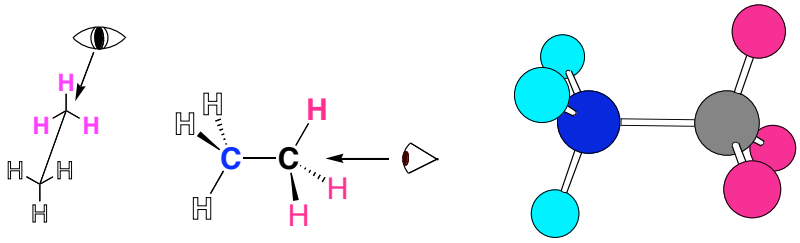
Ch. 3: Alkanes and Cycloalkanes: Conformations and cis-trans Stereoisomers

Stereochemistry: three-dimensional aspects of molecules

Conformation: different spatial arrangements of atoms that result from rotations about single (σ) bonds

Conformer: a specific conformation of a molecule

3.1: Conformational Analysis of Ethane



Sawhorse

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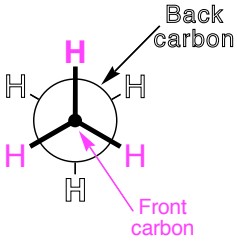
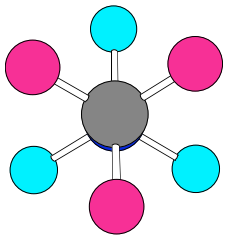
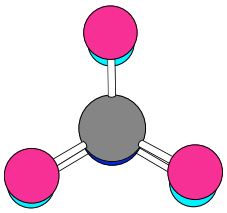
There are two conformations of ethane:







Newman projection Staggered Eclipsed

Dihedral (torsion) angle: angle between an atom (group) on the front atom of a Newman Projection and an atom (group) on the back atom

Dihedral angles of ethanes:

Staggered conformation: 60° (gauche), 180° (anti), and 300° (-60°, gauche)

Eclipsed conformation: 0°, 120°, and 240° (-120°)

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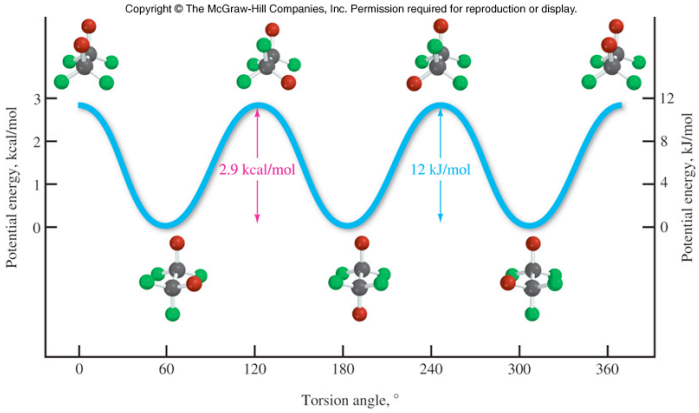
Energy vs. dihedral angle for ethane

http://www2.chem.ucalgary.ca/Flash/ethane.html



The barrier (E_{act}) for a 120° rotation of ethane (from one staggered conformer to another) is 12 KJ/mol. The eclipsed conformer is the barrier to the rotation. *An H-H eclipsing interaction = 4 KJ/mol*

Torsional Strain: strain (increase in energy) due to eclipsing interactions

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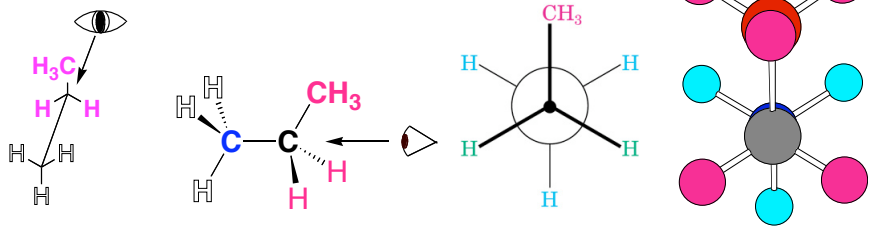
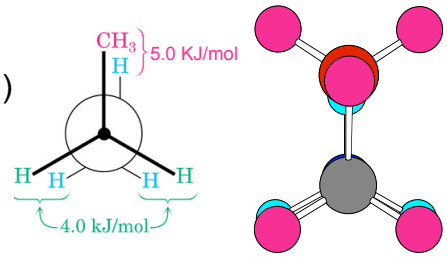
Conformations of Propane



The barrier to C-C rotation for propane is 13 KJ/mol = 1 (CH_3-H) + 2 (H-H) eclipsing Interactions.

A CH_3-H eclipsing interaction is 5 KJ/mol



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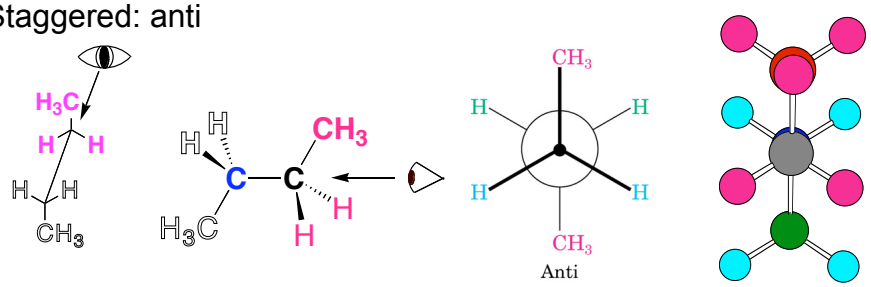
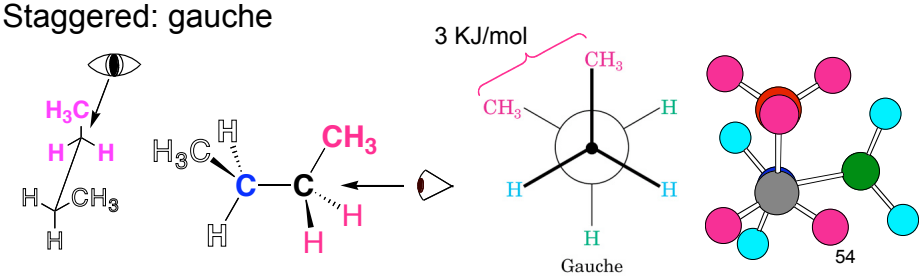
3.2: Conformational Analysis of Butane

Two different staggered and eclipsed conformations

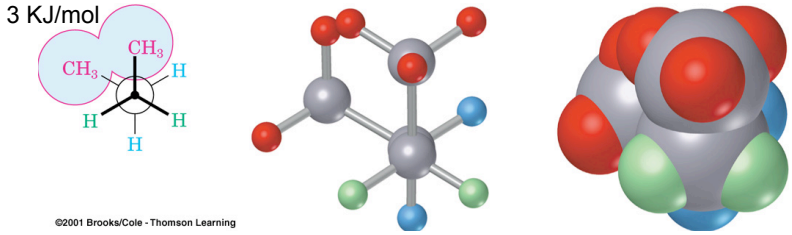
Staggered: anti



Staggered: gauche



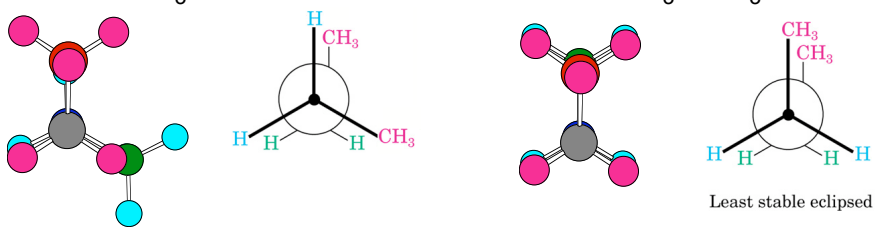
Steric Strain: repulsive interaction that occurs when two groups are closer than their atomic radii allow



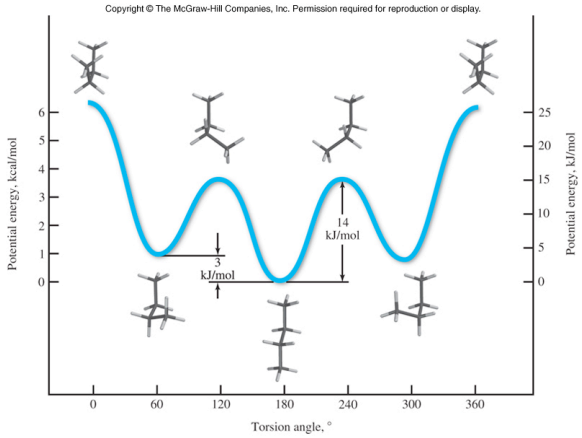
Eclipsed conformations of butane: rotational barrier of butane is 25 KJ/mol. *A CH_3-CH_3 eclipsing interaction is 17 KJ/mol.*

CH_3 - H

CH_3 - CH_3



Energy diagram for the rotation of butane



Summary:

H - H eclipsed	4.0 KJ/mol	torsional strain
H - CH_3 eclipsed	5.0 KJ/mol	mostly torsional strain
CH_3 - CH_3 eclipsed	17 KJ/mol	torsional + steric strain
CH_3 - CH_3 gauche	3.0 KJ/mol	steric strain

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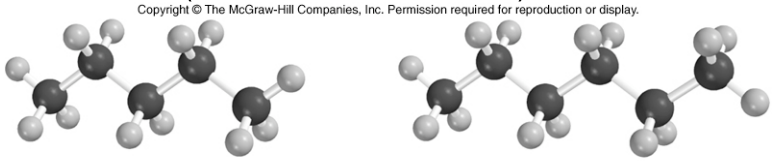
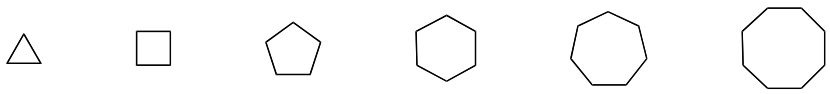
3.3: Conformations of Higher Alkanes - The most stable conformation of unbranched alkanes has anti relationships between carbons (extended carbon chain).



Pentane Hexane

3.4 The Shapes of Cycloalkanes: Planar or Nonplanar?

Angle Strain: strain due to deforming a bond angle from its ideal value (Baeyer Strain Theory)



60° 90° 108° 120° 128° 135°

Internal angles of polygons

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Heats of Combustion of Cycloalkane: the more strained a compound is, the more heat it releases upon combustion

C_nH_{2n} + O_2 ⟶ n CO_2 + (n+1) H_2O + heat

cycloalkane (can be measured)

Total Strain Energy = [Sample ΔH_{comb} per $-CH_2-$] − [Reference ΔH_{comb} per $-CH_2-$] • n

	Cycloalkane	Ring Size (n)	ΔH_{comb} KJ/mol	ΔH_{comb} per CH_2 KJ/mol		Total Strain Energy
strained rings	Cyclopropane	3	2091	697	(43)	129
	Cyclobutane	4	2721	681	(27)	108
common rings	Cyclopentane	5	3291	658	(4)	20
	Cyclohexane	6	3920	654	(0)	0
	Cycloheptane	7	4599	657	(3)	21
medium rings	Cyclooctane	8	5267	658	(4)	32
	Cyclononane	9	5933	659	(5)	45
	Cyclodecane	10	6587	659	(5)	45
large rings (> 12)	Cyclohexadecane	16	10466	654	(0)	0
	Alkane reference			654		0

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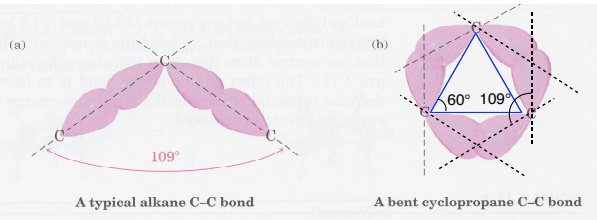
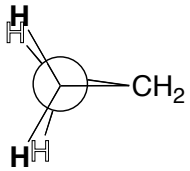
With the exception of cyclopropane, cycloalkane are not planar.

3.5 Small Rings: Cyclopropane and Cyclobutane

Bonding in Cyclopropane: reduced overlap of the sp^3-hybridized orbitals





Total strain for cyclopropane

= angle strain + torsional strain

all adjacent CH_2 groups are eclipsed

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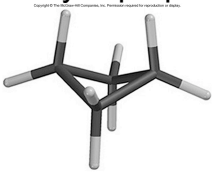
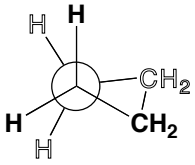
Cyclobutane - reduced angle and torsional strain relative to cyclopropane

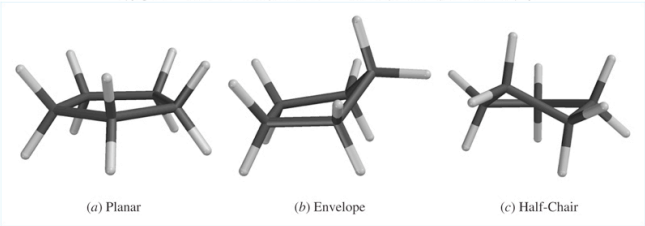


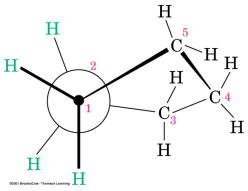


Puckering partially relieves torsional strain

3.6: Cyclopentane: planar conformation is strain free according to Baeyer; however, there is considerable torsional strain (10 H-H eclipsing interactions)

Envelope and half-chair conformations relieve much of the torsional strain





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3.7: Conformations of Cyclohexane - ΔH_{comb} suggests that cyclohexane is strain-free; favored conformation is a chair.

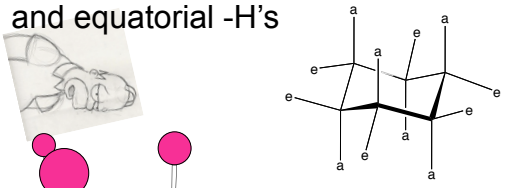
3.8: Axial and Equatorial Bonds in Cyclohexane

Chair cyclohexane has two types of hydrogens:

axial: C-H axis is "perpendicular" to the "plane of the ring"

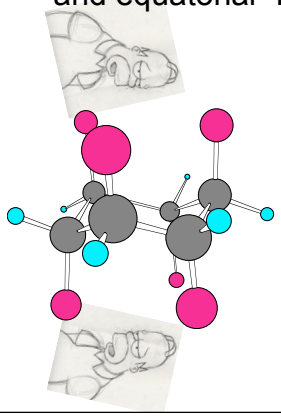
equatorial: C-H axis is "parallel" to the "plane of the ring"

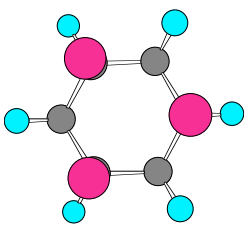
Chair cyclohexane has two faces; each face has alternating axial and equatorial -H's



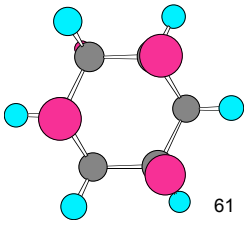
axial

equatorial





top face



bottom face

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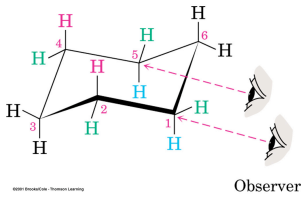
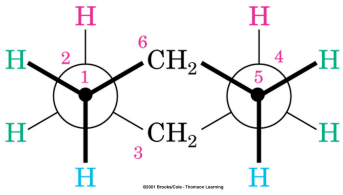
All H-H interactions are staggered - no torsional strain; minimal angle strain (~111°)

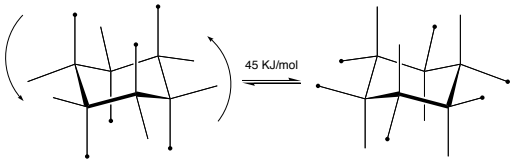




Other conformations of cyclohexane:
half chair; twist boat, and boat

3.9: Conformational Inversion (Ring-Flipping) in Cyclohexane

Ring flip interchanges the axial and equatorial positions. The barrier to a chair-chair interconversion is 45 KJ/mol.



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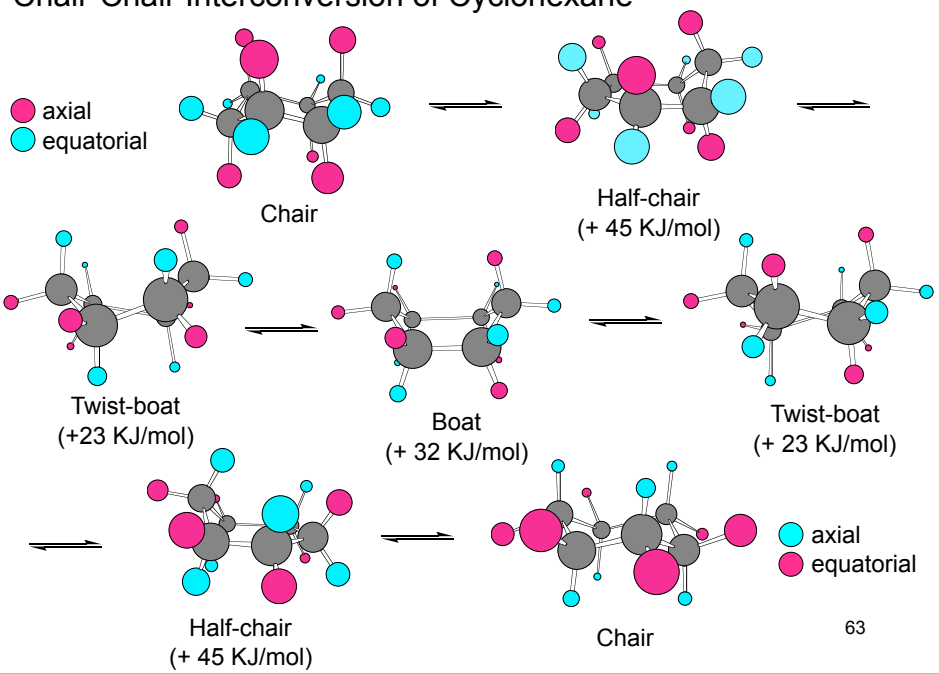
Chair-Chair Interconversion of Cyclohexane



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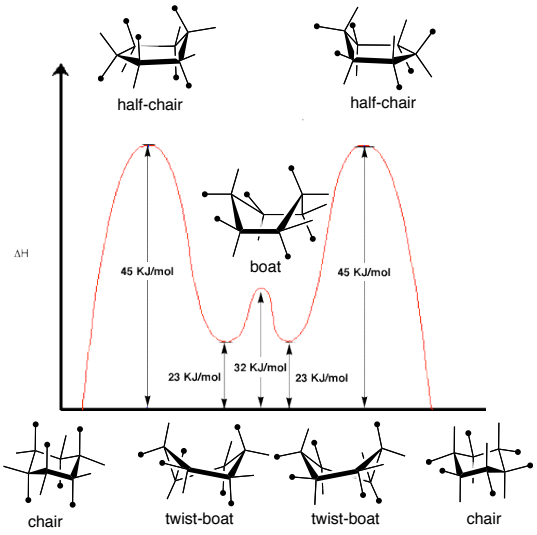
Energy Profile for the Chair-Chair Interconversion of Cyclohexane

http://www2.chem.ucalgary.ca/Flash/cyclohexane.html



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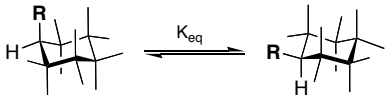
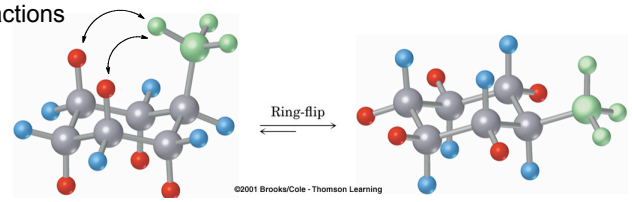
3.10: Conformational Analysis of Monosubstituted Cyclohexanes

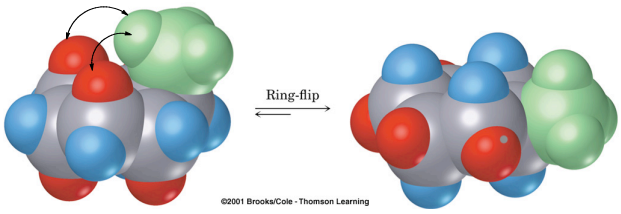
most stable chair conformation has the substituent in the equatorial position



R= -CH_3 5 : 95

1,3-diaxial interactions





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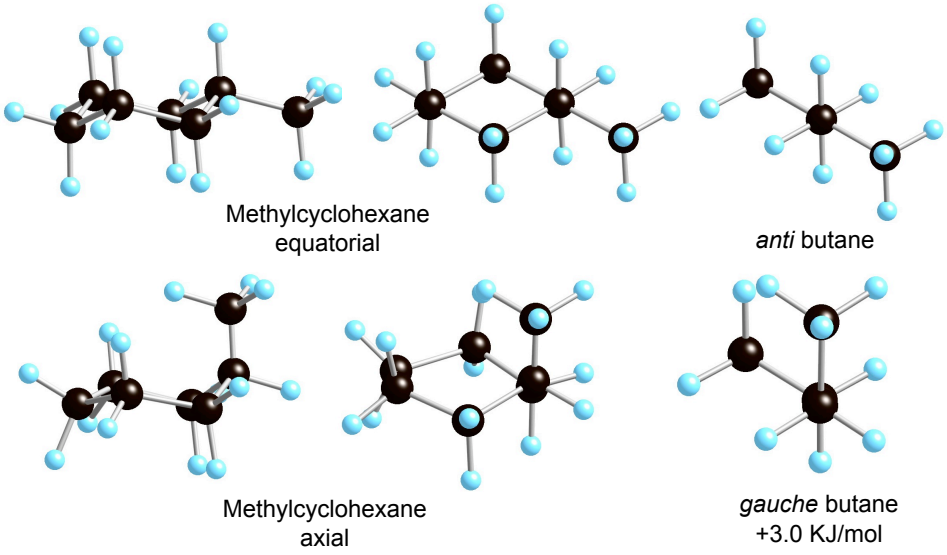

Methylcyclohexane equatorial

anti butane

Methylcyclohexane axial

gauche butane +3.0 KJ/mol

2 gauche butane interactions: 2 x 3.0 KJ/mol = 6.0 KJ/mol (actual 7.3 KJ/mol)

Axial position is more sterically congested (steric strain) and is therefore less favored thermodynamically

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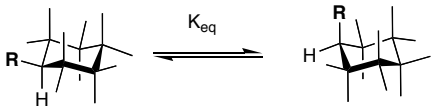


Substituent	per 1,3-diaxial interaction (KJ/mol)	total strain energy (A-value)	eq./axial
-F	0.5	1.0	60:40
-Cl	1.4	2.8	70:30
-Br	1.4	2.8	70:30
-I	0.85	1.7	65:34
-OH	2.1	4.2	85:15
$-NH_2$	2.7	5.4	90:10
$-N(CH_3)_2$	4.4	8.8	97:3
$-CH_3$	3.6	7.3	95:5
$-CH_2CH_3$	3.9	7.8	96:4
$-CH(CH_3)_2$	4.3	8.6	97:3
$-C(CH_3)_3$	> 8	16	>> 99.9:0.1
$-CH_2C(CH_3)_3$	4.2	8.4	97:3
$-C_6H_5$	6.3	12.6	99.5:0.5
CO_2H	2.9	5.8	92:8
-CN	0.4	0.8	60:40

$\Delta E = -RT \ln K_{eq}$, where R= 8.3 x 10^{-3} KJ/mol, T= 300 °K (room temp) 67

3.11: Disubstituted Cycloalkanes: Stereoisomers

Stereochemistry: three-dimensional arrangement of atoms (groups) in space

Isomers: different chemical compounds with the same formula

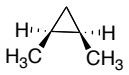
Constitutional isomers: same formula, but different connectivity of atoms (or groups)

ethylcyclopropane

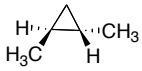
1,2-dimethylcyclopropane

C_5H_{10}

Stereoisomers: same connectivity, but different spatial arrangement of atoms or groups



cis-1,2-dimethylcyclopropane



trans-1,2-dimethylcyclopropane

ΔH_{comb} is ~ 5KJ/mol higher for the *cis* isomer

trans: on opposite sides of the ring
cis: on the same side of the ring

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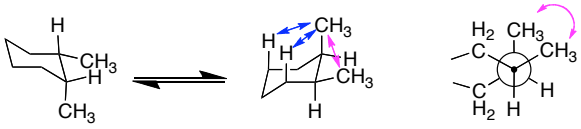
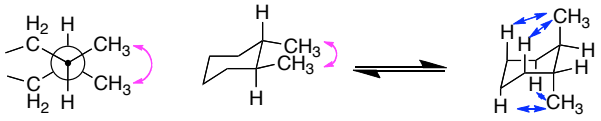
3.12: Conformational Analysis of Disubstituted Cyclohexanes

1,4-dimethylcyclohexane: ΔH_{comb} is 7 KJ/mol lower for the *trans* isomer
1,3-dimethylcyclohexane: ΔH_{comb} is 7 KJ/mol lower for the *cis* isomer
1,2-dimethylcyclohexane: ΔH_{comb} is 6 KJ/mol lower for the *trans* isomer



cis (one equatorial, one axial)
(2 x 3.0) + 3.0 = 9.0 KJ/mol



trans (two equatorial, no axial)
3.0 KJ/mol

trans (no equatorial, two axial)
2 (2 x 3.0) = 12.0 KJ/mol

ΔG = 9.0 KJ/mol K_{eq} = ~ 98:2

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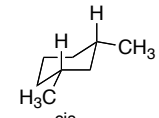
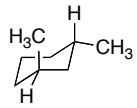
1,3-dimethylcyclohexane



cis
(two equatorial)

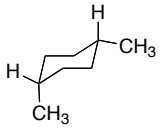
cis
(two axial)



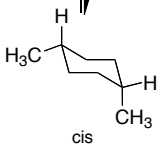
trans
(one equatorial, one axial)

trans
(one equatorial, one axial)

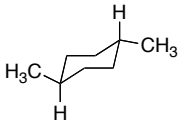
1,4-dimethylcyclohexane



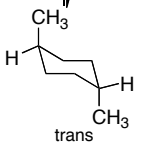
cis
(one equatorial, one axial)



cis
(one equatorial, one axial)



trans
(two equatorial)



trans
(two axial)

3.13: Medium and Large Rings (please read)

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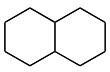
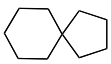
3.14: Polycyclic Ring Systems - contains more than one ring

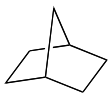
fused - two rings share a pair of bonded atoms
spirocyclic - one atom common to two rings
bridged bicyclic - nonadjacent atoms common to two rings



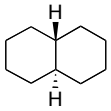
fused

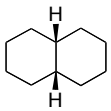


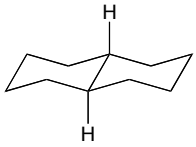
spiro



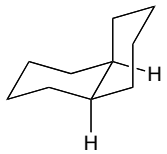
bridged







trans-decalin



cis-decalin

cis- and trans-decalin are stereoisomers, they do not interconvert into each other

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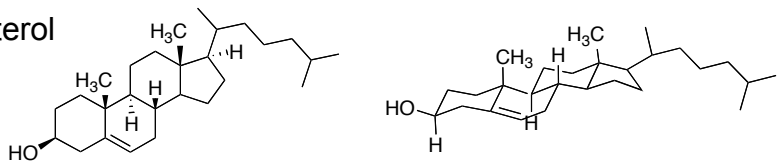
Cholesterol

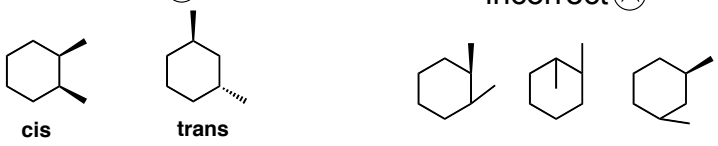


3.15: Heterocyclic Compounds (please read)
a cyclic compound that contains an atom other than carbon in the ring (typically N, O, S)

Drawing Structures

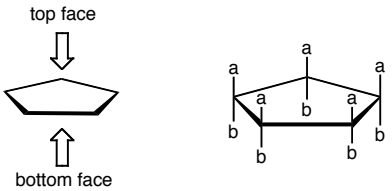
CYCLIC ALKANES: Substituents on a cycloalkane can be *cis* or *trans* to each other. You should draw the ring in the plane of the paper (solid lines) and use dashes and wedges to show whether substitutents are above or below the plane of the ring.

correct ☺ incorrect ☹



cis **trans**

On occasion you may wish to distinguish the faces of a cycloalkane.



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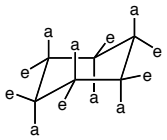
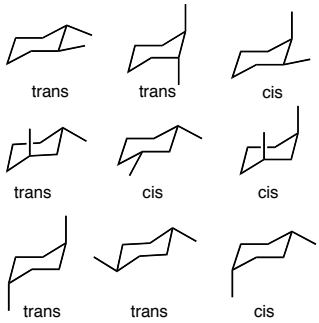
CYCLOHEXANE: For cyclohexanes you may be asked to draw a chair, in which case all substituents must be either axial or equatorial. The following is the correct way to draw chair cyclohexane. Note how the axial and equatorial substituents are represented off each carbon.

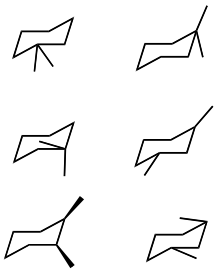


Disubstituted chair cyclohexanes:

correct ☺



incorrect ☹



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