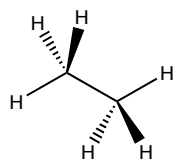
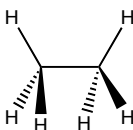
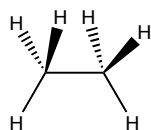


Structure, Conformations of Acyclic Alkanes (3.7)

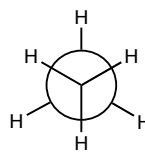
A. "Conformations" = "Conformers" = "Rotamers" = different 3-D arrangements resulting from rotation around a single bond



Normal zig-zag



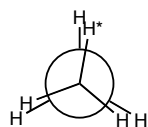
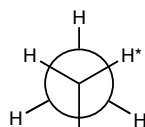
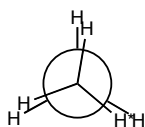
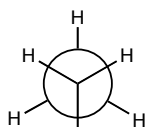
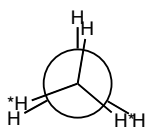
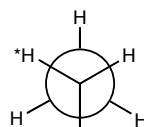
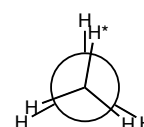
"sawhorse"



"Newman Projection"

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

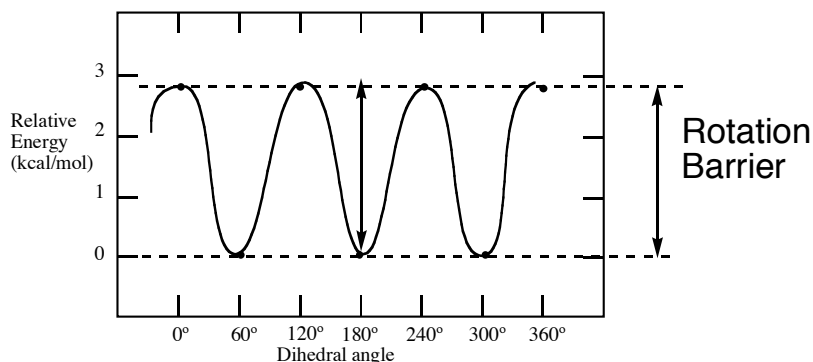
- If both bonded carbons are tetrahedral, there will be three bonds extending from the front carbon, and three more bonds extending from the back carbon
- Terms:
 - **Dihedral angle**: angle between a bond on the front atom relative to a bond on the back atom
 - **Eclipsed**: when bonds are aligned.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

 0°
eclipsed 60°
staggered 120°
eclipsed 180°
staggered 240°
eclipsed 300°
staggered 360°
eclipsedEnergy: 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.

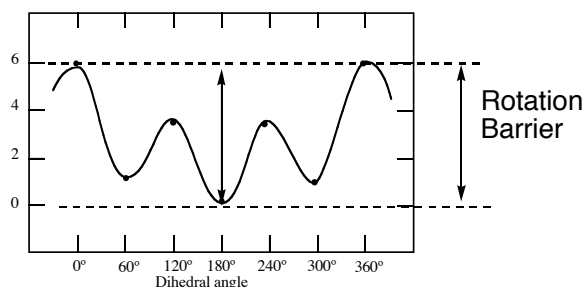
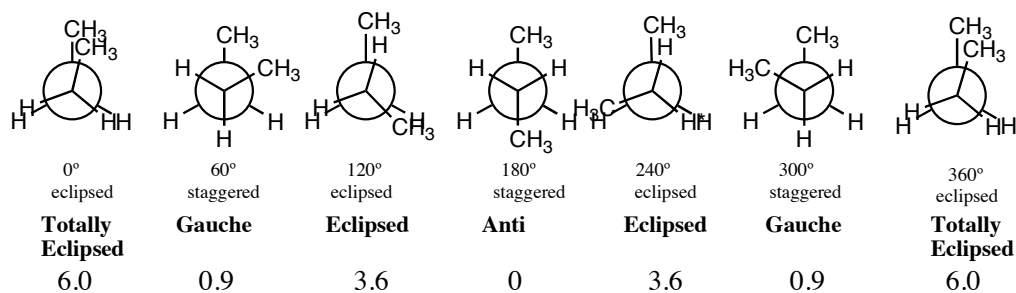
Rotation Barrier: energy gap between the best and worst conformation when you go through a full 360° rotation (as would take place in a full bond rotation)

- Draw in Energy diagram:



Conformations of Butane and Longer Alkanes (3.8)

$\text{CH}_3\text{CH}_2\text{-CH}_2\text{CH}_3$ is more complex. Focus down C2-C3 bond.

Questions

1. Draw the energy diagram
2. What would be the rotation barrier? 6 kcal/mol

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? Torsional strain.
2. Why is eclipsed better than totally eclipsed? Both have eclipsing and torsional strain. But the totally eclipsed conformation adds on severe steric strain.
3. Why is anti better than gauche? Both are staggered, so neither has any eclipsing or any torsional strain. But the gauche has a little bit of steric strain.
4. Why is gauche better than eclipsed? Gauche is staggered, with no torsional strain. Eclipsed is worse because of eclipsing/torsional strain. Plus the steric strain is a big worse.
5. Why is anti better than totally eclipsed? Both torsional strain and severe steric strain make the totally eclipsed way worse.

Summary

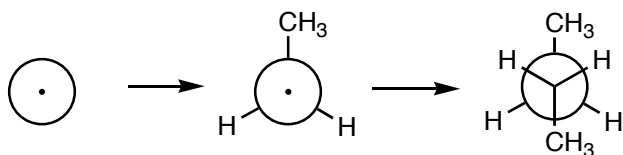
1. Anti < gauche < eclipsed < totally eclipsed
2. Steric and torsional reasons
3. The bulkier a substituent, the greater the steric strain in eclipsed and totally eclipsed conformations

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

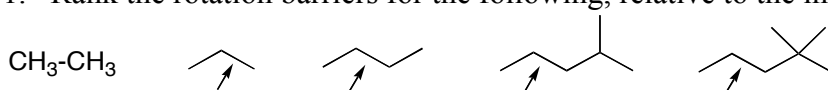
Steps to Drawing Newman Structure:

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



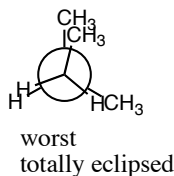
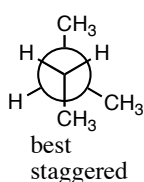
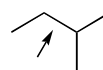
Problems

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



They increase from left to right. The rotation barrier is basically dominated by how bad things are in the worst possible, totally eclipsed conformation relative to a bond, and the steric interaction involved. From left to right, the worst eclipsing is between: H and H; CH₃ and H; CH₃ and CH₃; CH₃ and isopropyl; CH₃ and t-butyl

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.



Ring Stability and Ring Strain (Section 3.12)

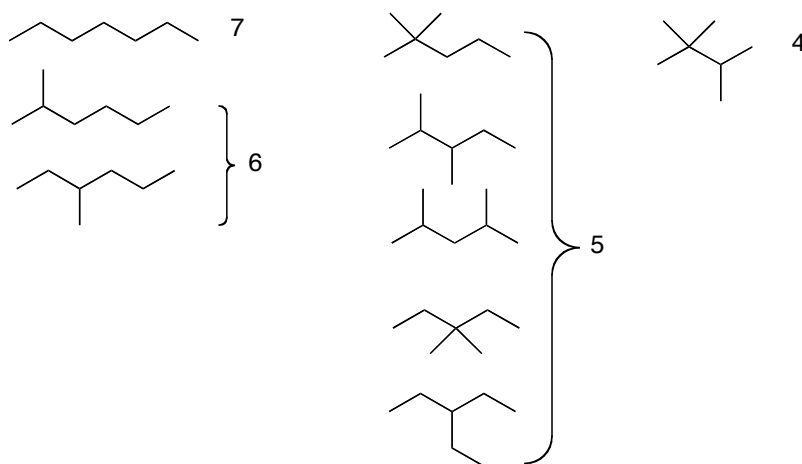
Ring Size	Total Ring Strain (kcal/mol)	Strain Per CH ₂	Main Source Of Strain
3	28	9	Angle Strain
4	26	7	Angle Strain
5	7	1	Torsional Strain (eclipsing)
6	0	0	-- STRAIN FREE
7	6	1	Torsional Strain (eclipsing)
8	10	1	Torsional Strain (eclipsing)

Structural Isomer Problems

- **Check formula first.** Is it an acyclic molecule, or not? (Cyclic alkane or an alkene or something...)
- **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.

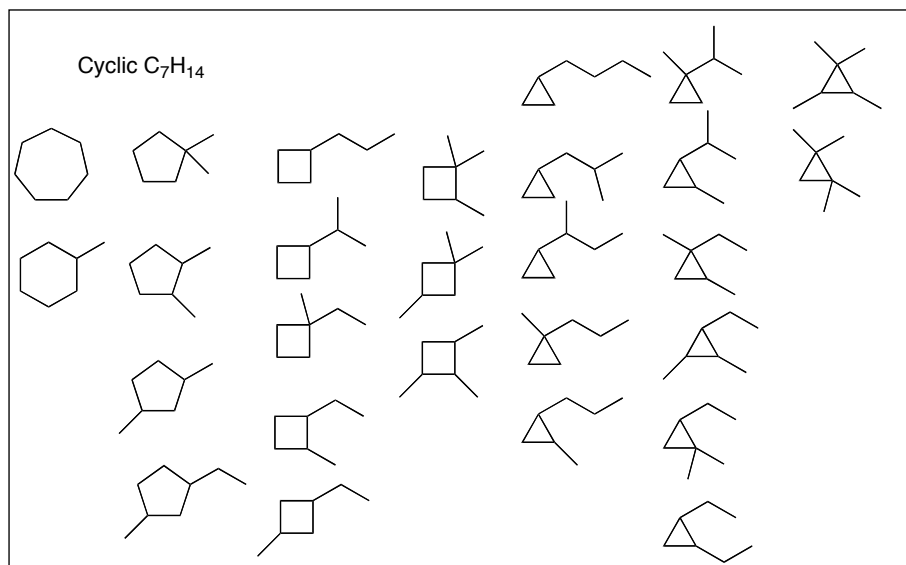
1. Draw all structural isomers of C_7H_{16} . (Be systematic; no duplicates!)

Formula proves acyclic alkane



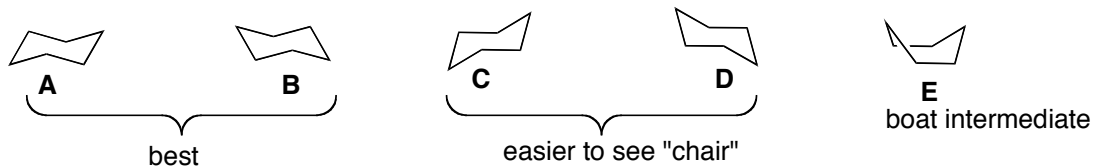
2. Draw all structural isomers of C_7H_{14} . (Be systematic; no duplicates!)

Formula proves either a cyclic alkane or an alkene. In addition to the 27 cycloalkanes shown, there are at least another couple dozen alkenes. Notice that these are 27 cycloalkane structure isomers; many of them could also have cis/trans issues, so where I drew just one, you could perhaps actually draw both a cis version and a trans version.

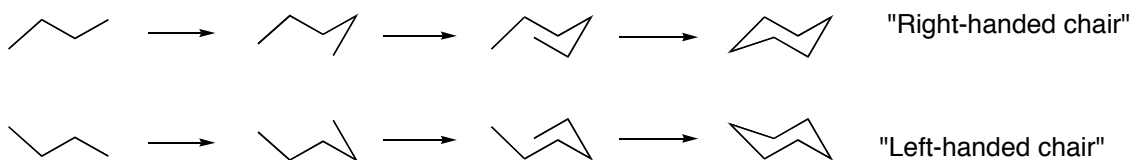


Cyclohexane Chair Conformations (Section 3-13,14)

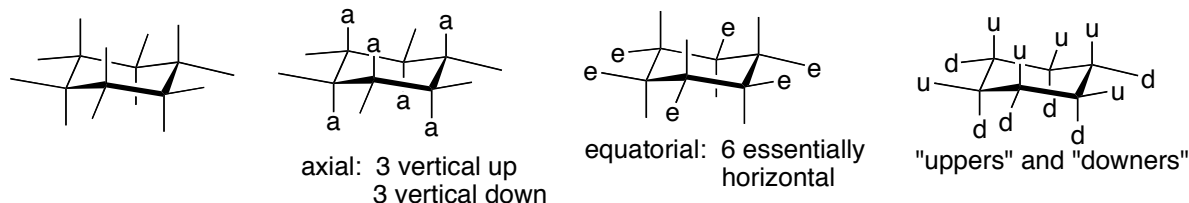
- Cyclohexane has no angle strain or torsional strain
- Cyclohexane has perfect 109° angles with staggered, non-eclipsed C-C bonds
- Obviously it is not flat (natural angle for a flat cyclohexane would be 120°)

Chair Conformations:

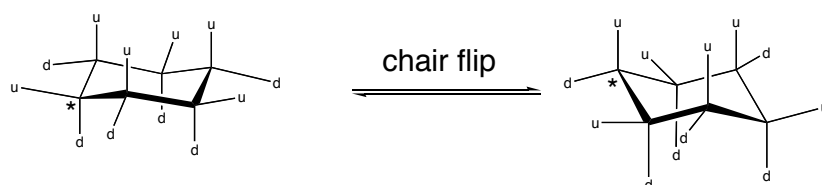
- Chairs **A** and **B** are constantly interconverting via "boat" **E**
- **A** and **B** are best to draw and work with.
- But **C/D** make it easier to visualize why it's called a "chair": 4 carbons make the seat of the chair, one makes backrest, one a footrest.

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 original 1st carbon
 - For a "left-handed chair", start up and zig-zag down.

"Axial" and "Equatorial" Positions for Substituents

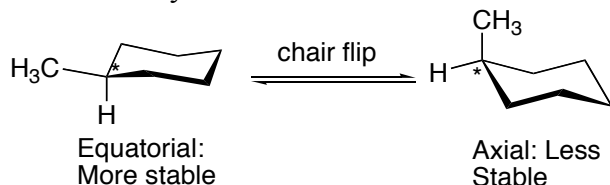
1. Each carbon has one axial and one equatorial H's
2. Always have six axial attachments
3. 3 axials up (on alternating carbons)
4. 3 axials down (on alternating carbons)
5. Always have six equatorial attachments
6. For processing cis/trans problems, it's helpful to recognize "upper" from "downer" positions
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)

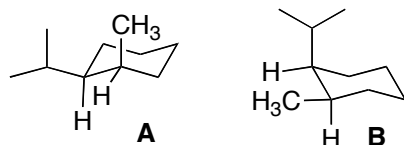
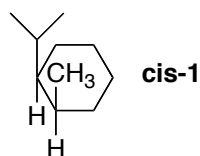
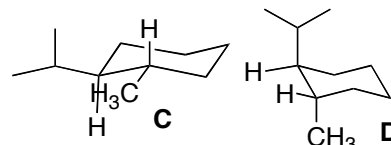
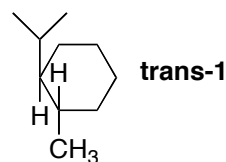
- Always attach the first substituent onto the leftmost carbon (easiest to draw)



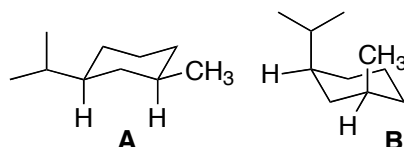
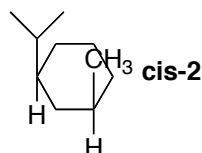
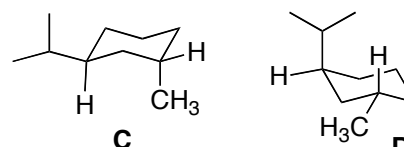
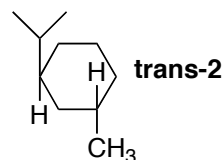
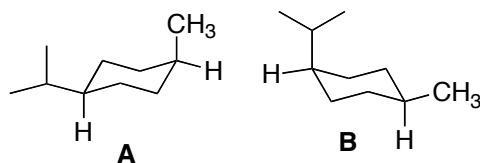
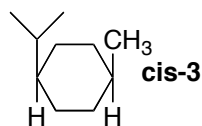
- Draw in the H on any substituted carbon, but skip on H-only carbons
- **Equatorial is better than axial for steric reasons.** In the axial configuration, the substituent has destabilizing steric interactions
 - 2 extra gauche interactions, and 1,3-diaxial interactions
- For disubstituted chairs, let 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 CyclohexanesQuestions:

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-
DiSubbedBest cis is **A > B**Best trans is **C > D**Best of all is **C (eq-eq)**, so trans-1 is better than cis-1

A > B and C > D because large isopropyl group wants to be equatorial

1,3-
DiSubbedBest cis is **A (eq eq) > B (ax ax)**Best trans is **C (eq ax) > D (ax eq)**Best of all is **A (eq-eq)**, so cis-2 is better than trans-21,4-
DiSubbedBest cis is **A (eq ax) > B (ax eq)**Best trans is **C (eq eq) > D (ax ax)**Best of all is **C (eq-eq)**, so trans-3 is better than cis-3