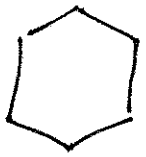
Chapter 5: Alkanes and Cycloalkanes

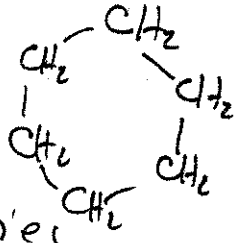
Alkanes: General Formula: C_nH_{2n+2} (saturated hydrocarbons)

ex: hexane; $CH_3CH_2CH_2CH_2CH_2CH_3$

C_6H_{14} 

Cycloalkanes: General Formula: C_nH_{2n} (1 unit of unsaturation)

ex: cyclohexane 



C_6H_{12}

Alkanes – have similar chemical properties but the physical properties vary with size and shape

(*)(*) Need to know the names of all straight chain alkanes

- Straight-chain alkanes → homologous series

CH_4 – methane (CH_3– methyl)

CH_3CH_3 – ethane (CH_3CH_2– ethyl)

$CH_3CH_2CH_3$ – propane ($CH_3CH_2CH_2$– propyl)

etc...

Table 5.1 Boiling Points and Melting Points for Some Alkanes

Molecular Formula	Name	Molecular Weight	bp, °C	mp, °C
CH_4	methane	16	−164	−182.5
C_2H_6	ethane	30	−88.6	−183.3
C_3H_8	propane	44	−42.1	−189.7
C_4H_{10}	butane	58	−0.6	−138.4
C_4H_{10}	2-methylpropane	58	−10.2	−138.3
C_5H_{12}	pentane	72	36.1	−129.7
C_5H_{12}	2-methylbutane	72	27.9	−159.9
C_5H_{12}	2,2-dimethylpropane	72	9.5	−16.6
C_6H_{14}	hexane	86	68.9	−93.5
C_7H_{16}	heptane	100	98.4	−90.6
C_8H_{18}	octane	114	125.7	−56.8
C_9H_{20}	nonane	128	150.8	−51.0
$C_{10}H_{22}$	decane	142	174.1	−29.7
$C_{20}H_{42}$	icosane	282	343	36.8

(*) Notice as chain length increases bpt + mpt increase

(*) Larger molecules have stronger Van der Waals interactions Therefore higher bpts + mpts.

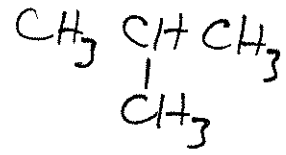
- 2-alkanes with the molecular formula C_4H_{10}

1-straight-chain alkane

$CH_3CH_2CH_2CH_3$

butane

1-branched-chain alkane



2-methylpropane

related as structural isomers

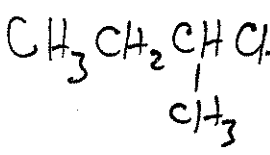
- 3-alkanes with the molecular formula C_5H_{12}

1-straight chain alkane

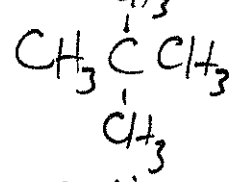
$CH_3CH_2CH_2CH_2CH_3$

pentane

2-branched-chain alkanes



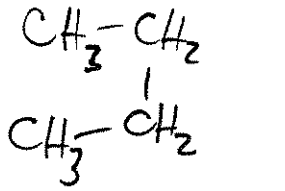
2-methylbutane

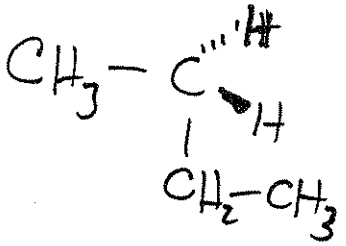


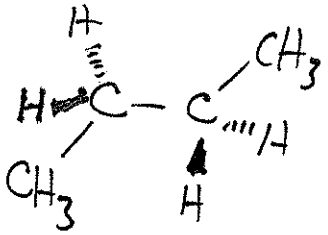
2,2-dimethylpropane

✡ You need to recognize that the same molecule can be drawn many different ways.

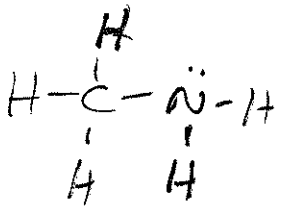
Butane $CH_3CH_2CH_2CH_3$

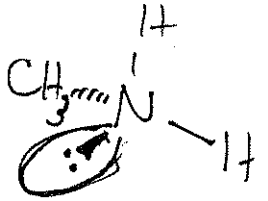


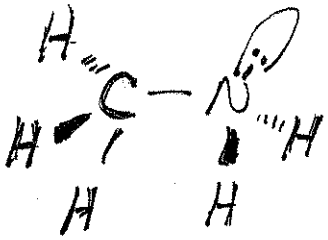




- methylamine CH_3NH_2



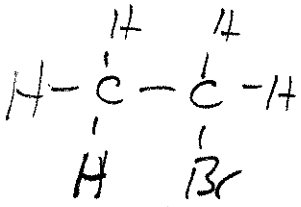




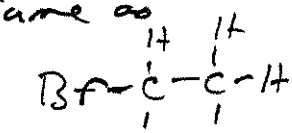
- **ETHANE**: CH_3CH_3

→ replace 1 hydrogen with Br (can replace any H)

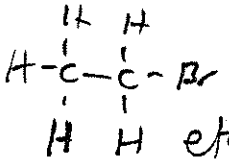
get CH_3CH_2Br



⇐ (same as



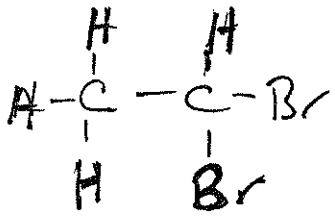
(or)

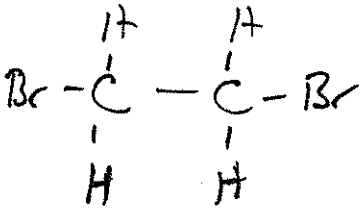


etc.)

→ If one replaces 2 hydrogens with bromines you can get two different compounds (depending on which Hs are replaced)

CH_3CHBr_2 and $BrCH_2CH_2Br$





Constitutional or structural isomers

PROPANE

$\overset{1^\circ}{CH_3}\ \overset{2^\circ}{CH_2}\ \overset{1^\circ}{CH_3}$

1° = primary (1-carbon attached)
2° = secondary (2-carbons attached)
3° = tertiary (3-carbons attached)

$CH_3CH_2CH_2-$

propyl group

ex $CH_3CH_2CH_2Br$ ← 1° alkyl halide

n-propyl bromide (common name)

"normal" straight chain

1-bromo propane (IUPAC name)

$CH_3CH(CH_3)-$ ← Alternative IUPAC (propan-2-yl)

isopropyl group (1-methylethyl)

$CH_3CH(Br)CH_3$ ← 2° alkyl halide

isopropyl bromide (common name)

2-bromo propane (IUPAC name)

BUTANES

→ 2 compounds with C_4H_{10} mol. formula

$CH_3CH_2CH_2CH_3$

butane

$CH_3-C(H)(CH_3)-CH_3$

isobutane or 2-methylpropane (common / IUPAC)

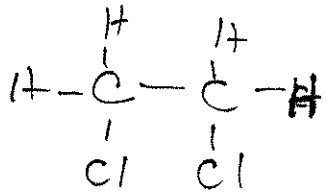
- Butane derivatives:

	IUPAC	Common
$CH_3CH_2CH_2CH_2-Br$	1-bromo butane	n-butyl bromide
$CH_3CH(Br)CH_2CH_3$	2-bromo butane	sec-butyl bromide
$CH_3-C(H)(CH_3)-CH_2-Br$	1-bromo-2-methyl propane	isobutyl bromide
$CH_3-C(CH_3)_2-Br$	2-bromo-2-methyl propane	tert-butyl bromide

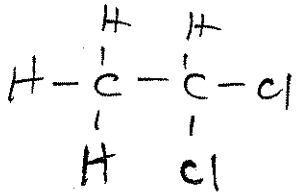
5-4

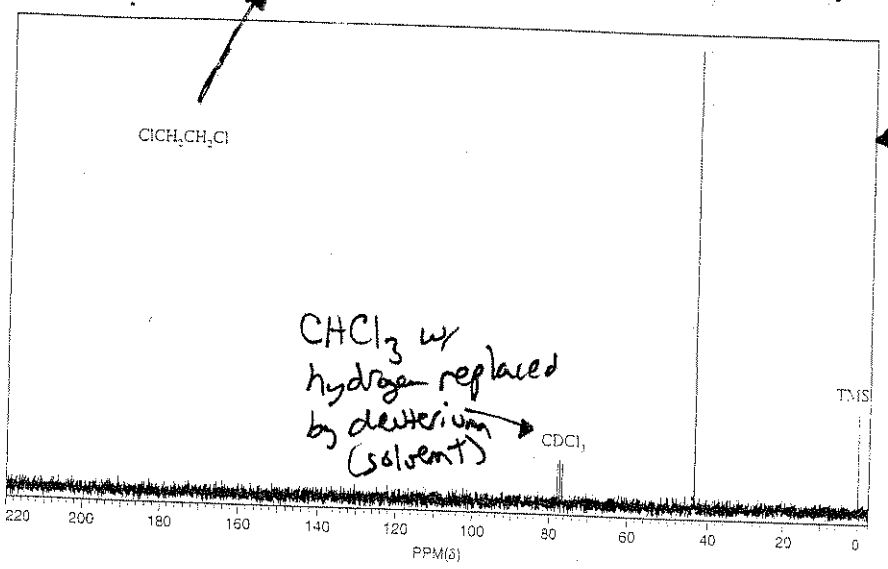
Nuclear Magnetic Resonance as a Tool for the Study of Molecular Structures

⊛ Compare two molecules with the same molecular formula $C_2H_4Cl_2$ but different structural formulas (different connectivities)



and

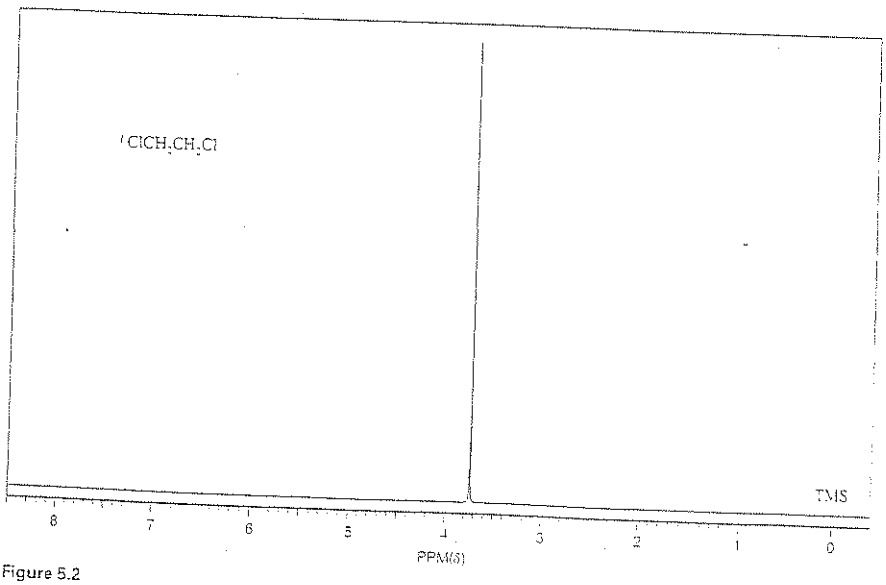




← ^{13}C-NMR

- only 1 type of carbon in ^{13}C-NMR spectrum

TMS = tetramethyl silane (internal std)



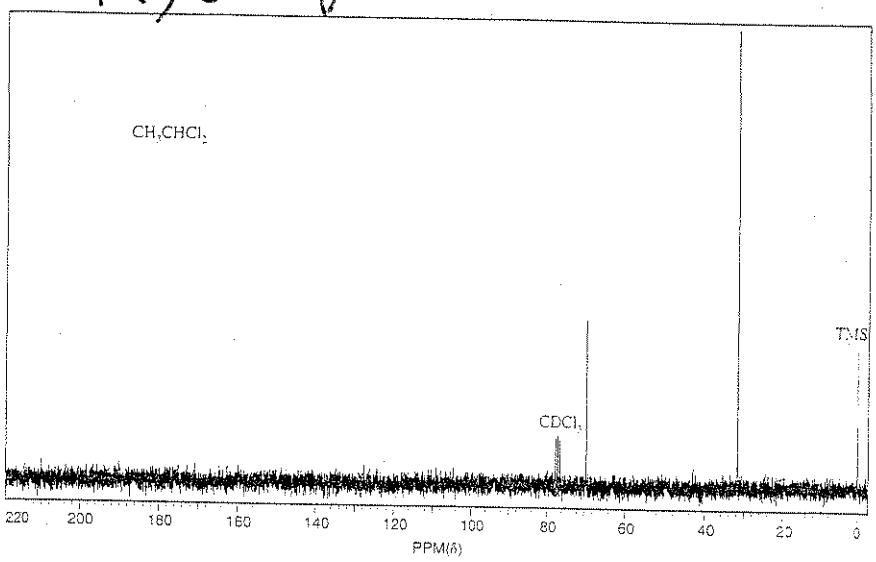
← ^{1}H-NMR

- only 2 type of hydrogen in ^{1}H-NMR spectrum

← Fig 5.2 p148 in text

Figure 5.2
Nuclear magnetic resonance spectra of 1,2-dichloroethane: *(top)* carbon spectrum; *(bottom)* proton spectrum.

Fig 5.3 p 149 in text



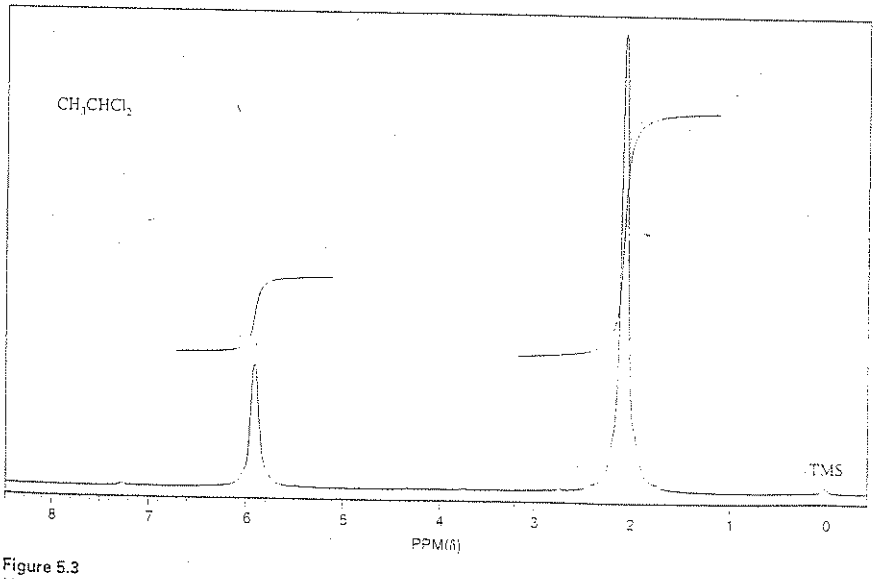
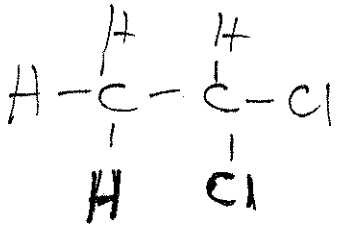


Figure 5.3
Nuclear magnetic resonance spectra of 1,1-dichloroethane: *(top)* carbon spectrum; *(bottom)* proton spectrum.



← ^{13}C-NMR

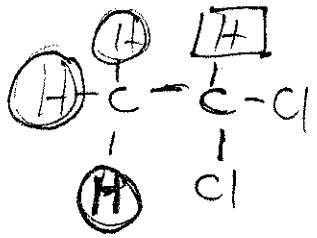
- two types of carbons in ^{13}C-NMR spectrum

← ^{1}H-NMR

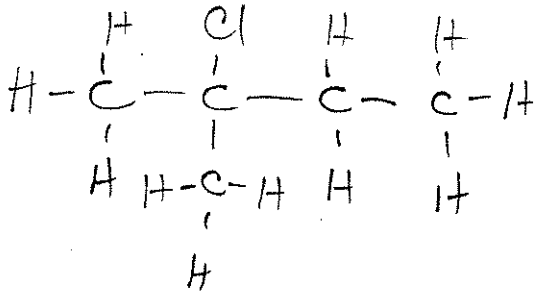
- two types of hydrogens in ^{1}H-NMR spectrum

$\int\int$ ← represents integration of area under the peaks

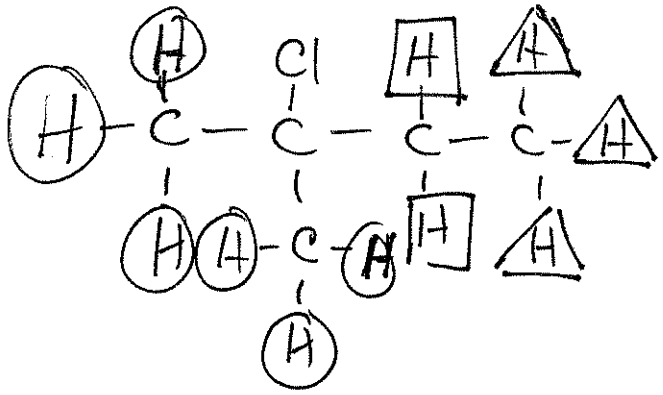
→ can tell relative # of hydrogens



A Closer Look at Equivalence of Groups and Atoms in Molecular Structure



What does it mean for atoms to be equivalent?



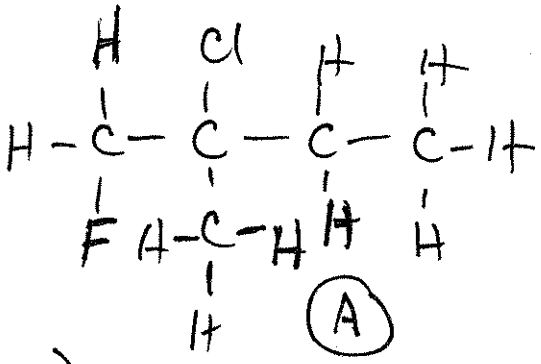
- 3 types of hydrogen atoms are in this molecule

(H) → 6 equivalent H-atoms

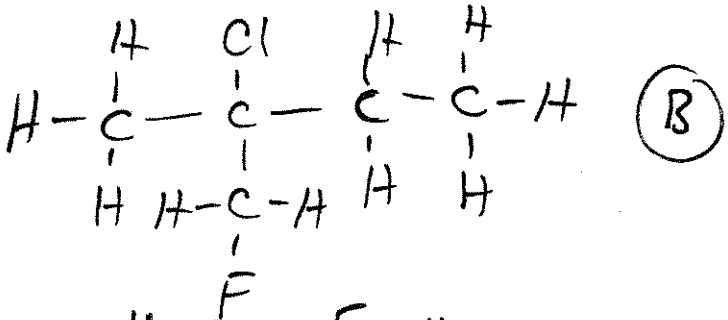
[H] → 2 equivalent H-atoms

△H → 3 equivalent H-atoms

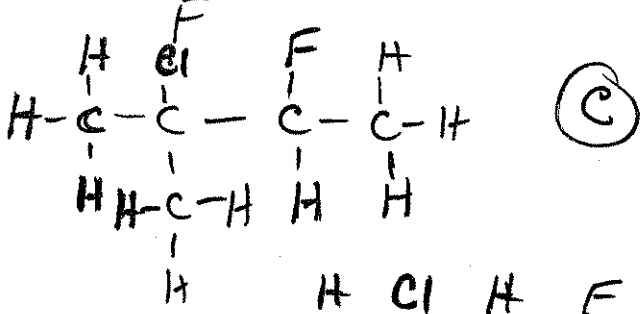
⇒ If we substitute a fluorine atom for 1-hydrogen we get:



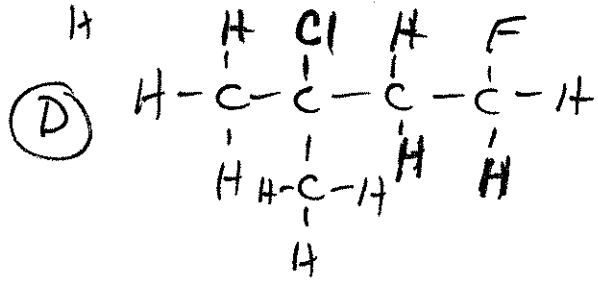
(A)



(B)



(C)



(D)

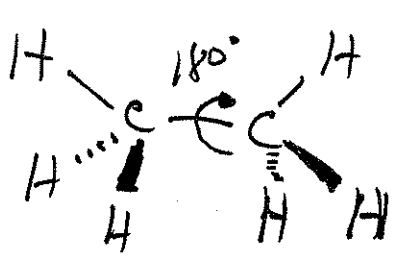
★ a) How many types of H-atoms are in each molecule and b) which are equivalent H-atoms? (circle w/ O □ + △, ⬭)

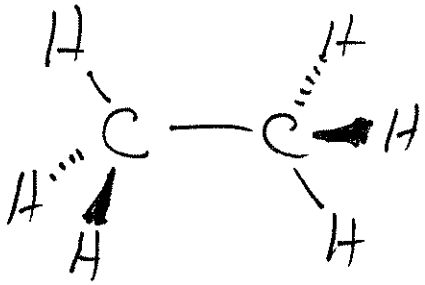
- Look closely at structures (A) + (B). Are they different molecules or the same?

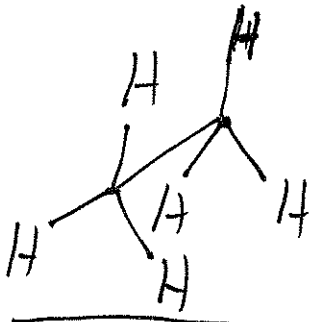
Conformations of Simple Alkanes

- Alkanes have different conformations ⇒ structures that differ only by rotation about 1 or more bonds.

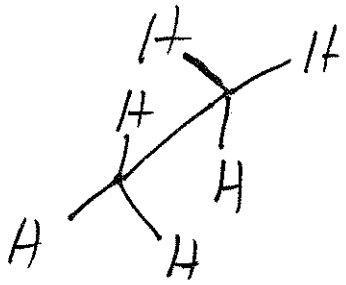
ex: Ethane





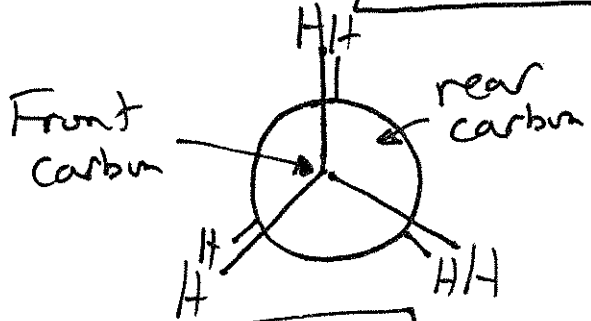


eclipsed

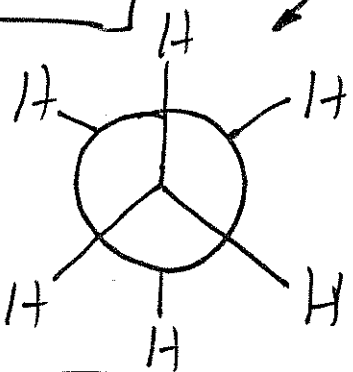


staggered

Sawhorse Projections



eclipsed

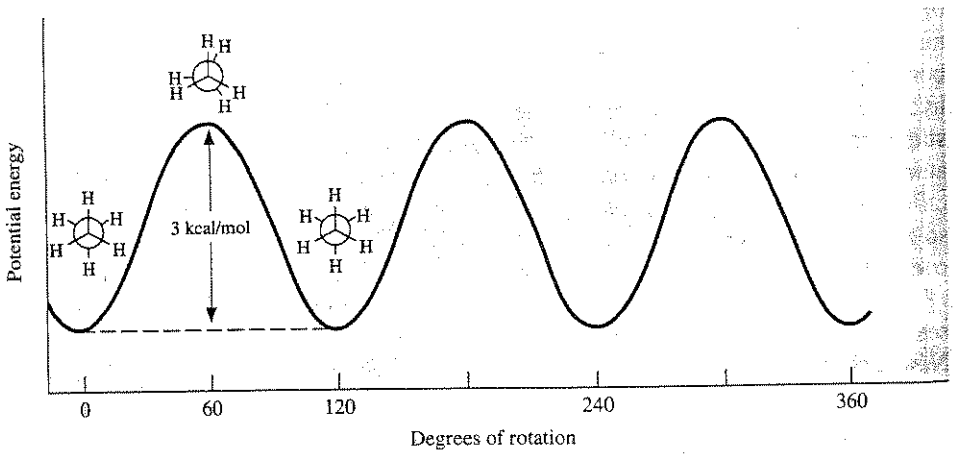


staggered

maximal separation that can be achieved ⇒ 60°

Newman Projections

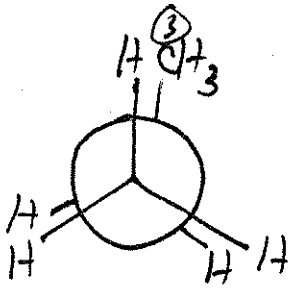
- Staggered conformation → more stable (by 3 kcal/mol) due to minimization of repulsions between hydrogen orbitals (5-8)



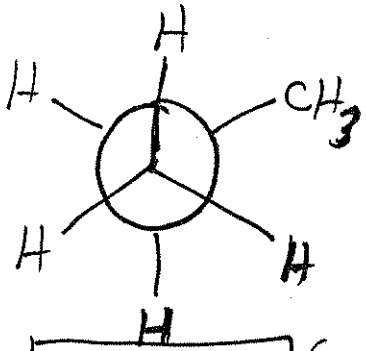
p162 in text

Figure 5.8
Energy diagram showing the energy difference between the staggered and eclipsed conformations of ethane.

Propane $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_3$ → Newman projection down C1–C2 bond

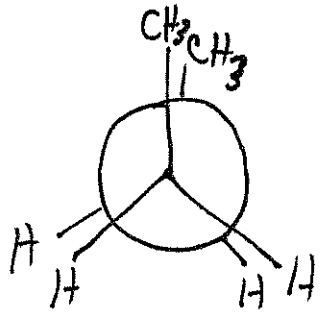


eclipsed



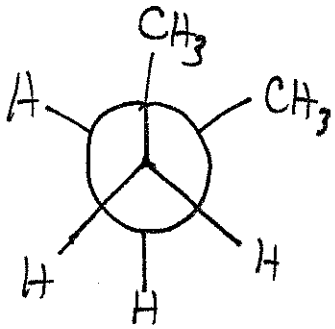
Staggered (more stable)

Butane $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3$ → Newman projection down C2–C3 bond

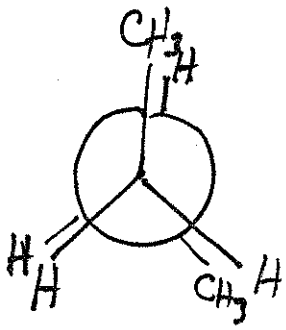


Totally eclipsed

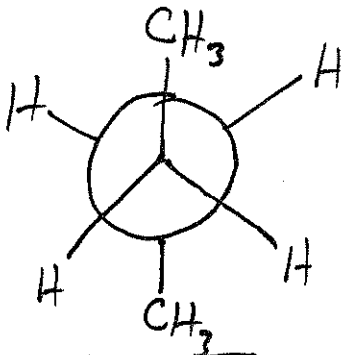
↑ Highest energy Conformation (steric hindrance: (interaction between 2 bulky methyl groups)



Gauche



eclipsed



anti (Staggered)

↑ Lowest energy conformation (steric interactions minimized; C-1 + C-4 methyls 180° apart)

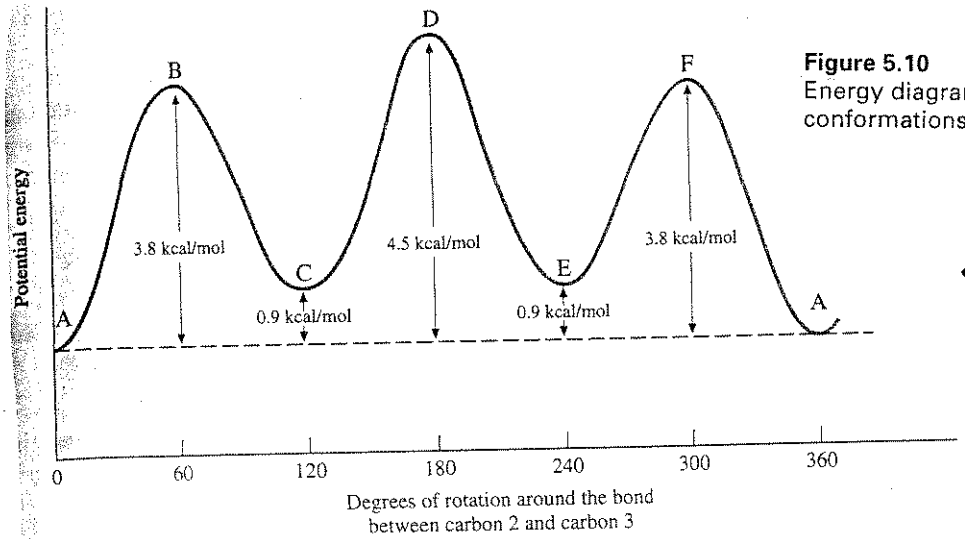
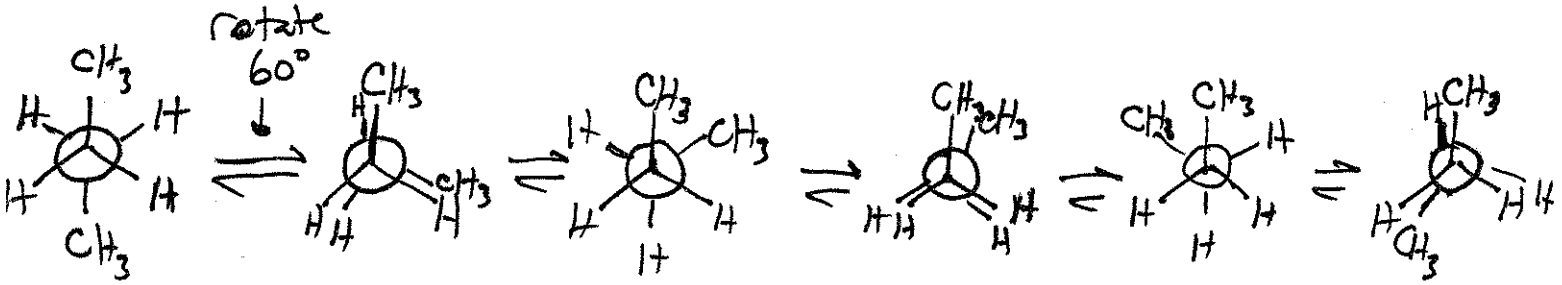


Figure 5.10
Energy diagram for the conformations of butane.

← p 168 in text



A Anti

B eclipsed

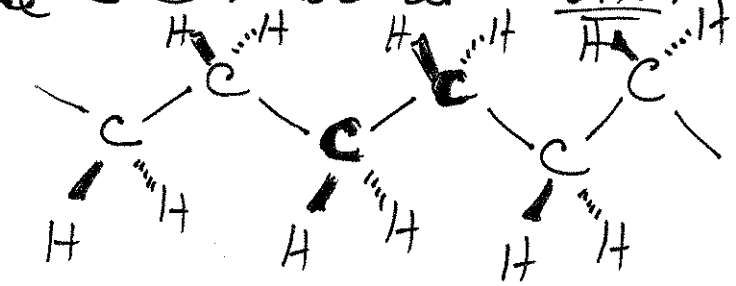
C gauche

D totally eclipsed

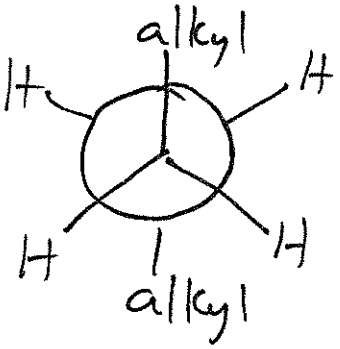
E gauche

F eclipsed

Higher n-alkanes ⇒ exist primarily in the conformation where the C-C bonds are anti.



⇒



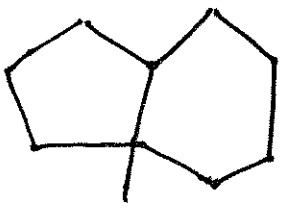
All anti-conformations →

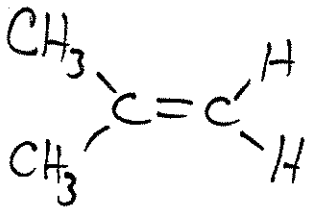
- Conformers with the least steric interactions among bulky groups will be the most stable.

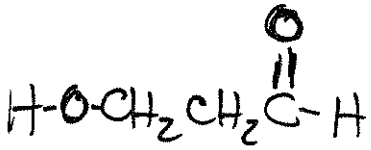
5-10

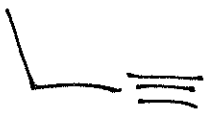
Review of Line-Angle Formulas of Organic Compounds

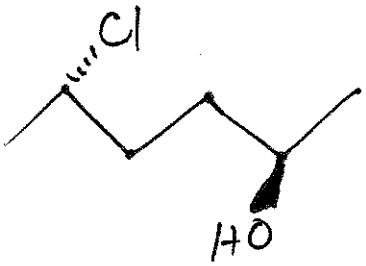
Line-Angle Formula	Condensed Structural Formula

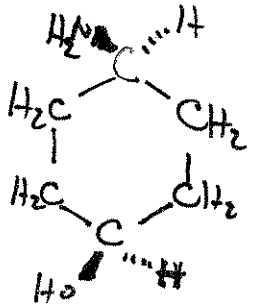












Nomenclature

- Before The 19th Century Compounds were named based on Thier origin (ex: urea – from urine)
  - in The late 1800's - IUPAC was formed

IUPAC - International Union of Pure and Applied Chemistry

IUPAC - developed a system of nomenclature based on numerous rules

→ IUPAC Nomenclature limitations:

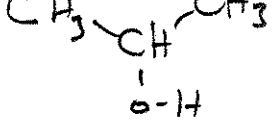
a) many compounds had common names before IUPAC started

b) many IUPAC names are cumbersome

Two types of nomenclature

1) Common
2) Systematic (IUPAC)

ex:



isopropyl alcohol (common)

2-propanol (IUPAC)

Table 5.2 The Names of Some Straight-Chain Alkanes

Molecular Formula	Name
CH_4	methane
C_2H_6	ethane
C_3H_8	propane
C_4H_{10}	butane
C_5H_{12}	pentane
C_6H_{14}	hexane
C_7H_{16}	heptane
C_8H_{18}	octane
C_9H_{20}	nonane
$C_{10}H_{22}$	decane
$C_{11}H_{24}$	undecane
$C_{12}H_{26}$	dodecane
$C_{16}H_{34}$	hexadecane
$C_{18}H_{38}$	octadecane
$C_{20}H_{42}$	icosane

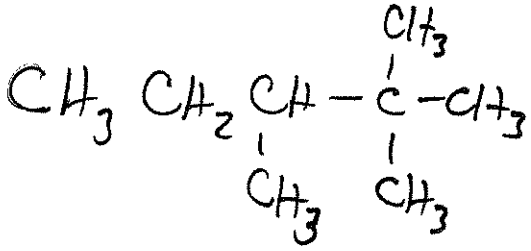
p 172 in text

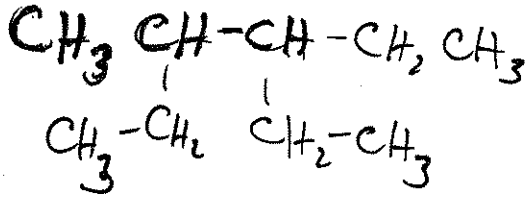
Reminder: KNOW The names of The straight chain alkanes up to **C10.**

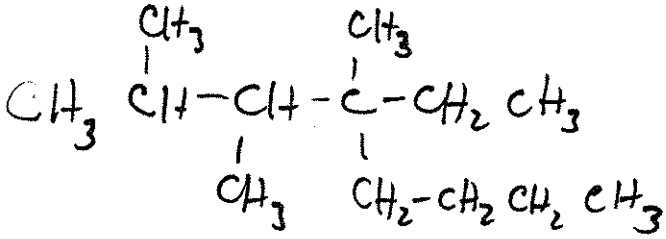
Rules for Naming Branched-Chain Alkanes

1. Select the longest chain and name as the n-alkane (parent chain)
2. Number the parent chain starting at the end of the chain nearest the 1st substituent.
3. Use the numbers obtained by application of rule #2 to designate the location of the substituent group(s) and name the substituents as alkyl groups.
4. List substituent groups alphabetically, along with the location number, before the parent chain name. (ie ethyl before methyl)
5. When two or more substituents are present on the same carbon, use the # twice.
6. When two or more substituents are identical, use the prefixes di, tri, tetra ... etc (These aren't used when alphabetizing)
   ⊛ (sec-butyl and tert-butyl → sec + tert not used in alphabetizing)
7. When chains of equal length compete for selection as the base chain, choose the chain with the greater # of substituents.
8. When branching 1st occurs at an equal distance from either end of the longest chain, choose the name that gives the LOWER # at the 1st point of difference.

IUPAC Name





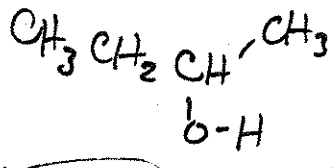


Nomenclature of Alkyl Halides and Alcohols

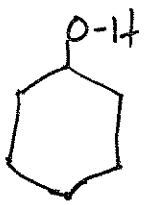
- Alcohols → change the "e" on the end of the alkane name to "ol" (IUPAC)

ex:

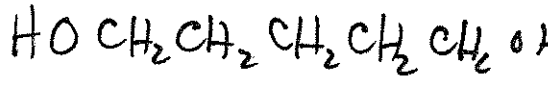
Common IUPAC



IUPAC Common

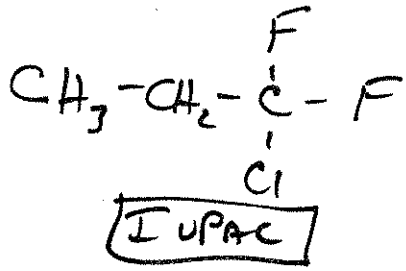


IUPAC

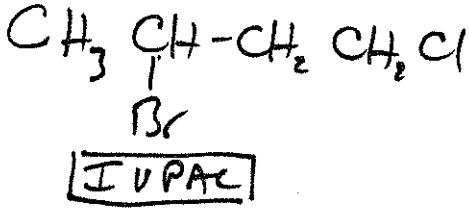


IUPAC

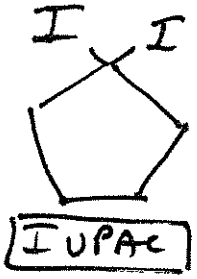
Alkyl Halides



IUPAC

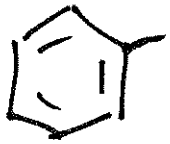


IUPAC

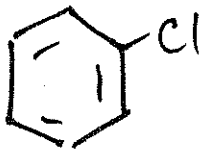


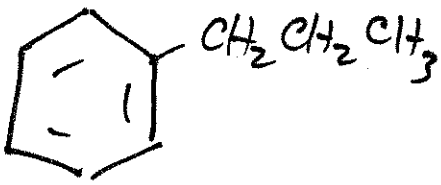
IUPAC

- **Phenyl group** → derived from benzene (remove 1-H)

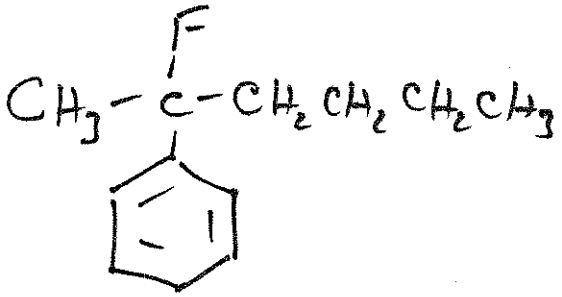


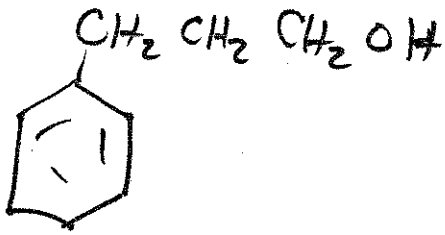
- also called an "aryl" group





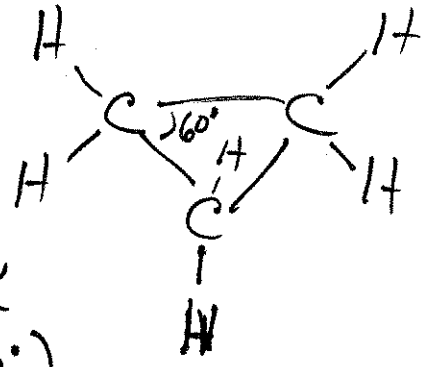
- If carbon chain is complex or 5 carbons or more The "phenyl" is used (The ring is named as a substituent





Structure and Conformations of The Simple Cycloalkanes

- **Cyclopropane** ≡



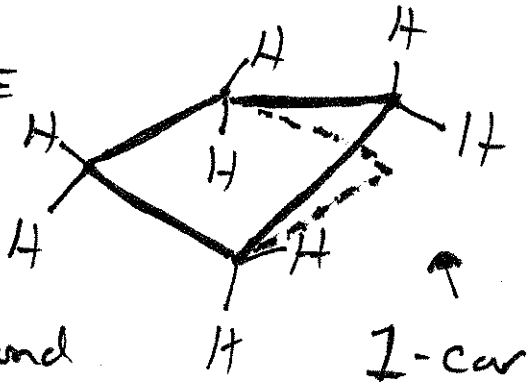
⇒ C-C bond angles of 60° Therefore RING STRAIN (109.5° compressed to 60°)

⇒ all hydrogen are eclipsed 3 above The ring, 3 below (torsional strain)

⇒ 3 carbons are in a plane

⇒ weaker Than normal C-C bonds because of inefficient overlap of orbitals (non-linear overlap)

Cyclobutane (liquid at rt + pressure) ≡



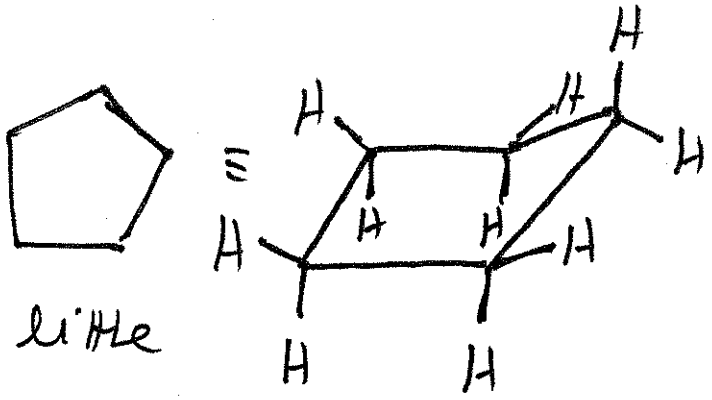
⇒ less strained because of presence of ≅ 90° bond angles

⇒ not planar; ring distorted 20° to prevent eclipsing of hydrogens → (doesn't prevent all eclipsing interactions, however)

1-carbon is up + out of The plane

⇒ pseudorotation occurs - a partial rotation about 2 bonds so That each carbon takes a turn out of plane

Cyclopentane

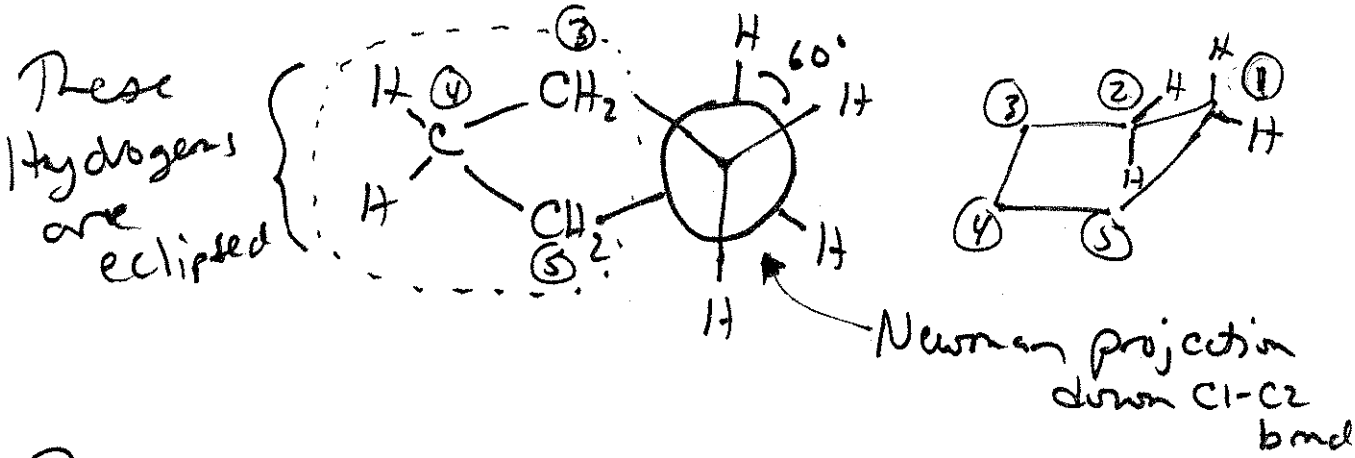


⇒ bond angles 108° (very little ring strain)

⇒ eclipsing of hydrogen relieved by distortion of the ring → ENVELOPE CONFORMATION (somewhat)

⇒ Four of the carbons lie in the same plane

⇒ pseudo rotation occurs (complete rotation is not allowed); each carbon takes a turn out of plane



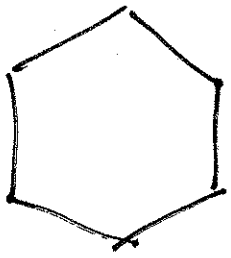
- Ring strain - effects reactivity. If you have more ring strain then the C-C bonds are weaker.

Cyclopropane (weaker bonds)
→ less energy given off when C-C bonds broken

cyclopentane (stronger bonds)
→ more energy given off when C-C bonds broken

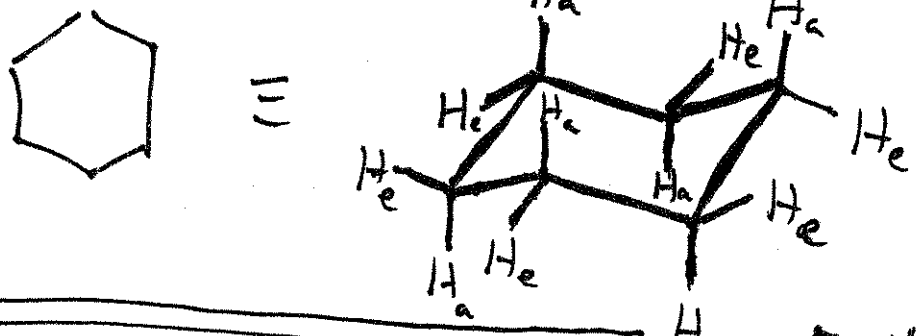
Cyclohexane - strain free

- no angle strain (has C-C bond angles of 109.5°)
- no torsional strain due to eclipsing hydrogens



- If cyclohexane were planar (all carbons in the same plane) then the bond angles would be 120° (tetrahedral carbon prefers 109°)

- To get 109° bond angles cyclohexane exists in a chair conformation



H_a = axial hydrogen

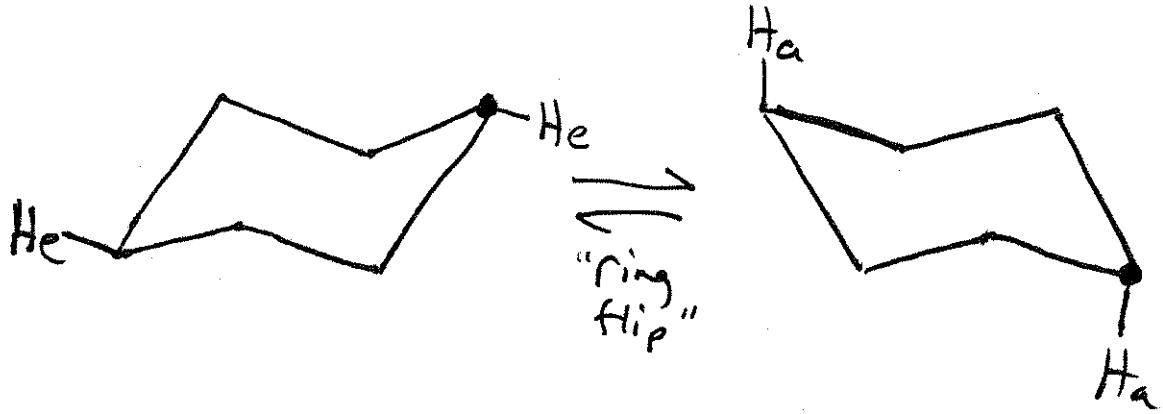
H_e = equatorial hydrogen

⇒ **You need to know how to draw**

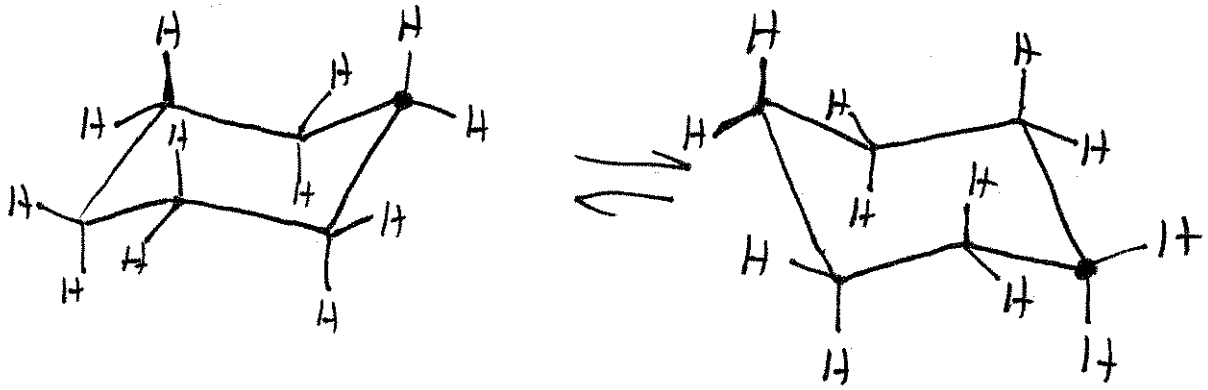
- You should practice so you can draw a chair conformation rapidly & accurately

Lets practice:

In cyclohexane 1-chair form is in equilibrium with the other chair form



- an equatorial substituent becomes an axial substituent when the ring "flips"



⇒ In chair conformation drawings: equatorial hydrogen C-H bonds are PARALLEL to the C-C bond 1-bond away

⇒ To do the "ring flip" between the two chair conformations cyclohexane undergoes pseudorotation (ring flip takes energy)

Conformations of Cyclohexane

Figures on this page are from a different textbook – Org. Chem. L.G. Wade

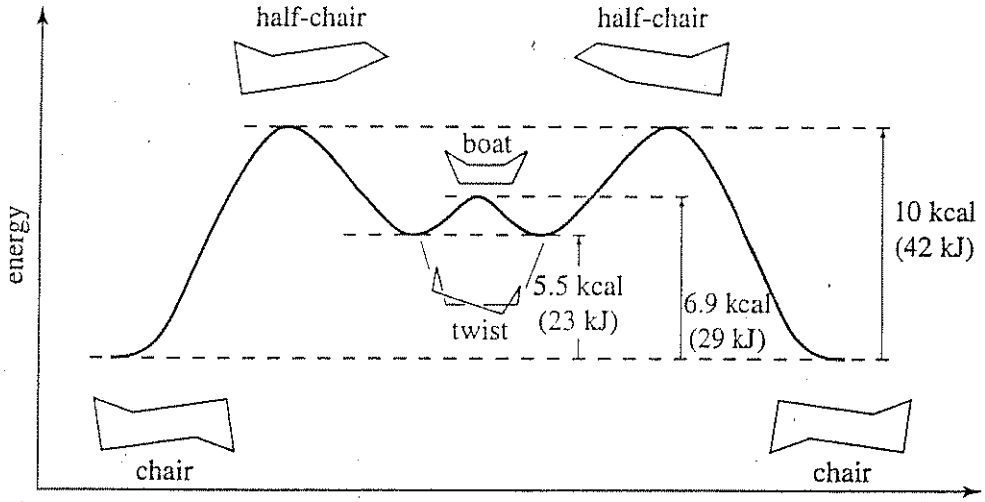
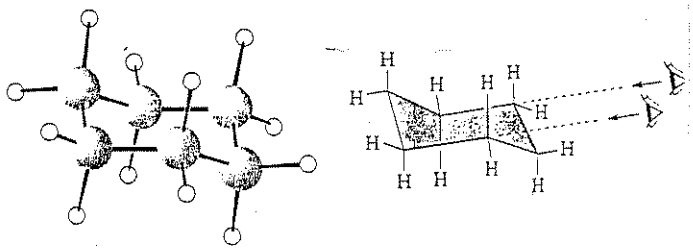


FIGURE 3-21 Conformational energy of cyclohexane. The chair conformation is most stable, followed by the twist boat. To convert between these two conformations, the molecule must pass through the unstable half-chair conformation.



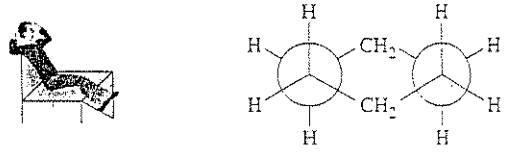
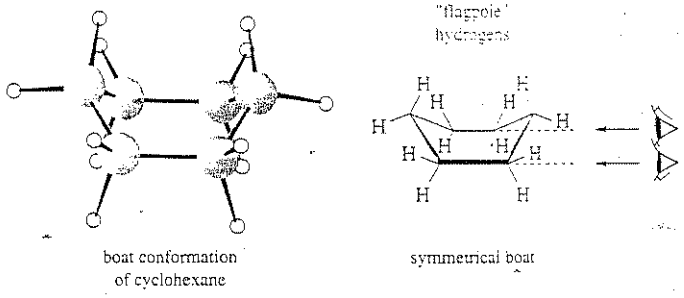


FIGURE 3-19 The chair conformation of cyclohexane has one methylene group puckered upward and another puckered downward. Viewed from the Newman projection, the chair conformation has no eclipsing of the carbon–carbon bonds. The bond angles are 109.5°.



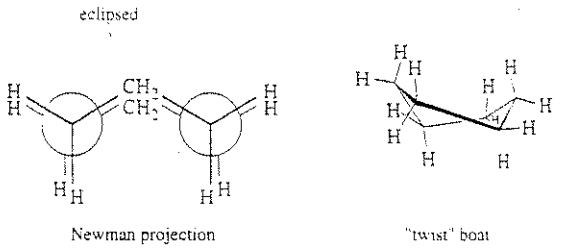
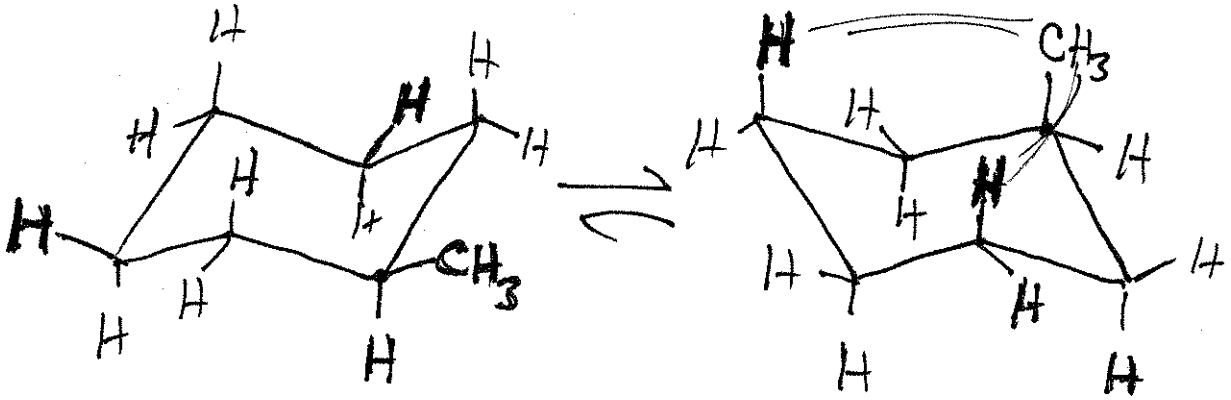


FIGURE 3-20 In the symmetrical boat conformation of cyclohexane, eclipsing of bonds results in torsional strain. In the actual molecule, the boat conformation is skewed to give the twist boat, a conformation with less eclipsing of bonds and less interference between the two flagpole hydrogens.

Monosubstituted Cyclohexanes: favored conformations often adopted



Favored Conformation

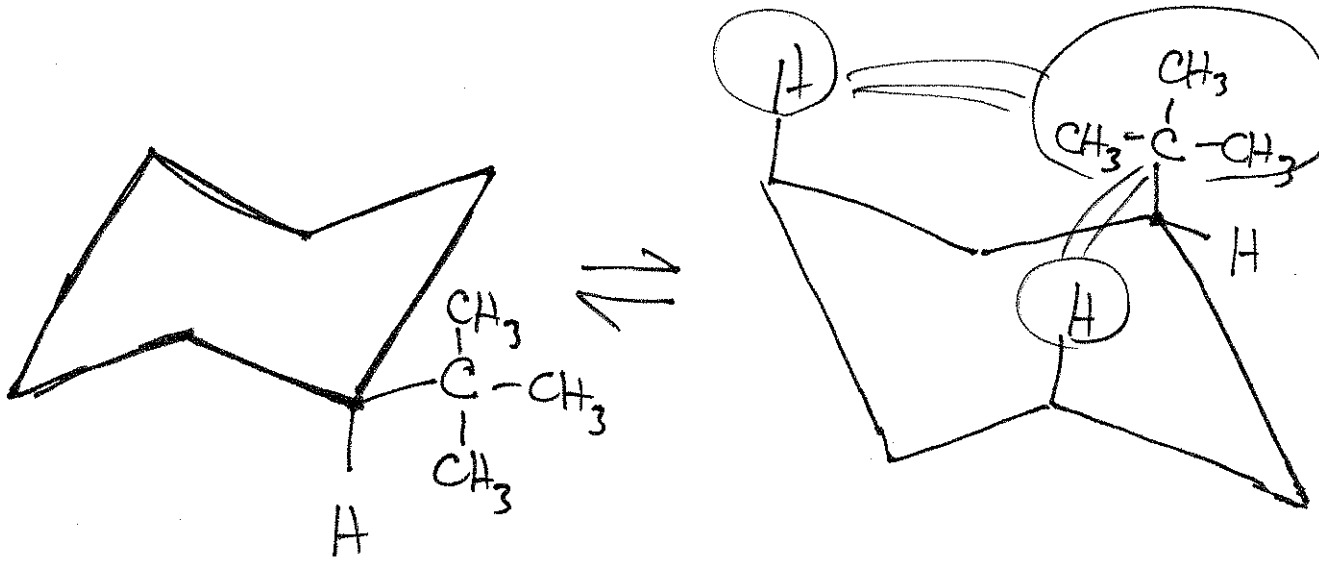
⊛ no 1,3-diaxial interactions w/ CH_3 group

→ less stable by 1.7 kcal/mole

• 1,3-diaxial interactions destabilize this conformation

• If the cyclohexane has bulkier substituents (than CH_3) then the substituent in the equatorial position is even more favored

ex: isopropyl group or t-butyl group



favored by 5.6 kcal/mol

Chemical Properties of Alkanes

Alkanes – mostly chemically inert

Three Main Types of Rxns

a) Combustion (fuels)

b) Hydrocracking (Oil refining)
↑
(breaks down large hydrocarbons into smaller ones w/ H_2 + catalyst)

c) Free-radical halogenation

ex: Propane – combustion

$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

ex: methane – free radical halogenation

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + CH_2Cl_2$$

↑ initiates free radical rxn mechanism