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Organic Chemistry I, CHM 3140, Dr. Laurie S. Starkey

Klein Chapter 4: Alkanes & Cycloalkanes

Chapter Outline

1) Nomenclature (alkanes & cycloalkanes: 4.1, 4.2, alky halides: 7.2)
2) Isomers (4.3), Molecular Formula, Degrees of Unsaturation/HDI (14.16)
3) Physical Properties, Source and Use of Alkanes (4.5)
4) Conformations (4.6, 4.7, 4.8)
5) Cycloalkanes (4.9, 4.14, 4.15)
   A) Cyclohexane (4.10 to 4.13)

skip section 4.4 & SkillBuilder 4.5

1) Alkane Nomenclature (4.2)

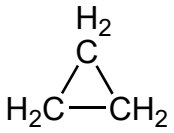
Alkanes are **saturated hydrocarbons** (only carbon and hydrogen, and with the maximum number of hydrogens - so no pi bonds, only sigma/single bonds)

alkane formula: $\mathbf{C_nH_{2n+2}}$

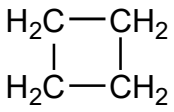
CH_4	methane	CH_4	C_5H	pentane	C_8H	octane
CH_3CH_3	ethane	C_2H_6	C_6H	hexane	C_9H	nonane
$CH_3CH_2CH_3$	propane	C_3H_8	C_7H	heptane	$C_{10}H$	decane
$CH_3(CH_2)_2CH_3$	butane	C_4H__				

line drawing for decane:

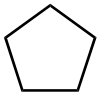
cycloalkane formula: $\mathbf{C_nH_{2n}}$

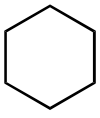


cyclopropane



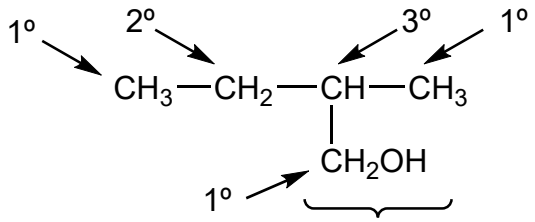
cyclobutane





Types of carbons

primary (1º)	attached to one carbon
secondary (2º)	attached to two carbons
tertiary (3º)	attached to three carbons
quaternary (4º)	attached to four carbons



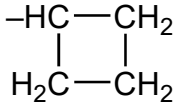
described as a primary alcohol (1º ROH)

IUPAC Rules for naming alkanes

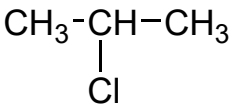
1. Find the longest carbon chain (if there is a tie, choose chain with the most substitutents). Name parent (one C = methane, two C's = ethane, three C's = propane, etc.).
2. Number the carbon chain, starting from the end closest to the first substituent.
3. Name and number the substituents (use di, tri, tetra, etc., prefixes for groups that appear more than once). Insert dashes between numbers and letters, and commas between numbers
4. Alphabetize* and list substituents before the parent name. *Ignore all prefixes other than iso.

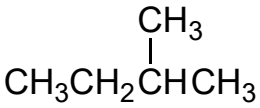
Alkyl Substituents (R–)
(groups attached to parent)

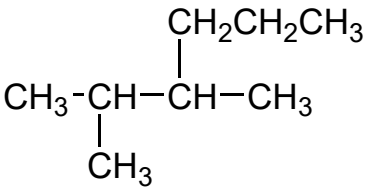
$–CH_3$	methyl (Me)
$–CH_2CH_3$	ethyl (Et)
$–CH_2CH_2CH_3$	propyl (Pr)
$–CH_2(CH_2)_2CH_3$	butyl (Bu)

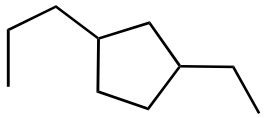


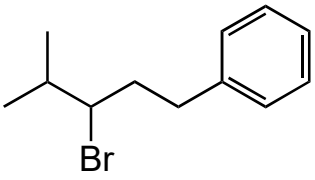
cyclobutyl

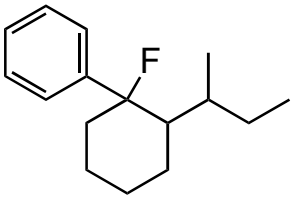


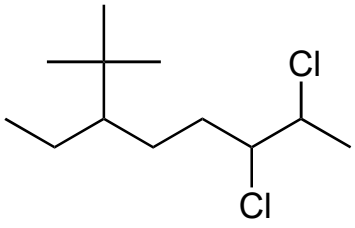












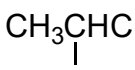
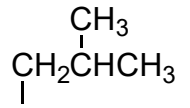
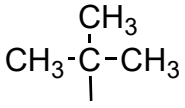
Other Substituents
(groups attached to parent)

–F	fluoro
–Cl	chloro
–Br	bromo
–I	iodo

phenyl

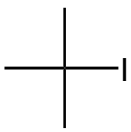
Note: phenyl is described as an aryl (Ar–) group since benzene is described as an "aromatic" compound

Common names for alkyl groups

$–CH_2CH_2CH_3$	*n*-propyl (*n*-Pr)
	isopropyl (*i*-Pr)
$–CH_2(CH_2)_2CH_3$	*n*-butyl (*n*-Bu)
	sec-butyl (*s*-Bu)
	isobutyl (*i*-Bu)
	*tert*-butyl (*t*-Bu)

sec-butyl alcohol

n-propyl alcohol



see SkillBuilders 4.1, 4.2, 4.3, 4.4

2) Molecular Formula and Degrees of Unsaturation (14.16) to Draw Isomers (4.3)

"saturated" alkane formula: $\mathbf{C_nH_{2n+2}}$

want to add a ring?

want to add a π bond?

every 2 missing H's = a degree/site of unsaturation (DU) (aka HDI, hydrogen deficiency index)

Determine the DU

C_9H_{16} $C_6H_{11}OCl$ 

How is DU helpful? Draw isomers of $\mathbf{C_5H_{12}}$

see SkillBuilder 4.6

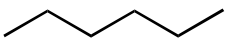
3) Physical Properties (4.4, 4.5)

- nonpolar, hydrophobic

- isolated from petroleum/oil

- fairly unreactive (all strong σ bonds, no π bonds or lone pairs)
  - used a fuel

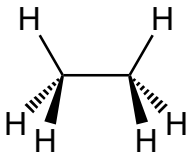
  - can undergo free-radical halogenation (R-H $\rightarrow$ R-Br, Klein Chapter 10)

	$CH_3CH_2CH_3$		$C_{31}H_{64}$	Overall trend:
bp ºC	- 42	69	> 300	

4) Conformations of Alkanes (4.6, 4.7)

conformers - structures that differ only by rotation about single/sigma (σ) bonds
(con**form**ers are different **forms** of the same molecule - they are interconvertible)

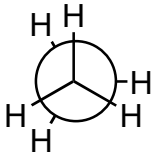
Ethane



60º rotation ⇌

rapidly interconverting conformers (~1,000,000 times/second!)

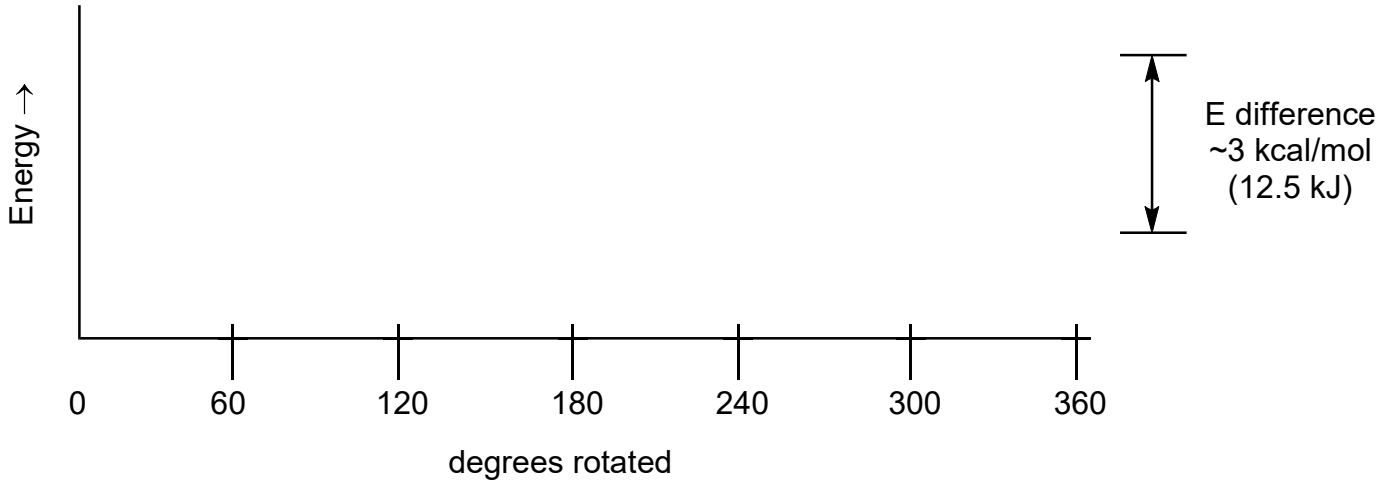
Newman Projection (view down a C-C bond)



60º rotation ⇌

eclipsed conformation is higher/lower in energy than staggered

due to "torsional strain" (a resistance to twisting)

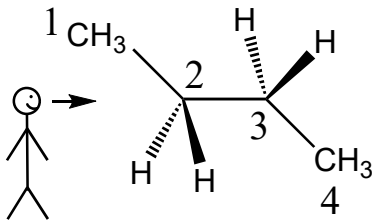


see SkillBuilders 4.7, 4.8

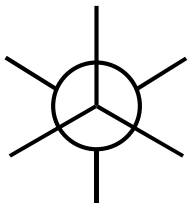
Conformations of Butane (4.8)

$CH_3-CH_2-CH_2-CH_3$

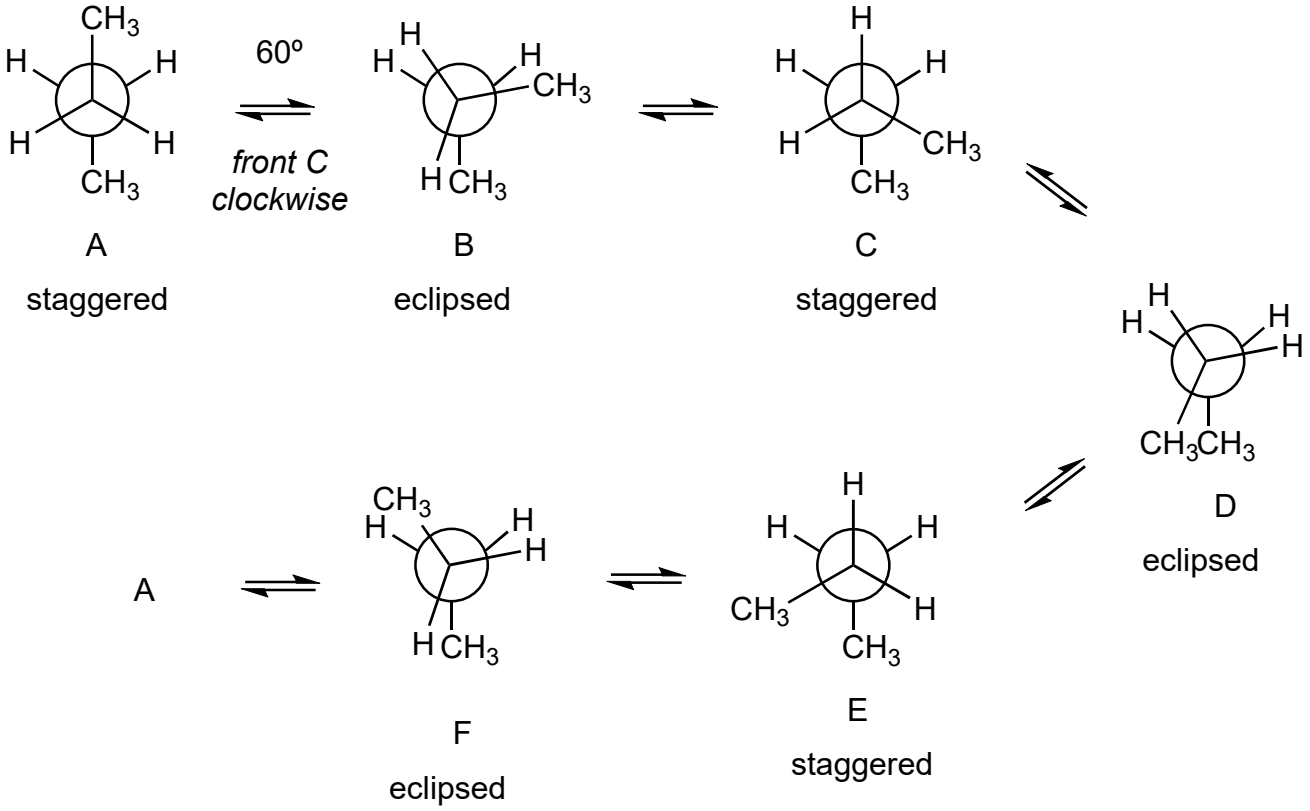
butane

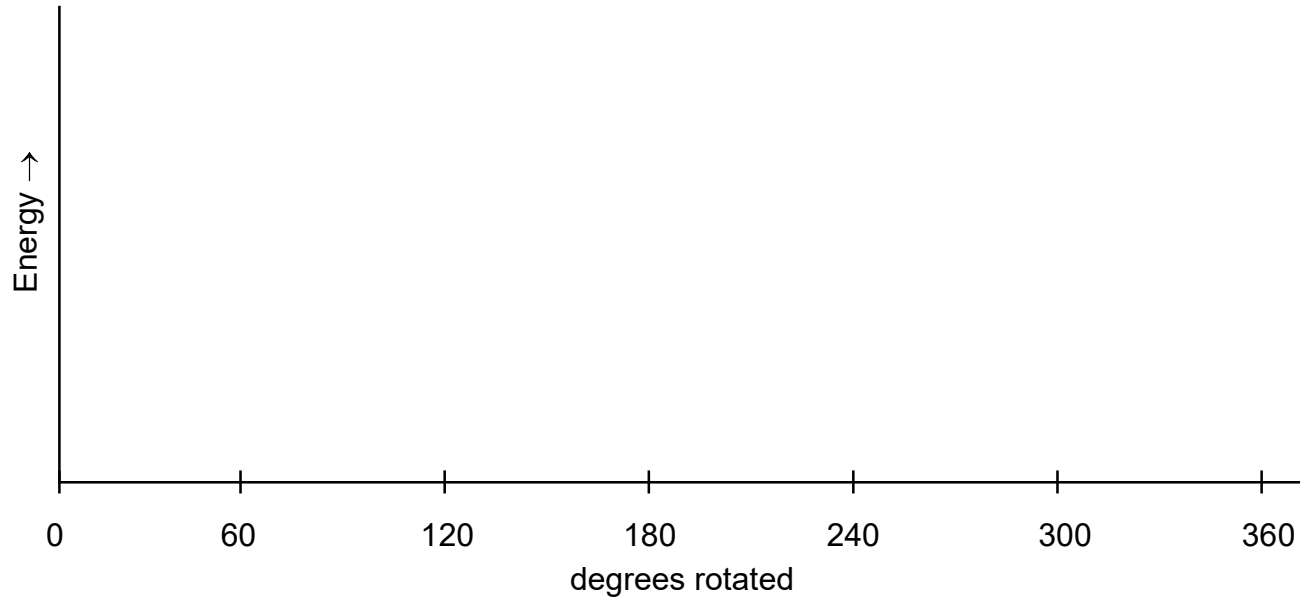


Newman Projection
(view down C2-C3 bond)

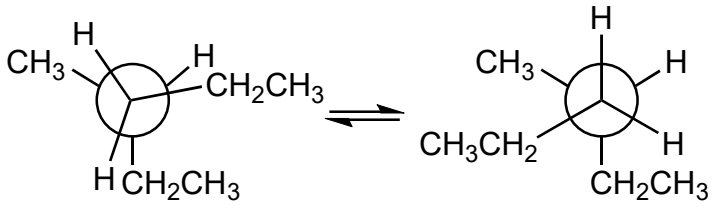


steric hindrance (sterics)
- interaction between large/bulky groups
- causes instability





Group work: 1) Provide the **IUPAC name of** the compound below (it may help to redraw it).
2) Determine the **direction** of the equilibrium. Explain.
3) Draw the **lowest** and **highest energy** conformations of this compound.



lowest Energy: *highest Energy:*

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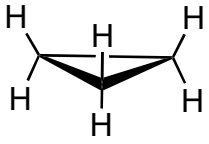
5) Structure and Conformations of Cycloalkanes (4.9)

cyclopropane

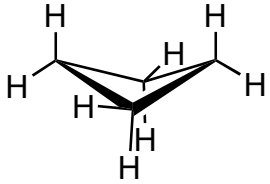


- sp^3 bond angle can't be 109.5º

- eclipsing H's

** these small rings have a large amount of "ring strain" **

cyclobutane



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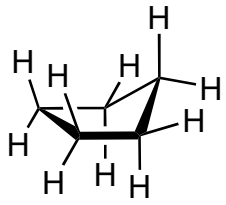
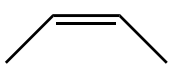
cyclopentane
- has very little ring strain



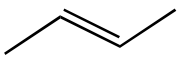
the envelope conformation

Cis-Trans Isomerism in Cycloalkanes (4.14)

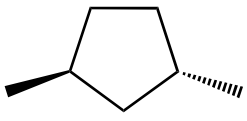
cis means two groups are on the same side
trans means two groups are on opposite sides



cis alkene



trans alkene



trans-1,3-dimethyl-cyclopentane

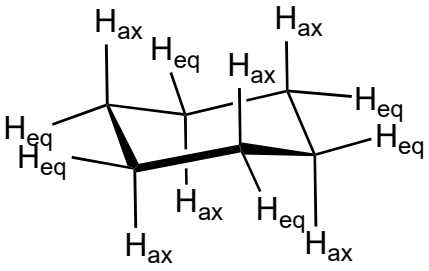
cis-1,3-dimethyl-cyclopentane

A) Cyclohexane (4.10-4.14)

- has NO ring strain!
- six-membered rings are commonly found in nature
- YouTube tutorials http://bit.ly/1fzyjZp

drawing a chair:

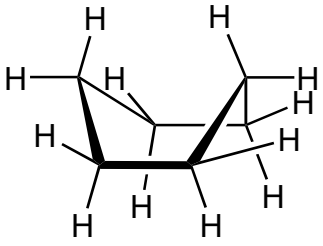
opposite sides are parallel



chair conformation

H_{ax} = axial position (straight up or down)

H_{eq} = equatorial position (slightly up or down)

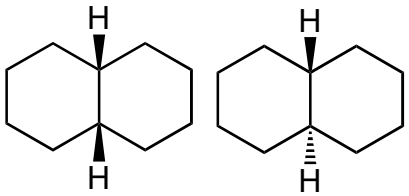


boat conformation

Draw a cyclohexane chair:

Group work: Decalin is composed of two fused cyclohexane rings.

1) Draw all of the missing hydrogen atoms on the numbered decalin framework shown. (Start by adding the axial hydrogens.)
2) Identify whether each of the following substituents would be in an equatorial (eq.) or axial (ax.) position.
3) Is the numbered drawing *cis*- or *trans*-decalin? Explain.



cis-decalin *trans*-decalin

a) A group at the C-3 position pointing UP. _____

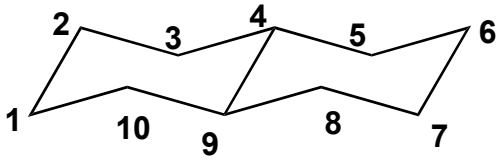
b) A group at the C-7 position pointing DOWN. _____

c) A group at the C-2 position pointing UP. _____

d) A group at the C-9 position pointing DOWN. _____

e) A group at the C-10 position pointing DOWN. _____

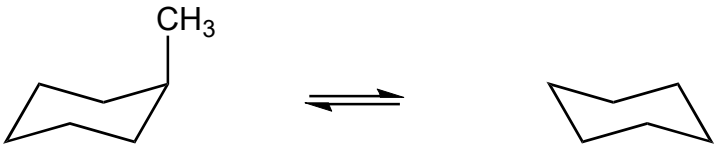
f) A group at the C-1 position pointing UP. _____



cis or *trans* decalin?

see SkillBuilders 4.9, 4.10

Draw and compare stabilities of the two chair conformations of methylcyclohexane (chair "flip").



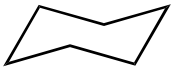
Group work: Draw the two chairs of *cis*-1-*t*-butyl-4-methylcyclohexane. Which is more stable?

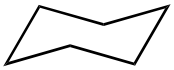
Group	"a value" ΔG (ax-eq)
–H	0
–Cl	0.5
$-CH_3$	1.7
$-CH_2CH_3$	1.9
–t-Butyl	4.9
$-C\equiv CH$	0.2

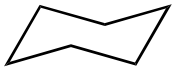
see SkillBuilders 4.11, 4.12, 4.13

Group work: Draw each of the following compounds and determine which one is the most thermodynamically stable.

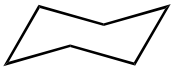
A) *cis*-1,4-dimethylcyclohexane B) *trans*-1,4-dimethylcyclohexane C) 1,1-dimethylcyclohexane

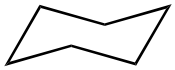




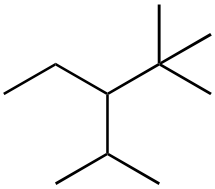


D) *cis*-1,2-dimethylcyclohexane E) *trans*-1,3-dimethylcyclohexane





Provide the IUPAC name for the given compound.



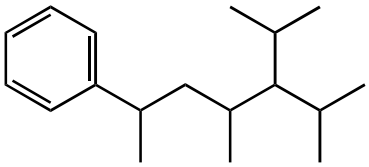
Provide a drawing for the following name:

(1,1-dimethylethyl)cyclohexane

Provide the IUPAC name for the given compound.

$CH_3CH_2C(CH_3)_2CHBrCH(CH_3)_2$

Provide the IUPAC name for the given compound.



Which is the correct IUPAC name for **2-*sec*-butylpentane**? (draw and rename)

Chapter 4 Summary (Klein textbook): Alkanes & Cycloalkanes

I. Nomenclature (4.2, 7.2) **SkillBuilders 4.1, 4.2, 4.3, 4.4**
- A) alkane names $C_1 - C_{10}$ (methane – decane)
- B) IUPAC rules, naming complex substituents
- C) common names (*n*-Pr, i-Pr, *n*-Bu, *s*-Bu, i-Bu, *t*-Bu)
- D) identifying primary (1º), secondary (2º), tertiary (3º), and quaternary (4º) carbons

II. Degrees of Unsaturation (DU) or Hydrogen Deficiency Index (HDI) (14.16)
- A) C_nH_{2n+2} is the formula for a saturated hydrocarbon (alkane)
  - i) halogens (F, Cl, Br, I) count as a hydrogen; oxygens are ignored
- B) every 2 "missing" hydrogens means 1 site/degree of unsaturation (1 DU)
- C) each site of unsaturation can be a ring or a π bond
- D) use DU to help draw isomers of a given formula **SkillBuilder 4.6**

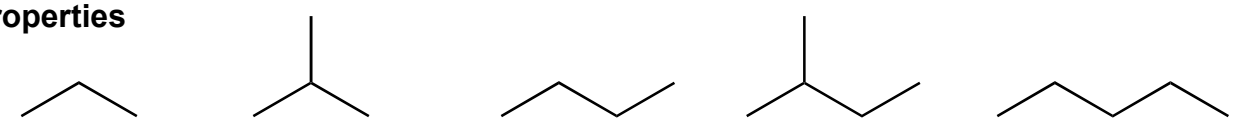
III. Sources, Uses and Physical Properties of Alkanes (4.5)
- A) nonpolar, hydrophobic
- B) used as fuels
- C) boiling point (bp) increases with MW (larger surface area; more van der Waals)

IV. Conformations of Alkanes (4.6 – 4.8) **SkillBuilders 4.7, 4.8**
- A) staggered vs. eclipsed conformations
- B) Newman Projections
- C) Energy diagrams, relative stability of conformers (torsional strain, sterics)

V. Cycloalkanes (4.9, 4.15)
- A) ring strain in cyclopropane, cyclobutane (torsional + angle strain)
- B) cis-trans isomerism in cycloalkanes (4.14)
- C) conformations of cyclohexane (4.10 – 4.13) **SkillBuilders 4.9, 4.10, 4.11, 4.12, 4.13**
  - i) chair vs. boat
  - ii) axial and equatorial positions
  - iii) chair flips
  - iv) predicting stability of chairs for substituted cyclohexanes
    - a) axial positions have sterics called 1,3-diaxial interactions
    - b) larger groups prefer equatorial position

skip: section 4.4 and SB 4.5, and problems 11-13, 39, 44,
add: Ch. 7: 7.17, 7.47, 7.48g; Ch. 14: 14.30 (all but c), 14.32, 14.48 (all but f and g).

Physical Properties of Alkanes



Formula	C_3H_8	C_4H_{10}	C_4H_{10}	C_5H_{12}	C_5H_{12}
bp (ºC)	-42.1	-11.7	-0.6	27.9	36.1
	propane	2-methylpropane	butane	2-methylbutane	pentane

Summary: ↑ Molecular weight, ↑ bp. Only if MW is same, **THEN** ↑ branching, ↓ bp