

ASSIGNED READINGS:

TODAY'S CLASS: Ch.2

- 2.1-2.7 Naming organic compounds
- 2.8-2.9 Relating physical properties & structure
- 2.10-2.14 Molecular flexibility: conformations of alkanes

NEXT CLASS: finish Ch.2, start Ch.3

(1)

Naming organic compounds: NOMENCLATURE

Two systems of nomenclature:

1. Common names

- Historical
- Not necessarily based on structure
- Too many to memorize for all known compounds...but...
- Still in use for common compounds
 - on chemical bottles...
 - need to know motifs: *normal, iso, neo*

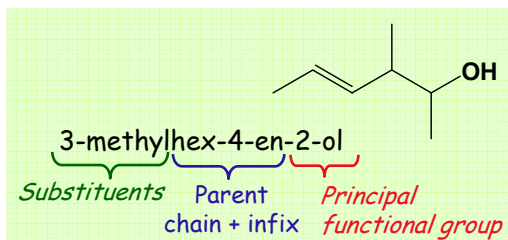
2. Systematic names (IUPAC)

- Unambiguous names
- Based on structure
 - Length of carbon chain
 - Bonding in chain
 - Positions of substituents
 - *etc.*
- Once you learn the rules, you can figure out names as required (less memorizing)
- *First: learn alkyl groups & functional groups*

Important: A compound can have more than one name, but a name must specify only one compound

Systematic names: one long word, made up of 3 main parts:

PREFIX	INFIX	SUFFIX
Based on length of longest continuous C chain (<i>parent</i>)	Based on C-C bond types in backbone	Based on most important (<i>principal</i>) functional group
PRECEDED BY: positions, #s, & names of substituents (in alphabetical order)		Except: • halides & ethers always treated as substituents
<u>Substituents:</u> alkyl halo hydroxy amino alkoxy	<u>Infix:</u> single only: -an- ≥ 1 double: -en- ≥ 1 triple: -yn-	<u>Suffix:</u> <i>more soon</i> Alkanes: -e Alcohols: -ol Amines: -amine
<u>Numbers:</u> 2 = di 3 = tri 4 = tetra 5 = penta (3) 6 = hexa...	<u>Parent:</u> meth- eth- prop- but- pent- hex- hept- oct- non- dec- undec- dodec-	



Some nit-picky details about names

- Substituents are always listed in alphabetical order (by name)
 - prefixes that indicate HOW MANY are not used in alphabetization
di, tri, tetra...
 - prefixes that DESCRIBE substituent are used in alphabetization
cyclo, iso, neo --- *except: sec & tert ...don't know why!*

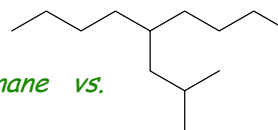
- Numbers are used only in systematic names, not in common names

- Hyphens vs commas:** number & word ⇨ separated by hyphen
number & number ⇨ separated by a comma



- A **branched substituent** is best named systematically, in parentheses with point of attachment to parent chain labeled as C-1 of the substituent

5-(2-methylpropyl)nonane vs. 5-isobutylnonane



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Class & text section	Example Draw line structures...	Common name	Systematic name Best approach - always unique.
Alkyl halides (2.4)	$\text{CH}_3\text{CHFCH}_2\text{CH}_2\text{CH}_3$	Alkyl group + halide <i>sec-pentyl fluoride?</i> <i>(Bad - not unique!)</i>	Halo-substituted alkane
Ethers (2.5)	$\text{CH}_3\text{OCH}_2\text{CH}_3$	Alkyl groups + ether ethyl methyl ether	Alkoxy-substituted alkane
Alcohols (2.6)	$(\text{CH}_3)_3\text{COH}$	Alkyl group + alcohol t-butanol	Suffix = -ol
Amines (2.7)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$	Alkyl groups + amine methylpropylamine	Suffix = -amine N-methylpropanamine

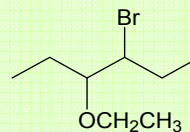
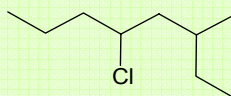
See Table 2.3

What about when the chains are more complicated?

2.2-2.5 Naming alkanes & substituted hydrocarbons

- Find parent chain: longest continuous chain of Cs containing...
 - max. # of principal Funct'l Gp substituents
 - max. # of double/triple bonds
 - max. length
 - max. # substituents (lower priority than principal gp)
- # Cs in direction that gives substituents lowest position #s (i.e., substituents are closest to the "start" of the parent chain)
 - lowest position # for principal Funct'l Gp subs
 - lowest position # for double, then triple, bonds
 - lowest position # for non-principal substituents
 - if same #s in each direction: lowest # for 1st substit. in name

Which unique name is correct?



parent chain:

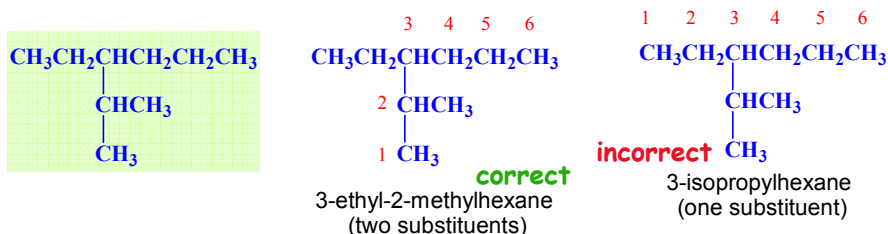
substituents:

Name (blank #s):

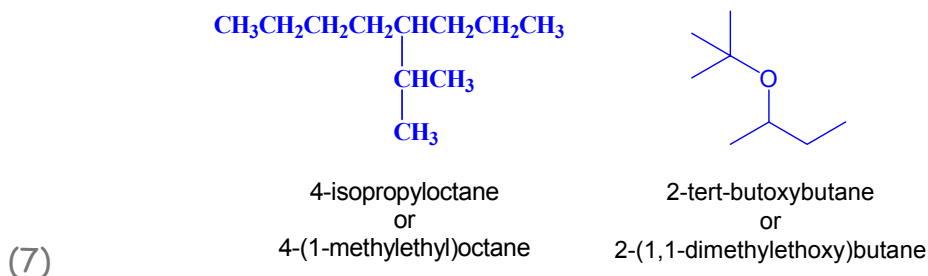
With # direction 1:

With # direction 2:

If two hydrocarbon chains in molecule have same # Cs:
parent = one with the most substituents (normal rule!):

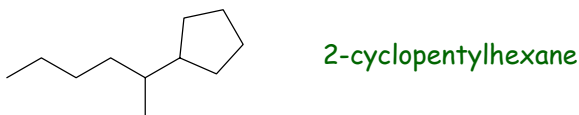


Common nomenclatures that ARE used in IUPAC system:
for common branched substituents (when parent chain obvious)



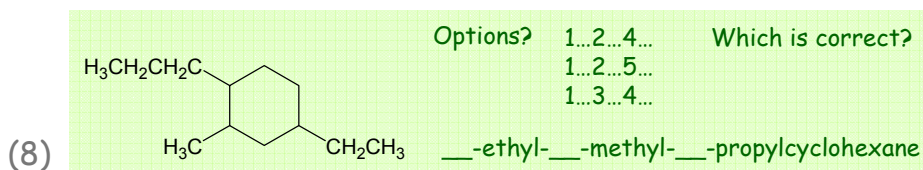
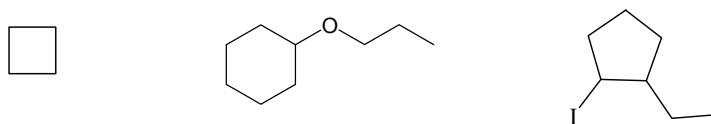
2.3 Naming cyclic organic compounds

1. If ring = substituent (ring NOT longest chain): **cycloalkyl-**



2. If ring = parent: add **cyclo** immediately before parent chain's name

- with 1 substituent: position # 1 implied (omitted)
- with 2 substituents: 1st in alpha. gets lower # (same #s each direction...)
- ≥ 3 substituents: choose C-1 to minimize other #s



Naming compounds with high-priority functional groups...

GROUP PRIORITY	Highest											Lowest		NAMED ONLY AS SUBSTITUENTS	
FUNCTIONAL GROUP	$\begin{matrix} O \\ \\ -C-OH \end{matrix}$	$\begin{matrix} O & O \\ & \\ -C-O-C- \end{matrix}$	$\begin{matrix} O \\ \\ -C-OR \end{matrix}$	$\begin{matrix} O \\ \\ -C-X \end{matrix}$	$\begin{matrix} O \\ \\ -C-NR_2 \end{matrix}$	$-C\equiv N$	$\begin{matrix} O \\ \\ -C-H \end{matrix}$	$\begin{matrix} O \\ \\ -C- \end{matrix}$	$-OH$	$-SH$	$-NR_2$	$-X$	$-OR$		
COMPOUND CLASS	Carboxylic acid	Anhydride	Ester	Acid halide	Amide	Nitrile	Aldehyde	Ketone	Alcohol	Thiol	Amine	Alkyl halide	Ether		
AS PRINCIPAL GROUP (SUFFIX)	-oic acid	-oic anhydride	-oate <small>OR group</small>	-oyl halide	-amide	-nitrile	-al	-one	-ol	-thiol	-amine	/	/		
NAME IF SUBSTITUENT	/	/	/	/	/	Cyano-	/	-oxo-	hydroxy-	mercapto-	amino-	halo-	alkoxy-		

Name constructed by... starting with principal chain

1) cite principal group: position #, suffix

2) if no principal gp: substituted hydrocarbon $\begin{matrix} \text{ane} \\ \text{ene} \\ \text{yne} \end{matrix}$

3) add substituents: position #, prefix

↑
alphabetical by group name
NOT by di, tri etc

- ① max. # principal group substituents (highest priority)
- ② max. # double/triple bonds (considered together)
- ③ max. length
- ④ max. # substituents (lower than princip gp) on chain
→ cited as prefixes in name

then:

PRINCIPAL CHAIN NUMBERING:

- ① lowest # for principal gp
- ② lowest #s for double, then triple, bonds
- ③ lowest #s for other substituents
(decided by 1st point of difference, NOT #SUM!)
- ④ lowest # for 1st substituent named (alphabetical...)

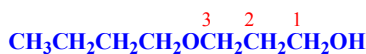
(9) IUPAC conventions -- from Loudon's *Organic Chemistry* 4th Ed, 2002; Appendix I

2.6 Nomenclature of Alcohols

"-OL"

PRINCIPAL FUNCTIONAL GROUP determines:

- (i) which is parent chain
- (ii) where #ing starts (at end closest to it)



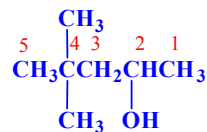
3-butoxypropanol

OR 3-butoxy-1-propanol

OR 3-butoxypropan-1-ol

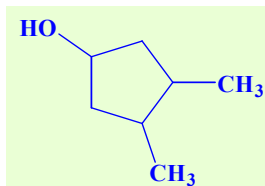
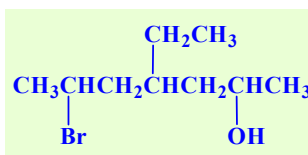
Position # for PRINCIPAL FUNCT'L GP can appear either:

- (i) before "-ol" suffix
- or
- (ii) before parent chain name



4,4-dimethyl-2-pentanol

OR 4,4-dimethylpentan-2-ol



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2.7 Nomenclature of Amines

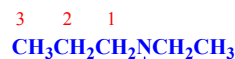
"-AMINE"



1-butanamine
or
butan-1-amine

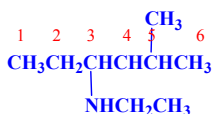


N-ethyl-3-hexanamine
or
N-ethylhexan-3-amine

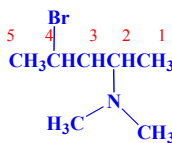


N-ethyl-N-methyl-1-propanamine
or
N-ethyl-N-methylpropan-1-amine

- The substituents are listed in alphabetical order & a # or an "N" is used to label their positions



N-ethyl-5-methyl-3-hexanamine



4-bromo-N,N-dimethyl-2-pentanamine



TO DO: Describe each amine here as: 1°, 2°, 3°

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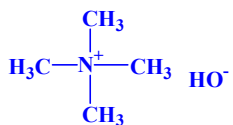
Naming Quaternary Ammonium Salts

Ionic compounds: name cation first, then name anion

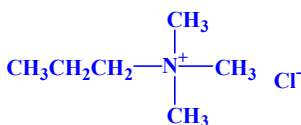
Common names:

- Name all substituents on the nitrogen
- Use suffix "-ammonium"
- Name the counterion

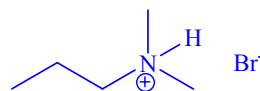
Don't worry about their IUPAC names



tetramethylammonium
hydroxide



ethyltrimethylammonium
chloride



dimethylpropylammonium
bromide

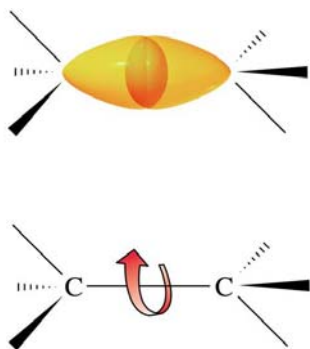
*We'll see how alkylammonium salts can form later...
but we DO know that amines can be protonated (act as base!)*

(12)

Drawing molecules based on their names

(13)

2.10 Conformations of Alkanes: rotation about carbon-carbon bonds



For any σ -bond:

Overlap of end-on overlapping orbitals is not diminished by rotation about the internuclear axis

- ⇒ rotation about a single bond does NOT break the bond
- ⇒ the energy barrier to rotation is quite small

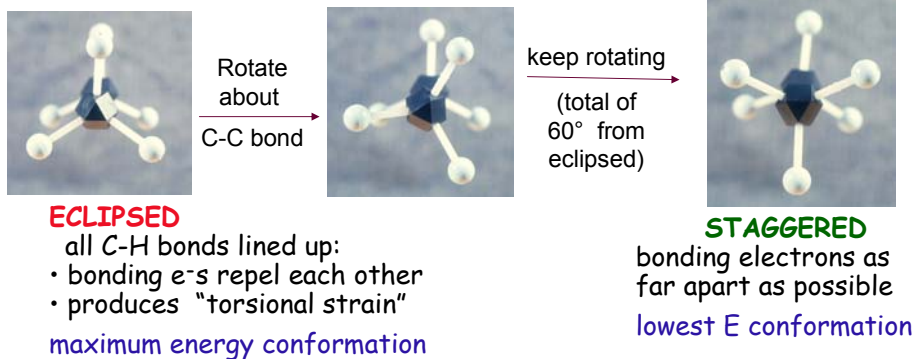
**At room temperature:
single bonds rotate freely!**

(14) Fig.2.3

Conformations: different 3D arrangements of atoms in molecule due to rotation around single bonds

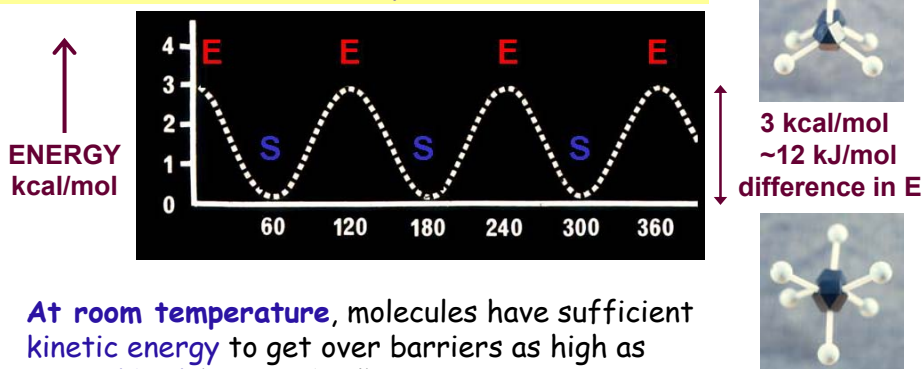
- different confo's = **rotational isomers**
conformational isomers
"conformers"

For ethane:



(15)

Via "Conformational analysis": find relative E...

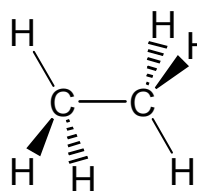


⇒ at R.T., have constant rotation around C-C bonds (& all other single bonds) ⇒ **conformational flexibility**

However: molecules spend most of their time in the more stable **staggered** conformations (energetically favorable)

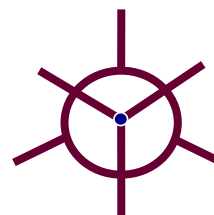
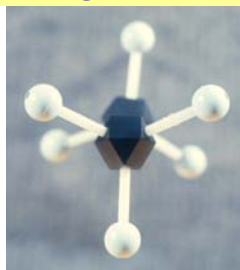
(16)

Newman projections: looking down a C-C bond...



Perspective drawing of staggered conformation

If we look this way down the C-C bond... we'll see \Rightarrow



Newman projection

A Newman projection: a view of a molecule down the axis of a carbon-carbon bond

- \rightarrow the carbon in the front = the point where the 3 bonds intersect
- \rightarrow the carbon in the back = a circle

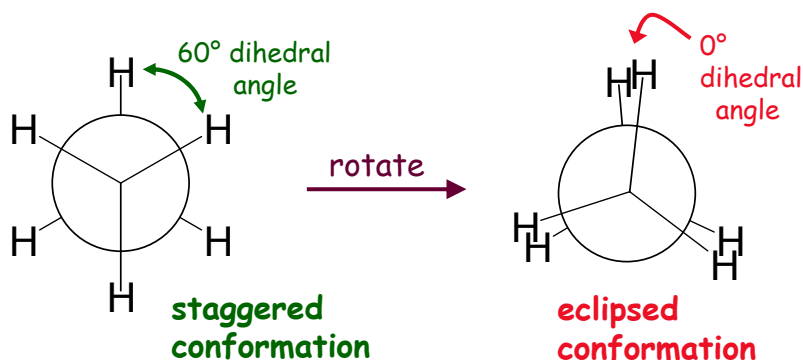
Helps visualize interactions within the molecule...

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Visualize spatial relationship between atoms bonded to adjacent carbon atoms

- \rightarrow get feeling for torsional strain in different conformers
- \rightarrow predict which conformation most molecules will adopt!

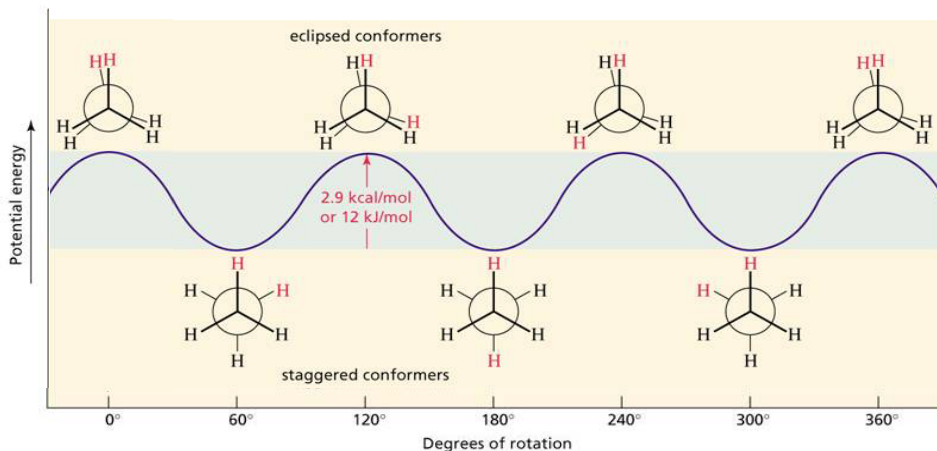
Dihedral angle (θ) = angle between groups on adjacent atoms as viewed in the Newman projection



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Different Conformations of Ethane

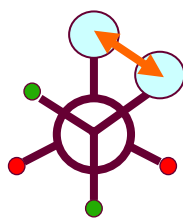
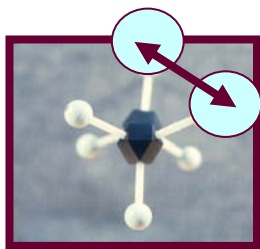
- **Torsional strain** = repulsion between pairs of bonding e⁻s
- Staggered conformers more stable than eclipsed conformers



(19)

If have substituents on the C-C bond...

→ must consider their "STERIC" demand (bulkiness)

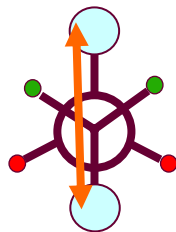
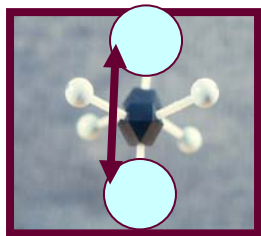


60° dihedral angle

between these two positions

Interaction between them
= a "gauche" interaction

→ introduces "steric strain"
*repulsion of electron clouds
of these groups*



180° dihedral angle

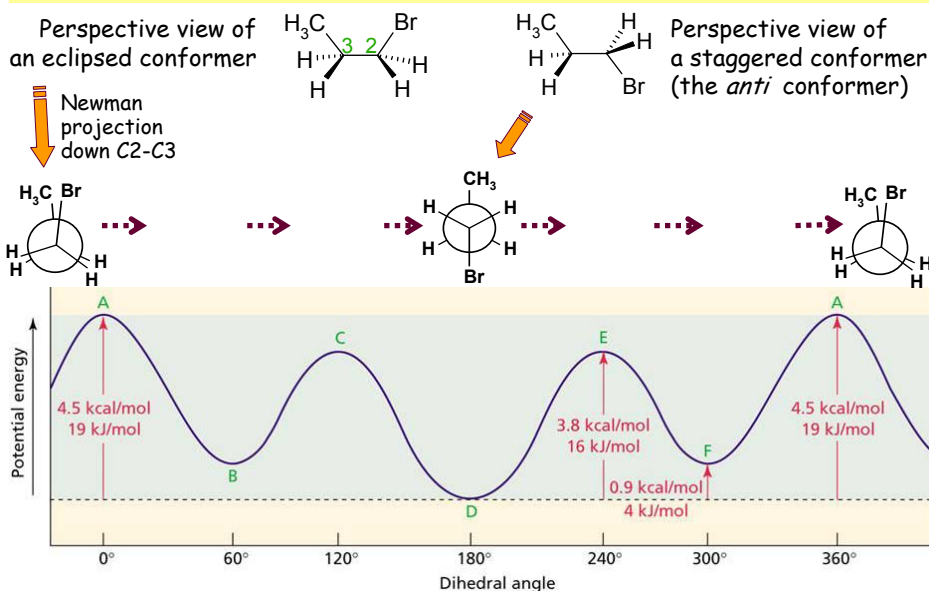
between these positions

Interaction between them
= an "anti" interaction

→ very little steric strain

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Looking down a substituted C-C bond: e.g., bromopropane



Bruice Fig.2.5 - for butane's conformations, looking down C2-C3 bond
 → CH₃-Br steric repulsions not exactly same as CH₃-CH₃, but same general trend

2.11 Cycloalkanes: Ring Strain

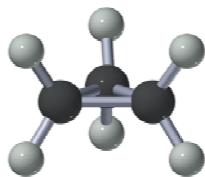
- **Angle strain** results when bond angles deviate from 109.5°
 - destabilization due to decrease in efficiency of orbital overlap
 - σ -bonds *should* be straight, not bent like a banana!



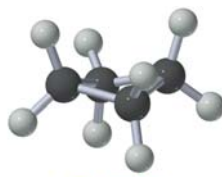
Conformations of Cycloalkanes: C_nH_{2n}

MOST STABLE CONFORMATIONS = puckered, in order to minimize angle strain & torsional strain

cyclopropane



cyclobutane



cyclopentane

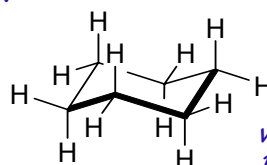


banana bonds

Cannot pucker
Cannot avoid angle strain
→ Highly reactive!



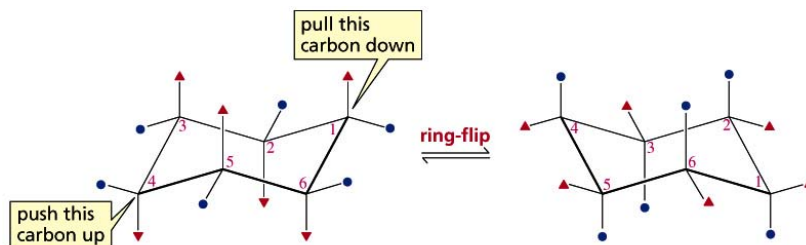
cyclohexane



very stable
 109.5° angles

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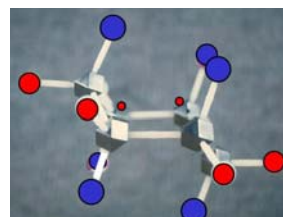
"Ring Flipping" in Cyclohexane: chair-chair interconversion



"axial"

"equatorial"

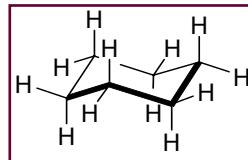
"axial"



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CYCLOHEXANE: the chair conformation

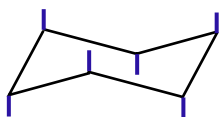
1st: Draw parallel lines



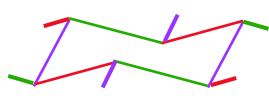
2nd: Connect the lines with lop-sided shallow "V"s
(or...make parallel lines to outline seat, then connect to head & toe)



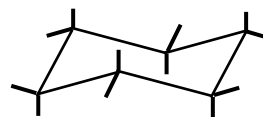
3rd: Add axial & equatorial bonds: 1 of each on each carbon
(axial point straight up/down; equatorial off to the sides...)



Axial bonds



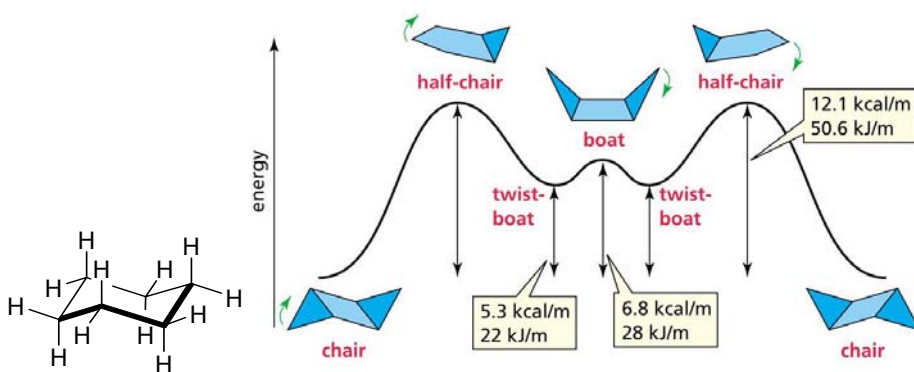
Equatorial bonds



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CYCLOHEXANE: 6-membered rings common in nature... study in more detail its "ring-flipping":

Fig.2.10



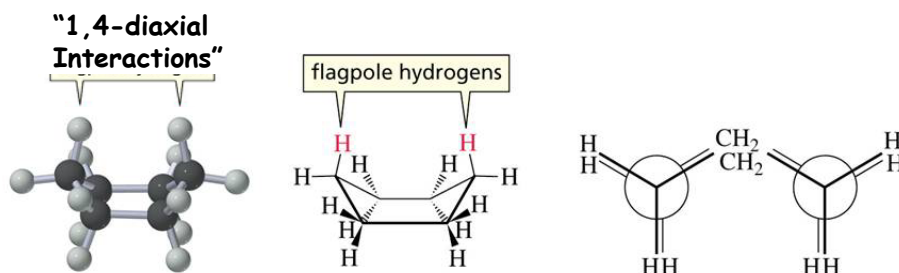
(26)

Torsional and steric strain in cyclohexane:

Bruice
Fig.2.9

Why is the **BOAT** conformation so unstable?

- 1.) lots of eclipsed bonds (torsional strain)
- 2.) 1,4-diaxial interactions (H-H steric strain)

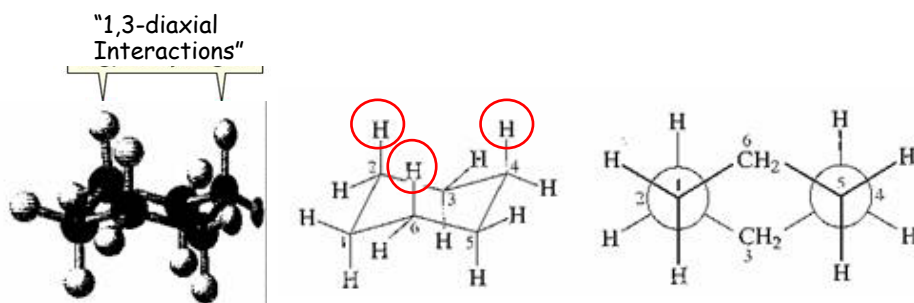


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Why is the **CHAIR** conformation so stable?

- 1.) no eclipsed bonds (minimal torsional strain)
- 2.) no major steric interactions:
 - H-R gauche interactions = very minor
 - H-H "1,3-diaxial interactions" = very minor

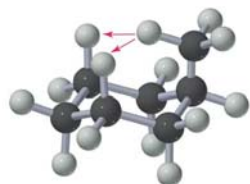
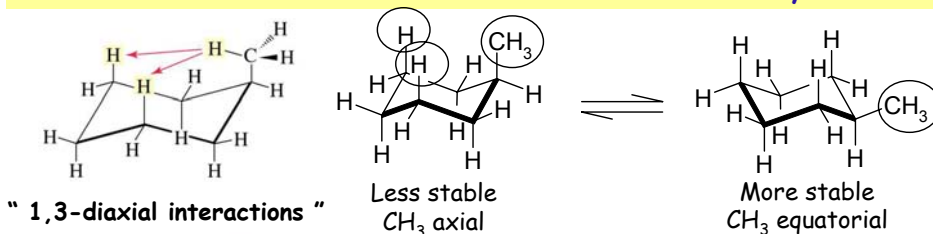
Bruice
Fig.2.7



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2.13 Substituted cyclohexanes

increased steric interactions: 2 chair confo's not necessarily same E



BULKIER SUBSTITUENTS PREFER TO SIT IN EQUATORIAL POSITIONS
because of fewer steric interactions

⇒ Less strain ⇒ increased stability
⇒ in a sample: most of the molecules will adopt the most stable conformation

⇒ can predict most likely way molecules will look!
⇒ useful for predicting reactivity later...

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Larger substituents prefer equatorial positions

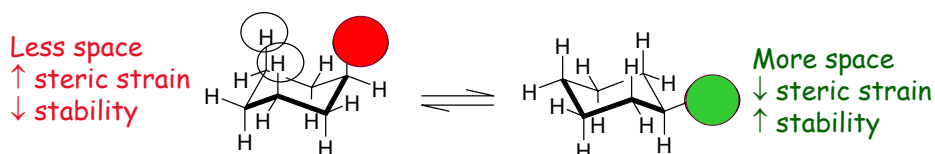


Table 2.10 Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C

Substituent	Axial \rightleftharpoons Equatorial	K_{eq}	Substituent	Axial \rightleftharpoons Equatorial	K_{eq}
H		1	CN		1.4
CH ₃		18	F		1.5
CH ₃ CH ₂		21	Cl		2.4
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH} \end{array}$		35	Br		2.2
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C} \\ \\ \text{CH}_3 \end{array}$		4800	I		2.2
			HO		5.4

$$K_{eq} = \frac{[\text{R equatorial}]}{[\text{R axial}]}$$

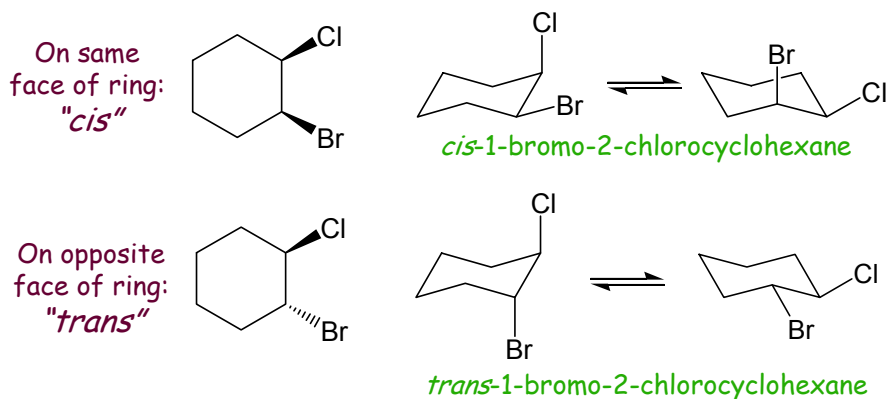
larger K_{eq}
⇒ eq. preferred

Good way to get a feeling for "steric bulk"

(30)

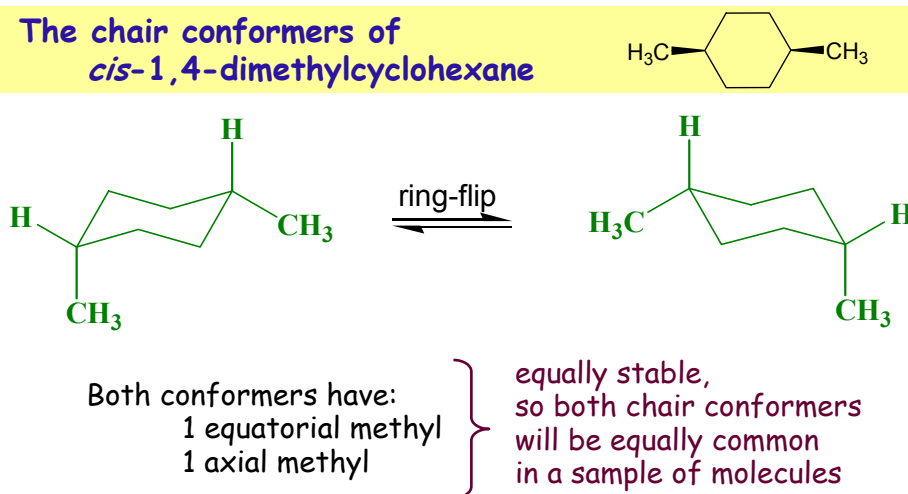
2.14 Conformations of disubstituted cyclohexanes

Naming convention: describes relative orientation of substituents to distinguish between *geometric isomers*
= isomers with same connectivity of atoms, but different spatial orientations



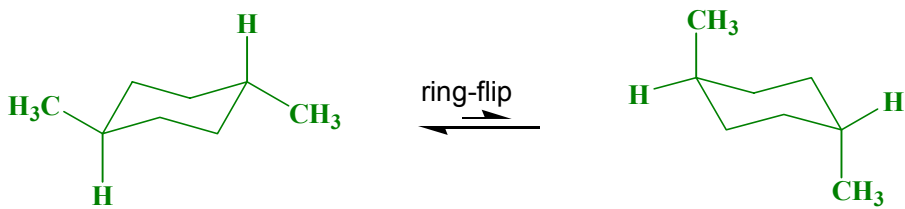
(31)

The chair conformers of *cis*-1,4-dimethylcyclohexane



(32)

The chair conformers of *trans*-1,4-dimethylcyclohexane

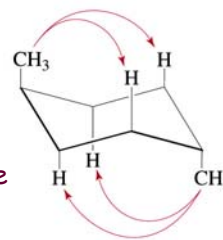


This conformer has:
2 equatorial methyls

More stable
Thus: most common
conformation in which
to find this compound

This conformer has:
2 axial methyls

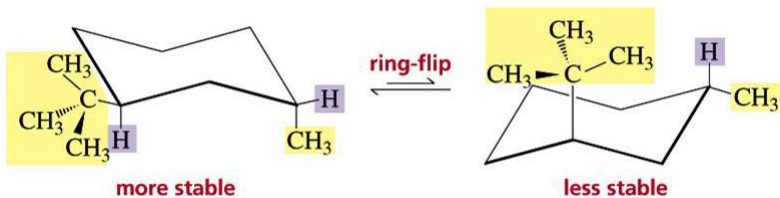
Four
1,3-diaxial
interactions
→ Less stable



(33)

Differences between geometric isomers

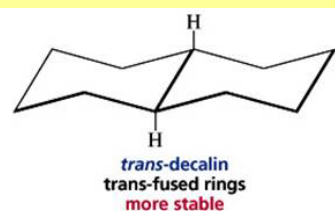
trans-1-*tert*-butyl-3-methylcyclohexane



cis-1-*tert*-butyl-3-methylcyclohexane

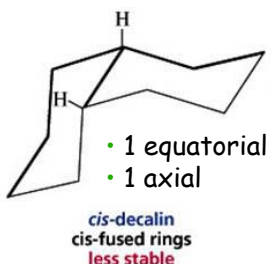
(34)

2.15 Conformations of fused rings



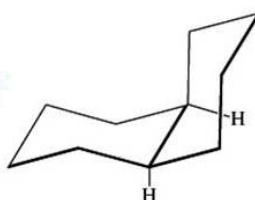
Think of the 2nd ring as a substituent on the 1st ring:

- both substituents equatorial
- quite a stable conformation (ring flip would yield both axial, so compound will remain as shown)



- 1 equatorial
- 1 axial

ring-flip



- after ring flip: still 1 eq, 1 ax
- both confo's less stable than trans-fused rings

Trans-fused cyclohexane rings are more stable than cis-fused rings (note: would have to break C-C bonds to change geometry of ring fusion...)

(35)

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Ch.2

Practice: drawing & naming compounds (IUPAC)
visualizing molecular conformations

- Newman projections
- using molecular model kits

drawing cyclohexanes & "ring flipping"

(36)