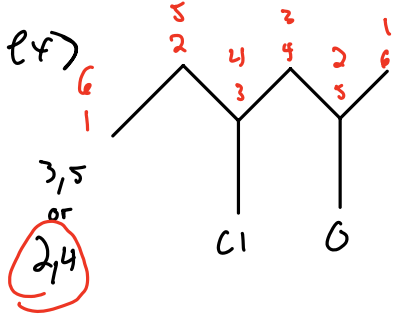
Ch 4 Alkanes and Cycloalkanes

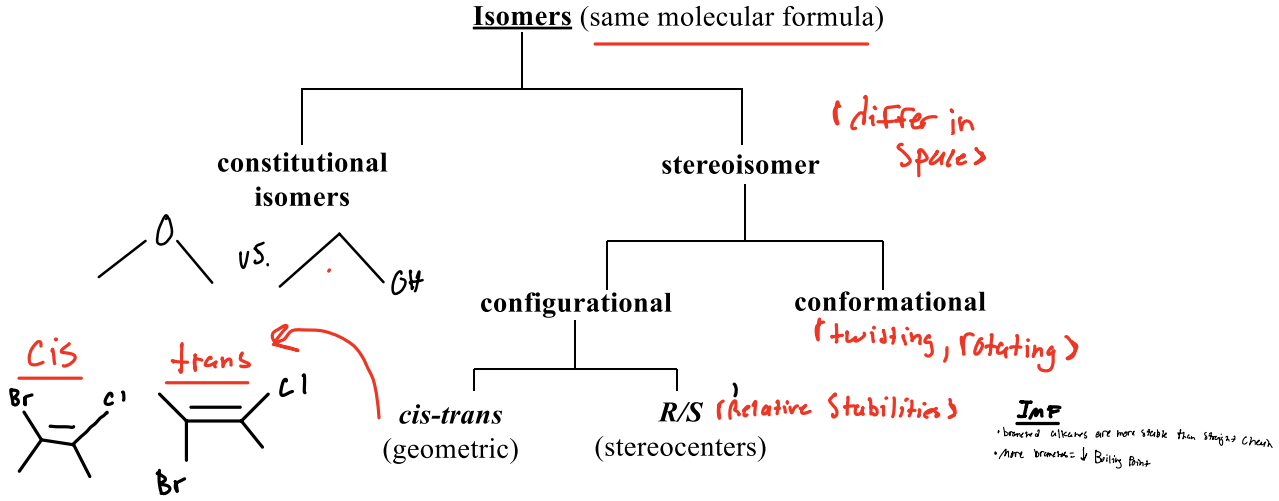


I. Nomenclature
   a. IUPAC rules
   b. handout
      i. find parent chain
      ii. name substituents
      iii. assign number locant to substituents (keep numbers as low as possible)
      iv. alphabetize substituents

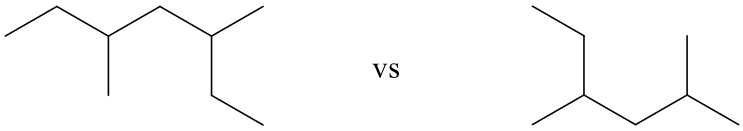
4-chloro-2-methyl hexane

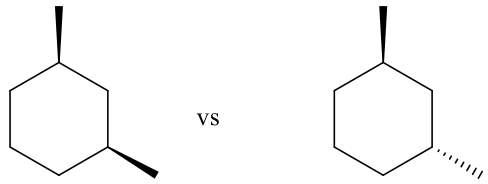
stereo – substituents – parent – unsaturation – functional group

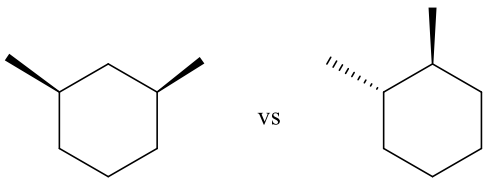
II. Constitutional isomers



Constitutional isomers have _____

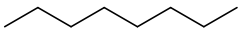


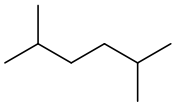


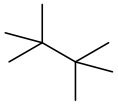


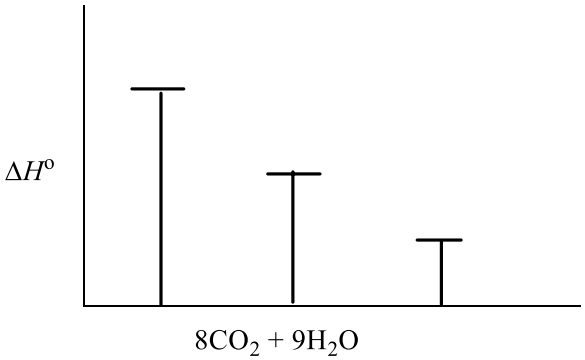
Relative stabilities of alkanes are determined by combustion

branched alkanes are more stable than straight-chain alkanes

I C_8H_{18}  $\Delta H^o = -5470$ kJ/mol

II C_8H_{18}  $\Delta H^o = -5460$ kJ/mol

III C_8H_{18}  $\Delta H^o = -5452$ kJ/mol



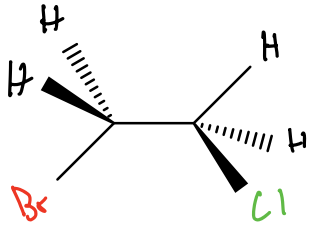
different views of the molecule

(think 3-D)

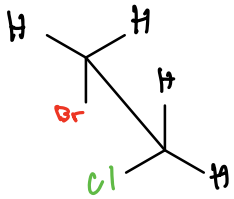
. from wedge & Dash to Newman you rotate the molecule 180°

III. Newman projections (look at handout)

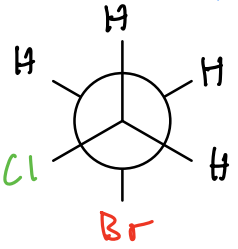
a. convert: wedge and dash → sawhorse → Newman projection, and vice versa



wedge & Dash



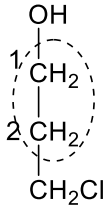
Sawhorse

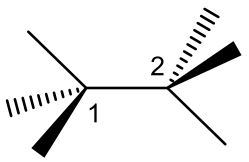


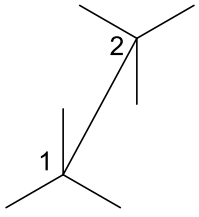
Newman

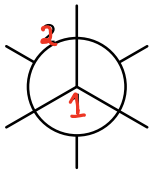
Let's take a look at 3-chloropropan-1-ol

look down C-1 to C-2





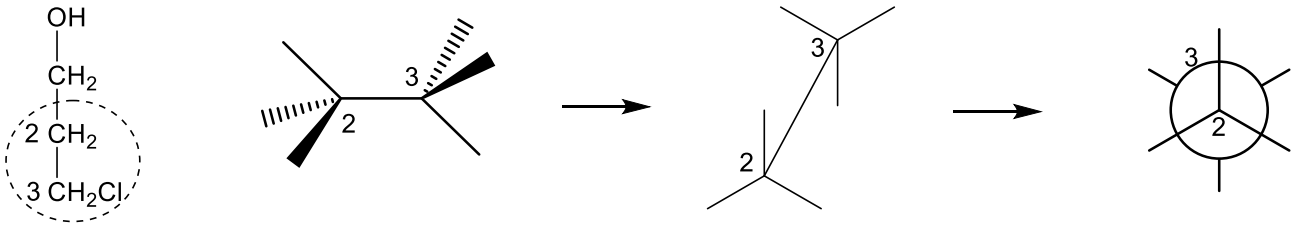




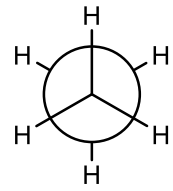
1 = front carbon

2 = Back carbon

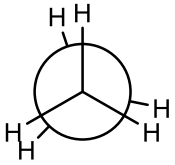
look down C-2 to C-3



Conformations of ethane



Staggered



Eclipse

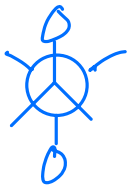
• implies the H's are perfectly aligned

The angle between the H-atoms is called the dihedral or _____.

IV. Conformational analysis

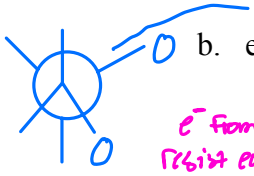
a. Terms

i. staggered - H atoms (groups) are as far apart as possible



ii. eclipsed - H atoms are as close as possible (one behind the other)

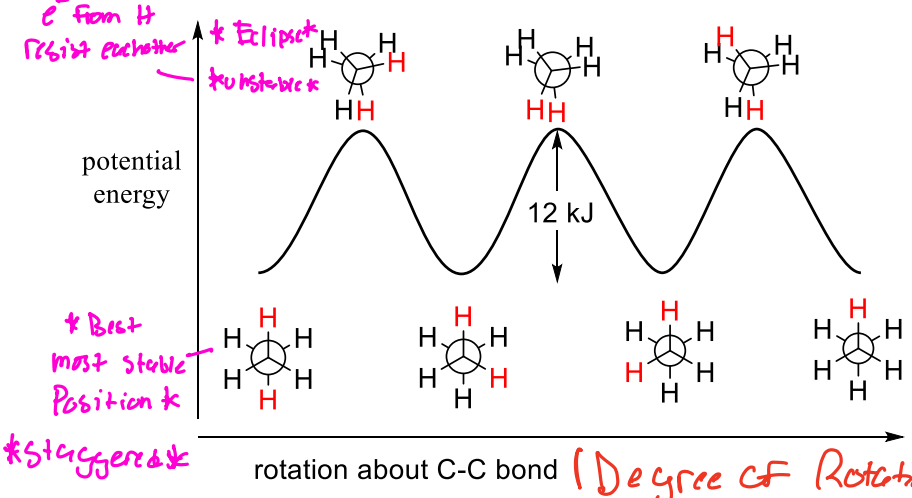
iii. anti-periplanar – Bulky groups are as far apart as possible



iv. gauche – Staggered conformer where bulky groups are only 60° apart

b. ethane

ETHANE



e⁻ from H resist each other

* Eclipsed * Most unstable *

* Best most stable Position *

Staggered

(Degree of Rotation) (Rotated 360° by the end)

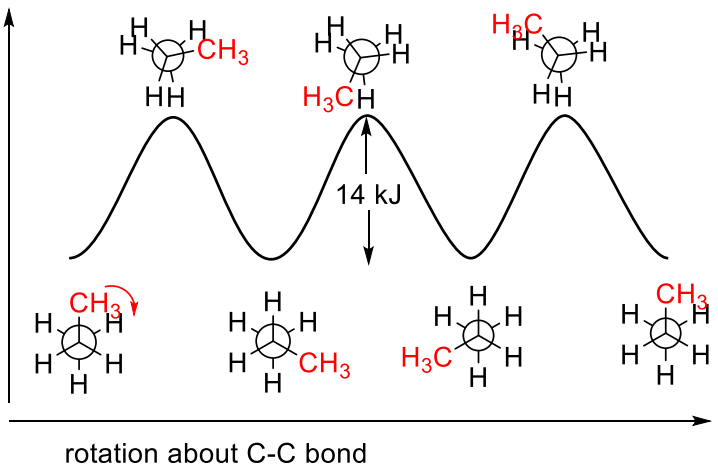
we are rotating the front carbon and holding the carbon in the back steady

c. propane

PROPANE – only thing different than ethane is the energy barriers (14 kJ)

* Peaks always eclipse *

* Valleys always staggered *

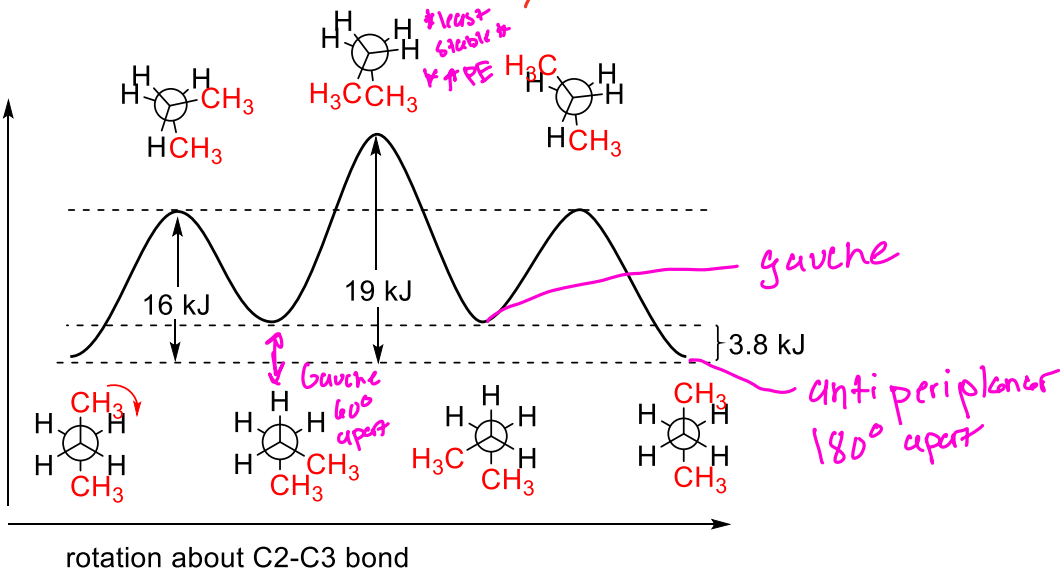


d. butane (a little more complicated) – 2 energy barriers

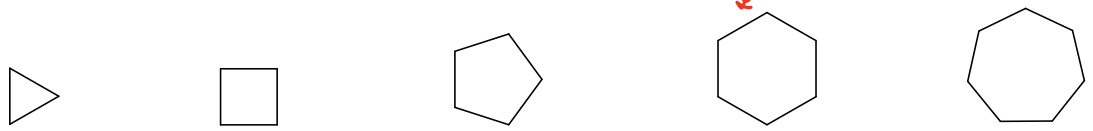
* Peaks always eclipse *

* Valleys are Gauche or antiperiplanar

BUTANE



V. Cycloalkanes — Cyclohexane → Preffered



60° 90° 108° 120°

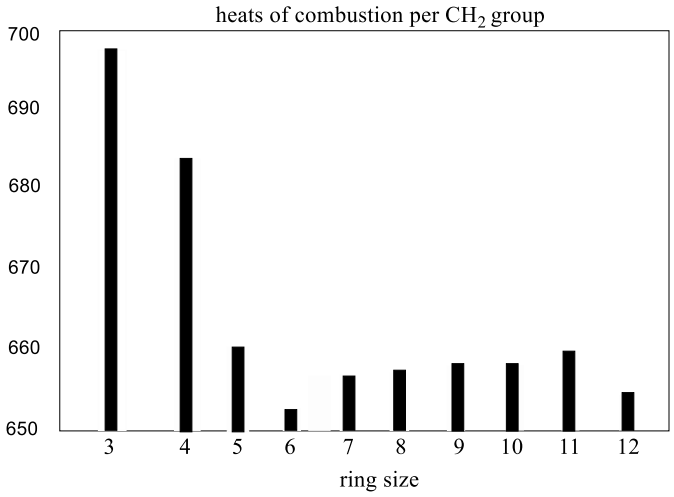
- Sp^3 carbon rings are not flat they "pucker" (deviation from 109.5°)

all of the above contain sp^3 carbons

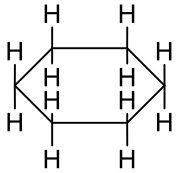
ring strain is a combination of torsional strain (dihedral angle / eclipsing) and angle strain

Cyclohexane is the most stable

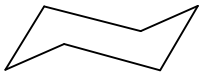
- all H-atoms can stagger
- Sp^3 carbons can have 109.5° angle



So why does cyclohexane appear to be the most stable?



flat

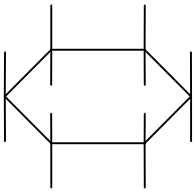


puckered

what 6-C actually look like

VI. Conformations of cyclohexane

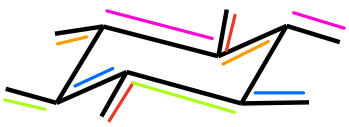
- Cyclohexane can twist into other shapes but the chair is always most stable/lowest energy
- *cis* and *trans* stereoisomers of cyclohexane



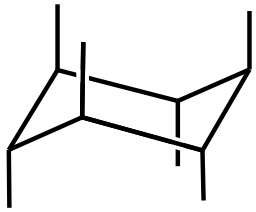
- everything is parallel
- Only use Chair Conformer (Most Stable)

a. axial and equatorial positions

- Must be Parallel



Equatorial



Axial

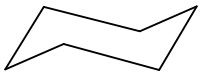
- if it hints at going up or down

Ring flip

b. stability of chair conformations

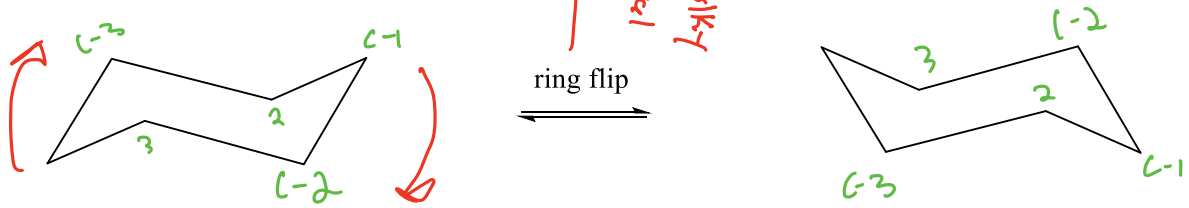
bulky groups are more stable in equatorial position, *if possible*

i. 1,3-diaxial interactions



ring flip puts Bulky group in equatorial position

ii. monosubstituted



iii. disubstituted - one group is more bulky

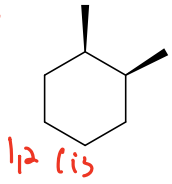
• favored Conformer exists

1, 2

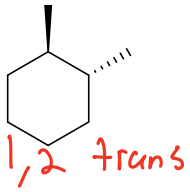
1, 3

1, 4

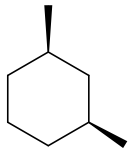
cis and trans



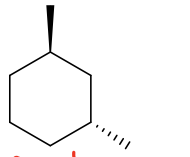
1,2 cis



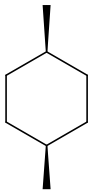
1,2 trans



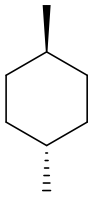
1,3 cis



1,3 trans

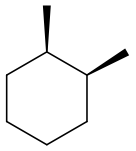


1,4 cis

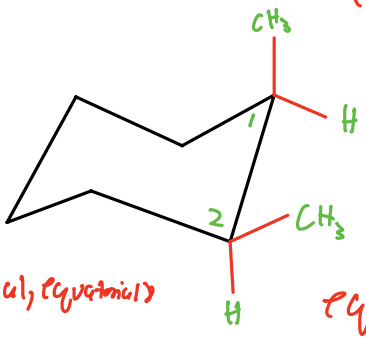


1,4 trans

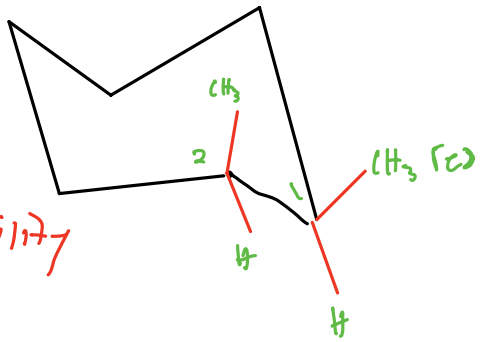
let's do 1,2



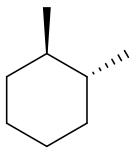
cis



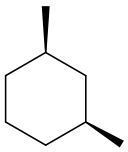
(axial, equatorial)

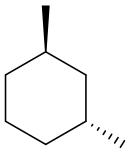


equal energies/ Stability

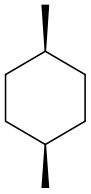


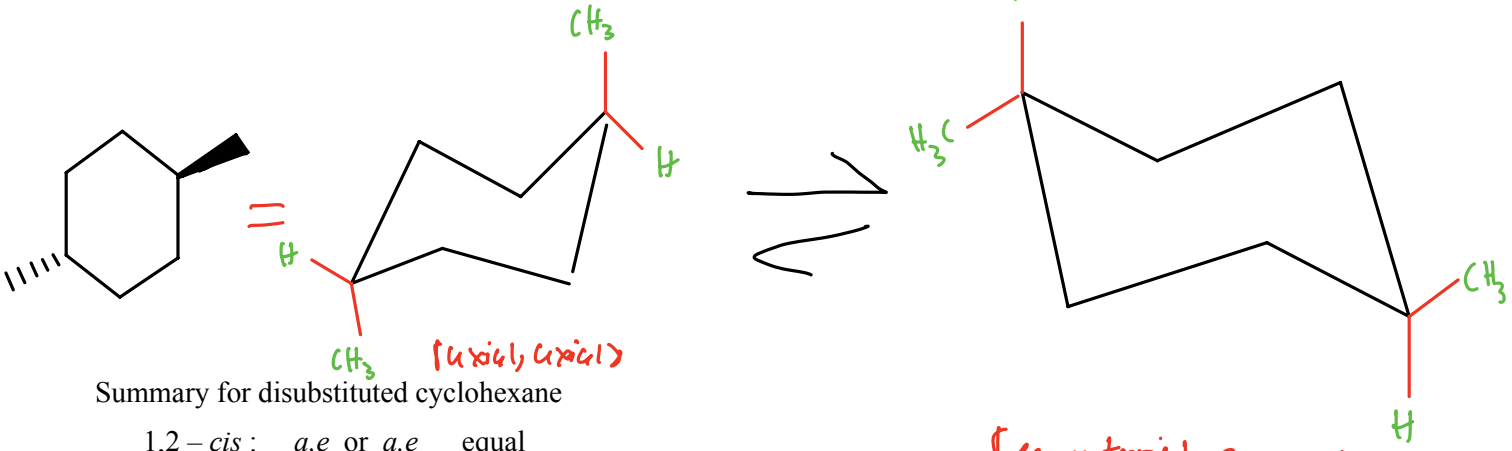
let's do 1,3 – *cis* and *trans*





let's do 1,4 – *cis* and *trans*





Summary for disubstituted cyclohexane

1,2 – *cis* : *a,e* or *a,e* equal

1,2 – *trans* : *a,a* or *e,e*

1,3 – *cis* : *a,a* or *e,e*

1,3 – *trans* : *e,a* or *a,e* equal

1,4 – *cis* : *a,e* or *e,a* equal

1,4 – *trans* : *a,a* or *e,e*

iv. polysubstituted

the bulkiest group should be equatorial, usually

	1,3−diaxial energy	*e*:*a* ratio
–Cl	2.0 kJ/mol	70:30
–OH	4.2	83:17
$-CH_3$ (Me)	7.6	95:5
$-CH_2CH_3$ (Et)	8.0	96:4
$-CH(CH_3)_2$ (*i*-Pr)	9.2	97:3
$-C(CH_3)_3$ (*t*-Bu)	22.8	9999:1

v. polycyclics – *cis* and *trans* decalin

consider the H-atoms on two fused C-atoms