ALKANE NAMES, Formulas, Properties (Memorize) (Sections 3.2,4)

# C's	Name	Formula	Bp (ºC)	Structure
1	Methane	CH_4	-162	H-(CH_2)-H
2	Ethane	C_2H_6	-89	H-(CH_2)$_2$-H
3	Propane	C_3H_8	-42	H-(CH_2)$_3$-H
4	Butane	C_4H_{10}	0	H-(CH_2)$_4$-H
5	Pentane	C_5H_{12}	36	H-(CH_2)$_5$-H
6	Hexane	C_6H_{14}	69	H-(CH_2)$_6$-H
7	Heptane	C_7H_{16}	98	H-(CH_2)$_7$-H
8	Octane	C_8H_{18}	126	H-(CH_2)$_8$-H
9	Nonane	C_9H_{20}	151	H-(CH_2)$_9$-H
10	Octane	$C_{10}H_{22}$	174	H-(CH_2)$_{10}$-H

Notes: (Including some alkane properties, Section 3.5)

1. Memorize names
2. Names all end in "ane"
3. From 5 up, come from Greek
4. Boiling points: more C's → high boiling point (London force)
5. Formula: for **acyclic alkanes → C_NH_{2N+2}**
   - Basically 2H per carbon (2N), plus 2 extra H's at the ends (+2)
   - Branched isomers for acyclic alkanes still have **C_NH_{2N+2}**
6. **Cyclic Alkanes**: names start in "cyclo" (cyclopentane, cyclooctane, etc.)
7. Formula for **cyclic alkanes → C_NH_{2N}**
   - Basically 2H per carbon (2N), but without the extra two H's at the ends
   - Cyclic alkanes with side-chains still have **C_NH_{2N}**
8. Solubility: nonpolar
   - → insoluble in water
   - → soluble in nonpolar, hydrophobic solvents
9. Density: < 1 (less than water)
   - → float on top of water

Industrial Alkanes (3.5)

Name	# C's	Boiling Range	Use
Natural Gas	C_1-C_3 (70% methane)	Gas	Fuel
"Petroleum Gas"	C_2-C_4	<30º	Heating, Gas
Propane	C_3	-42º	Propane tanks, camping, etc.
Gasoline	C_4-C_9	30-180º	Car fuel
Kerosene	C_8-C_{16}	160-230º	Jet fuel
Diesel	C_{10}-C_{18}	200-320º	Truck fuel
Heavy Oils	C_{16}-C_{30}	300-450º	
Motor Oils		High temp	
Paraffin		Vacuum	
Asphalt		Never Distills	
Coke		Never Distills	

Nomenclature of Alkanes (Sections 3.3-4)

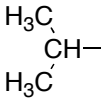
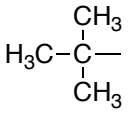
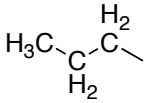
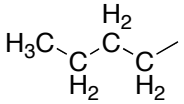
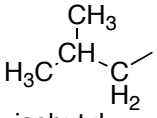
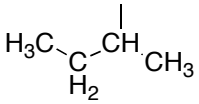
Systematic IUPAC Rules for Branched and Substituted Alkanes

1. Longest continuous C-chain → "core name"
2. Number core chain from an end nearest a substituent
3. Name substituents as "alkyl" groups:
4. Specify the location of substituents using numbers (hyphenate the #'s)
   - If >2 substituents, list alphabetically
   - Use di-, tri-, tetra- if the same substituent is repeated. (But ignore these in alphabetizing).

Punctuation Notes:

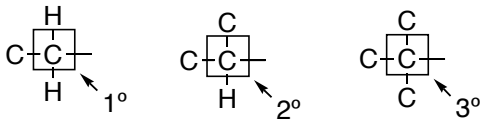
- Hyphenate numbers
- Do not put a space between substituents and the core name

Special Names for Some 3 or 4-carbon Substituents

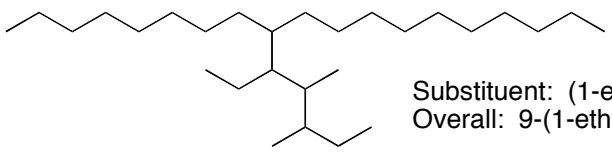
Memorize	 Isopropyl	 t-butyl or tert-butyl		
Others	 n-propyl (n for "normal")	 n-butyl	 isobutyl	 s-butyl

Another Classification System

Primary (1º): with one attached carbon
Secondary (2º): with two attached carbons
Tertiary (3º): with three attached carbons

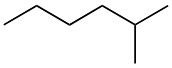


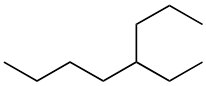
Very Complex Substituents (Not responsible)

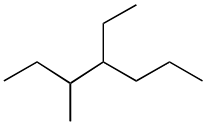


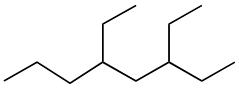
Substituent: (1-ethyl-2,3-dimethylpentyl)
Overall: 9-(1-ethyl-2,3-dimethylpentyl)nonadecane

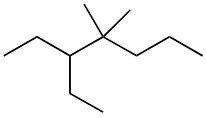
Nomenclature Example Problems

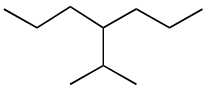
1. 

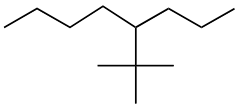
2. 

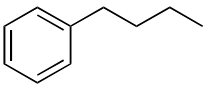
3. 

4. 

5. 

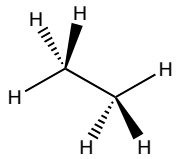
6. 

7. 

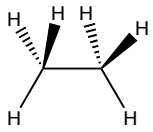
8. 

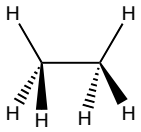
Structure, Conformations of Acyclic Alkanes (3.7)

A. "Conformations" = "Conformers" = "Rotamers" = different 3-D arrangements resulting from rotation around a single bond

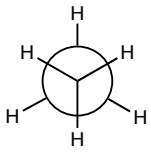


Normal zig-zag





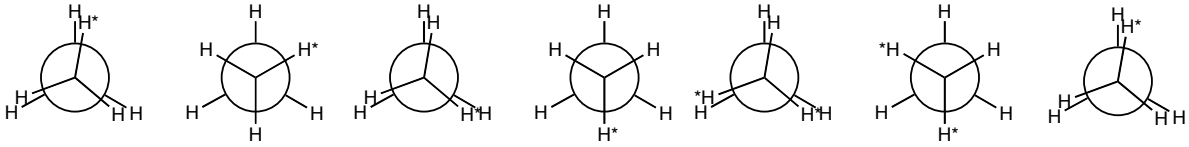
"sawhorse"



"Newman Projection"

B. "Newman Projections": look straight down one C-C bond

- If both bonded carbons are tetrahedral, there will be three bonds extending from the front carbon, and three more bonds extending from the back carbon
- Terms:
  - **Dihedral angle**: angle between a bond on the front atom relative to a bond on the back atom
  - **Eclipsed**: when bonds are aligned. 0º, 120º, 240º, 360º dihedral angles
  - **Staggered**: when bonds are as far apart as possible: 60º, 180º, 300º
  - **Skew**: anything else in between the eclipsed and staggered extremes



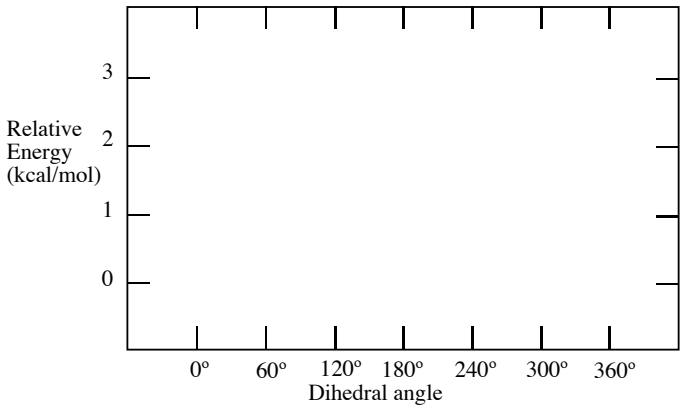
0º eclipsed | 60º staggered | 120º eclipsed | 180º staggered | 240º eclipsed | 300º staggered | 360º eclipsed

Energy: **Staggered best, eclipsed worst**

- Why: Torsional strain. **Repulsion between bonding electron pairs** is reduced in the staggered conformation, and is worst in the eclipsed conformation.

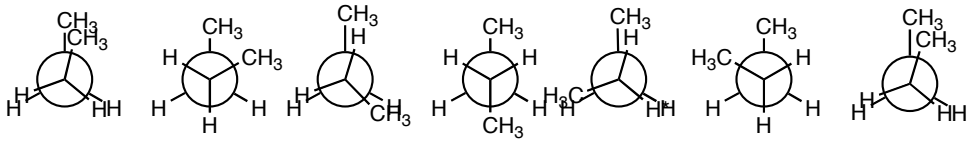
Rotation Barrier: energy gap between the best and worst conformation when you go through a full 360º rotation (as would take place in a full bond rotation)

- Draw in Entergy diagram:

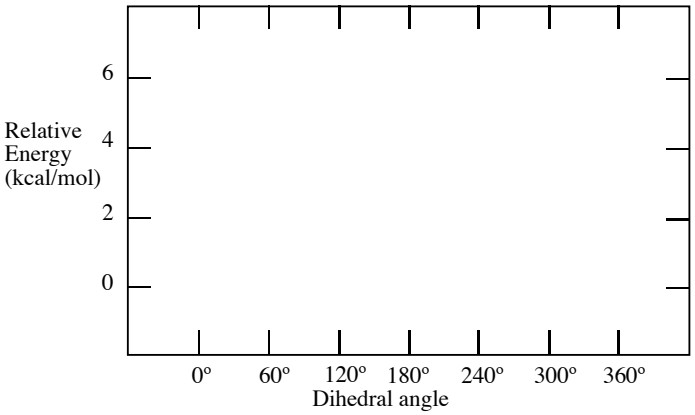


Conformations of Butane and Longer Alkanes (3.8)

CH_3CH_2-CH_2CH_3 is more complex. Focus down C2-C3 bond.



0° eclipsed	60° staggered	120° eclipsed	180° staggered	240° eclipsed	300° staggered	360° eclipsed
Totally Eclipsed	**Gauche**	**Eclipsed**	**Anti**	**Eclipsed**	**Gauche**	**Totally Eclipsed**
6.0	0.9	3.6	0	3.6	0.9	6.0



Questions

1. Draw the energy diagram

2. What would be the rotation barrier?

Strain Energy Factors:

1. **Torsional** strain (why all of the eclipsed type conformations are worse). Repulsion between bonded electrons
2. **Steric** strain: When atoms themselves get too close. Atom-atom repulsion.
3. **Angle** strain: When bond angles can't achieve ideal VSEPR angles. (No angle strain in ethane or butane)

Total Strain =	Torsional strain (are any bonds eclipsed?) + Steric strain (are any atoms too close) + Angle strain (are any bond angles forced to be other than ideal?)

Questions

1. In general, why are staggered better than eclipsed?

2. Why is eclipsed better than totally eclipsed?

3. Why is anti better than gauche?

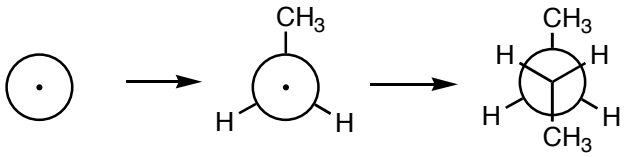
4. Why is gauche better than eclipsed?

5. Why is anti better than totally eclipsed?

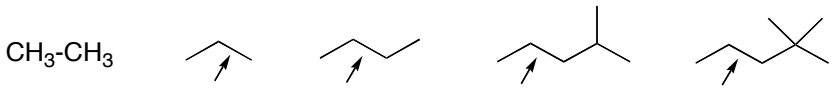
Summary
1. Anti < gauche < eclipsed < totally eclipsed
2. Steric and torsional reasons
3. The bulkier a substituent, the greater the steric strain in eclipsed and totally eclipsed conformations

Skills. Be Able to:
1. predict relative rotation barriers
2. write a conformational analysis (rotation/energy diagram)
3. draw Newman pictures for any bond in any structure
4. identify anti/gauche/eclipsed/totally eclipsed conformations

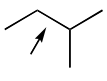
Steps to Drawing Newman Structure:
1. Draw a circle (back carbon) with a dot in the middle
2. Add three sticks extending from the periphery of the circle, with one of them straight up
3. Add three sticks extending from the center dot (front carbon) to illustrate the bonds radiating from the front carbon



Problems
1. Rank the rotation barriers for the following, relative to the indicated bonds



2. Draw Newman projections for the best and worst conformations of the structure shown, relative to the indicated bond. Use the 3rd carbon in the back.



Higher Alkanes
-for any alkane, anti conformations best = zig-zag layout

3.10 Cycloalkanes
Nomenclature: cyclopropane, cyclobutane, etc..

General formula: C_NH_{2N}
-this is also true for cycloalkanes with chain(s) attached

3.11 Substituted Cycloalkanes and cis/trans Isomers in Disubstituted Cycloalkanes
Nomenclature:

- Monosubstituted: alkylcycloalkane
- Disubstituted: cis- (or trans-)-x-alkyl-y-alkylcycloalkane
    1. "Cis"-same side "trans" – opposite sides
    2. Number ring so as to minimize numbers

3.12 Ring Stability and Ring Strain (Section 4.4-8)

Ring Size	Total Ring Strain (kcal/mol)	Strain Per CH_2	Main Source Of Strain
3	28	9	Angle Strain
4	26	7	Angle Strain
5	7	1	Torsional Strain (eclipsing)
6	**0**	**0**	**-- STRAIN FREE**
7	6	1	Torsional Strain (eclipsing)
8	10	1	Torsional Strain (eclipsing)

Structural Isomer Problems (3.2, 3.10)

- **Check formula first**. Is it an acyclic molecule (C_NH_{2N+2}), or not? (C_NH_{2N} could be a cyclic alkane, or perhaps an alkene …)
- **Be systematic**. Try the longest possible chain (or largest ring size) first, then systematically shorten it and find the branched isomers.
- **Avoid duplicates**!
- Beware of things that look different but are really the same thing.

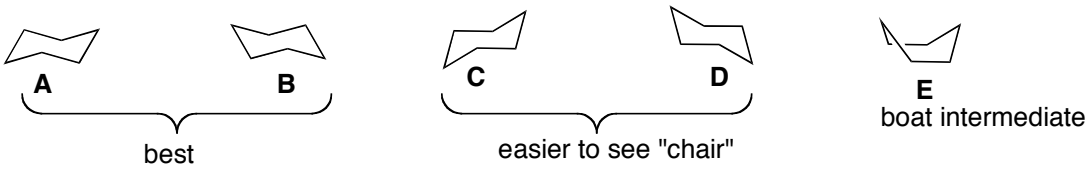
1. Draw all structural isomers of C_7H_{16}. (Be systematic; no duplicates!)

2. Draw all structural isomers of C_7H_{14}. (Be systematic; no duplicates!)

3.13 **Cyclohexane Chair Conformations**

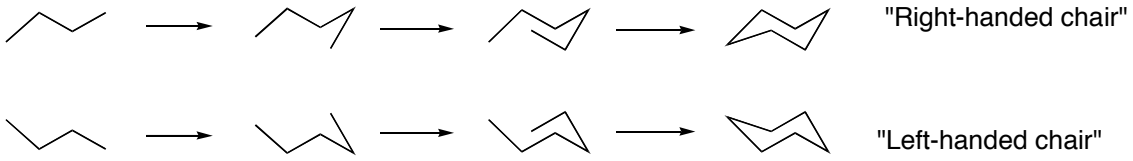
- Cyclohexane has no angle strain or torsional strain
- Cyclohexane has perfect 109º angles with staggered, non-eclipsed C-C bonds
- Obviously it is not flat (natural angle for a flat cyclohexane would be 120º)

Chair Conformations:



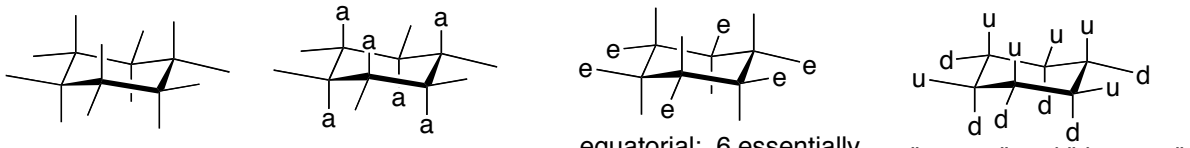
- Chairs **A** and **B** are constantly interconverting via "boat" **E**
- **A** and **B** are best to draw and work with.
- But **C**/**D** make it easier to visualize why it's called a "chair": 4 carbons make the seat of the chair, one makes backrest, one a footrest.

Process for Drawing Both Chairs:



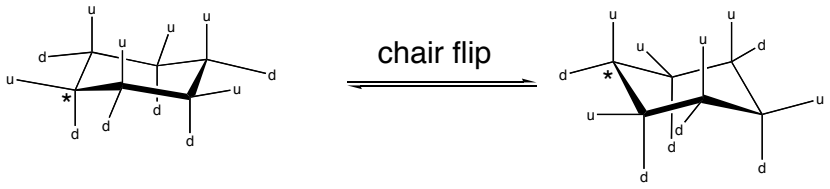
1. Draw a 4-carbon zig-zag. It helps if your left-most carbon is a little lower than your 3rd carbon
2. Add a 5th carbon and 6th carbon, but don't have them exactly underneath the 2nd and 3rd carbons.
3. Connect the 6th carbon to the orginal 1st carbon
   - For a "left-handed chair", start up and zig-zag down.

"Axial" and "Equatorial" Positions for Substituents



1. Each carbon has one axial and one equatorial H's
2. Always have six axial attachments
3. 3 axials up (on alternating carbons)

4. 3 axials down (on alternating carbons)
5. Always have six equatorial attachments
6. For processing cis/trans problems, it's helpful to recognize "upper" from "downer" positions
7. When a chair flips, what was equatorial becomes axial, and what was axial becomes equatorial

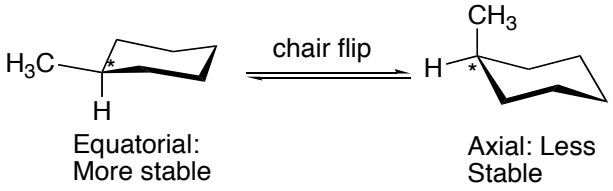


Drawing equatorial and axial bonds:

- Make axial straight up or straight down (3 each)
- Make equatorial bond lines almost exactly horizontal
- Equatorials are easiest to draw on left and right-most carbons

Drawing Mono- and DiSubstituted Cyclohexanes (Sections 3-14,15)

- Always attach the first substituent onto the leftmost carbon (easiest to draw)



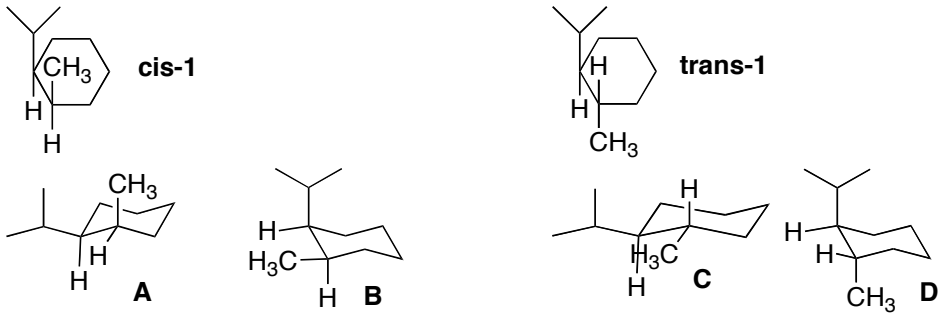
- Draw in the H on any substituted carbon, but skip on H-only carbons
- **Equatorial is better than axial for steric reasons**. In the axial configuration, the substituent has destabilizing steric interactions
  - 2 extra gauche interactions, and 1,3-diaxial interactions
- For disubstituted chairs, let the cis/trans relationship guide whether the second substituent should be in an "upper" or "lower" position relative to the original substituent.
- If one substituent is bigger than the other, the most stable chair will always have the larger substituent equatorial

Cis and Trans Disubstituted Cyclohexanes

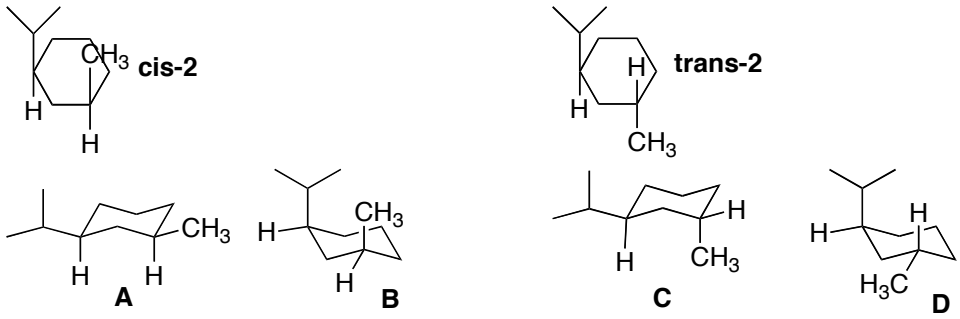
Questions:

1. Draw both chair forms for cis-2-methyl-1-isopropylcyclohexane.
2. Which is the best chair for cis-2-methyl-1-isopropylcyclohexane?
3. Draw both chair forms and identify the best chair for trans-2-methyl-1-isopropylcyclohexane.
4. Which is more stable, cis- or trans-2-methyl-1-isopropylcyclohexane?
5. Then answer the same questions for the 1,3- and 1,4- isomers.

1,2-DiSubbed



1,3-DiSubbed



1,4-DiSubbed