H/Me**   **Me/Me**

Cycloalkanes: Names and Ring Strain

cyclopropane
(27.6 kcal/mol)

cyclobutane
(26.4 kcal/mol)

cyclopentane
(6.5 kcal/mol)

cyclohexane
no ring strain!

cycloheptane
(6.3 kcal/mol)

cyclooctane
(9.6 kcal/mol)

Drawing Cyclohexane Chairs

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

(1)   **(2)**   **(3)**

Steps 4–6: Draw equatorial bonds parallel to ring bonds in bold

(4)   **(5)**   **(6)**

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

(7)   **(8)**   ≡

Ring Flip

- **Interconverts equatorial and axial substituents.**
- **Energetic barrier = 10 kcal/mol; occurs rapidly at room temperature.**

Substituted Cyclohexane

equatorial: C–X bond **anti** to ring bonds

axial: C–X bond **gauche** to two ring bonds

- This means that axial groups experience **1,3-diaxial interactions**; "bump into" other axial groups.

- **EQUATORIAL PREFERRED**

A-Values to Remember

–X	A-Value
–CH$_3$	1.74
–CH$_2$CH$_3$	1.8
–CH(CH$_3$)$_2$	2.1
–C(CH$_3$)$_3$	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 substituents equatorial.
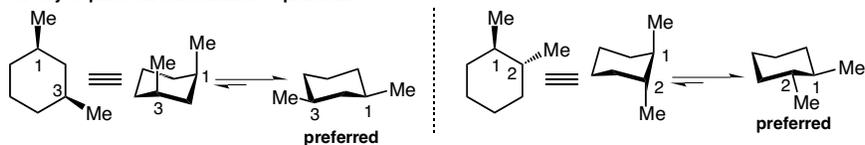
2. If you can't, place the substituent with the largest A-value equatorial.
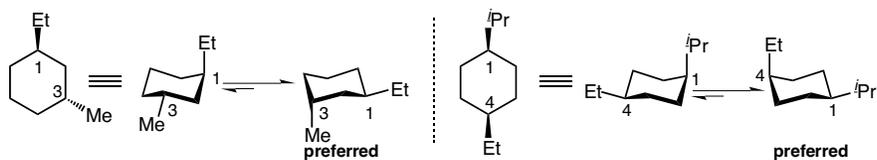
REMEMBER: Midterm #1 is Friday, February 21, in Walker. It will cover reading and lecture material through Tuesday, February 18. This means that not all of the material on this handout will be covered on the exam.