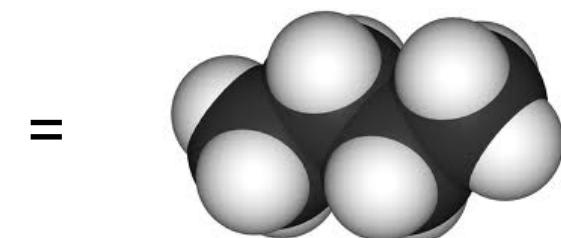
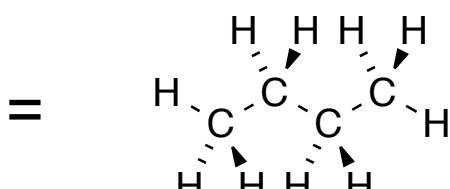
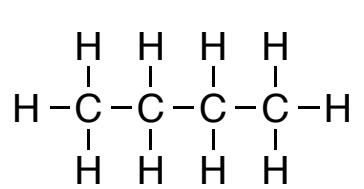


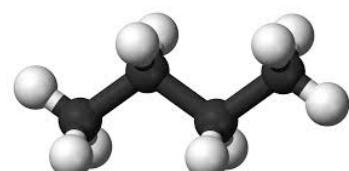
What will we cover in CH2310?

....and later in CH2320 and CH2330?

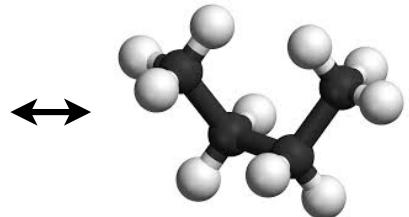
# Structure, Conformation, Stereochemistry & Nomenclature



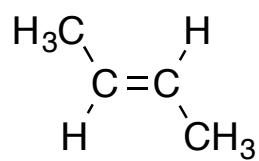
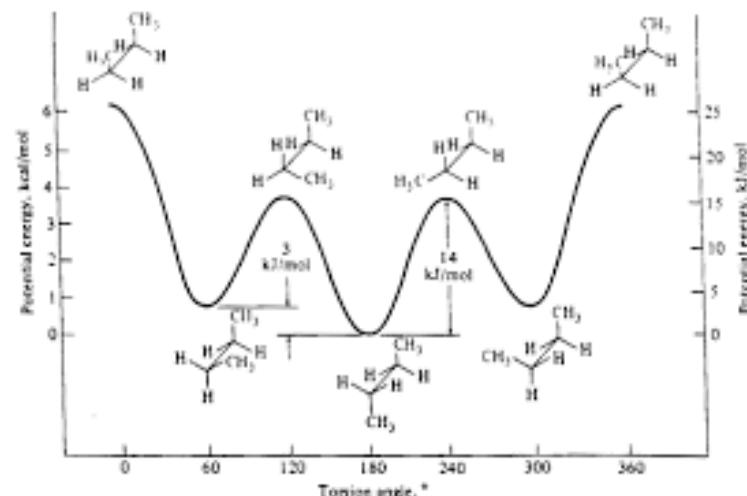
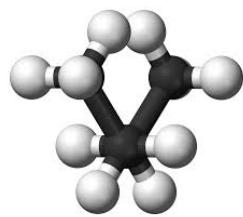
butane



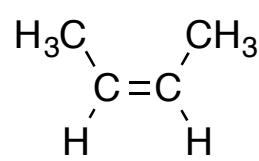
anti conformation



gauche conformation



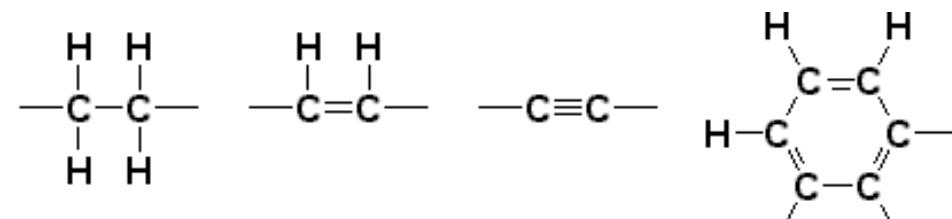
trans-but-2-ene  
(E)-but-2-ene



cis-but-2-ene  
(Z)-but-2-ene

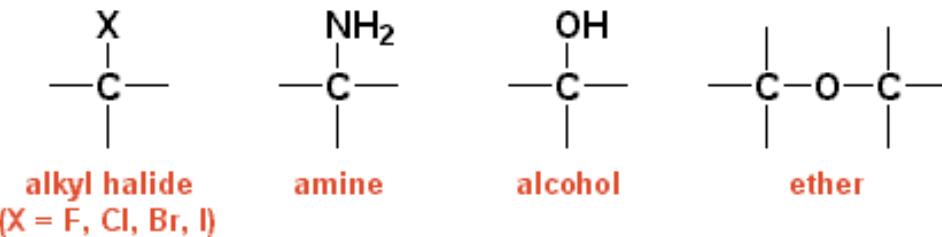
# Functional Groups - What are they & what chemistry do they do?

## Functional Groups - the main players



alkane      alkene      alkyne

phenyl

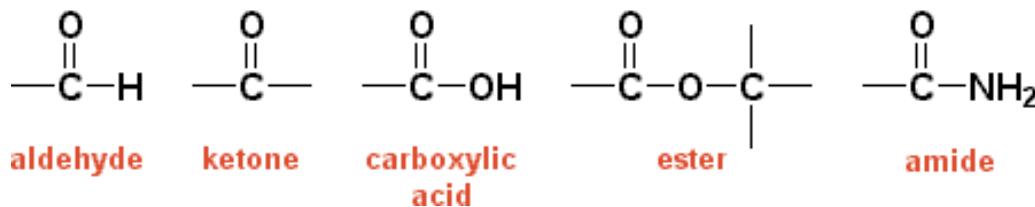


alkyl halide  
(X = F, Cl, Br, I)

amine

alcohol

ether



aldehyde

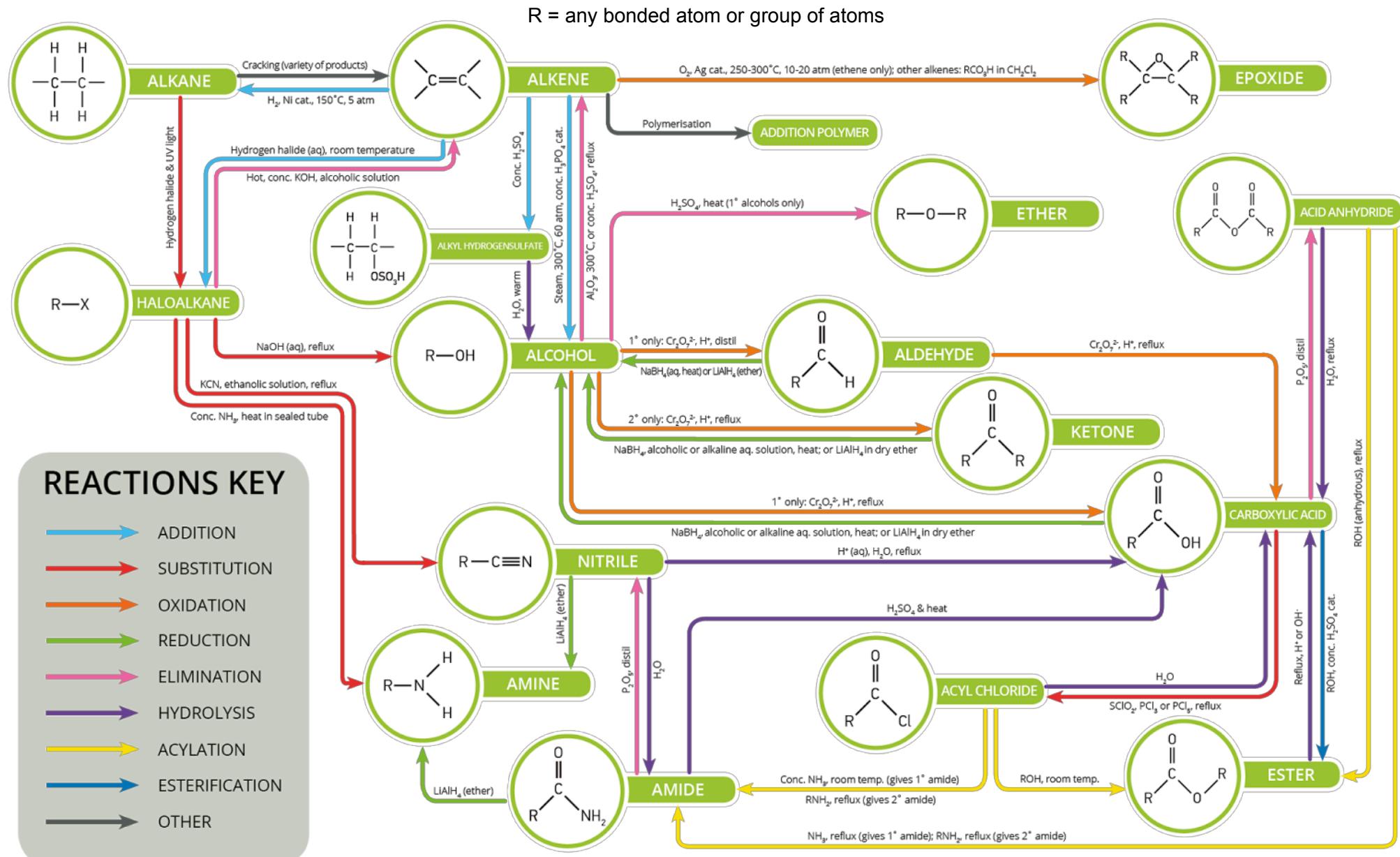
ketone

carboxylic acid

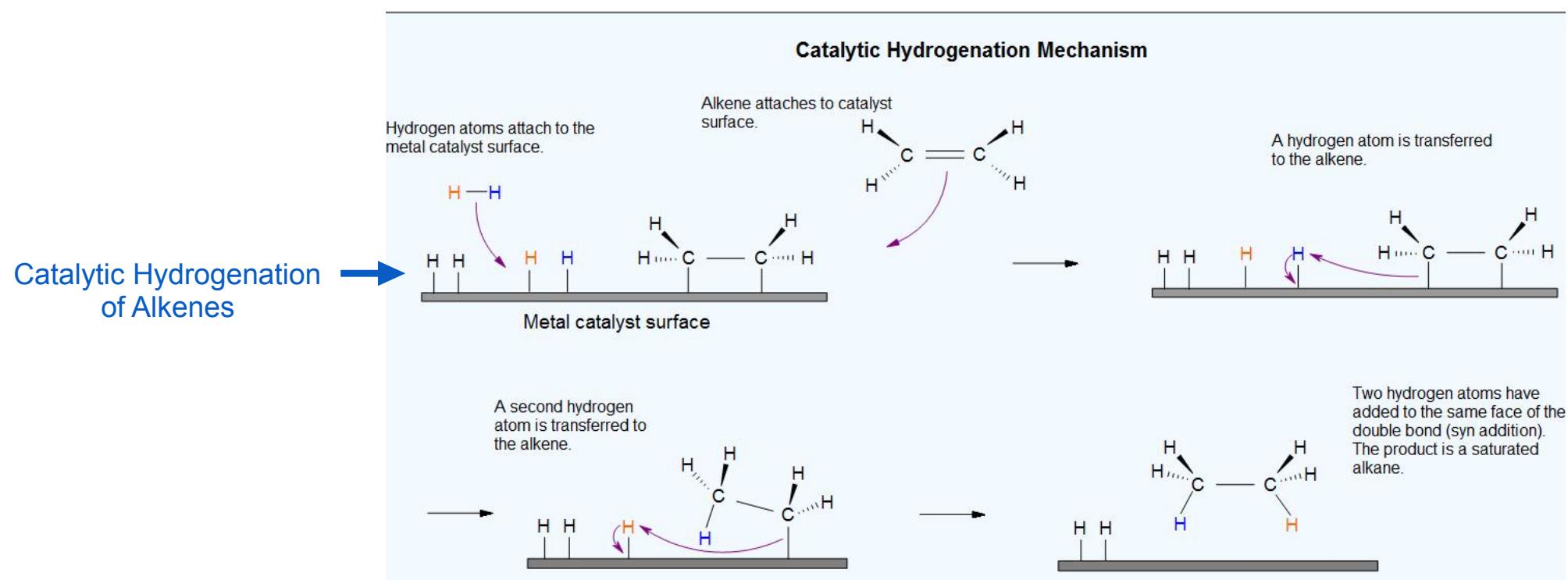
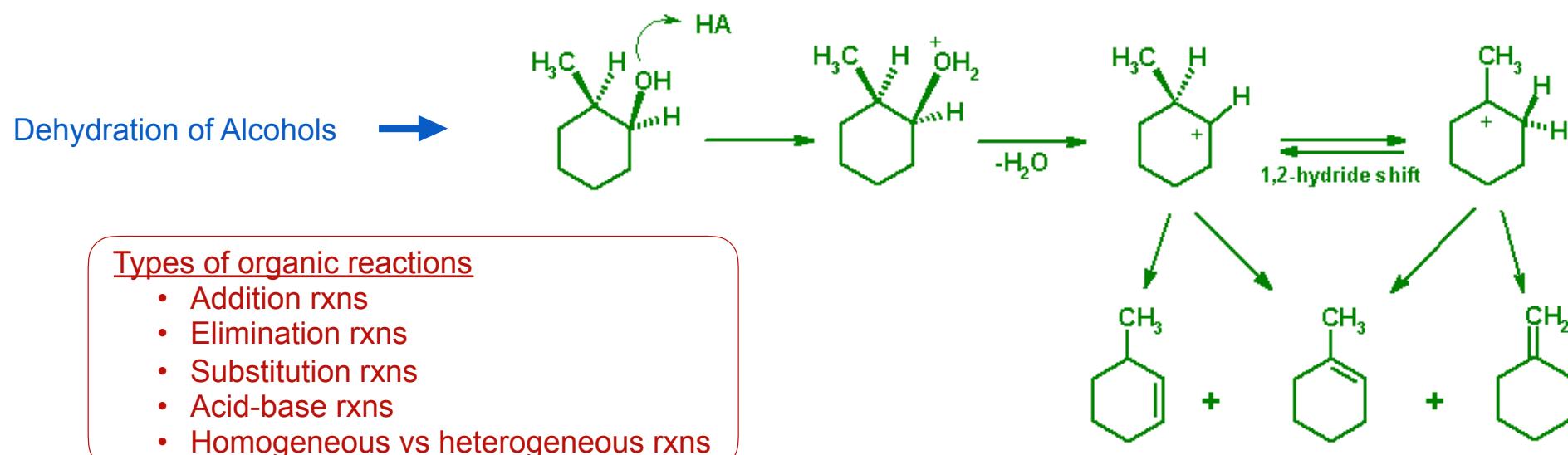
ester

amide

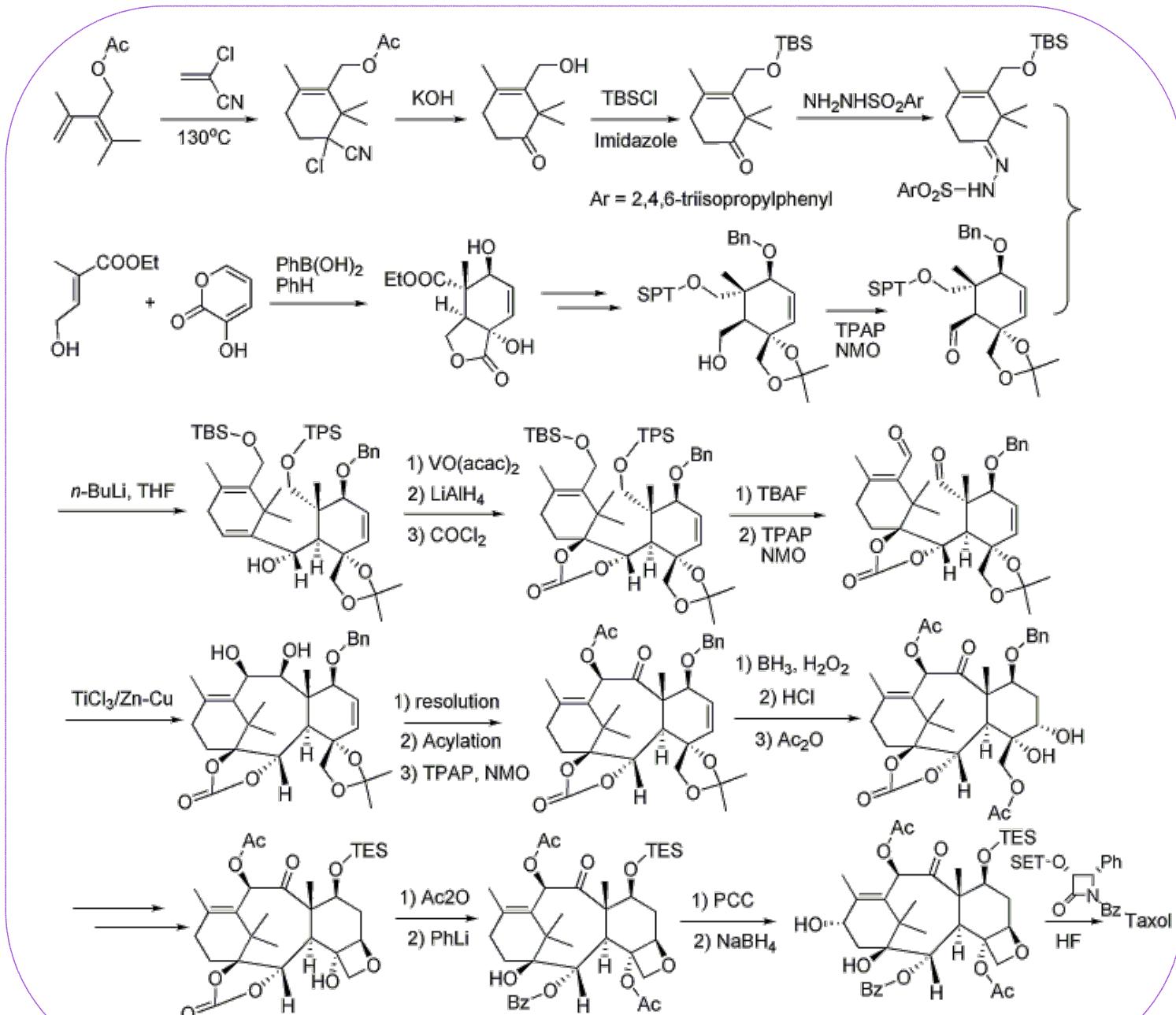
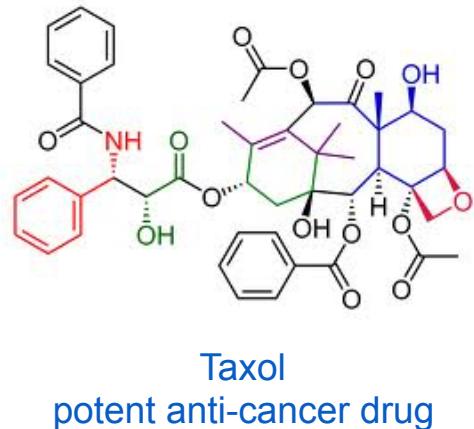
# Transformations of Functional Groups



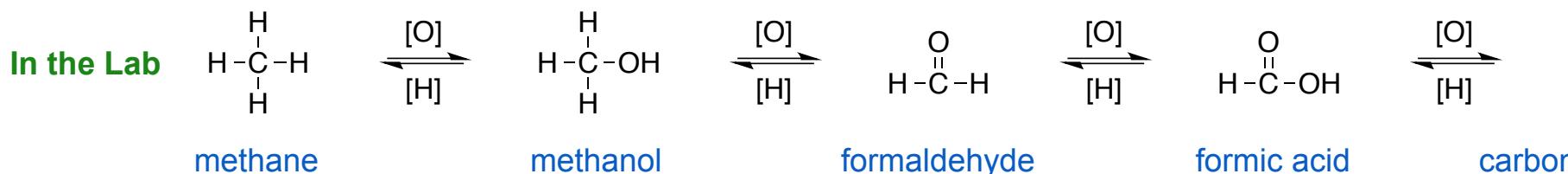
# Mechanisms of Reactions — Understanding How Reactions Work



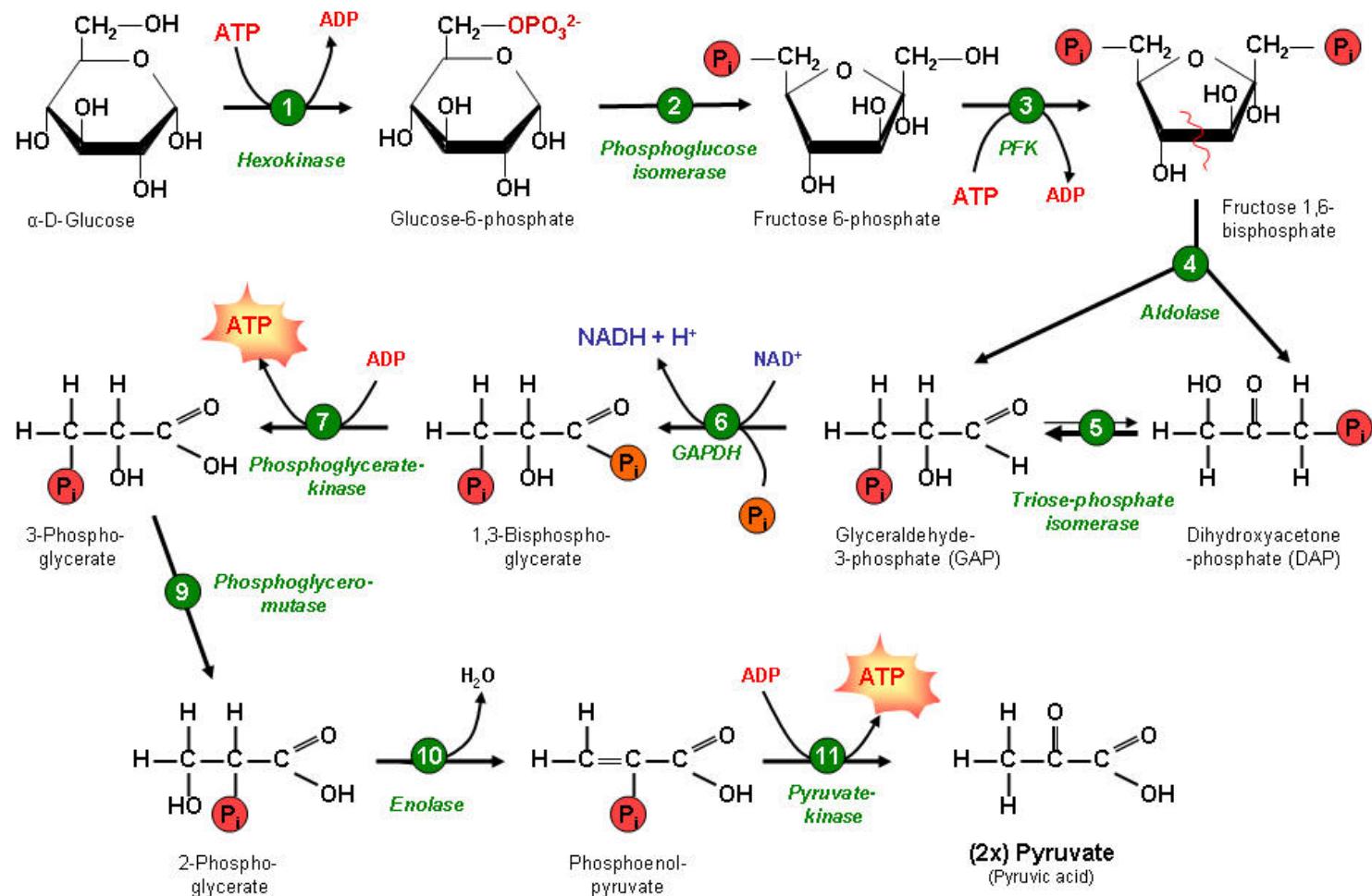
# Synthesis of Taxol — Synthesis in Multiple Steps



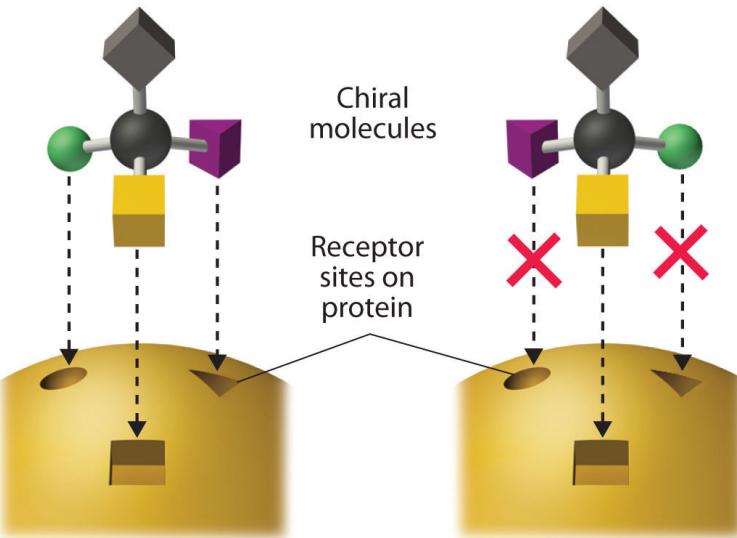
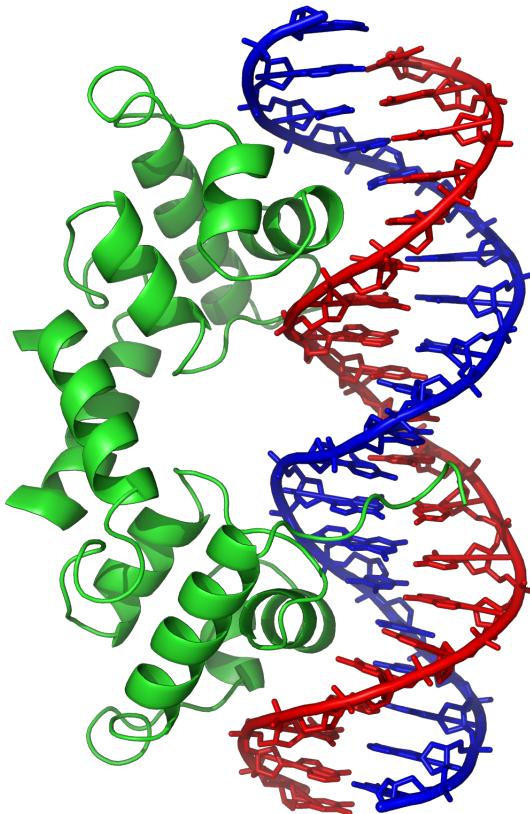
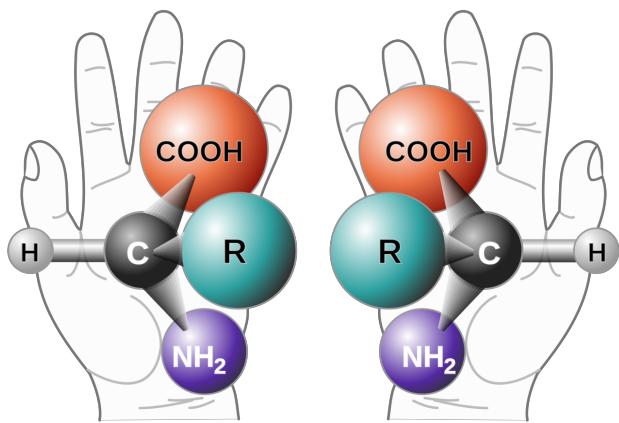
# Oxidation & Reduction



**In Organisms**

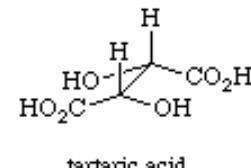
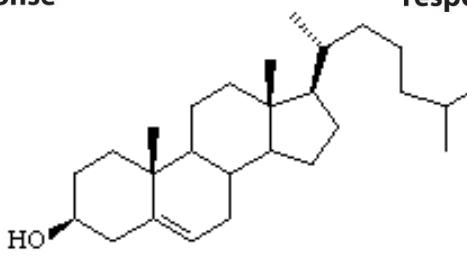
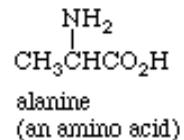


# Chirality & Asymmetric Carbon

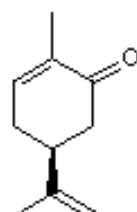
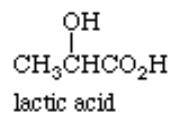


(a) Molecule fits receptor site, leading to a response

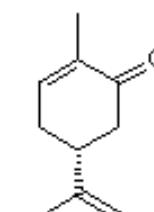
(b) Molecule does not fit receptor site; no response



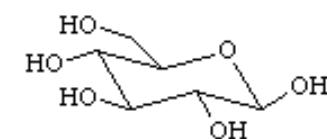
tartaric acid



(S)-carvone  
(caraway oil)



(R)-carvone  
(spearmint oil)



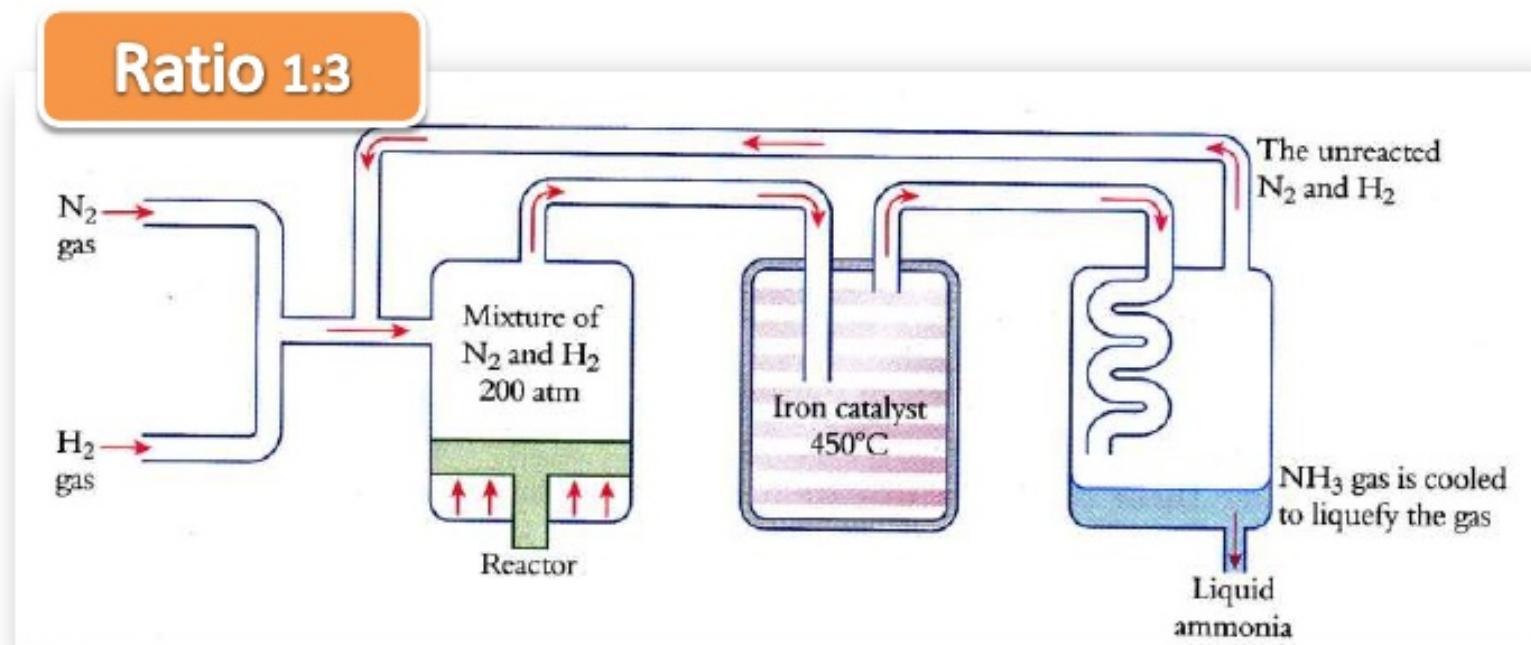
$\beta$ -(D)-glucopyranose  
(a cyclic form of glucose)

Why is knowing this stuff important?

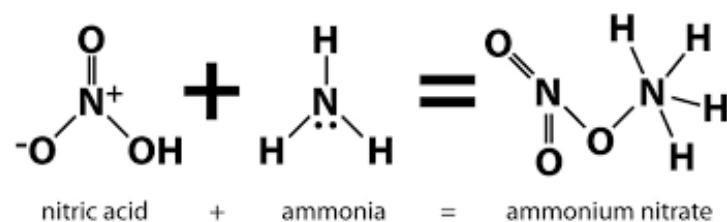
How can I use organic chemistry  
moving forward?

# Most important chemical reaction discovered in the last 100 years

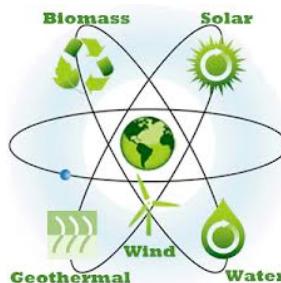
## The Manufacture of Ammonia, $\text{NH}_3$ through the Haber Process



Production of Ammonium Nitrate Fertilizer



# Where is chemical research headed today? What important problems need to addressed?



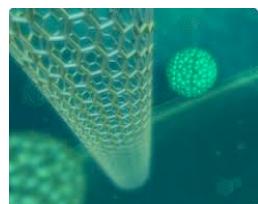
energy



raw  
materials



global  
warming



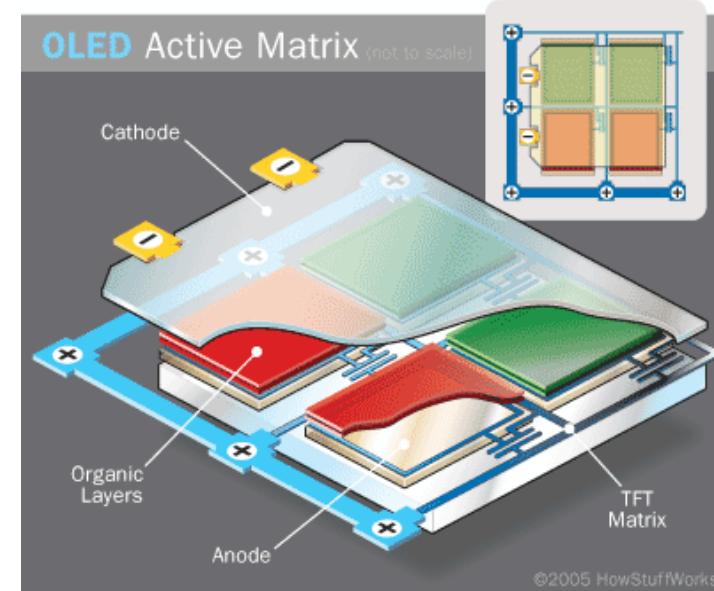
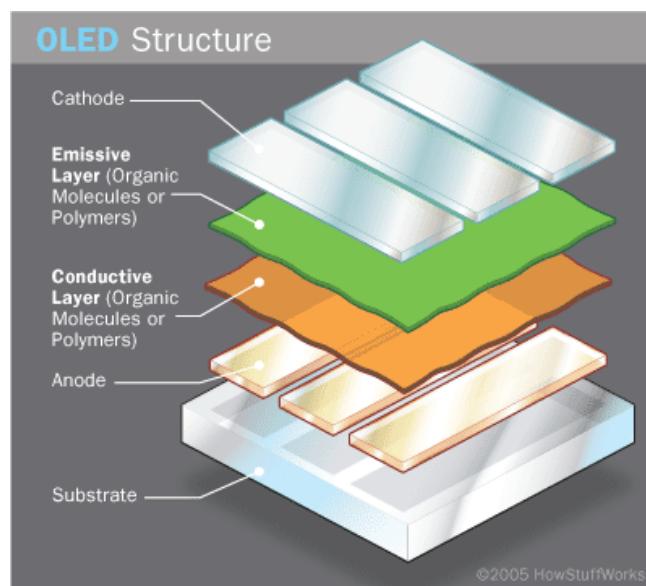
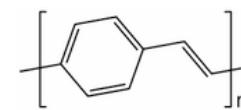
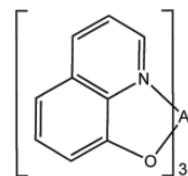
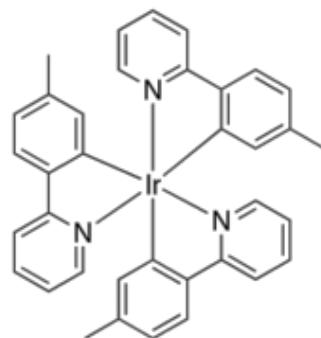
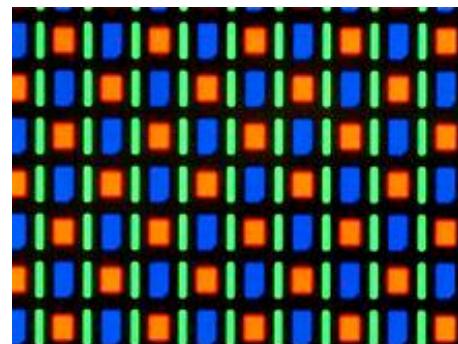
new  
materials &  
technology



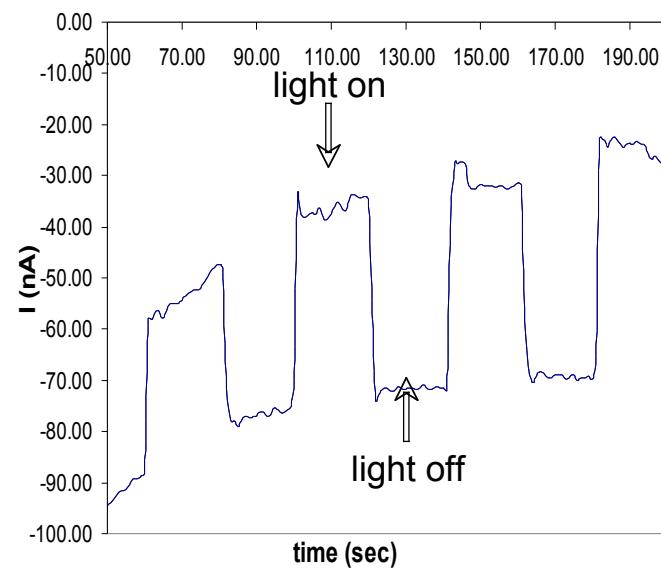
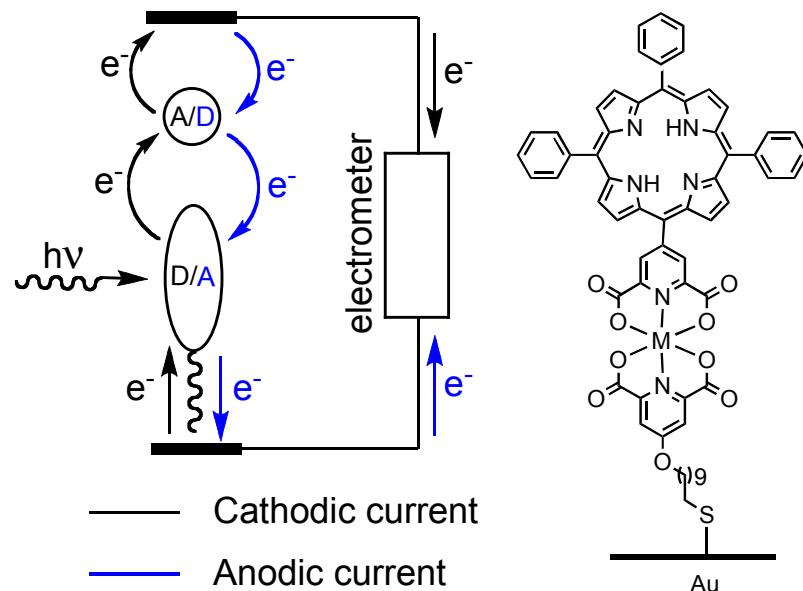
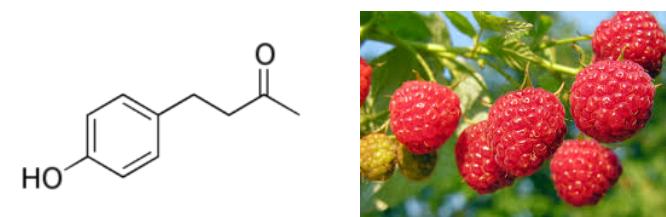
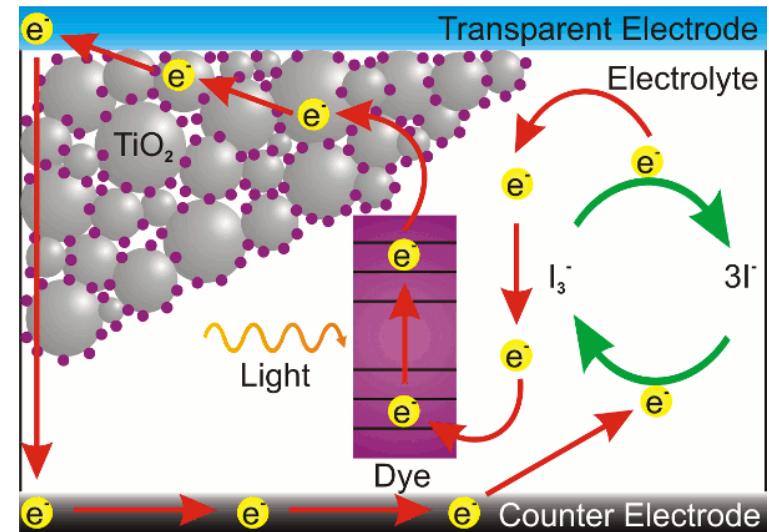
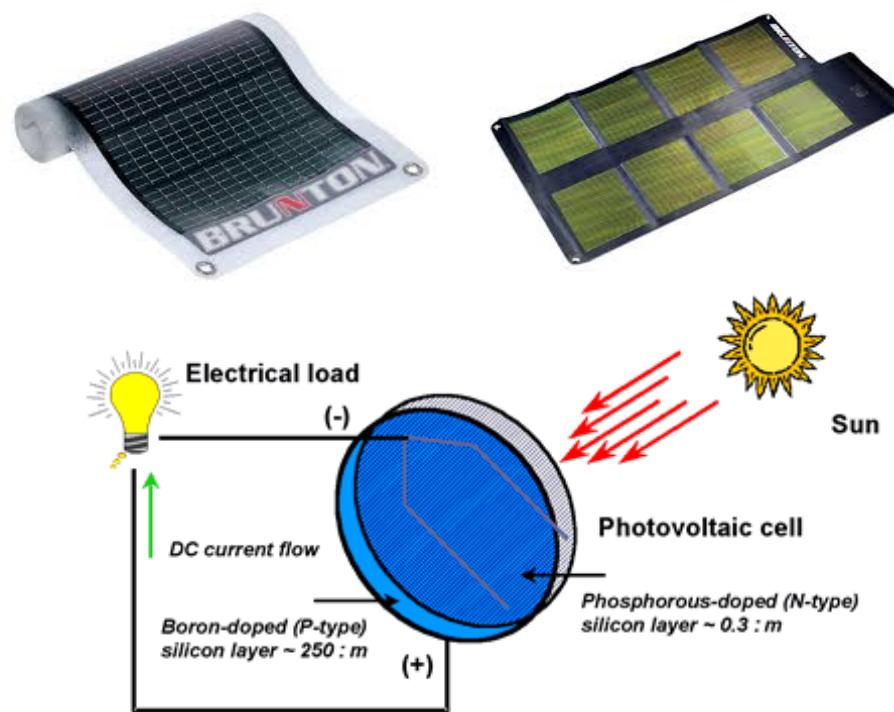
food



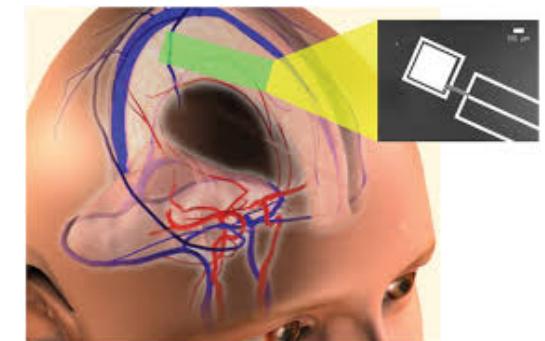
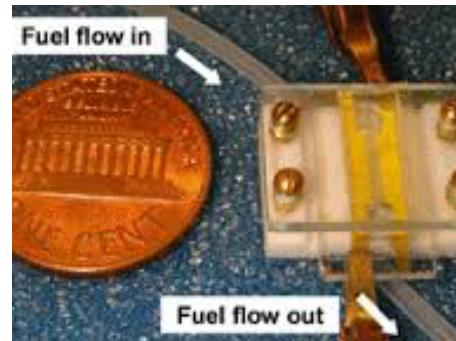
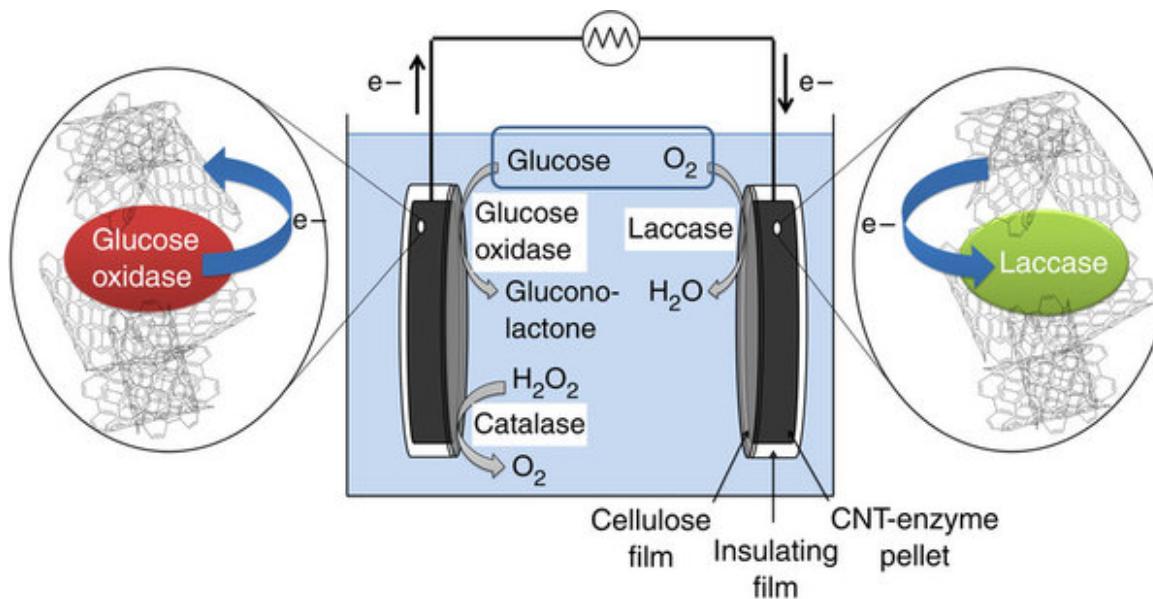
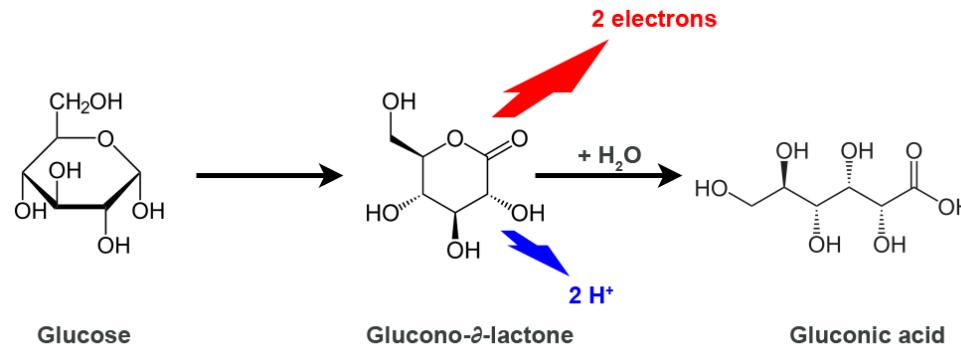
# Display Technology - OLED Molecular Electronics



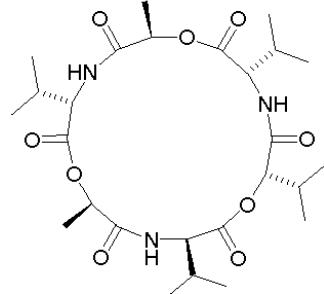
# Energy Technology - Organic Thin-Film Photovoltaics



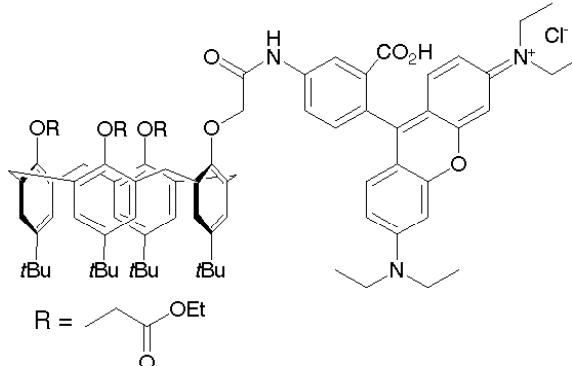
# Energy Technology - Glucose Biofuel Cell



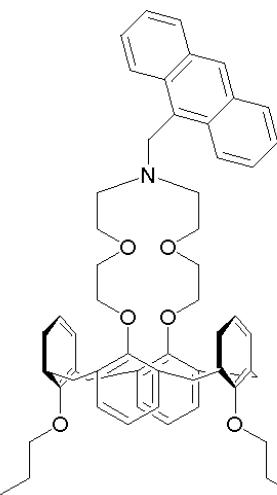
# Medical Technology - Sensors



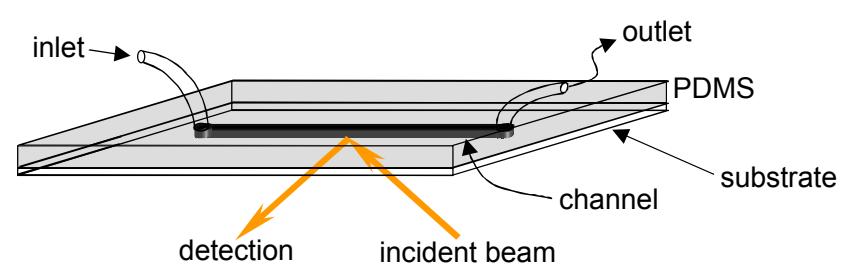
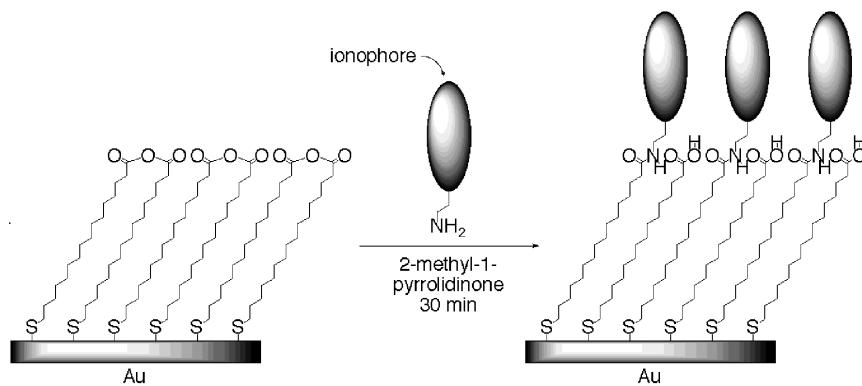
ammonium ionophore



sodium ionophore



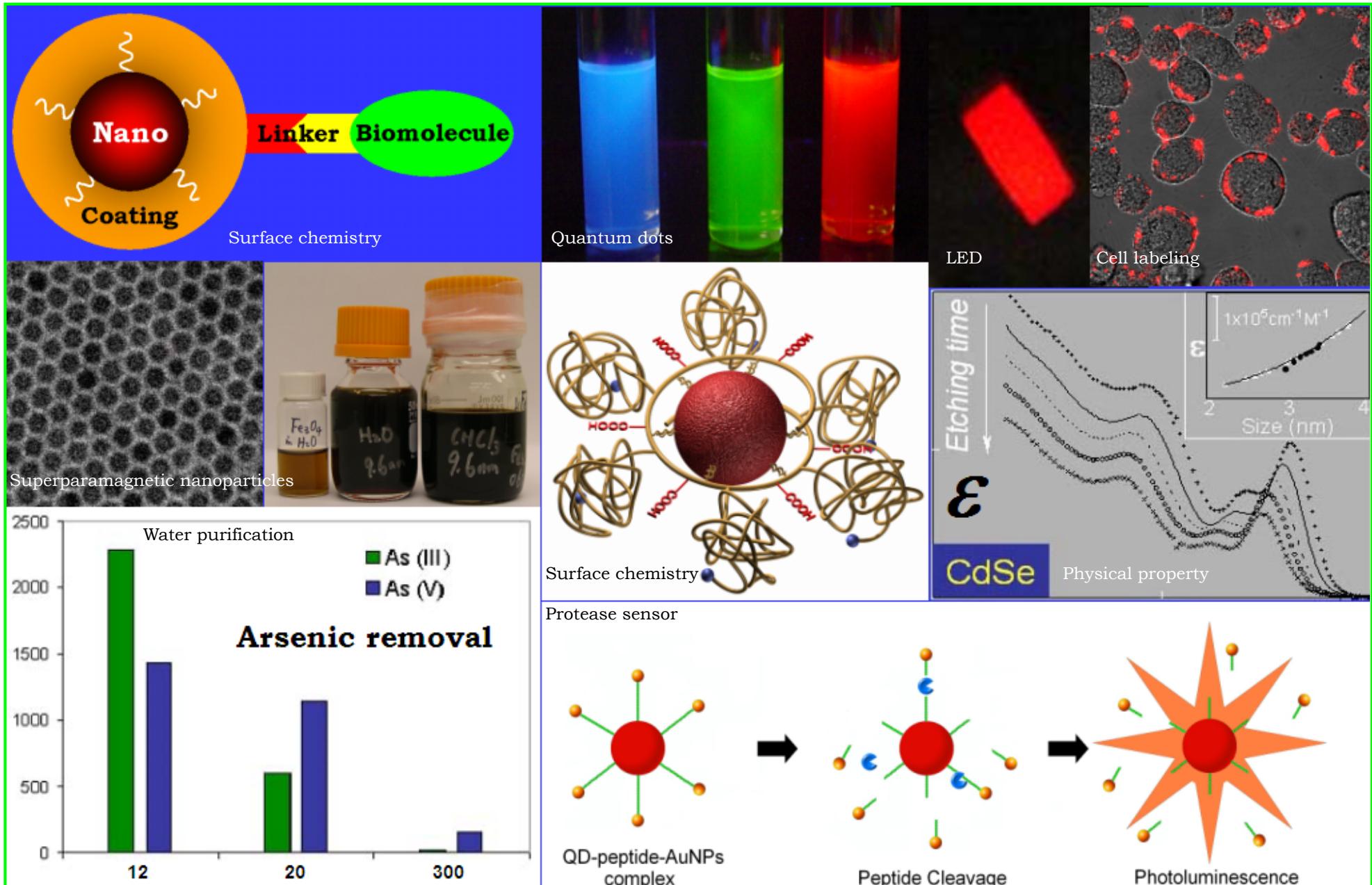
potassium ionophore



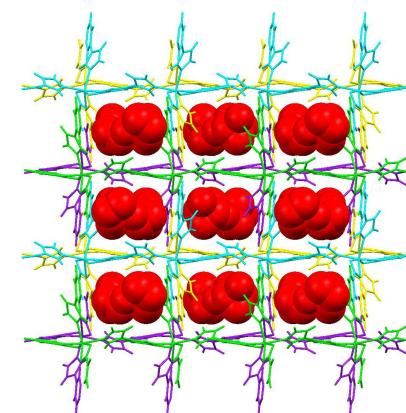
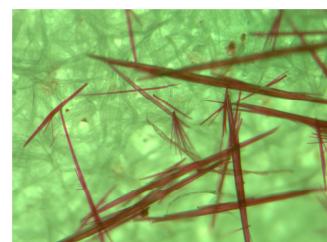
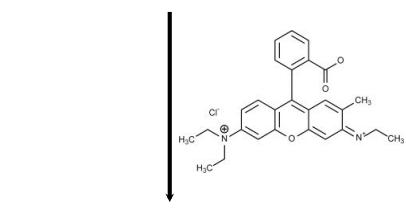
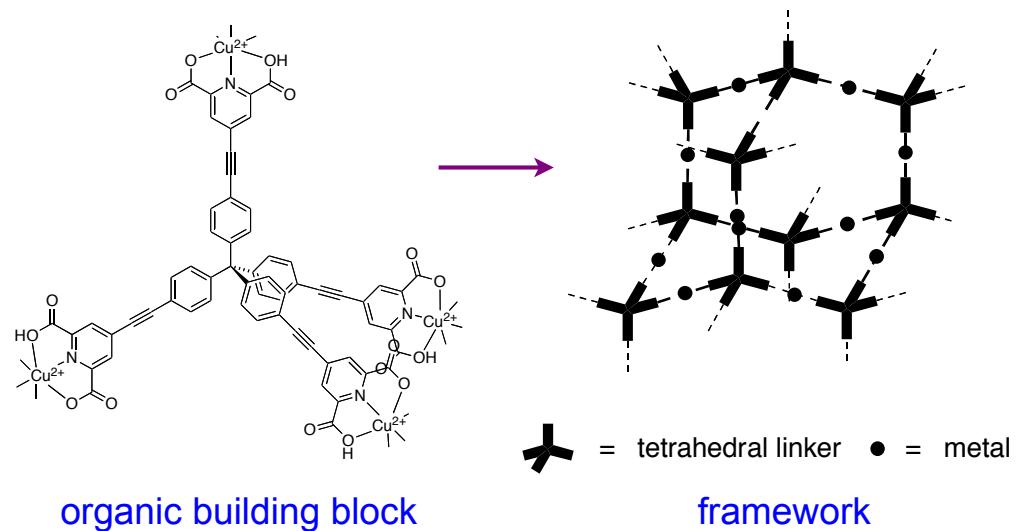
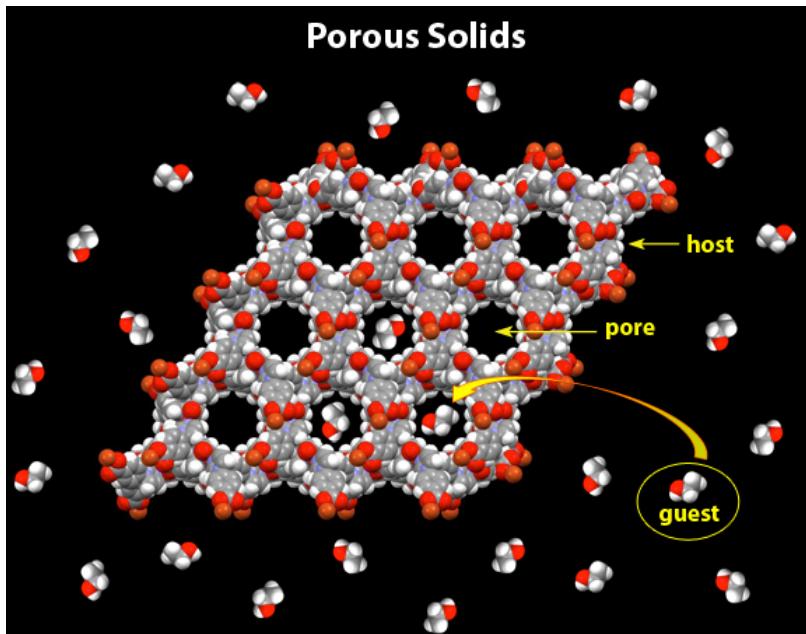
Glucose Sensor



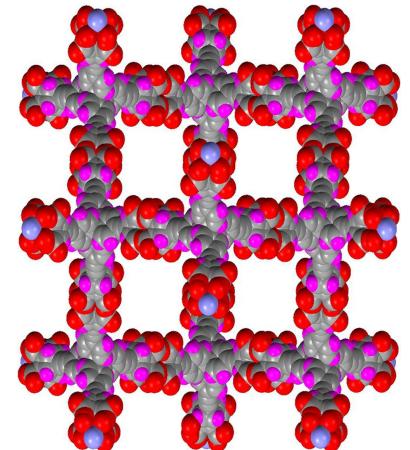
# Biomedical Technology - Imaging, Drug Delivery, Remediation



# Porous Materials - Separation, Storage, Purification of Molecules

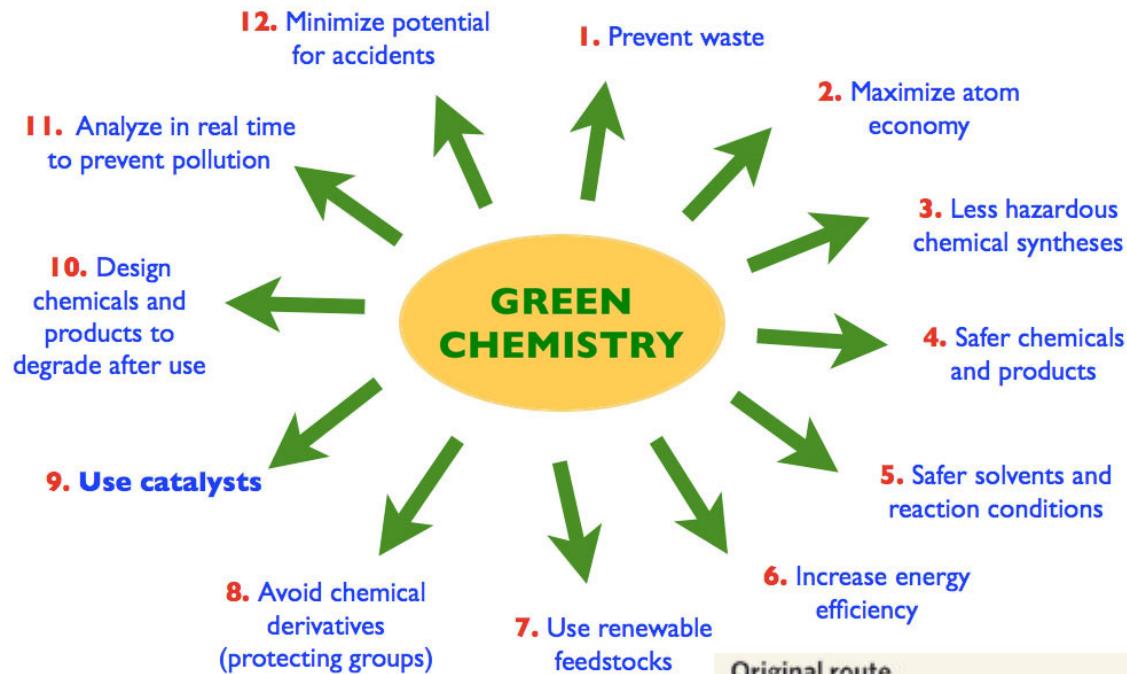


guest molecules sorbed inside

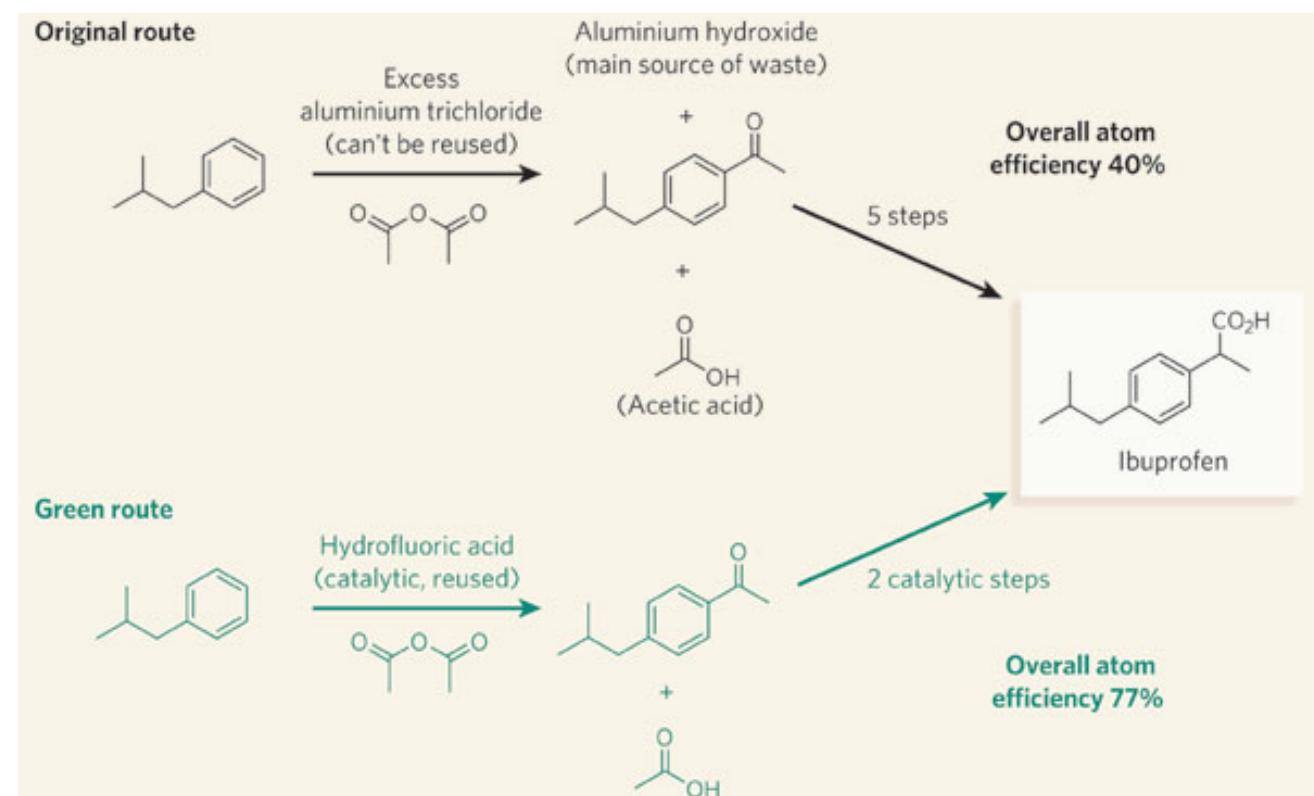


porous solid

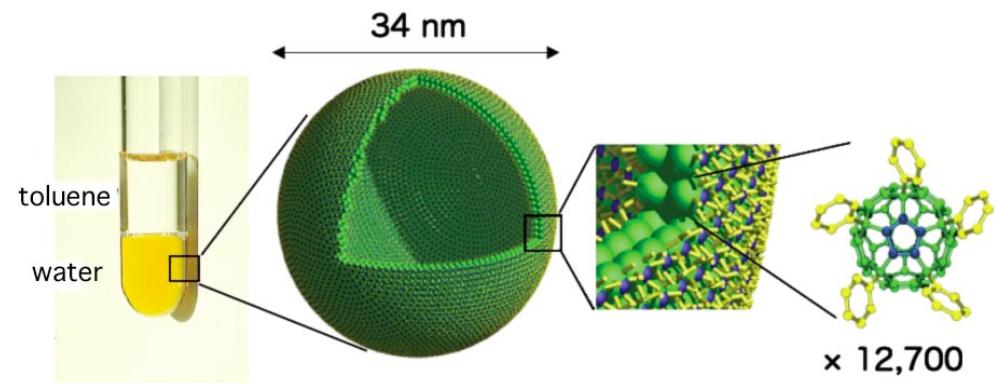
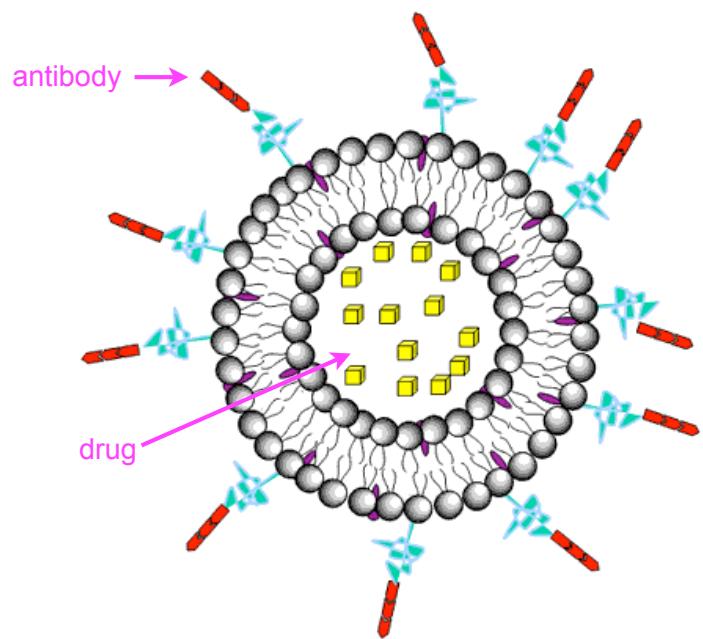
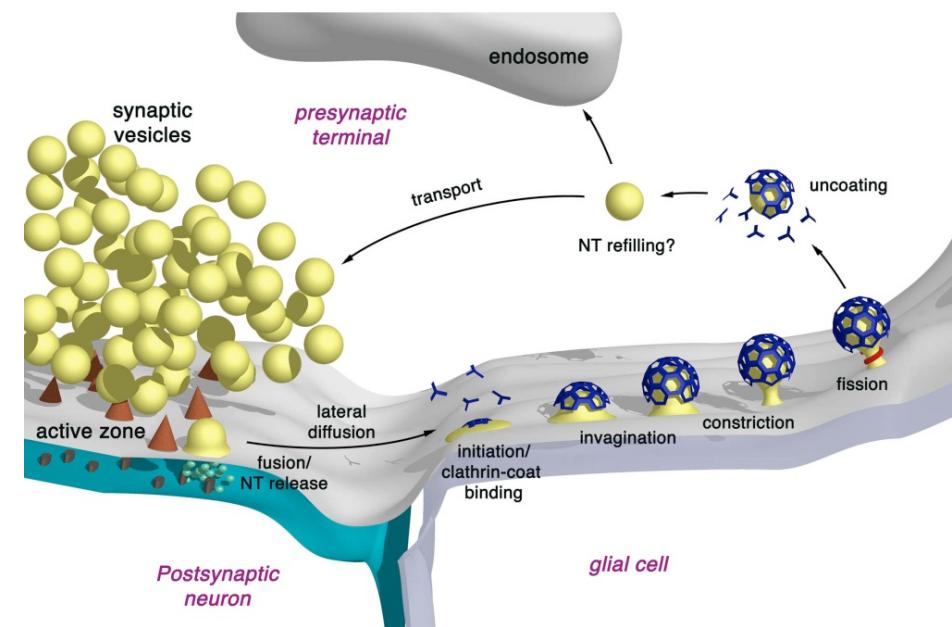
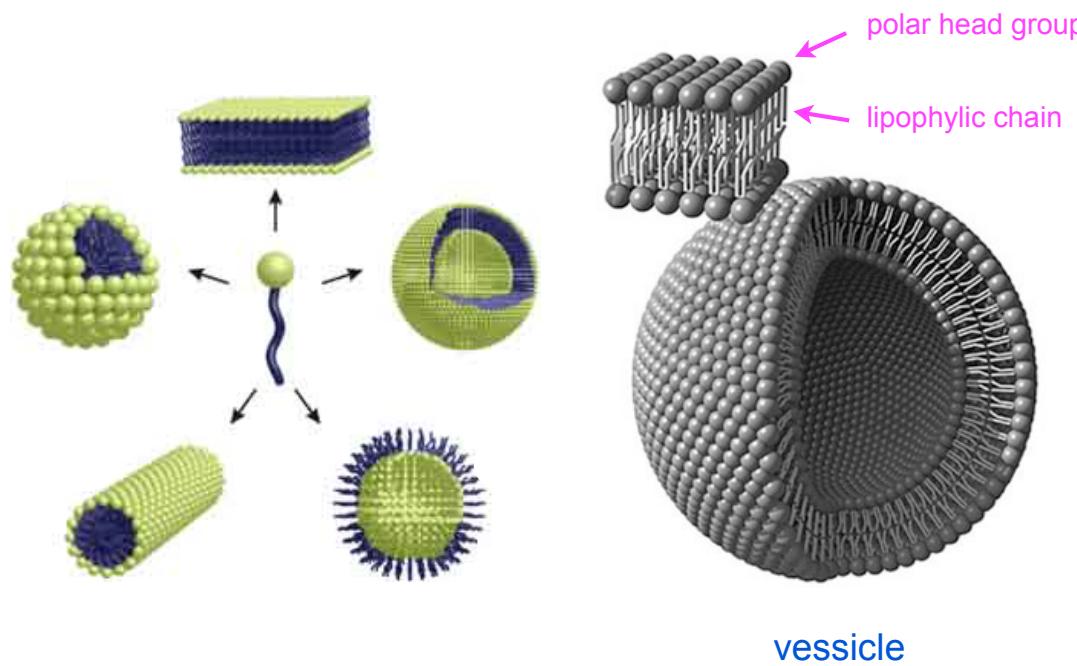
# Green Chemistry



Anastas and Warner (1998)



# Supramolecular Capsules for Molecular Storage & Delivery

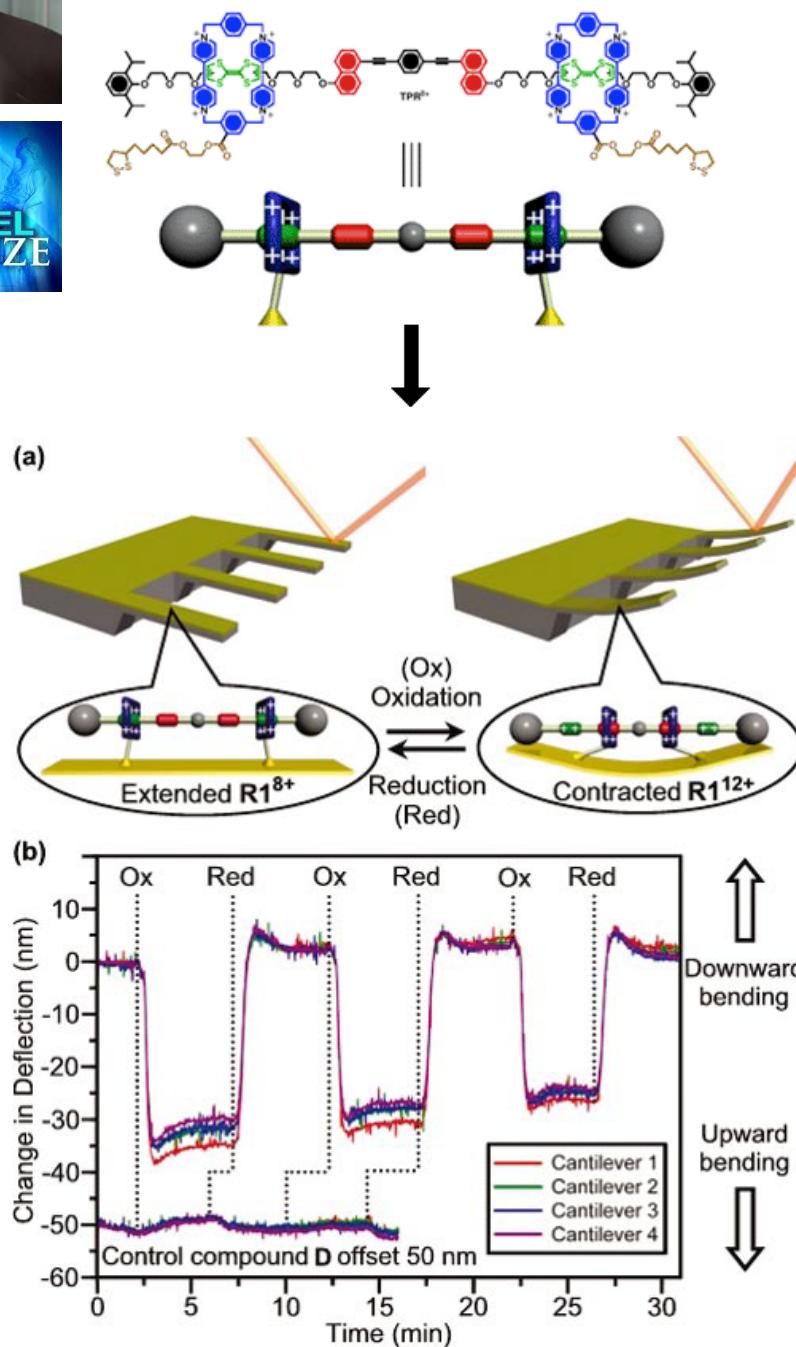


FULLERENE BILAYER VESICLE

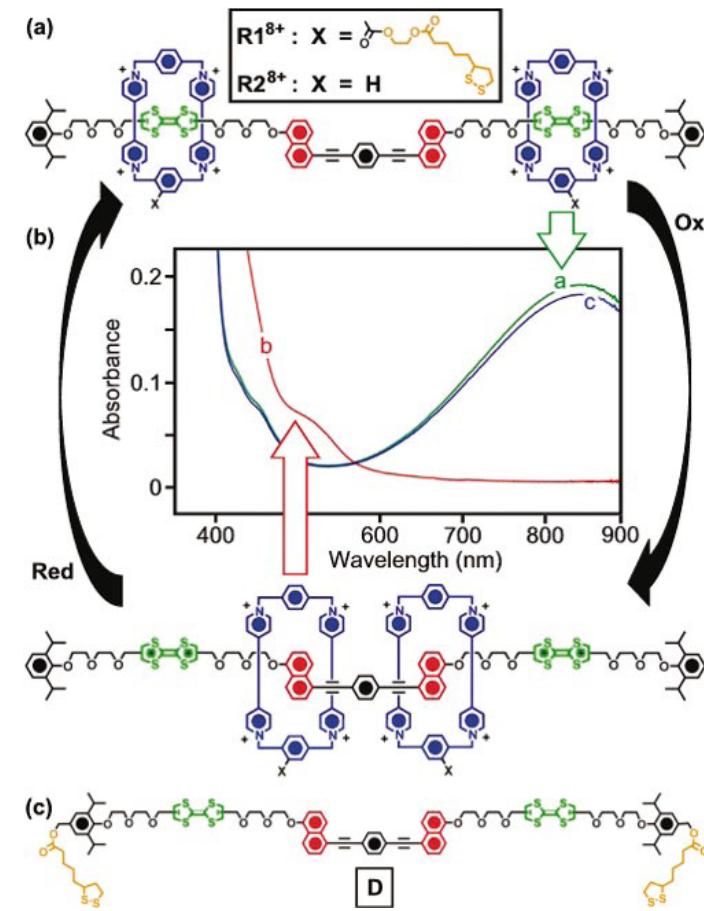


## A nanomechanical device based on linear molecular motors

Tony Jun Huang, Branden Brough, Chih-Ming Ho, Yi Liu, Amar H. Flood, Paul A. Bonvallet, Hsian-Rong Tseng, J. Fraser Stoddart, Marko Boller and Sergei Magonov  
Appl. Phys. Lett., 2004, 85, 5391-5393

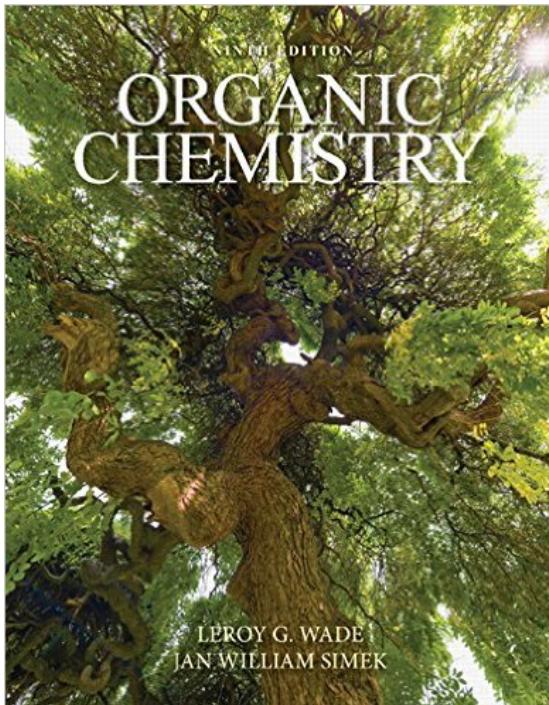


An array of microcantilever beams, coated with a self-assembled monolayer of bistable, redox-controllable [3]rotaxane molecules, undergoes controllable and reversible bending when it is exposed to chemical oxidants and reductants. Conversely, beams that are coated with a redox-active but mechanically inert control compound do not display the same bending. A series of control experiments and rational assessments preclude the influence of heat, photothermal effects, and pH variation as potential mechanisms of beam bending. Along with a simple calculation from a force balance diagram, these observations support the hypothesis that the cumulative nanoscale movements within surface-bound "molecular muscles" can be harnessed to perform larger-scale mechanical work.

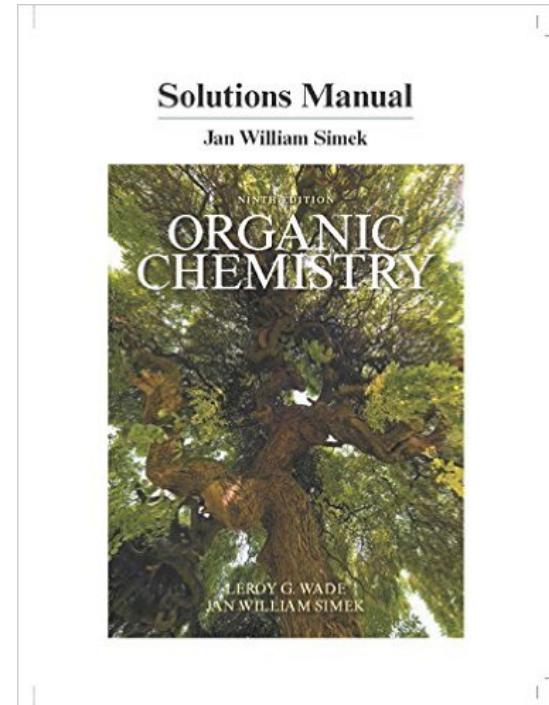


# Materials for the Course

Text

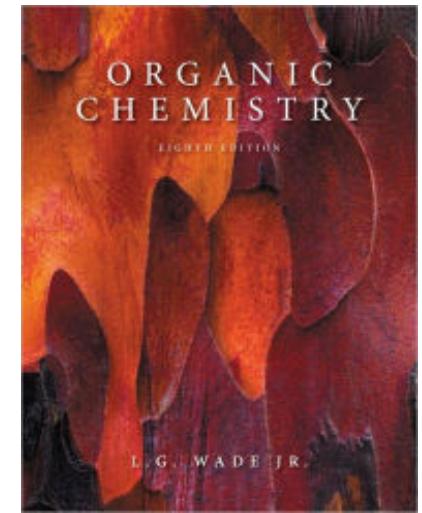


Wade, 9th Edition (required)



optional

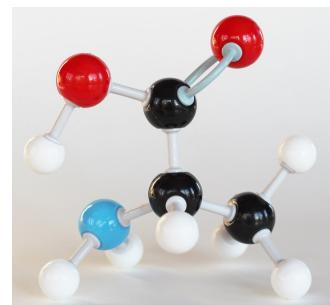
Can I use the 8th Edition?



Wade, 8th Edition

Molecular model kit: optional,  
but highly recommended

- Book Store
- Amazon



Duluth Labs Organic Chemistry Molecular Model Student Kit



MM-003 (\$25)  
ISBN-13: 978-0-9988678-0-9



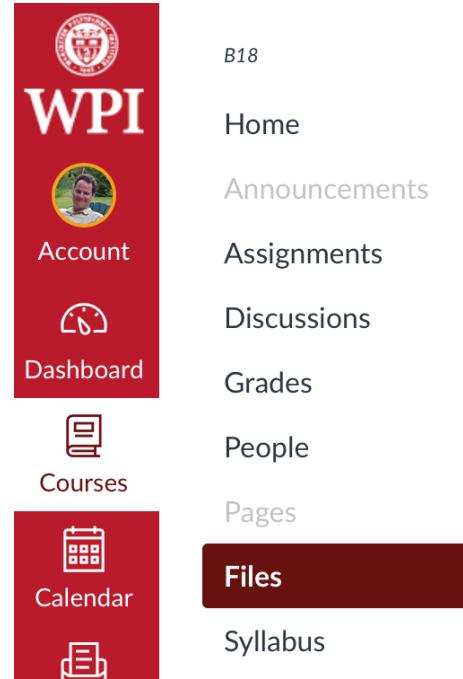
MM-004 (\$35)  
ISBN-13: 978-0-9988678-1-6

# Course Web Site

## Canvas

All material for the course is posted

- syllabus
- lecture presentations in class
- handouts
- problem sets & solutions
- exams & solutions
- grades



☰ CH2310-B18-B01 > Files

Search for files

- ▼ ORGANIC CHEMISTRY I
  - Exams & Solutions
  - ▼ Presentations in Class
    - Problem Sets & Solutions
    - Summaries of Reactions

Material in lectures will be presented using a combination of slides and chalk talks at the board

All presentations will be posted by chapter as **PDF** files

I recommend that you **bring a laptop or tablet, or print PDF files of presentations** and bring them to class

# Topics Covered in CH2310

Chapter 1: Introduction and Review

[Review on your own\\*](#)

Chapter 2: Structure and Properties of Organic Molecules

[Review on your own.\\* We'll go over some of this material as needed throughout the term](#)

 **We'll start here**

**Chapter 3: Structure and Stereochemistry of Alkanes**

Chapter 4: The Study of Chemical Reactions

[We'll work this material into the context of Chapters 5-8](#)

Chapter 5: Stereochemistry

Chapter 6: Alkyl Halides: Nucleophilic Substitution and Elimination

Chapter 7: Structure and Synthesis of Alkenes

Chapter 8: Reactions of Alkenes

**\*\*\* Use problem sets as a study guide \*\*\***

# Chapter 3: Structure & Stereochemistry of Alkanes

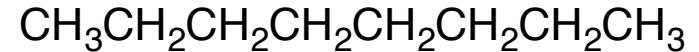
Ex: Common alkanes



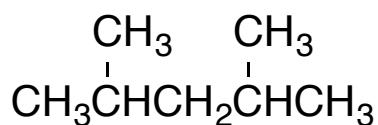
methane



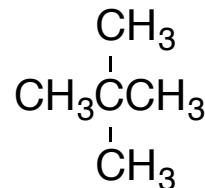
propane



octane



2,4-dimethylpentane



2,2-dimethylpropane

Q: What features do these compounds have in common?

## Alkanes

- Compounds that contain only carbon and hydrogen where every carbon atom is bonded to four other atoms
- Also called saturated hydrocarbons (lack C=C or C≡C bonds)
- Compounds that lack functional groups (chemically reactive groups)

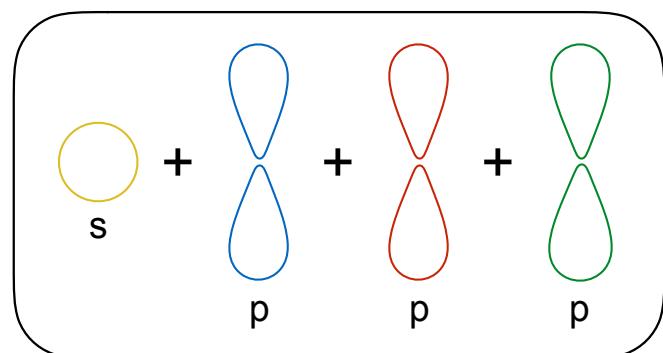
Q: Why start with alkanes when learning organic chemistry?

Q: Structure of carbon?

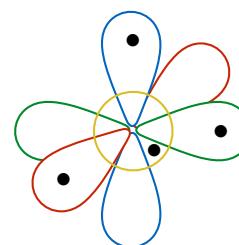
Q: What does saturated mean?

Q: What are functional groups? Why are they important?

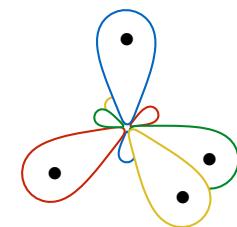
# Arrangement of valence electrons around carbon?



Q: What's wrong with this picture?



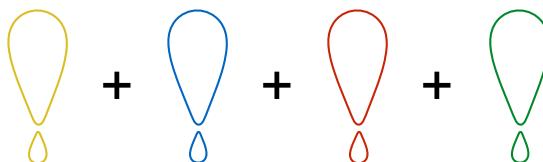
atomic orbitals



VSEPR!

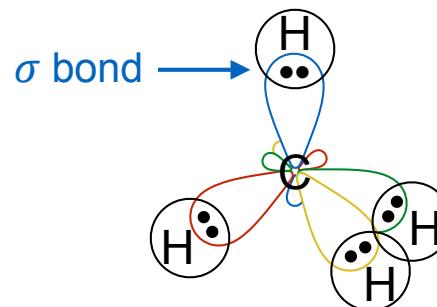
hybridized orbitals  
tetrahedral geometry

↓  
hybridization

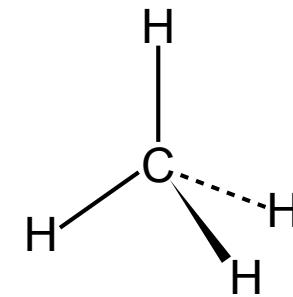


four  $sp^3$ -hybridized orbitals

Ex: Structure of methane,  $CH_4$



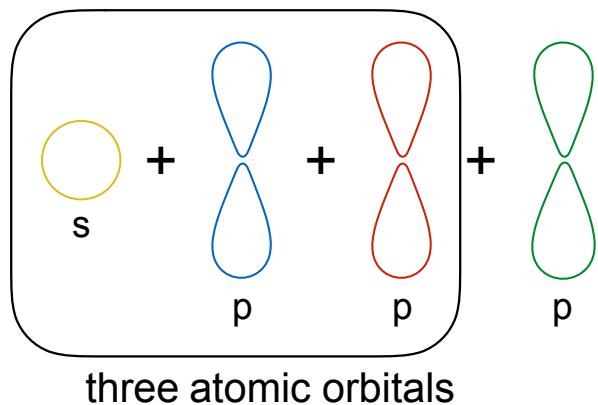
=



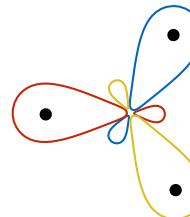
$sp^3$ -hybridized carbon  
tetrahedral carbon  
saturated carbon

Q: Relevance to other alkanes with more complex structures?

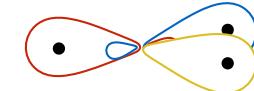
## Other ways to arrange valence electrons around carbon?



VSEPR!

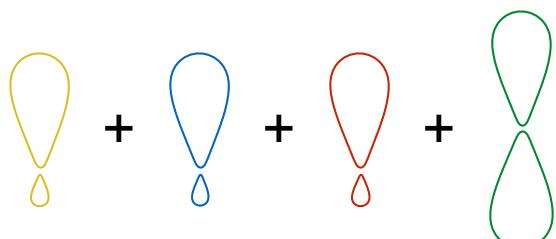


turn 90°



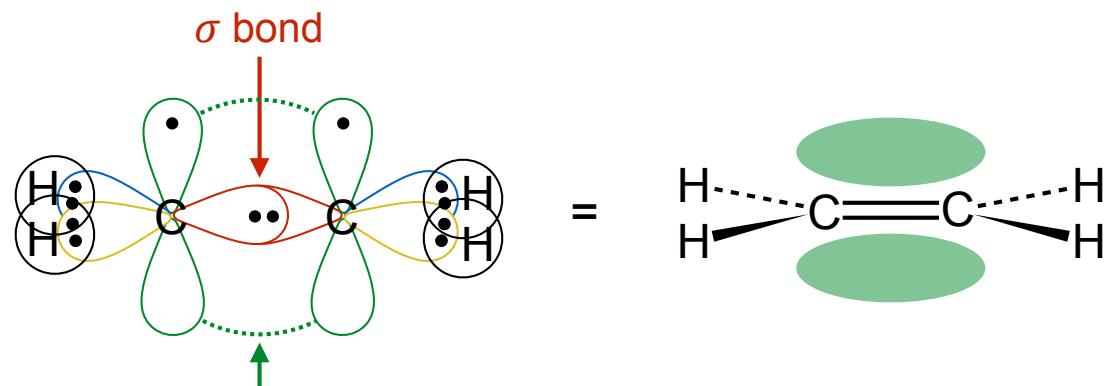
hybridized orbitals  
trigonal planar geometry

↓ hybridization



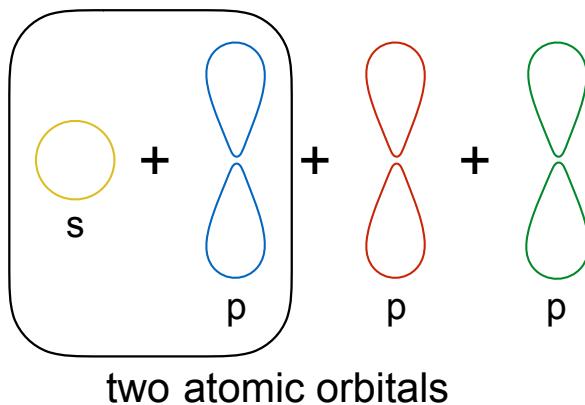
+  
one unhybridized atomic p orbital

Ex: Structure of ethene, H<sub>2</sub>C=CH<sub>2</sub>

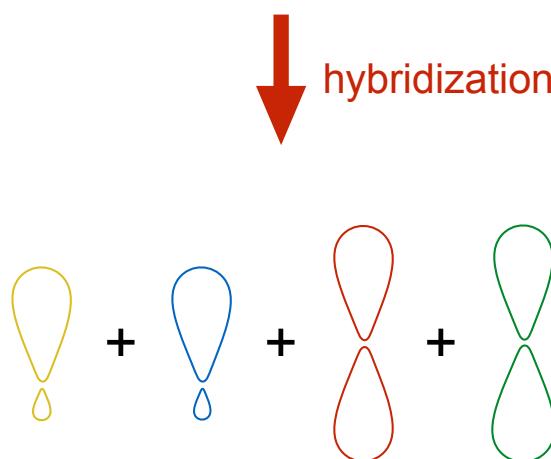


**sp<sup>2</sup>-hybridized carbon**  
**trigonal planar carbon**  
**unsaturated carbon**

## Other ways to arrange valence electrons around carbon?

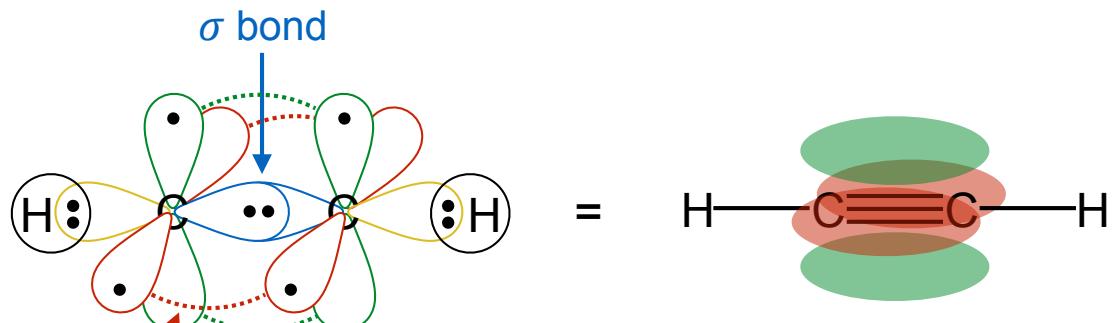


hybridized orbitals  
linear geometry



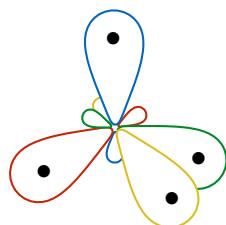
+  
two unhybridized atomic p orbitals

Ex: Structure of ethyne,  $\text{HC}\equiv\text{CH}$

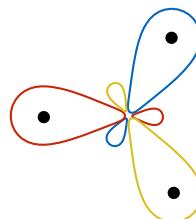


sp-hydrized carbon  
linear carbon  
unsaturated carbon

# Summary of the three bonding geometries of carbon



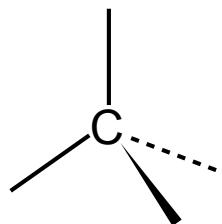
sp<sup>3</sup>-hybridized



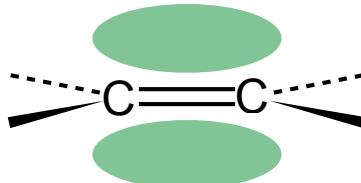
sp<sup>2</sup>-hybridized



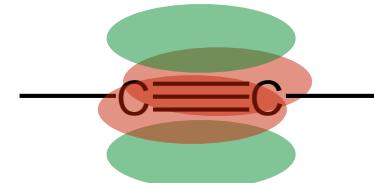
sp-hybridized



tetrahedral  
4  $\sigma$  bonds



trigonal planar  
3  $\sigma$  bonds + 1  $\pi$  bond



linear  
2  $\sigma$  bonds + 2  $\pi$  bonds

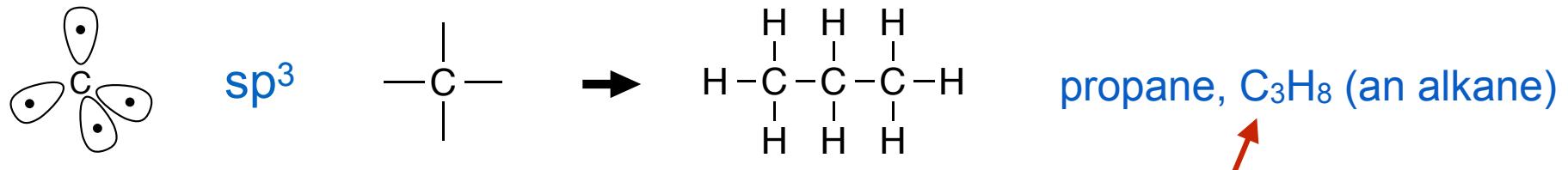
Alkanes contain only sp<sup>3</sup>-hybridized carbon atoms with tetrahedral geometry

Q: Why is knowing the bonding geometry of carbon important?

Q: Relationship between atomic hybridization and overall molecular structure?

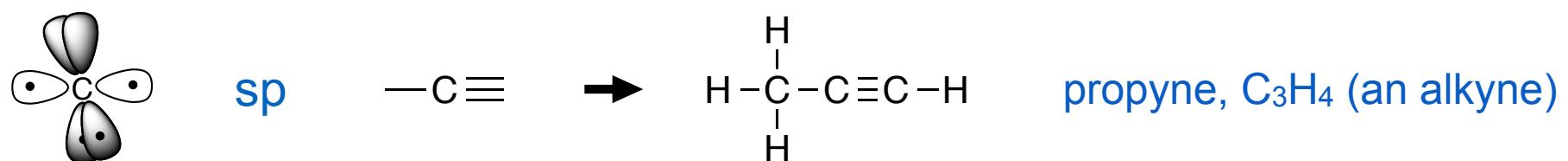
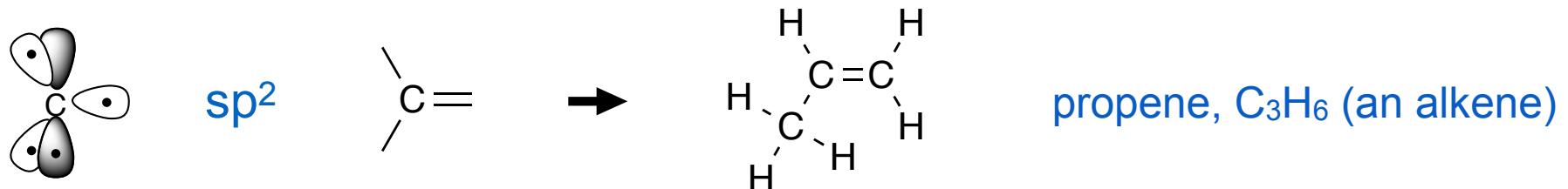
## Saturated vs. Unsaturated Hydrocarbons

Saturated: All carbon atoms are bonded to four other atoms via single ( $\sigma$ ) bonds—all carbon atoms are  $sp^3$ -hybridized



maximum number of hydrogen atoms (i.e., saturated) compared to unsaturated hydrocarbons with the same number of carbon atoms

Unsaturated: One or more carbon atoms are bonded to atoms via double/triple ( $\pi$ ) bonds—one or more carbon atoms are  $sp^2$ /sp-hybridized

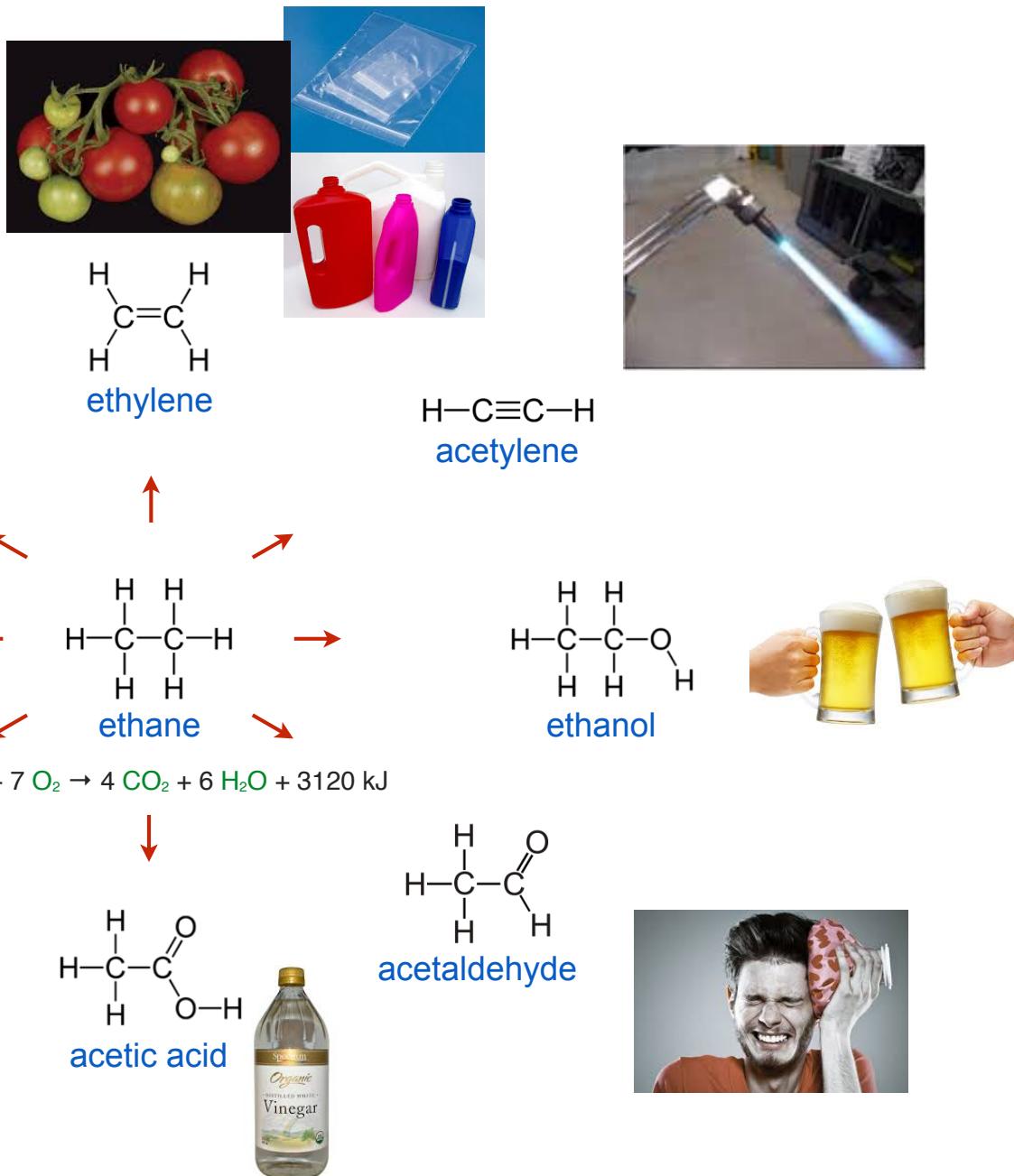
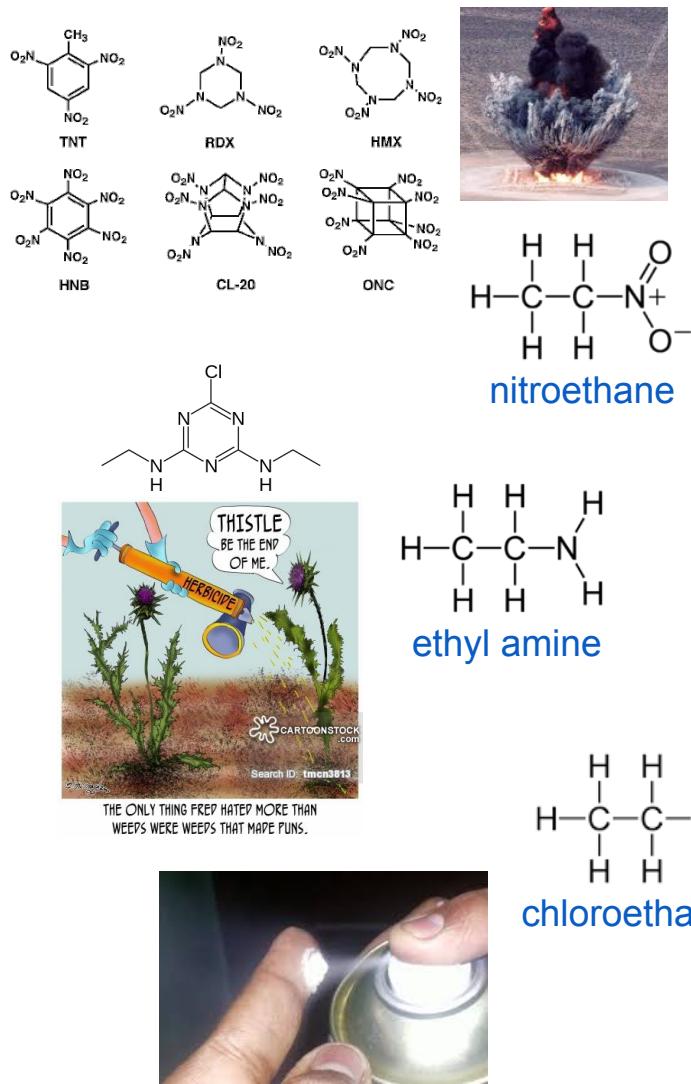


Q: What impact does saturation/unsaturation have on chemical behavior?

# Functional Behavior



# Q: Where does functionality come from in organic chemistry?



Organic functional groups - structural features that make it possible to classify compounds on the basis of their behavior, properties, and reactivity!

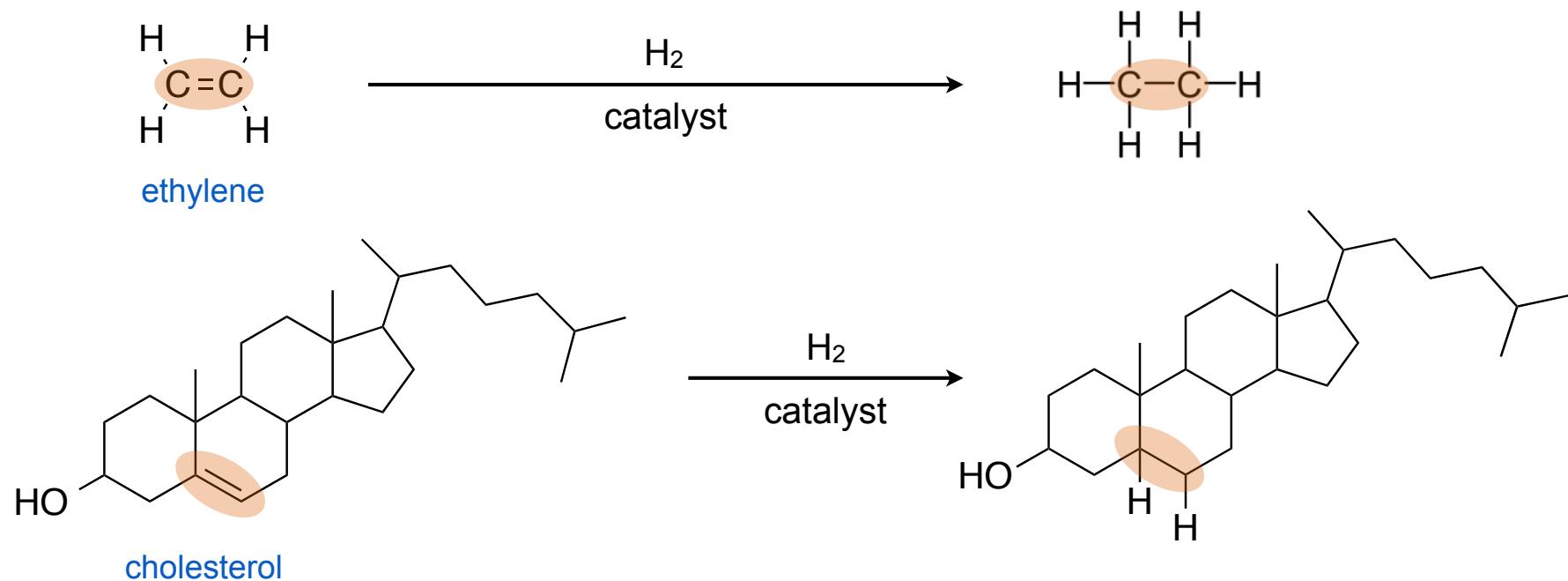
## Functional Group

Part of a larger molecule

An atom or group of atoms that exhibits a characteristic (predictable) chemical behavior

A functional group behaves the same way chemically in every compound it is part of

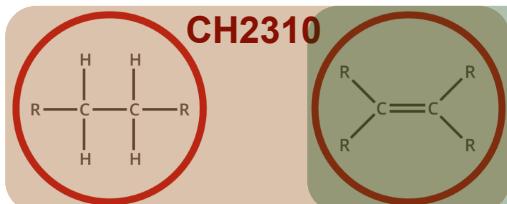
Ex: C=C bonds show similar reactivity



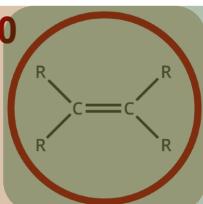
# FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

FUNCTIONAL GROUPS ARE GROUPS OF ATOMS IN ORGANIC MOLECULES THAT ARE RESPONSIBLE FOR THE CHARACTERISTIC CHEMICAL REACTIONS OF THOSE MOLECULES.  
IN THE GENERAL FORMULAE BELOW, 'R' REPRESENTS A HYDROCARBON GROUP OR HYDROGEN, AND 'X' REPRESENTS ANY HALOGEN ATOM.

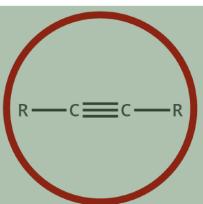
HYDROCARBONS SIMPLE OXYGEN HETEROATOMICS HALOGEN HETEROATOMICS CARBONYL COMPOUNDS NITROGEN BASED SULFUR BASED AROMATIC



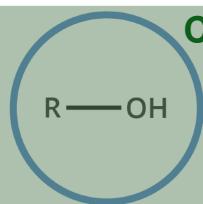
**ALKANE**  
Naming: -ane  
e.g. ethane



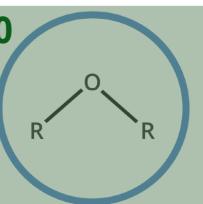
**ALKENE**  
Naming: -ene  
e.g. ethene



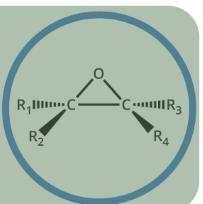
**ALKYNE**  
Naming: -yne  
e.g. ethyne



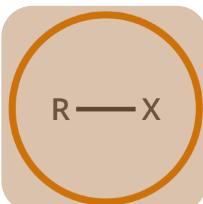
**ALCOHOL**  
Naming: -ol  
e.g. ethanol



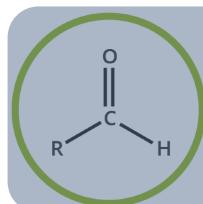
**ETHER**  
Naming: -oxy -ane  
e.g. methoxyethane



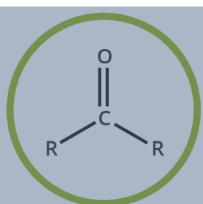
**EPOXIDE**  
Naming: -ene oxide  
e.g. ethene oxide



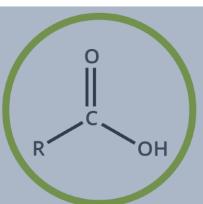
**HALOALKANE**  
Naming: halo-  
e.g. chloroethane



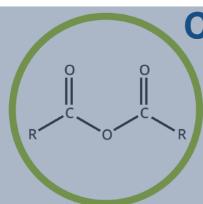
**ALDEHYDE**  
Naming: -al  
e.g. ethanal



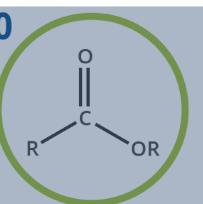
**KETONE**  
Naming: -one  
e.g. propanone



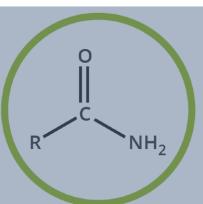
**CARBOXYLIC ACID**  
Naming: -oic acid  
e.g. ethanoic acid



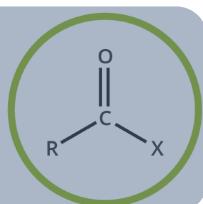
**ACID ANHYDRIDE**  
Naming: -oic anhydride  
e.g. ethanoic anhydride



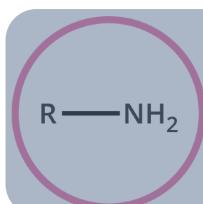
**ESTER**  
Naming: -yl -oate  
e.g. ethyl ethanoate



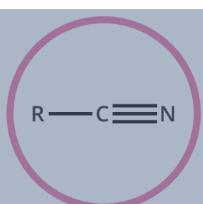
**AMIDE**  
Naming: -amide  
e.g. ethanamide



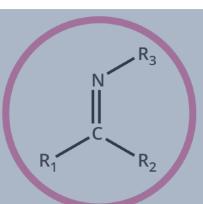
**ACYL HALIDE**  
Naming: -oyl halide  
e.g. ethanoyl chloride



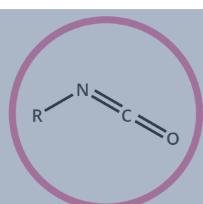
**AMINE**  
Naming: -amine  
e.g. ethanamine



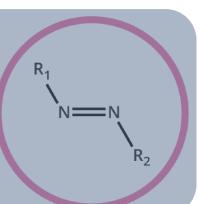
**NITRILE**  
Naming: -nitrile  
e.g. ethanenitrile



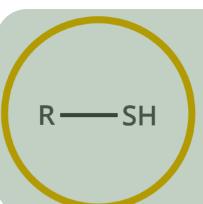
**IMINE**  
Naming: -imine  
e.g. ethanimine



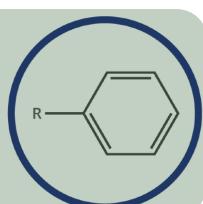
**ISOCYANATE**  
Naming: -yl isocyanate  
e.g. ethyl isocyanate



**AZO COMPOUND**  
Naming: azo-  
e.g. azoethane



**THIOL**  
Naming: -thiol  
e.g. methanethiol



**ARENE**  
Naming: -yl benzene  
e.g. ethyl benzene



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S

R = any bonded atom or group of atoms



Q: What are the functional groups?

Q: How do you recognize when a functional group is present?

→ Any atom or group of atoms that isn't saturated hydrocarbon!



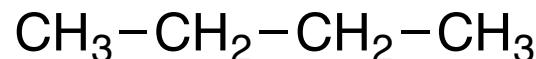
Read Ch. 2 sections 2-15, 2-16, and 2-17 in Wade

→ Learn to recognize organic functional groups!

You can avoid memorizing reactions if you learn how compounds will react based on the functional groups present!

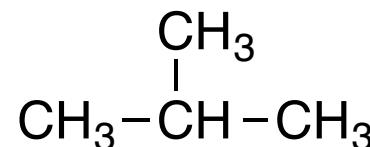
## Molecular formulas of alkanes - classification of alkanes (3-2)

Ex:



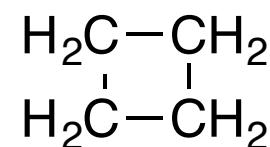
n-butane

normal or straight-chain



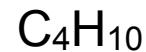
2-methylpropane

branched



cyclobutane

cyclic



same formula  
constitutional isomers

## Classification of alkanes

1. Straight-chain (normal) alkanes
2. Branched alkanes
3. Cyclic alkanes (we'll get to these in sec. 3-10)

Constitutional Isomers - Compounds that have the same molecular formula, but that differ in the connectivity between the atoms

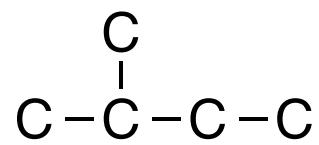
Ex: Isomers of C<sub>5</sub>H<sub>12</sub>

Q: How many isomers? Unique structures?

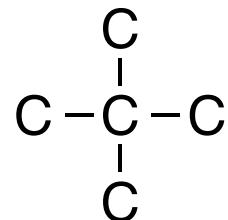
Hint: Ignore hydrogen and focus on connectivity between carbon atoms



start with  
straight chain

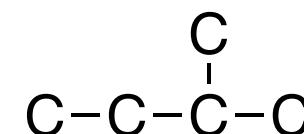
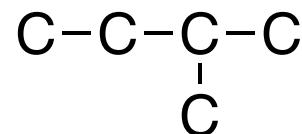
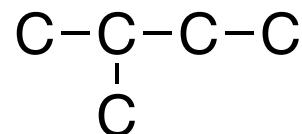


shorten straight chain by 1 C to  
make branched isomers

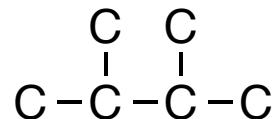
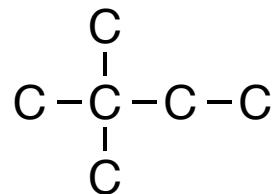
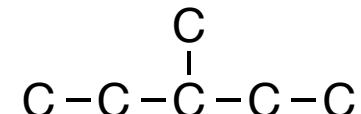
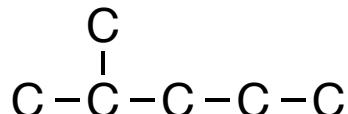
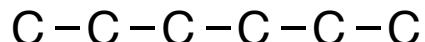


identical  
connectivity

Q: Any others? How about these?

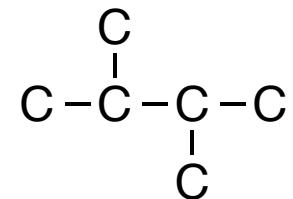
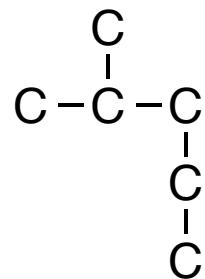
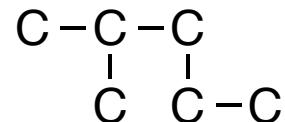
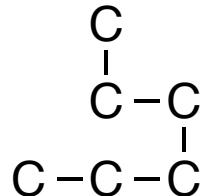


Ex: Isomers of C<sub>6</sub>H<sub>14</sub>?



Q: Any others?

Q: What about these?

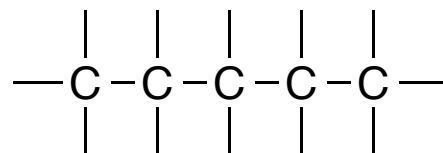
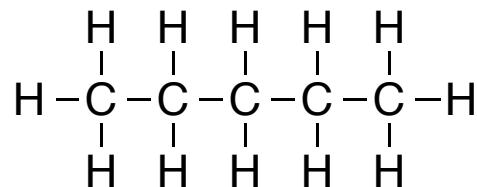


Q: How do you know if structures are unique?

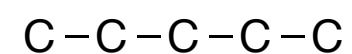
- Focus on connectivity and name them.  
Different isomers have different names.

## Different Ways to Draw Alkanes

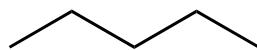
Ex: n-pentane



avoid this



avoid this



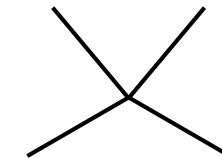
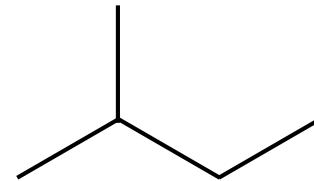
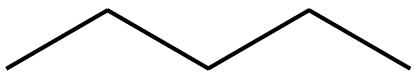
bond-line notation  
line-angle notation  
(H atoms are implied)



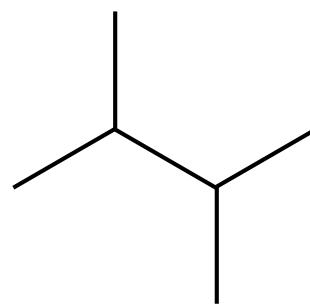
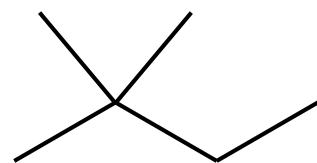
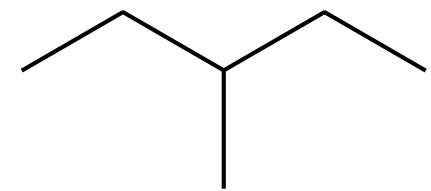
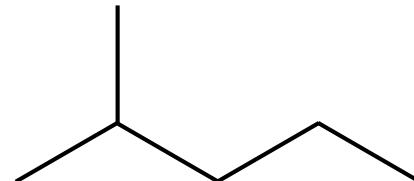
carbon skeletons can be drawn quickly!

There are many ways to draw alkanes  
Bond-line (line-angle) notation is most efficient → learn it!  
Review Chapter 1 Section 10

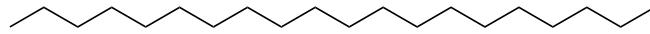
Ex: Bond-line notation for the three isomers of C<sub>5</sub>H<sub>12</sub>



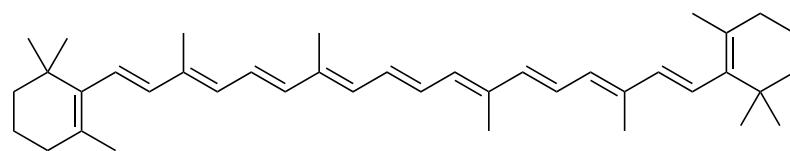
Ex: Bond-line notation for the five isomers of C<sub>6</sub>H<sub>14</sub>?



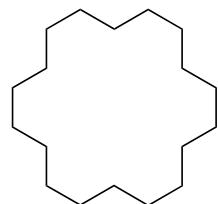
## Ex: Examples of more complex structures drawn with bond-line notation



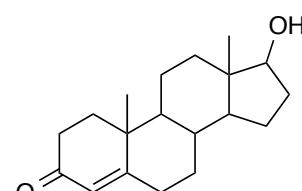
icosane



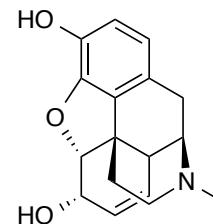
beta carotene



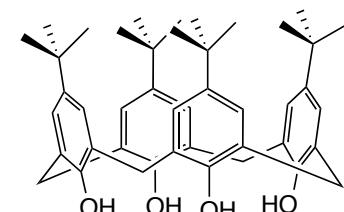
cyclooctadecane



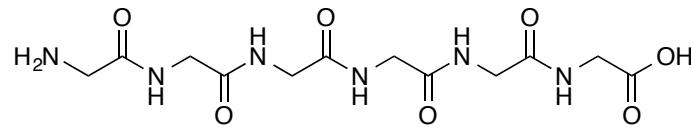
testosterone



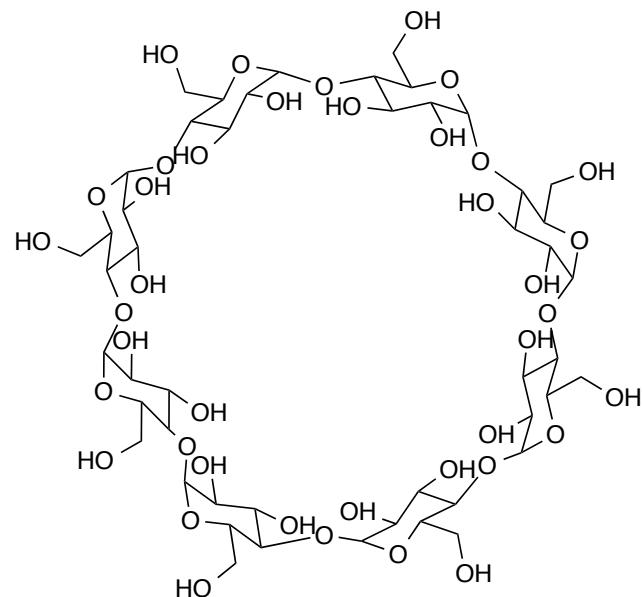
morphine



resorcinol

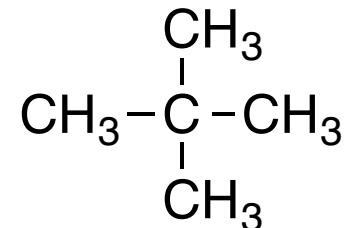
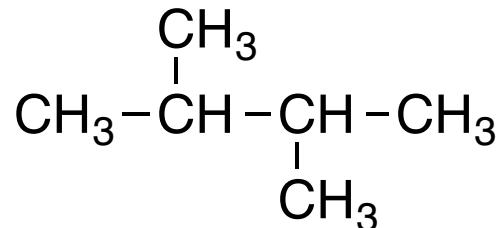
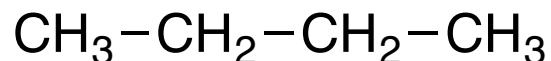


glycylglycylglycylglycylglycylglycine



cyclodextrin

## General Formula for Alkanes



$\text{C}_4\text{H}_{10}$

$\text{C}_6\text{H}_{14}$

$\text{C}_5\text{H}_{12}$

Q: What do these formulas have in common?

General Formula =  $\text{C}_n\text{H}_{2n+2}$



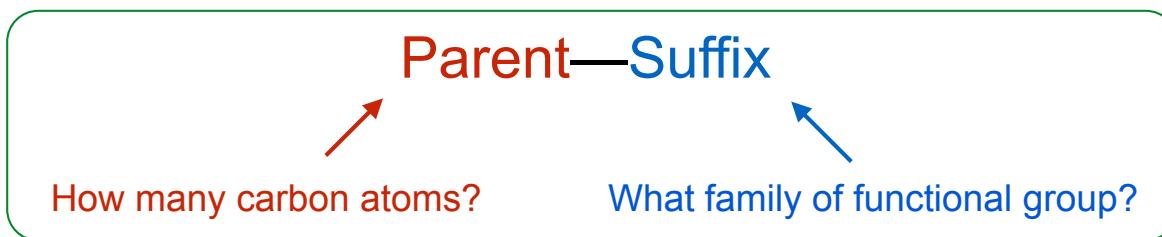
Formula for a saturated alkane

Note: General formula works only for acyclic (non-cyclic) alkanes

## Nomenclature of Alkanes (3-3)

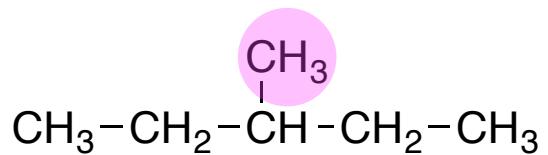
### Names of Straight-Chain (Normal) Alkanes

- Use Greek roots for the **parent name** (except C<sub>1</sub>-C<sub>4</sub>) to indicate the # of carbon atoms
- Add **-ane** as the suffix to indicate the functional group (an alkane)



<u>Name</u>	<u>Formula</u>	<u>Molecular Formula</u>	<u>Bond-Line Notation</u>
methane	CH <sub>4</sub>	CH <sub>4</sub>	
ethane	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	
propane	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	
butane	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	
pentane	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	
hexane	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	
heptane	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	
octane	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	
nonane	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	
decane	C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	
undecane	C <sub>11</sub> H <sub>24</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	
dodecane	C <sub>12</sub> H <sub>26</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	

Q: What about hydrocarbon groups on branched alkanes?

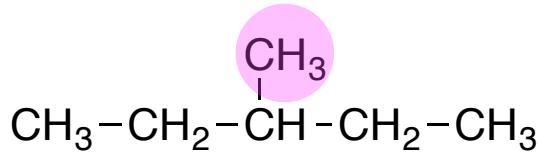


### Alkyl Groups

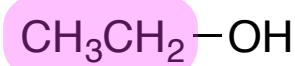
- Removing a H atom from an alkane creates an alkyl group—a substituent that is an alkane that is not part of the parent alkane
- Replace -ane with -yl as the suffix



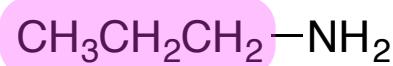
Ex:



3-methylpentane



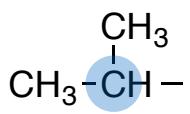
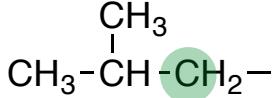
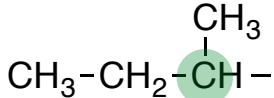
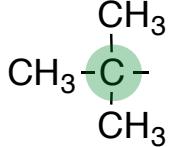
ethyl alcohol



n-propyl amine

## Commonly Occurring Alkyl Groups

- Alkyl groups with 1-4 carbon atoms often are substituents → Learn them!

<u>Alkyl Group</u>	<u>Name</u>	<u>Short-hand Abbreviation</u>
$\text{CH}_3-$	methyl	Me
$\text{CH}_3-\text{CH}_2-$	ethyl	Et
$\text{CH}_3-\text{CH}_2-\text{CH}_2-$	<i>n</i> -propyl	<i>n</i> -Pr
	isopropyl	iPr (no hyphen)
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	<i>n</i> -butyl	<i>n</i> -Bu
	isobutyl	iBu (no hyphen)
	<i>sec</i> -butyl	s-Bu
	<i>tert</i> -butyl	<i>t</i> -Bu

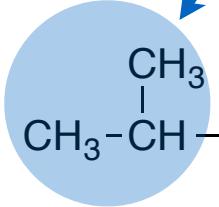
Q: What do *iso*, *sec*-, and *tert*- mean?

## Common Names for Alkyl Groups with a Terminal Branch

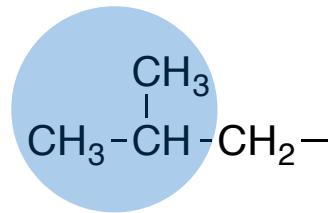
Q: What structural feature do these alkyl groups have in common?

Ex:

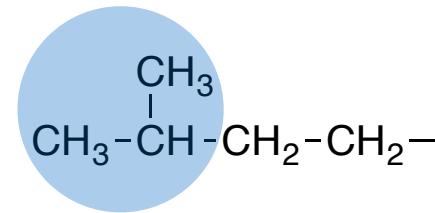
branched terminal methyl group



isopropyl



isobutyl

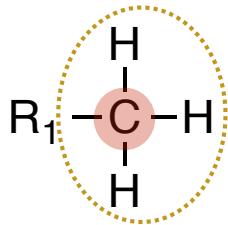


isopentyl

- The prefix iso indicates a branched methyl group at the end of a straight carbon chain
- The parent name is based on the total number of carbon atoms in the group (i.e., common name)—not the longest continuous carbon chain as in sec. 3-3 on IUPAC nomenclature
- Note: there is no hyphen separating iso and the parent name, and iso (i.e., “i”) is used when ranking substituents alphabetically

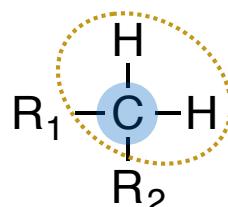
## Degree of Substitution on Carbon

methyl group



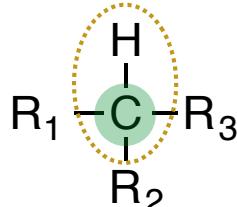
primary carbon  
1°

methylene group



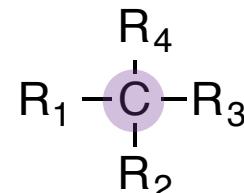
secondary carbon  
2°  
(prefix sec- or s-)

methine group



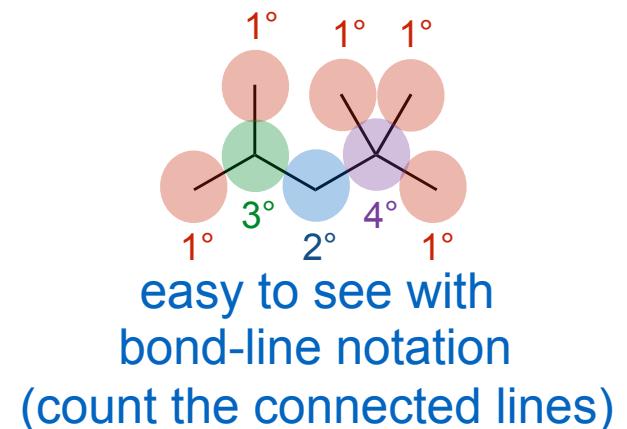
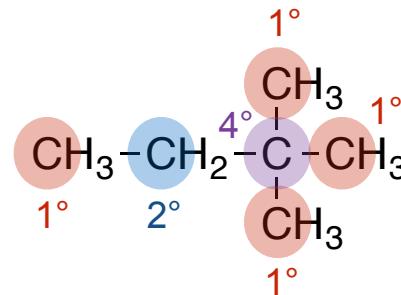
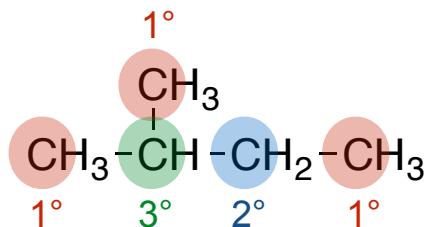
tertiary carbon  
3°  
(prefix tert- or t-)

R = any carbon group



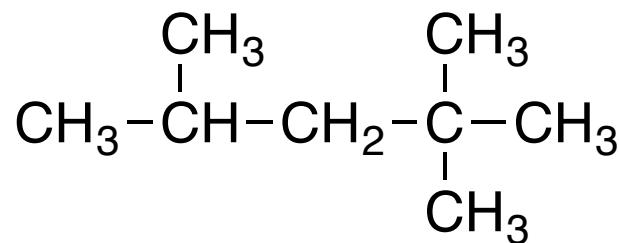
quaternary carbon  
4°

Ex: Label the degree of substitution on each carbon atom

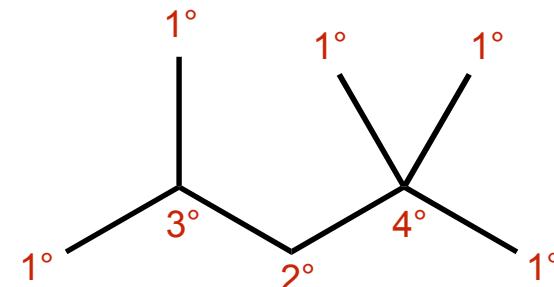


Q: Why does degree of substitution matter? What impact does it have?

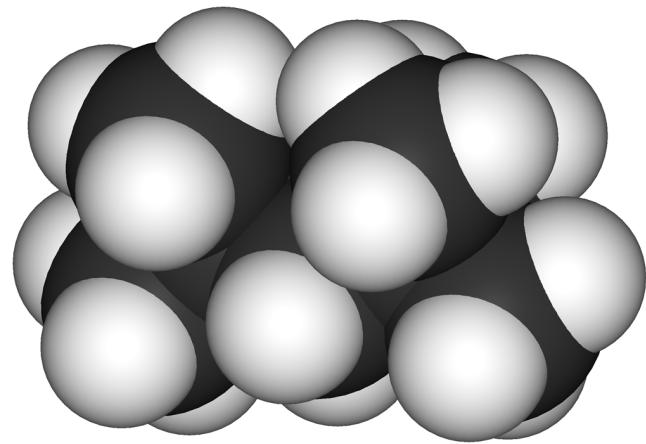
Ex: 2,2,4-trimethylpentane (isooctane) — a component of gasoline



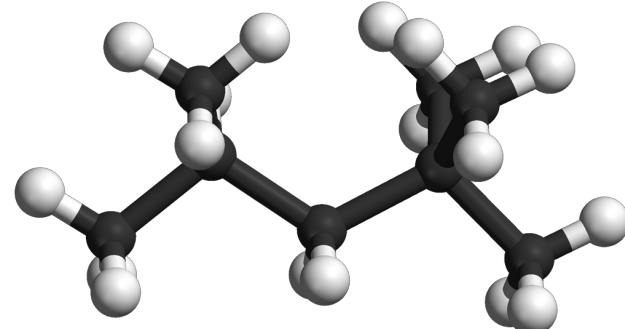
connectivity



bond-line notation



space-filling model



ball-&-stick model  
(make a model with a model kit)

Q: Accessibility of the carbon atoms as a function of degree of substitution?

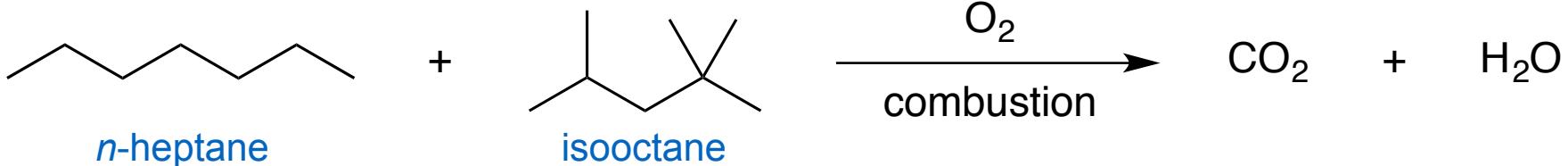
Q: Impact of accessibility on structure, conformation, and reactivity?

## Ex: Octane rating for gasoline

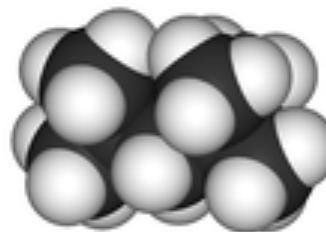


combustion characteristics compared to standard mixtures of isooctane/n-heptane

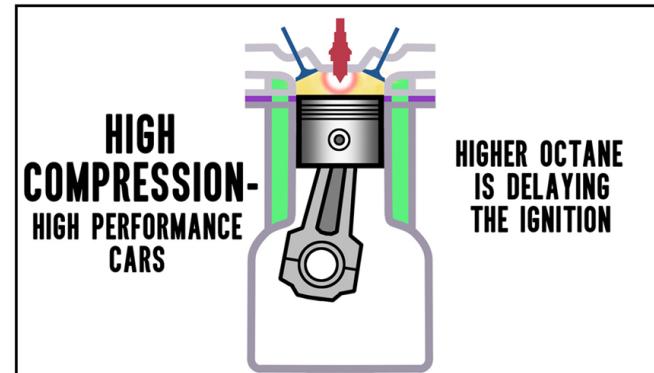
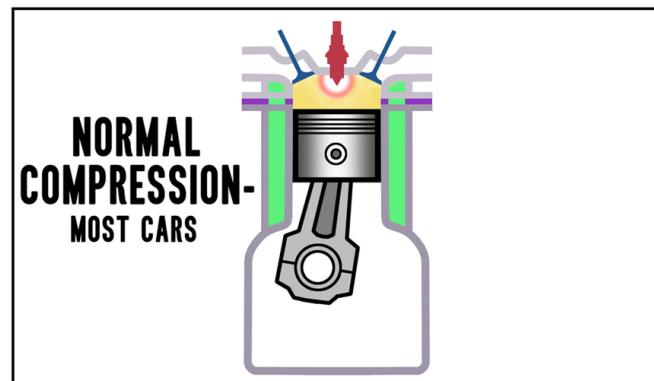
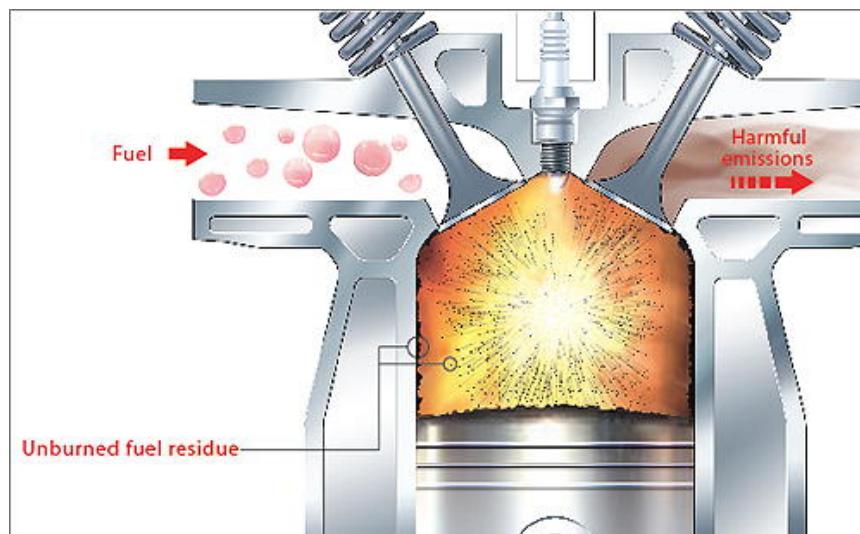
87 octane rating = 87% isoctane/13% n-heptane



higher surface area  
reacts at a faster rate  
burns explosively



lower surface area  
reacts at a slower rate  
burns smoothly



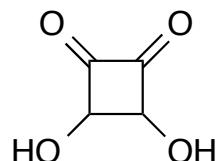
## Naming Organic Compounds

- Historically, organic compounds were named after people, shapes, smells, etc.

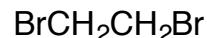
Ex:



cubane



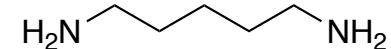
squaric acid



Newman's reagent



adamantane



cadaverone

Needed a simple, systematic set of rules for naming organic compounds (nomenclature) to communicate connectivity and structure unambiguously



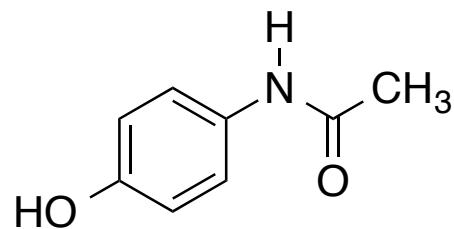
I U P A C



International Union of Pure & Applied Chemistry

est. 1892

## How are organic compounds named today?



Common or commercial names



Alvendon	Dafalgan	Genapap
Anacin	Doliprane	Panadol
Apra	Efferalgan	Panodil
Crosin	Feverall	Tylenol

Accepted IUPAC names



N-(4-hydroxyphenyl)acetamide  
N-(4-hydroxyphenyl)ethanamide

Q: Why is a systematic procedure for naming important?



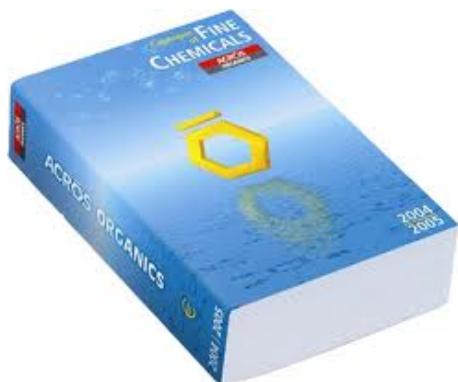
# Commercial Sources of Chemical Reagents



**SIGMA-ALDRICH**



**ACROS  
ORGANICS**



**Alfa Aesar®**  
A Johnson Matthey Company



<b>2,4-Dimethyl-1,3-pentadiene, 98%</b>					
[1000-86-8] Beil. I,257 $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ FW 96.17					
bp	94 °C	$n_D^{20}$	1.441		
density	0.744 g/mL, 25 °C	vp	67 mmHg (37.7 °C)		
R: 11-36/37/38 S: 16-26-36/37/39 EC No. 213-677-4 Fp: 10 °C (50 °F)					
126551-5G	glass btl	5 g	59.00		
126551-25G	glass btl	25 g	203.00		
<b>2,4-Dimethyl-2,3-pentadiene, 97%</b>					
Tetramethylallene					
[1000-87-9] Beil. I,IV,1030 $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ FW 96.17					
bp	87-88 °C	$n_D^{20}$	1.440		
density	0.701 g/mL, 25 °C				
R: 11-36/37/38-65 S: 16-26-33-35-62-7/9 EC No. 213-679-5 Fp: -12 °C (10 °F)					
272965-1G	ampule	1 g	155.50		
<b>2,2-Dimethylpentane, ≥99%</b>					
[590-35-2] Beil. I,IV,403 $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ FW 100.20					
bp	78 °C/43 mmHg	$n_D^{20}$	1.382		
density	0.674 g/mL, 25 °C				
R: 11-38-50/53-65-67 S: 9-16-29-33-60-61-62 EC No. 209-680-5 Fp: -9 °C (16 °F) LEL/UEL: 1.00%/8.30%					
110571-5G	ampule	5 g	98.70		
110571-10G	ampule	10 g	184.50		
<b>2,3-Dimethylpentane, ≥99%</b>					
[565-59-3] Beil. I,III,445 $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ FW 100.20					
bp	89-90 °C	vd	3.45 (vs air)		
density	0.695 g/mL, 25 °C	vp	2.35 psi (37.7 °C)		
R: 11-38-50/53-65-67 S: 9-61 EC No. 209-280-0 Fp: -7 °C (19 °F) LEL/UEL: 1.00%/7.00%					
D173207-5G	glass btl	5 g	31.10		
D173207-25G	glass btl	25 g	101.50		
D173207-100G	glass btl	100 g	301.50		
<b>2,4-Dimethylpentane, 99%</b>					
[106-08-7] Beil. I,IV,406 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$ FW 100.20					
mp	-123 °C	$n_D^{20}$	1.381		
bp	80 °C	vd	3.48 (vs air)		
density	0.673 g/mL, 25 °C	vp	3.29 psi (37.7 °C)		
R: 11-38-50/53-65-67 S: 9-16-29-33-60-61-62 EC No. 203-548-0 Fp: -7 °C (19 °F) LEL/UEL: 1.00%/7.00%					
D173401-5G	glass btl	5 g	46.40		
D173401-25G	glass btl	25 g	160.00		
<b>3,3-Dimethylpentane, 99%</b>					
[562-49-2] Beil. I,IV,409 $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_3\text{CH}_2\text{CH}_3$ FW 100.20					
mp	-135 °C	$n_D^{20}$	1.392		
bp	86 °C	vp	2.77 psi (37.7 °C)		
density	0.693 g/mL, 25 °C				
R: 11-38-50/53-65-67 S: 9-16-29-33-60-61-62 EC No. 209-230-8 Fp: -7 °C (19 °F) LEL/UEL: 1.00%/7.00%					
118451-1G	ampule	1 g	39.30		
118451-5G	ampule	5 g	121.50		

## IUPAC Rules for Systematically Naming Alkanes (3-3B)

- Read section 3-3: *Nomenclature of Alkanes* in Wade
- The rules for naming alkanes serve as the foundation for naming all organic compounds!

→ [Learn and practice the rules!](#)

# Naming Alkanes - IUPAC Nomenclature

Prefix—Parent—Suffix

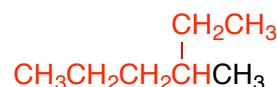
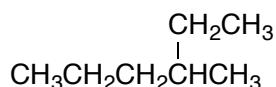
What substituents and where?

How many carbon atoms?

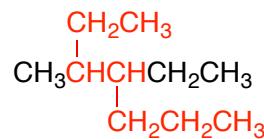
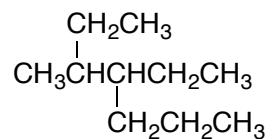
What family of functional group?

1. Find the parent hydrocarbon:

A. Find the longest continuous chain of carbon atoms present in the molecule and use the name of that chain as the parent name.

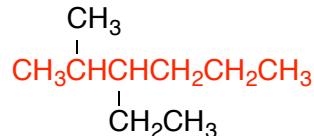
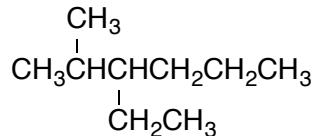


Name as a substituted hexane



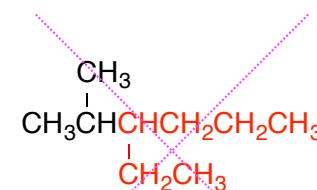
Name as a substituted heptane

B. If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.



not

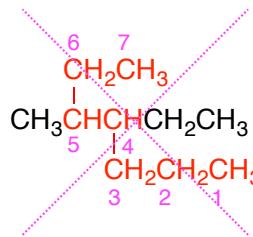
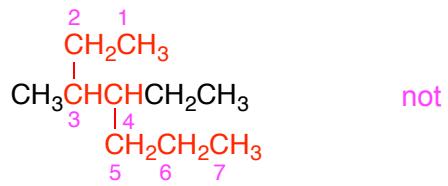
hexane with two substituents



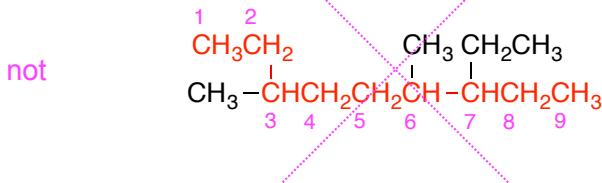
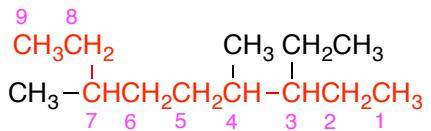
hexane with one substituent

2. Number the atoms in the parent chain:

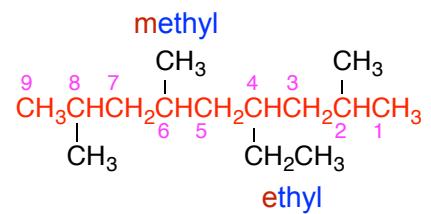
A. Beginning at the end nearer the first branch point, number each carbon atom in the parent chain.



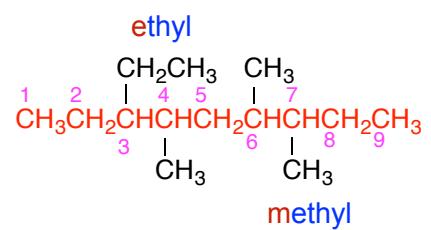
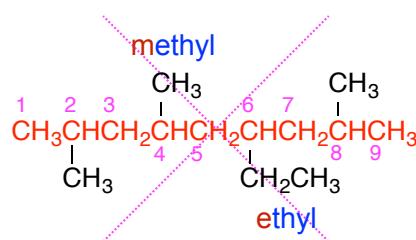
B. If branching is equidistant from both ends of the parent chain, begin numbering at the end nearer the second branch point.



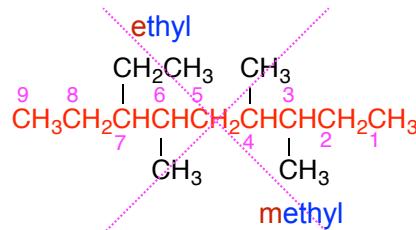
C. If multiple branch points are equidistant from both ends of the parent chain, begin numbering at the end nearer the branch point bearing the substituent with highest priority based on alphabetization.



not

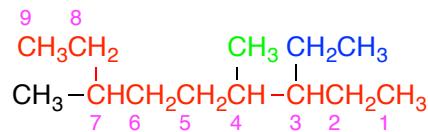


not



3. Identify and number the substituents:

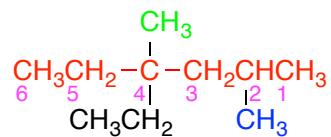
A. Assign a number to each substituent according to its point of attachment to the main chain.



Named as a nonane

Substituents: On C3, CH<sub>2</sub>CH<sub>3</sub> → 3-ethyl  
On C4, CH<sub>3</sub> → 4-methyl  
On C7, CH<sub>3</sub> → 7-methyl

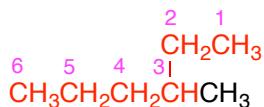
B. If there are two substituents on the same carbon, assign them the same number. There must be as many numbers in the name as there are substituents.



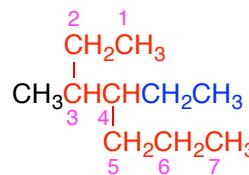
Named as a hexane

Substituents: On C2, CH<sub>3</sub> → 2-methyl  
On C4, CH<sub>3</sub> → 4-methyl  
On C4, CH<sub>2</sub>CH<sub>3</sub> → 4-ethyl

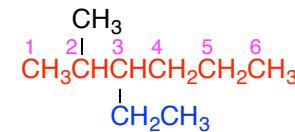
4. Write the name as a single word **using hyphens to separate numbers from words** and **using commas to separate numbers from numbers**. If two or more different substituents are present, **list them in alphabetical order**. If two or more identical substituents are present, **use one of the prefixes *di-*, *tri-*, *tetra-*, etc.** to indicate the total number of those substituents. Don't use those prefixes for alphabetizing. Note: "iso" is used in alphabetizing substituents.



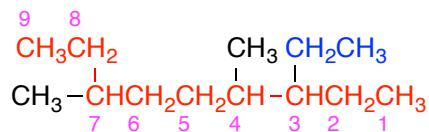
3-methylhexane



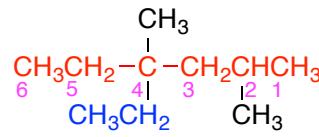
4-ethyl-3-methylheptane



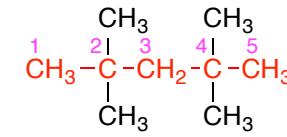
3-ethyl-2-methylhexane



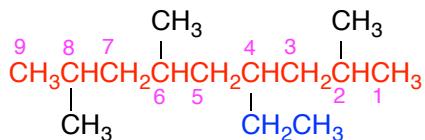
3-ethyl-4,7-dimethylnonane



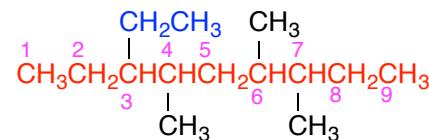
4-ethyl-2,4-dimethylhexane



2,2,4,4-tetramethylpentane



4-ethyl-2,6,8-trimethylnonane

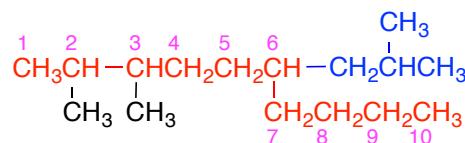
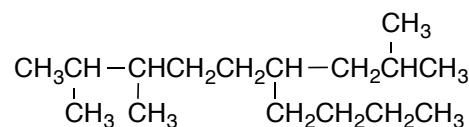


3-ethyl-4,6,7-trimethylnonane



Try drawing the structures from the names using bond-line notation

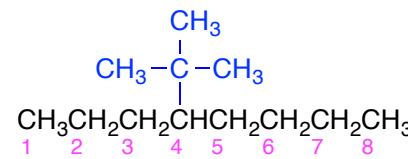
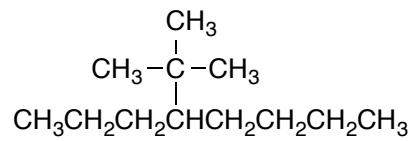
5. Complex branched substituents are named by applying the first four steps above **as if the complex branched substituent itself is an alkane**. Number the parent chain in the complex substituent starting at the point of attachment of the molecule. The name of the complex substituent is placed inside parentheses. Note: Use common names for complex substituents containing 3 or 4 carbon atoms.



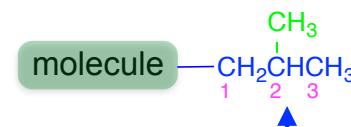
2,3-dimethyl-6-(2-methylpropyl)decane

6-isobutyl-2,3-dimethyldecano**e**

no hyphen



4-(1,1-dimethylethyl)octane  
4-*t*-butyloctane



2-methylpropane

2-methylpropyl group

isobutyl group



1,1-dimethylethane

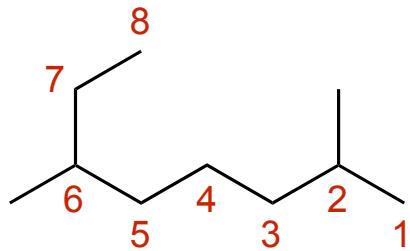
1,1-dimethylethyl group

*tertiary*-butyl group

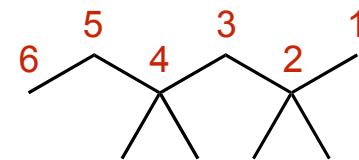
*tert*-butyl group

*t*-butyl group

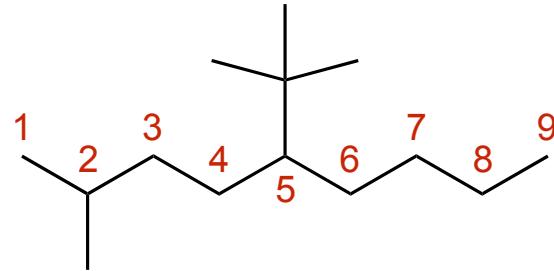
Ex: Name these alkanes



2,6-dimethyloctane



2,2,4,4-tetramethylhexane



5-*t*-butyl-2-methylnonane

2-methyl-5-(1,1-dimethylethyl)nonane

# ChemDraw Software

ChemDraw Professional File Edit View Object Structure Text Curves Colors Search Window Help

Atom Properties...  
Bond Properties...  
Bracket Properties...

Check Structure  
Clean Up Structure ⌘⌘K  
Clean Up Reaction  
Clean Up Biopolymer  
Expand Label  
Contract Label  
Expand Generic Structure

Add Multi-Center Attachment  
Add Variable Attachment  
R-Logic Query...  
Add 3D Property  
Enhanced Stereochemistry

Map Reaction Atoms  
Clear Reaction Map  
Analyze Stoichiometry

Predict  $^1\text{H}$ -NMR Shifts  
Predict  $^{13}\text{C}$ -NMR Shifts  
Make Spectrum-Structure Assignment

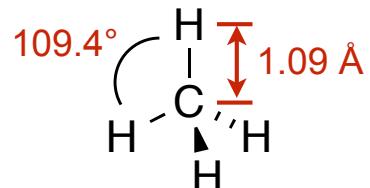
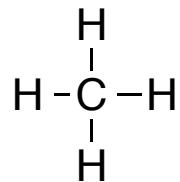
Define Nickname...  
Convert Name to Structure ⌘⌘N  
Convert Structure to Name ⌘⌘N

Untitled Document-1

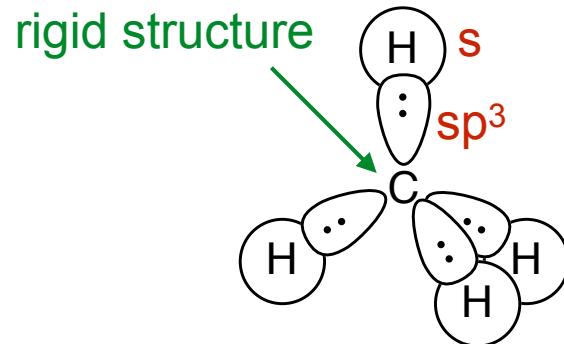
5-ethyl-4-isopropyl-2-methylheptane

## Structure and Conformations of Alkanes (3-7)

### Structure of methane (3-7A)



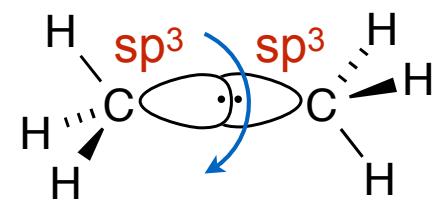
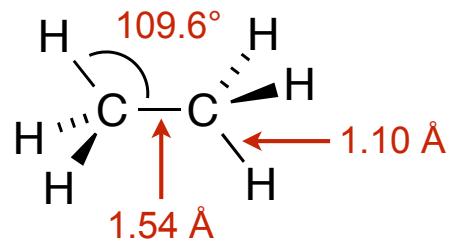
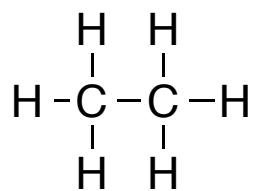
Lewis structure



VSEPR

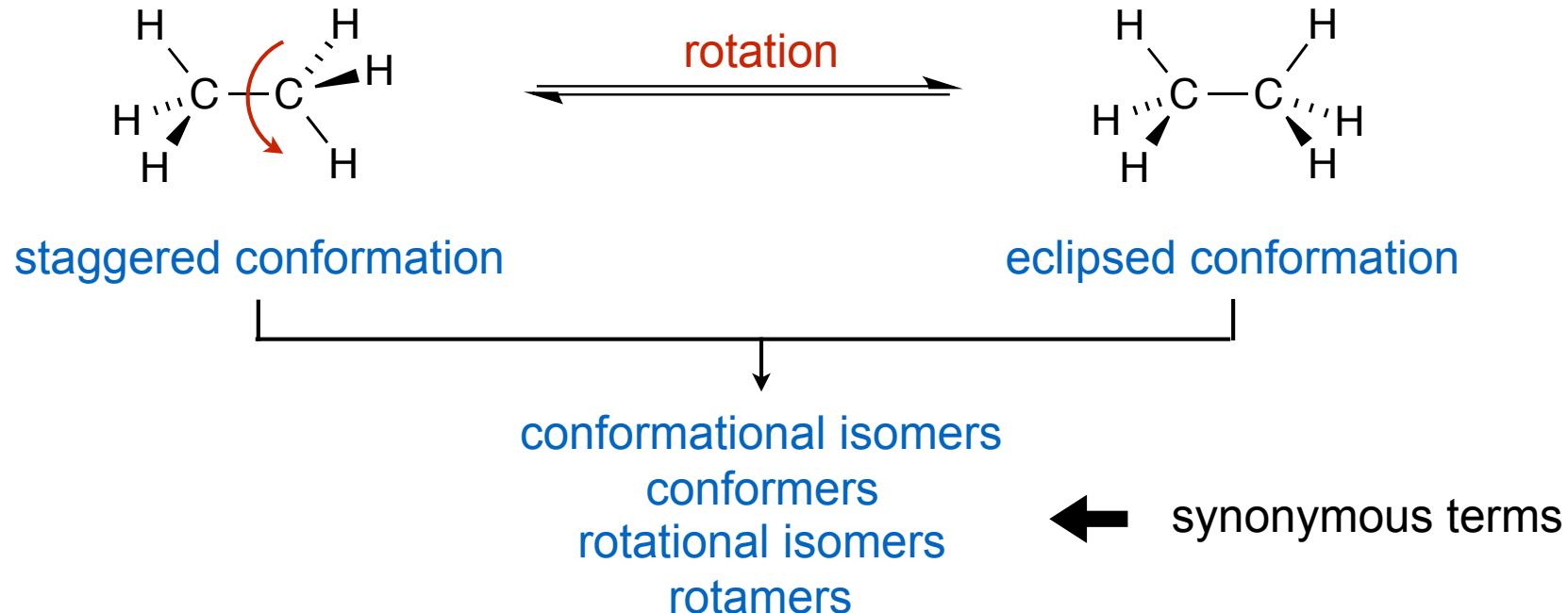
hybridization

### Structure and conformations of ethane (3-7B)



sigma bond allows free rotation  
of Me groups to give different  
conformations

Conformations: different molecular shapes or 3-D structures that result from rotation about single ( $\sigma$ ) bonds



Hint: use molecular models to visualize and compare structures easily!

Q: How many conformers of ethane exist?

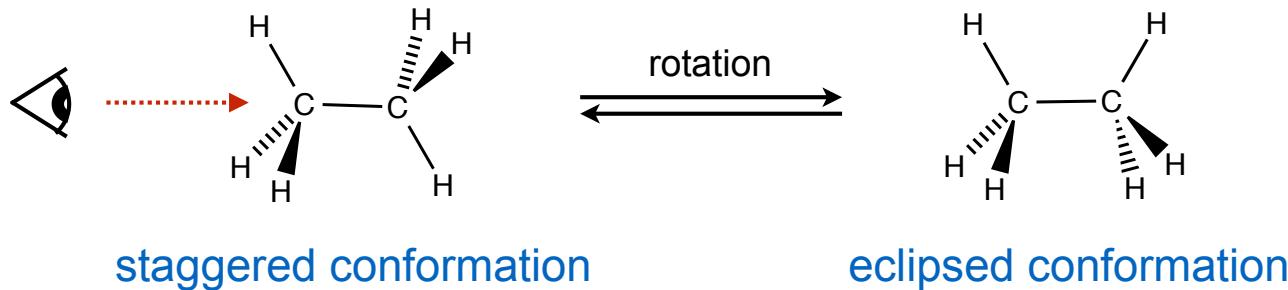
Q: Can different conformers be isolated?

Q: Do conformers have the same energy (stability)?

## Ways to Draw Conformational Isomers

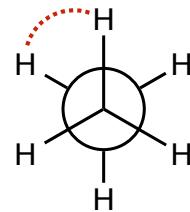
- Need to show 3-D structure clearly

Ex: Conformations of ethane



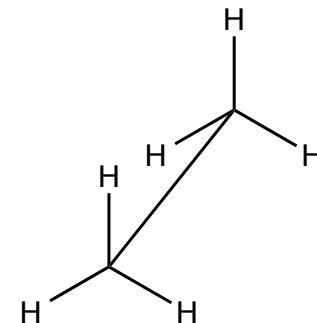
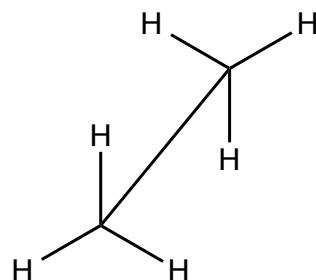
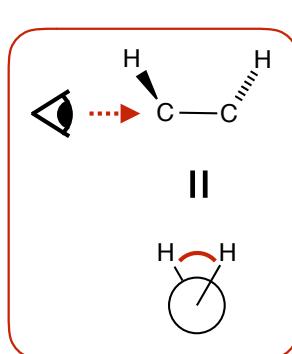
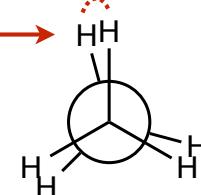
torsion angle  
dihedral angle

$$\longrightarrow \theta = 60^\circ$$



torsional strain from  
electronic repulsion  
causes energy to  
increase

$$\theta = 0^\circ$$

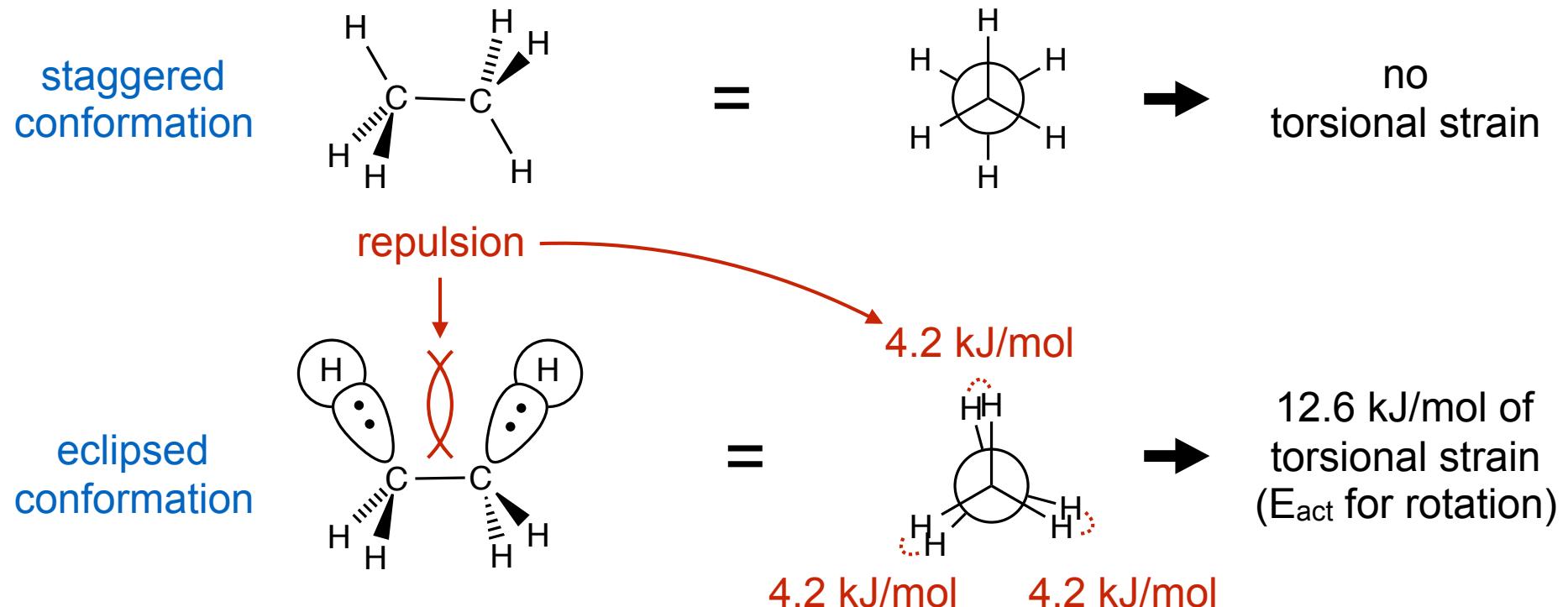


perspective  
drawings

Newman  
projections

sawhorse  
structures

Q: Origin of torsional strain?



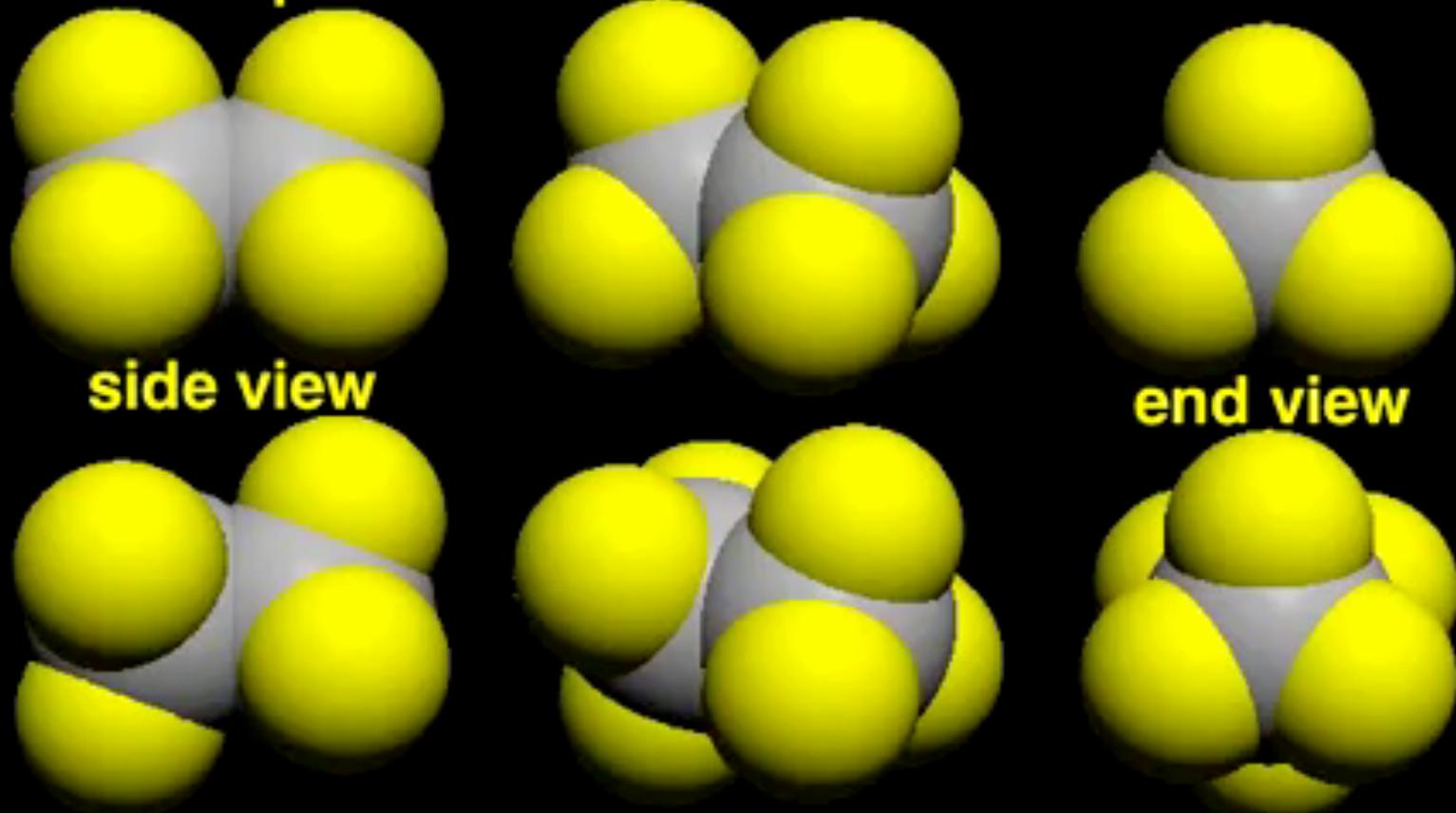
Note:  $E_{dissoc} \text{ C-C bond} = 378 \text{ kJ}$

Torsional strain: Increase in energy (destabilization) resulting from eclipsed bonds on adjacent atoms

- Eclipsing brings valence electrons into close proximity (i.e., coplanar) causing Coulombic repulsion
- Each H/H eclipsing interaction raises the energy by 4.2 kJ/mol relative to the staggered conformation

## Conformational Energy Profile of Ethane

**Ethane Newman Projection, Energies  
space filling models  
eclipsed conformation - least stable**

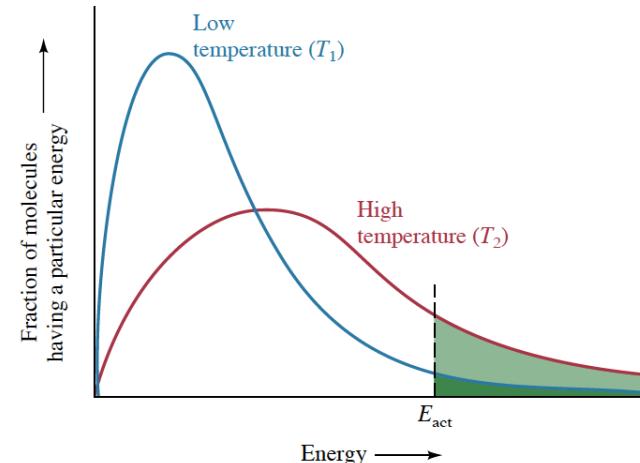


Q: At what rate do the methyl groups on ethane rotate at room temperature (RT)?

- Fast!!! <  $10^{-6}$  seconds for half of the molecules in a sample of ethane to go from one staggered conformation to another

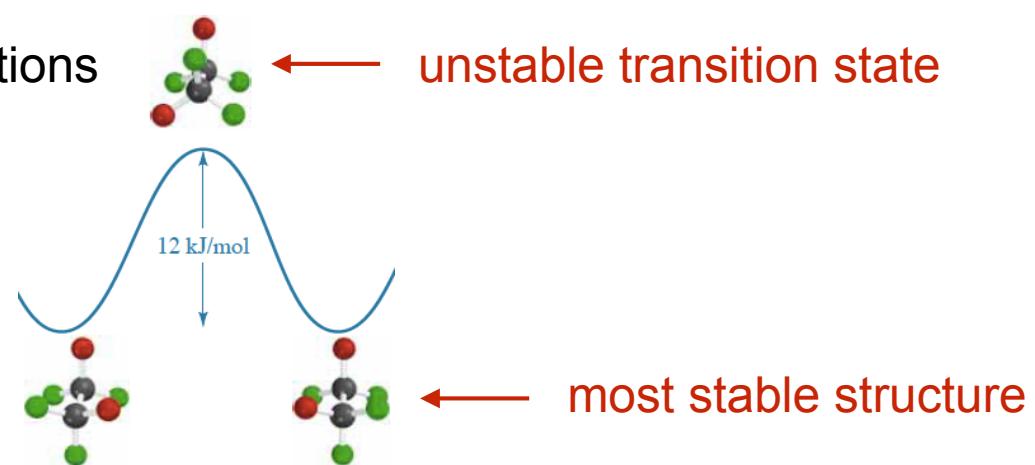
Q: What effect does temperature have on the rate of rotation?

- rate of rotation increases with temperature



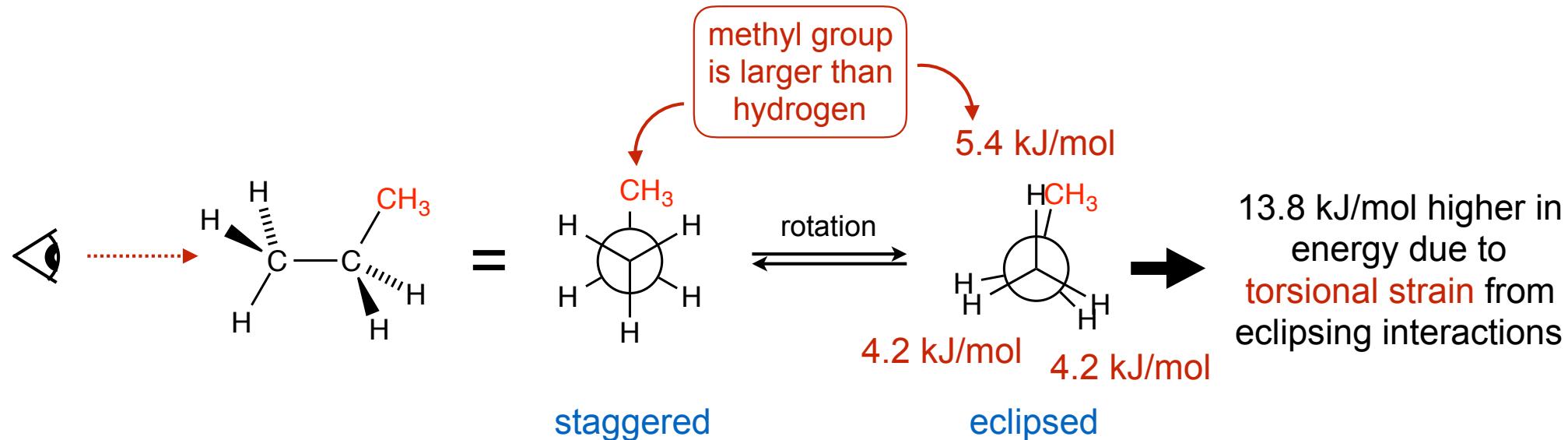
Q: Which conformations of ethane are present at RT? Which one dominates? Why?

- A distribution of all conformations
- Staggered (>>99%)
- Activation energy



Q: Why is any of this important for understanding organic reactions?

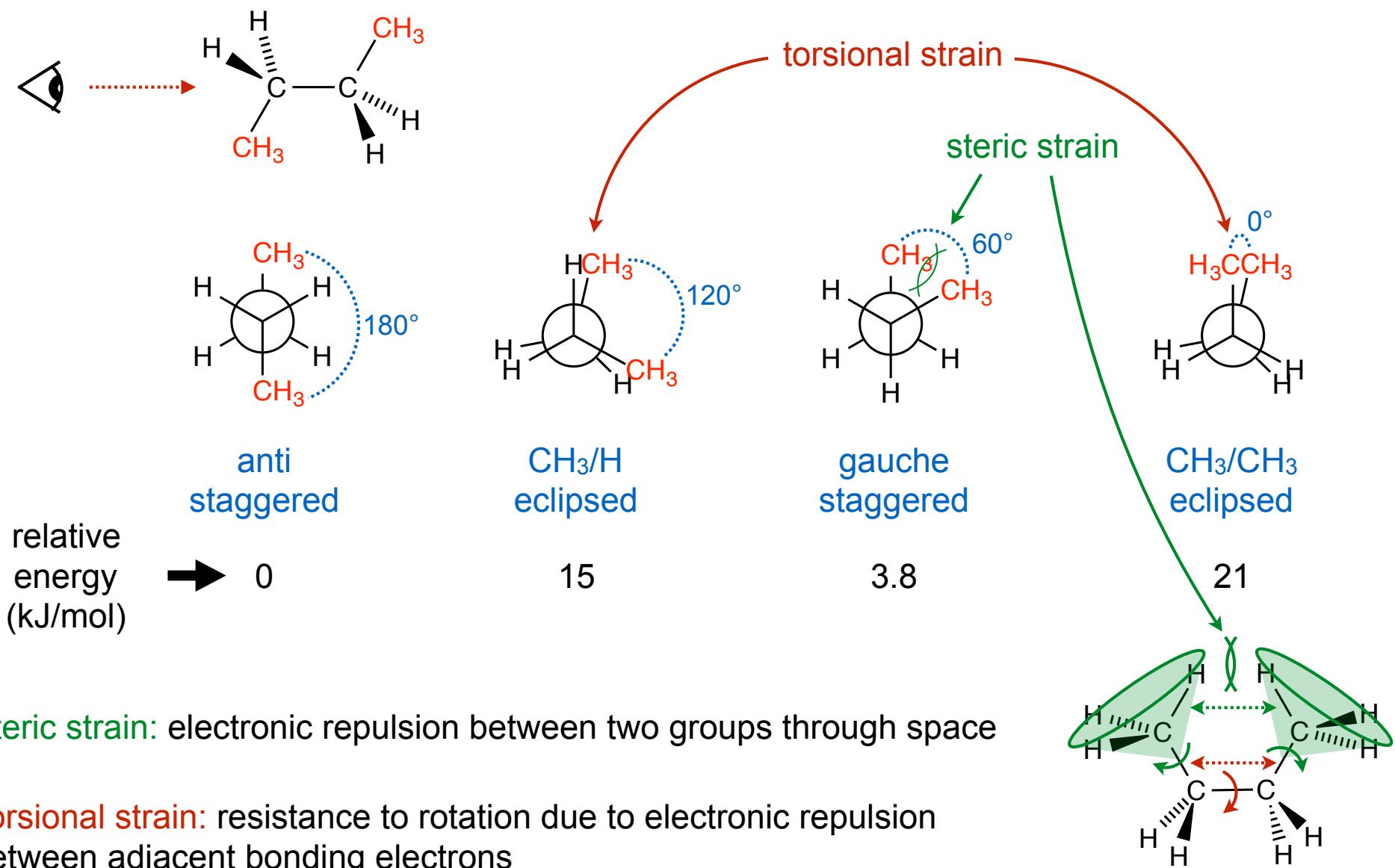
## Conformations of Propane (3-C)



<u>Group</u>	<u>Space-filling Model</u>	<u>Diameter</u>
H		2.2 Å
CH <sub>4</sub> /CH <sub>3</sub>		4 Å

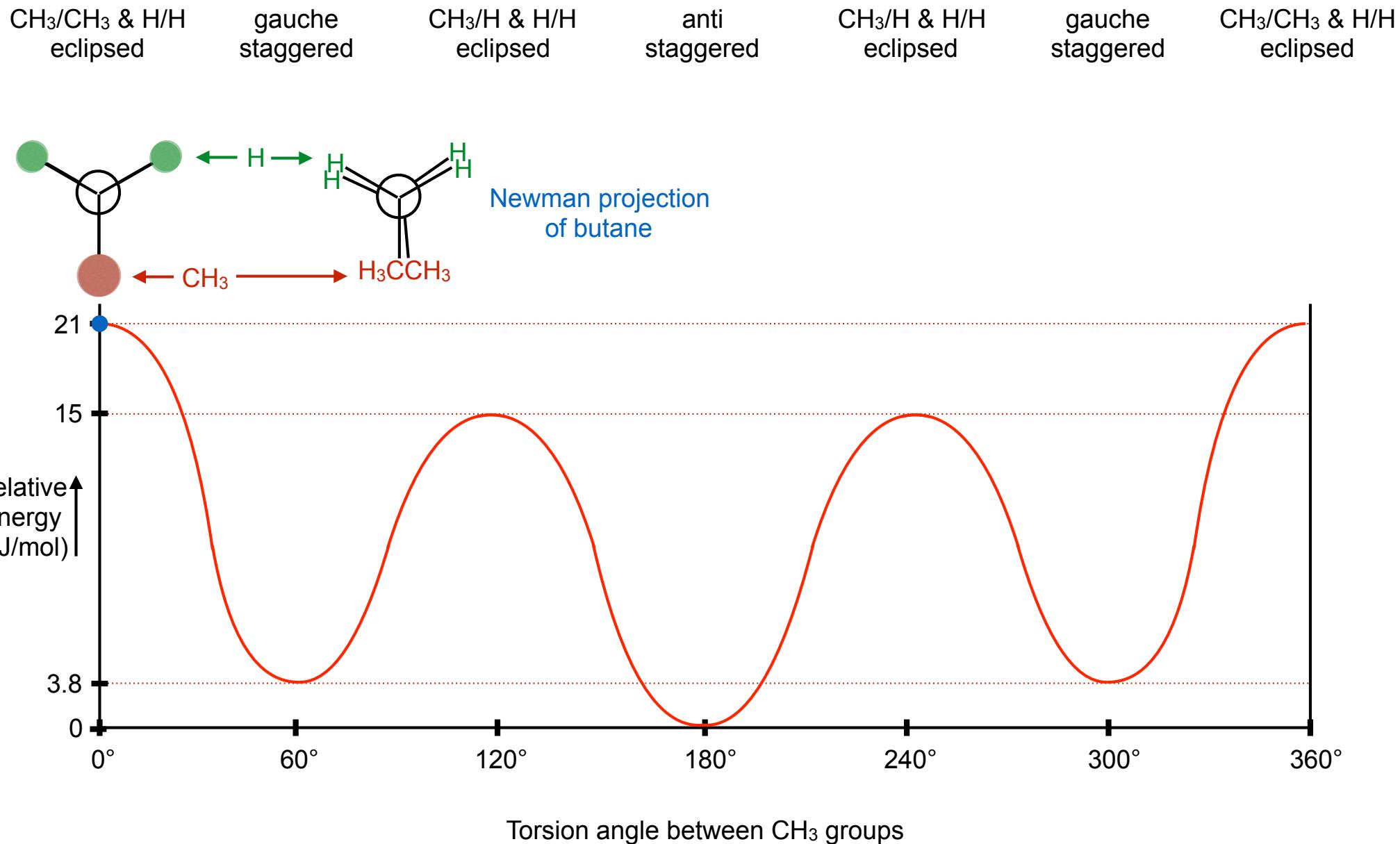
Q: What does the conformational energy diagram look like for propane?

## Conformations of Butane (3-8)



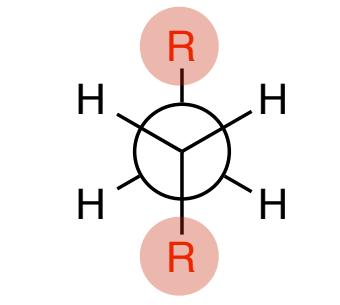
Q: What does the conformational energy diagram look like for butane?

# Conformational Energy Profile of Butane



Q: Which conformation will predominate?

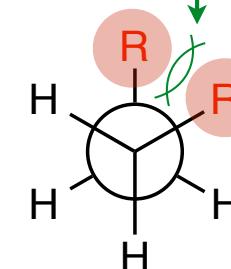
## Conformations of Higher Alkanes (3-9)



anti staggered  
lowest energy  
(most stable)

R = any carbon group

steric strain



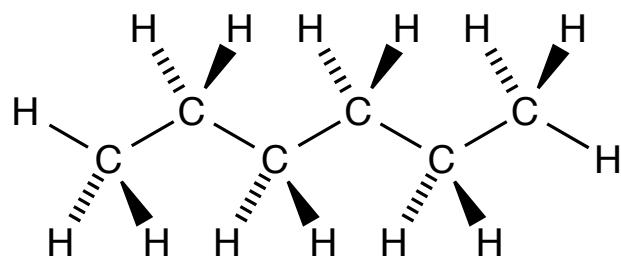
gauche staggered  
slightly higher energy  
(less stable)

energy increases  
with size

Anti conformations always are lowest in energy and favored over gauche conformations

Ex: n-hexane, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

Q: Lowest energy conformation?



=



all-anti conformation

Lowest energy conformation → methylene (CH<sub>2</sub>) groups all anti along the backbone!

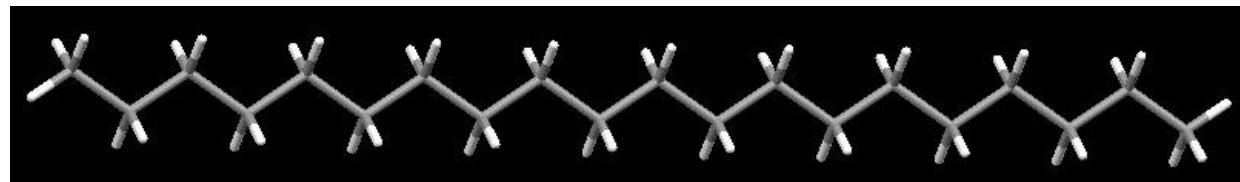
Ex: Eicosane ( $C_{20}H_{42}$ ) - a component of paraffin wax



molecular structure

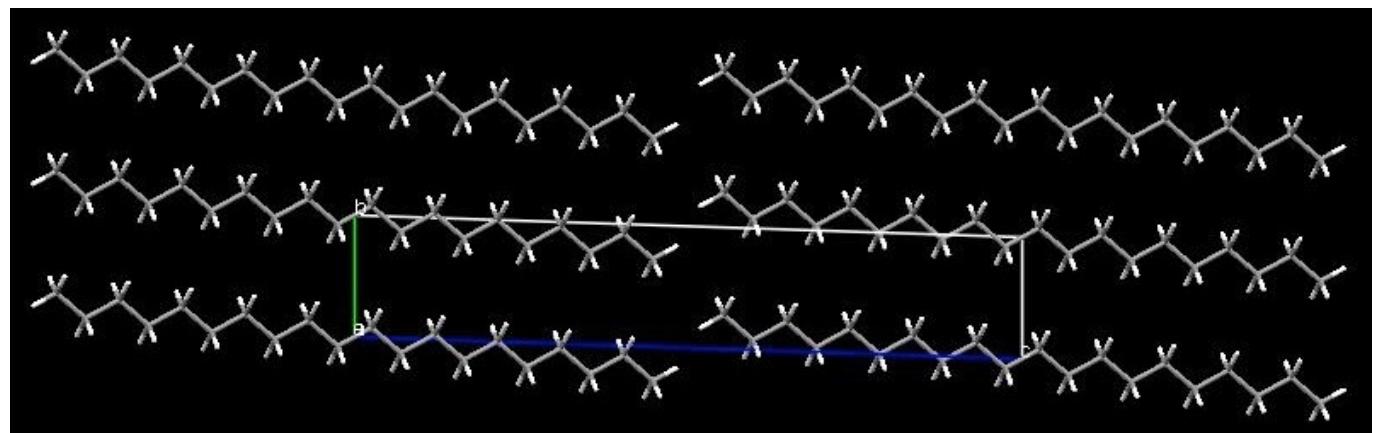
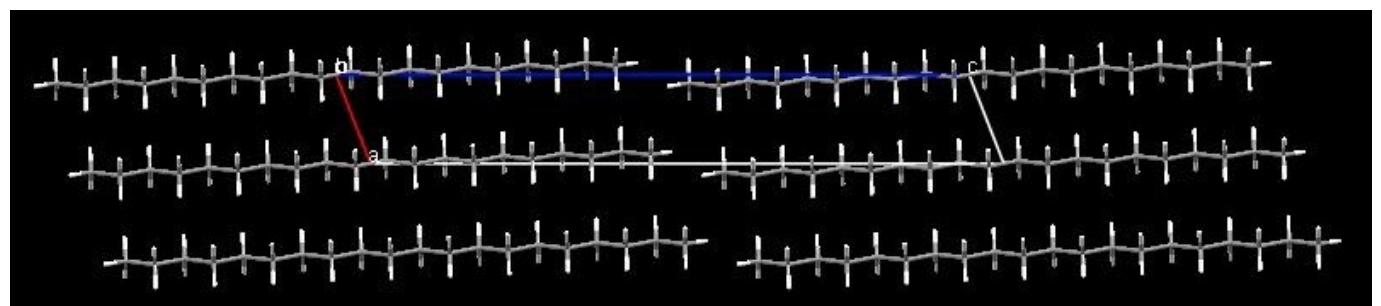
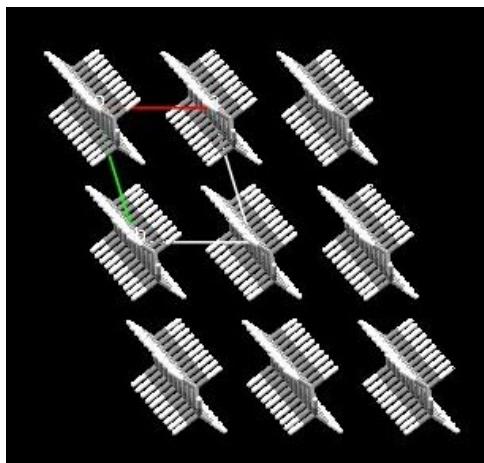


crystal structure



all-anti conformation

crystal packing





Published on Web 08/27/2003

## Highly Oriented Self-Assembled Monolayers as Templates for Epitaxial Calcite Growth

A. Markus Travaille, Lotte Kaptijn, Paul Verwer, Bas Hulsken,  
Johannes A. A. W. Elemans, Roeland J. M. Nolte, and Herman van Kempen\*

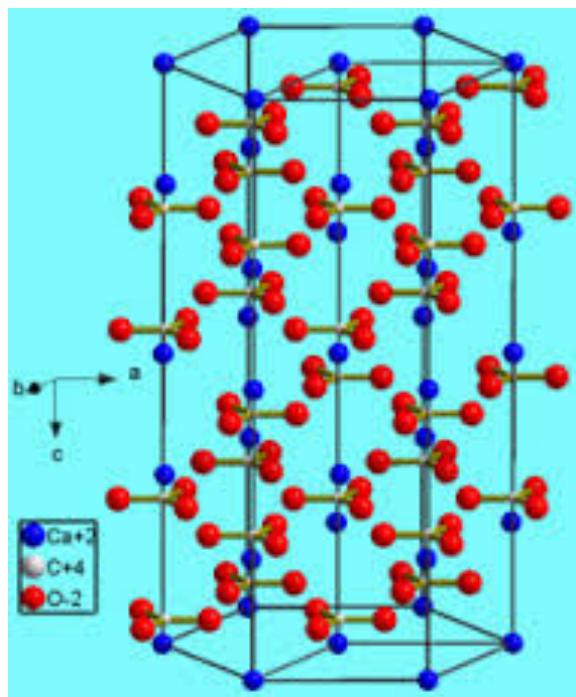
*Contribution from the NSRIM Institute, University of Nijmegen, Toernooiveld 1,  
6525 ED Nijmegen, The Netherlands*

Received February 12, 2003; E-mail: hvk@sci.kun.nl

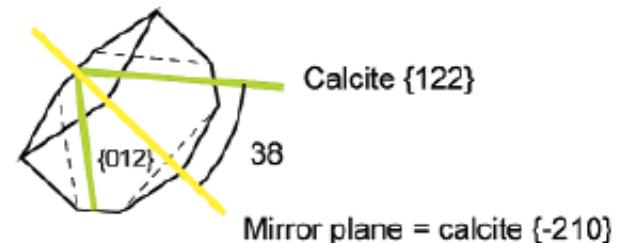
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**Abstract:** The lateral alignment of {012} habit-modified calcite crystals with respect to a carboxylic acid terminated self-assembled monolayer (SAM) of thiols has been determined. The crystals were grown from a Kitano solution (pH 5.6–6.0), and the samples were investigated with scanning electron microscopy, X-ray diffraction, and polarization microscopy. For the first time, a lattice match in one direction, which is the nearest neighbor direction of the SAM and the calcite ⟨100⟩ direction, has been experimentally shown. The experimental results are in good agreement with the theoretical models proposed in previous work, and it is expected that this method can be applied to similar systems where inorganic crystals nucleate with a preferred orientation to a SAM.

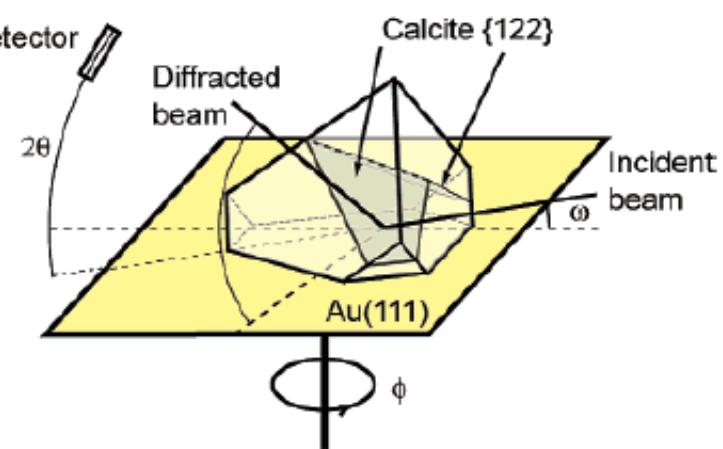
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(a)

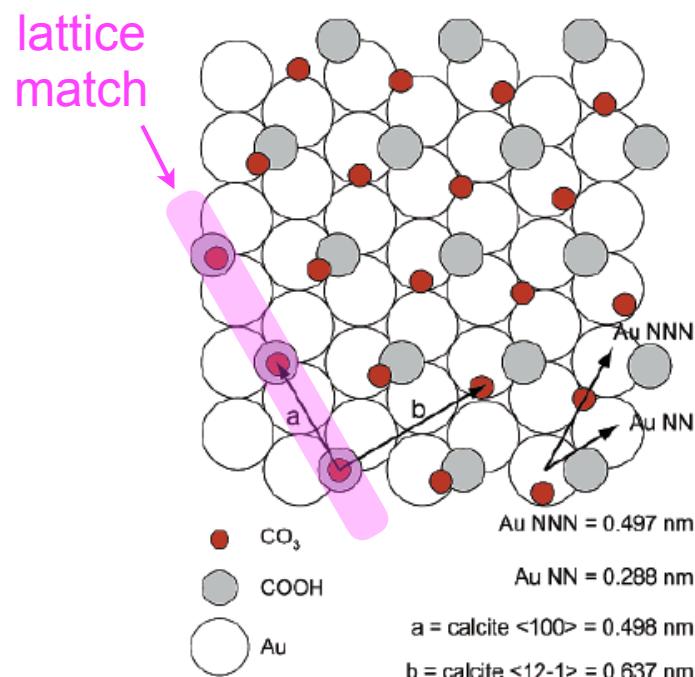
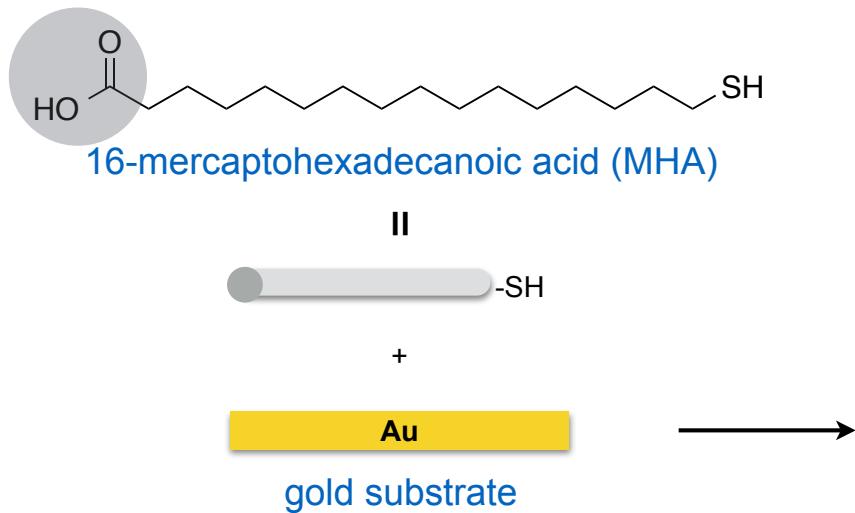


(b)

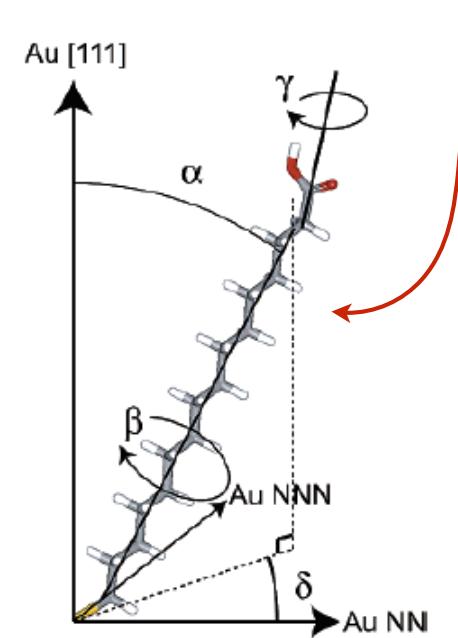
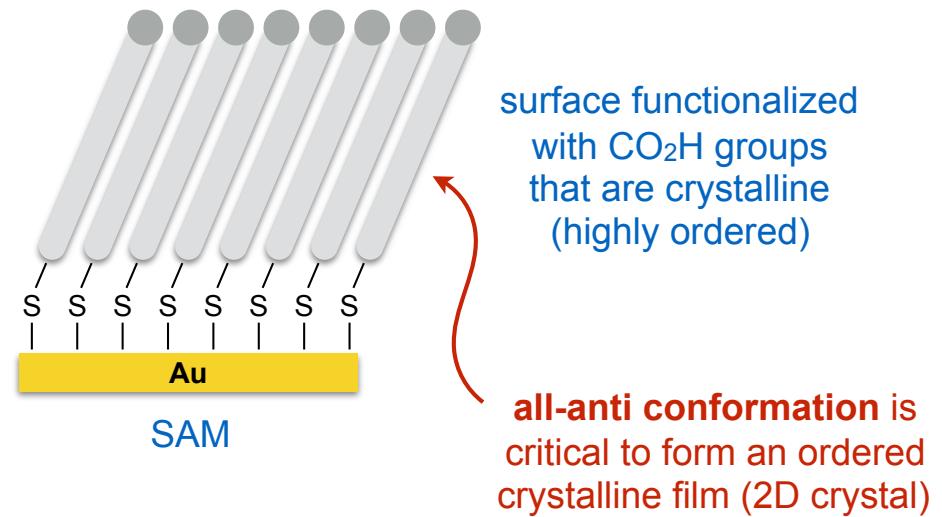


**Figure 3.** (a) Model of a {012} oriented calcite crystal. The yellow line, which represents the mirror plane, which is the {−210} calcite plane and is perpendicular to the {012} face and parallel to the [001] axis, determines the lateral orientation of the crystal. The green lines represent the lateral orientations of the {122} planes. (b) Schematic model of the diffraction setup. The angle between the incident beam and the detector ( $2\theta$ ) is such that only diffraction from the calcite {122} planes will be detected. When the sample is rotated about  $\varphi$ , diffraction will occur every time the calcite {122} plane is correctly aligned with respect to the incoming beam and the detector. The incident angle ( $\omega = \theta - \alpha$ ) is varied around the equilibrium value to correct for the misalignment between the Au[111] axis and  $\varphi$ , where  $\alpha$  is the angle between the Au(111) plane and the calcite {122} plane.

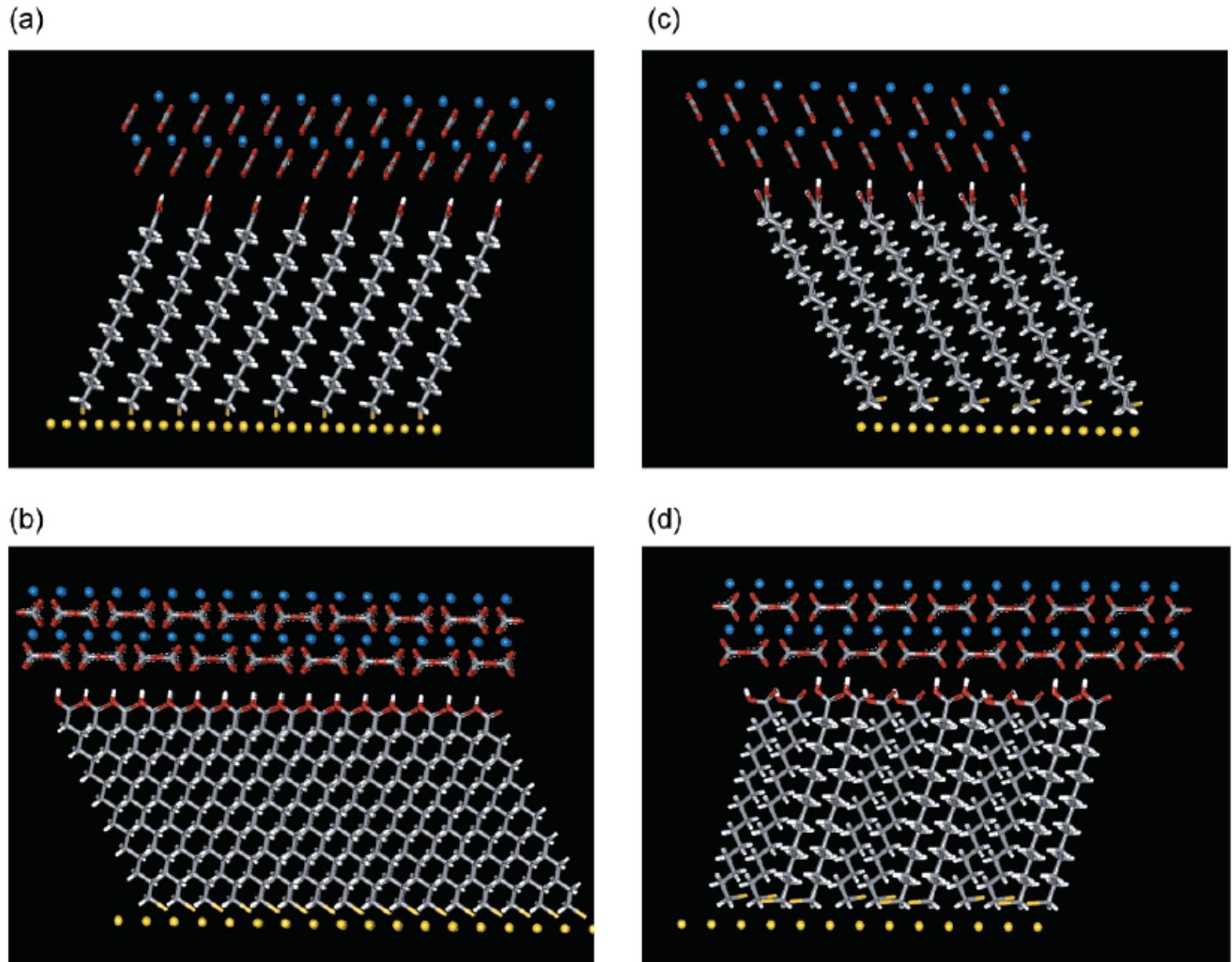
# Self-Assembled Monolayers (SAMs)



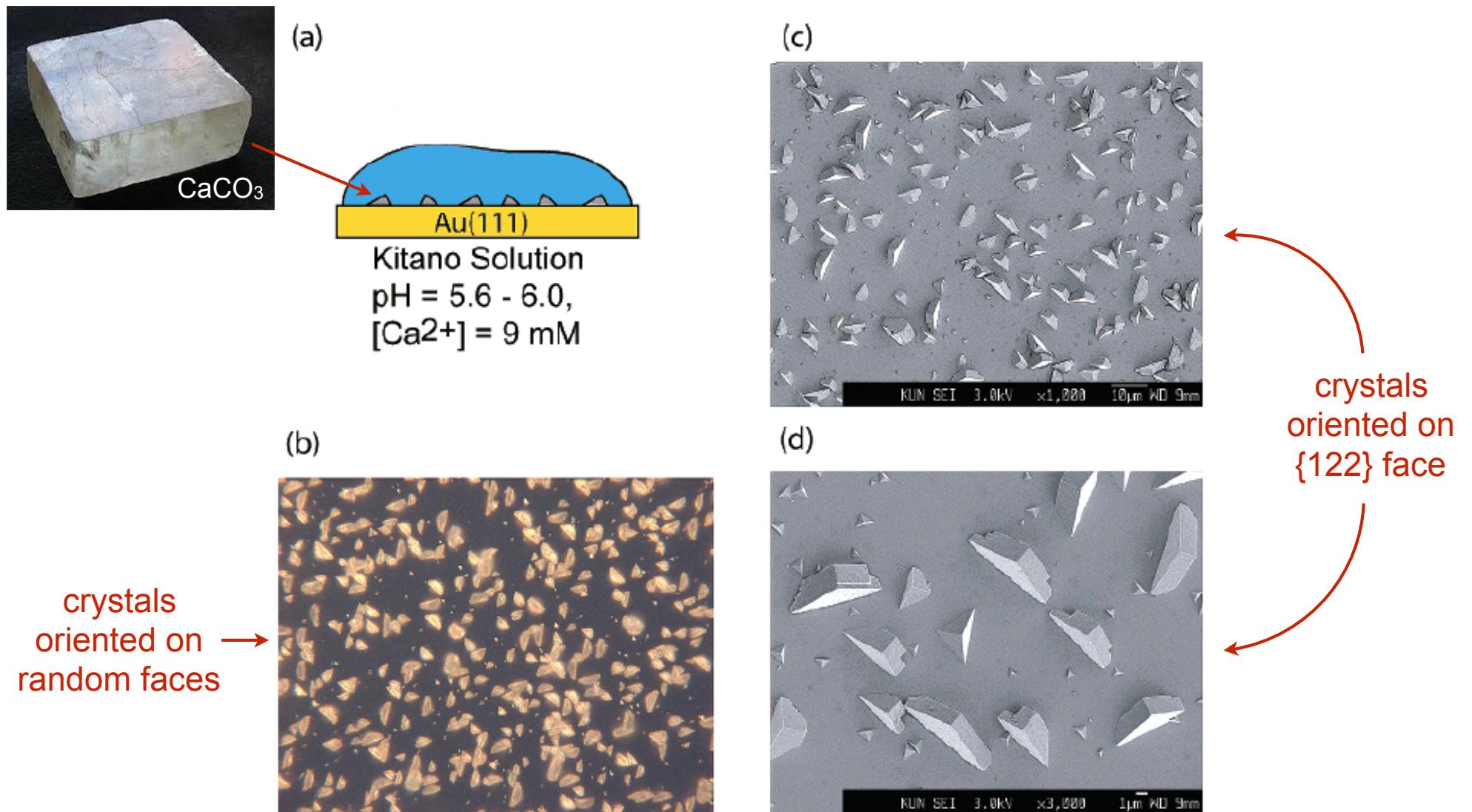
**Figure 5.** Schematic drawing of the lattices of the Au(111) plane, the carboxylic acid endgroups of the SAM, and the carbonate ions of the calcite lattice. The lattice match in the  $a$ -direction is almost perfect, but there is a large mismatch in the  $b$ -direction. All three lattices can be translated in any direction; therefore, their precise positions remain unclear.



**Figure 6.** 16-Mercaptohexadecanoic acid (MHA) and its degrees of freedom. In our models, the tilt angle  $\alpha$  is  $32^\circ$  and the tilt direction  $\delta$  is  $22.7^\circ$ . The twist angle for the  $R30^\circ(\sqrt{3} \times \sqrt{3})$  model is  $\beta = 55^\circ$  and for the  $C2 \times 4$  model is  $\beta = +35^\circ$  and  $-55^\circ$ . The carboxylic acid endgroup is free to rotate around  $\gamma$ .

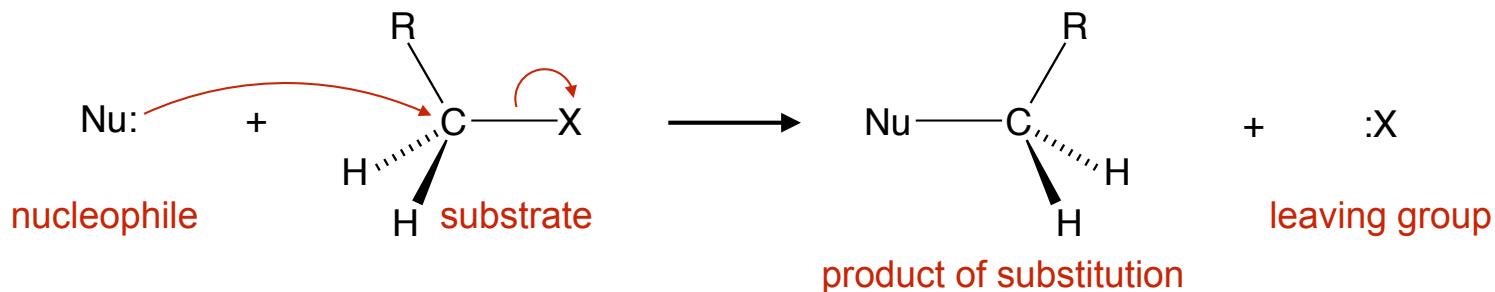


**Figure 7.** 3D models of calcite crystals nucleated with their {012} faces on a SAM of MHA on Au(111). (a) R30°( $\sqrt{3} \times \sqrt{3}$ ) structure viewed in the *a*-direction of Figure 5. Note the directional match between the carboxylic acid endgroups and the carbonate ions. (b) R30°( $\sqrt{3} \times \sqrt{3}$ ) structure viewed in the *b*-direction of Figure 5. In this direction, a lattice match exists between the SAM and the carbonate ions. (c) C2 × 4 structure viewed in the *a*-direction of Figure 5. Note the directional match between one-half of the carboxylic acid endgroups and the carbonate ions. (d) C2 × 4 structure viewed in the *b*-direction of Figure 5. In this direction, a lattice match exists between the SAM and the carbonate ions, although it is obvious that in this model the interaction is less directional.

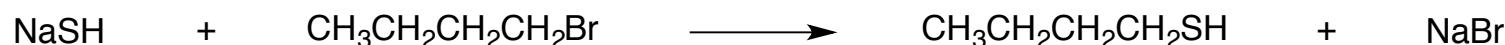


**Figure 1.** (a) Calcite growth from a droplet of a Kitano solution. (b) Polarization micrograph of growing calcite crystals (1000 $\times$ ). (c) Scanning electron micrograph of calcite grown on a self-assembled monolayer of MHA (1000 $\times$ ). (d) Scanning electron micrograph zoomed in on laterally aligned calcite crystals (3000 $\times$ ).

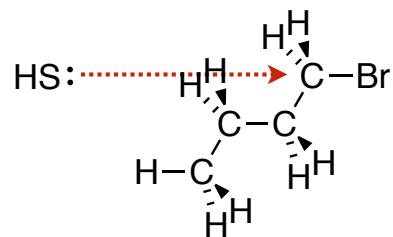
## Impact of Conformation on Chemical Reactivity?



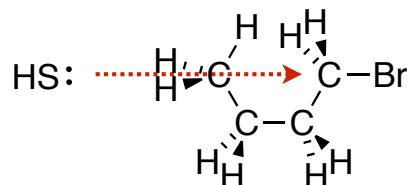
Ex: Synthesis of thiols



Q: Does the conformation of the substrate matter?



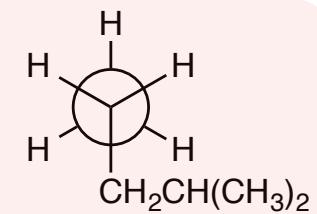
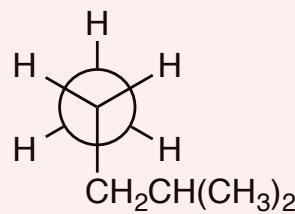
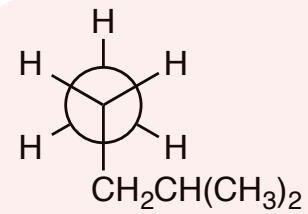
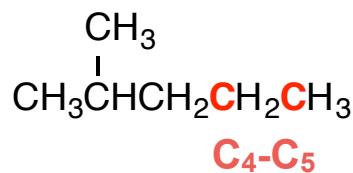
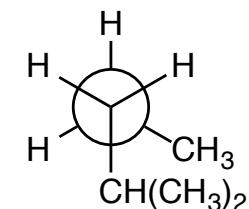
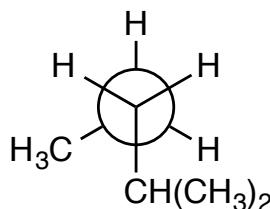
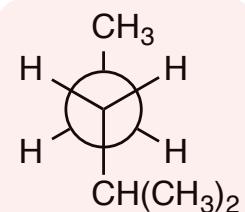
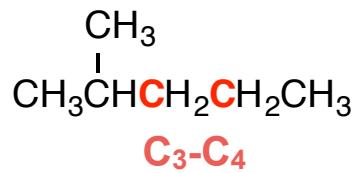
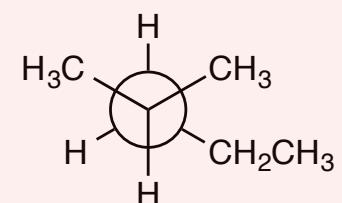
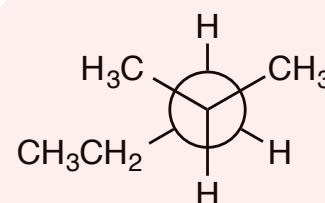
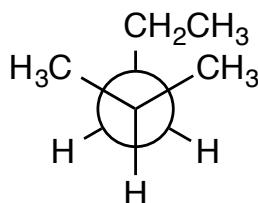
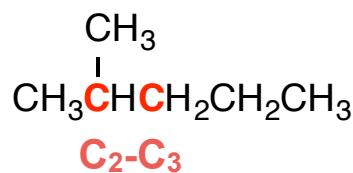
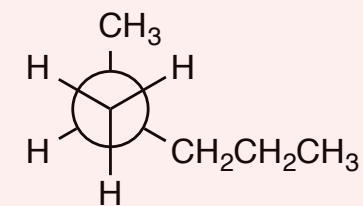
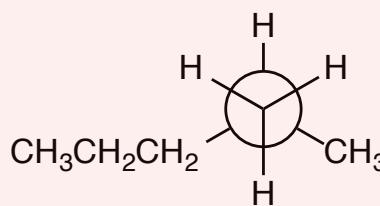
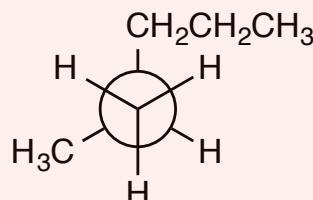
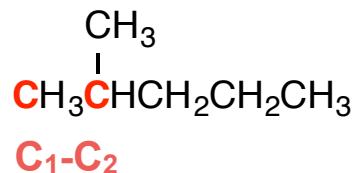
all *anti* staggered  
conformation  
(>> 99%)



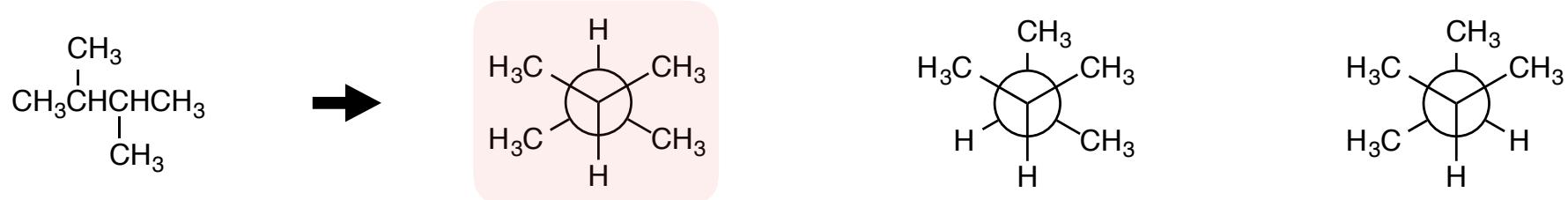
an eclipsed  
conformation

Q: Is it possible to change conditions to favor one conformation over another?

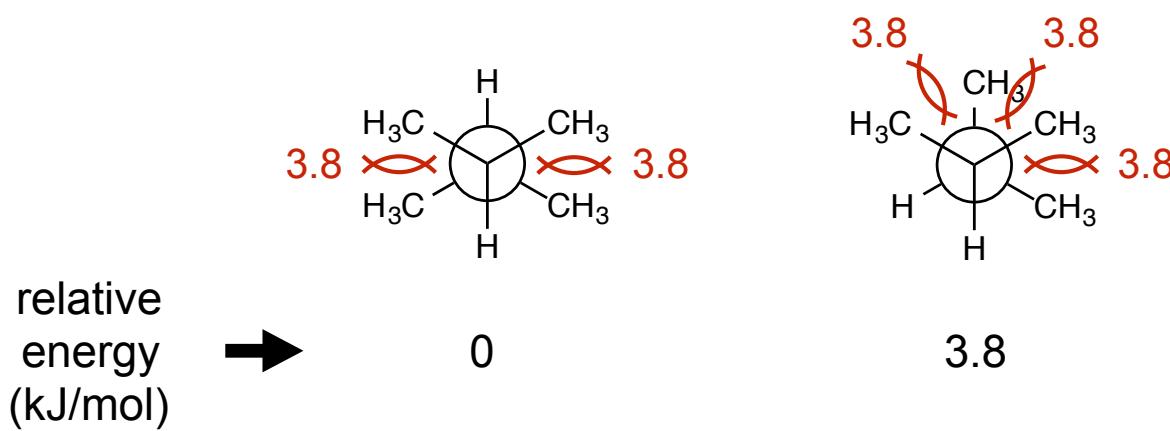
Q: Which conformation of 2-methylpentane is lowest in energy?



Q: Which conformation of 2,3-dimethylbutane is lowest in energy?



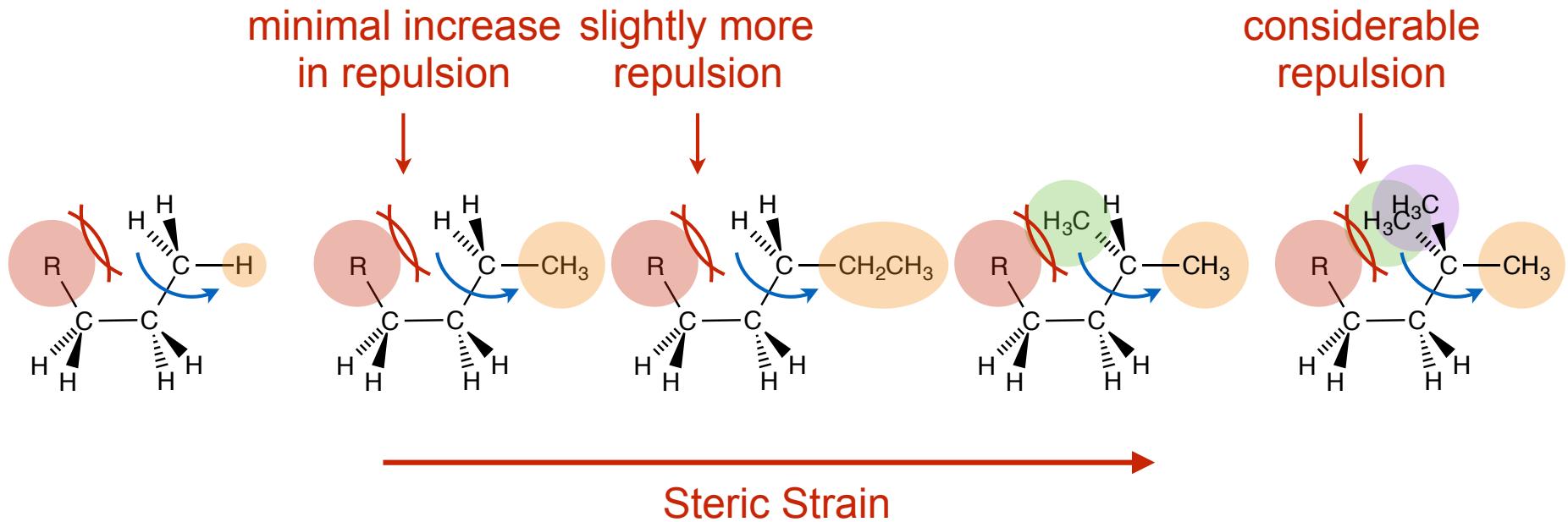
Q: How much lower in energy is the most stable conformer?



Q: Which conformations exist at room temperature?

Q: Which conformation is most highly populated at any temperature?

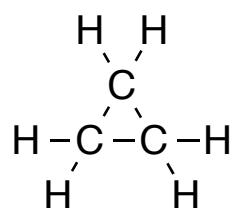
## Influence of Increasing Size of Substituents on Steric Strain



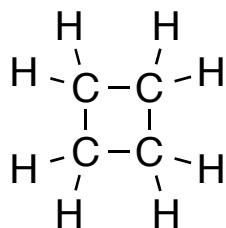
- Steric strain increases as the size (steric bulk) of substituents increases
- Unbranched substituents (e.g.,  $\text{Me} \rightarrow \text{Et}$ ,  $\text{Et} \rightarrow n\text{-Pr}$ ) increases strain slightly when lengthened
- Branched substituents (e.g.,  $i\text{Pr}$ ,  $t\text{-Bu}$ ) increase strain dramatically

Q: Impact of increasing steric strain on conformation?

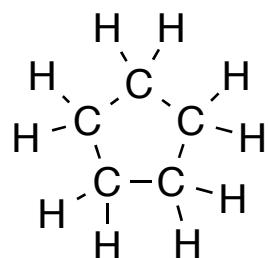
## Cycloalkanes (3-10)



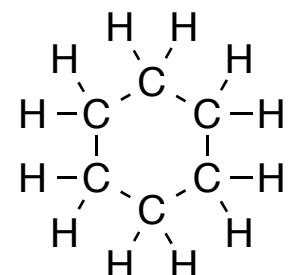
cyclopropane  
 $\text{C}_3\text{H}_6$



cyclobutane  
 $\text{C}_4\text{H}_8$



cyclopentane  
 $\text{C}_5\text{H}_{10}$

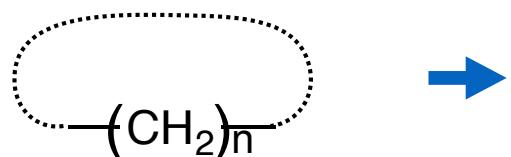


cyclohexane  
 $\text{C}_6\text{H}_{12}$

Cycloalkanes - saturated hydrocarbons where the carbon atoms form a ring

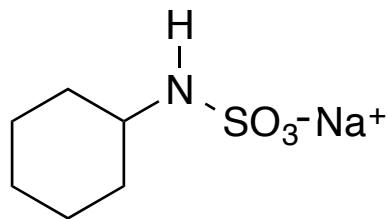
Q: General formula of cycloalkanes?

Cycloalkanes have two fewer H atoms than the corresponding acyclic alkanes

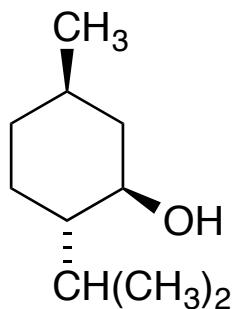


General formula =  $\text{C}_n\text{H}_{2n}$

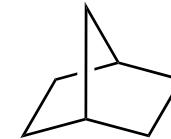
## Ex: Molecules that contain cycloalkanes



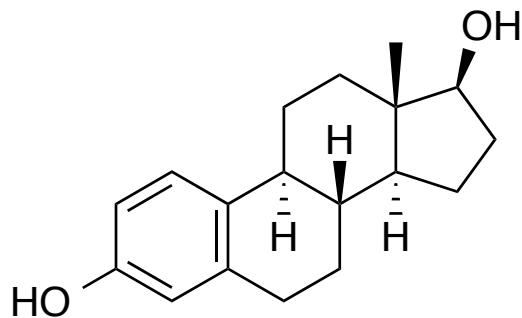
cyclamate  
artificial sweetener



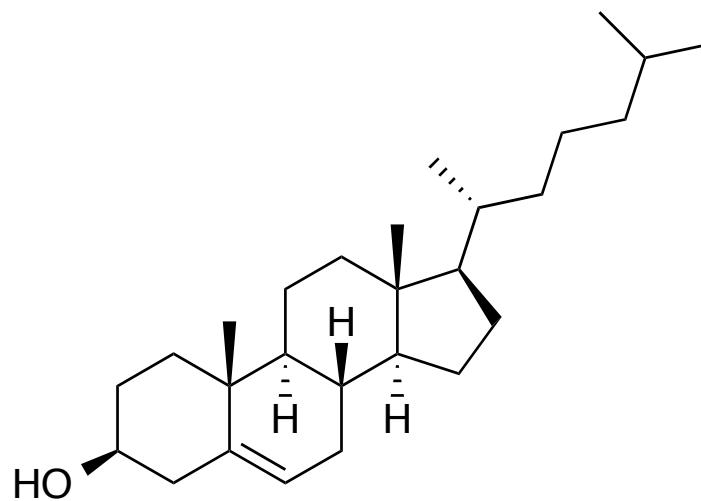
menthol  
natural flavoring



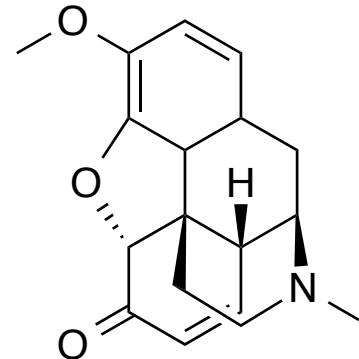
norbornane  
component of terpentine  
(bicyclic ring system)



estradiol  
reproductive hormone  
(fused-ring system)



testosterone  
steroid  
(fused-ring system)



hydrocodone  
analgesic  
(Oxycontin, Percocet, Vicodin)

## Nomenclature of Cycloalkanes (3-10C)

Cycloalkanes are named similarly to alkanes using IUPAC rules

1. The **parent** ring is named as a **cycloalkane**

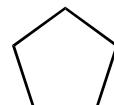
Ex:



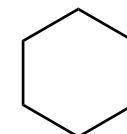
cyclopropane



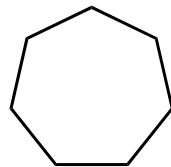
cyclobutane



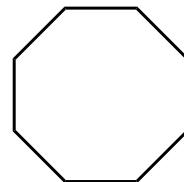
cyclopentane



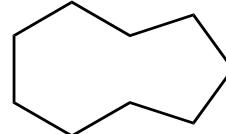
cyclohexane



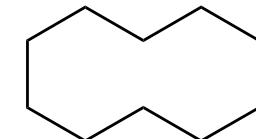
cycloheptane



cyclooctane



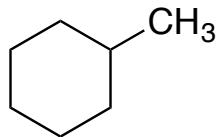
cyclononane



cyclodecane

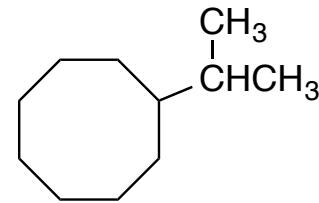
2. Numbering the ring is not required for cycloalkanes with **one** substituent

Ex:



methylcyclohexane

not  
1-methylcyclohexane



isopropylcyclooctane

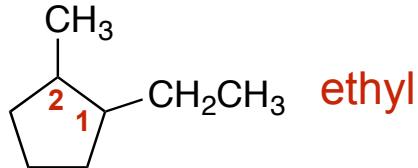
not  
1-isopropylcyclooctane

3. When **two or more** substituents are present:

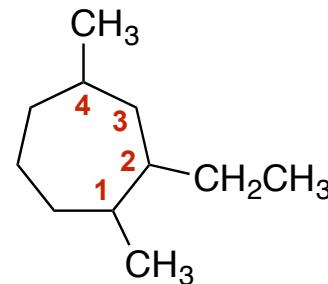
- Number the carbon atoms in the ring to give the **lowest numbering sequence** via the shortest path that includes all substituents.
- Start numbering at the carbon atom that is **more substituted**. If two or more carbon atoms are substituted equally, start at the one with the substituent that comes **first alphabetically**.
- List substituents alphabetically.

Ex:

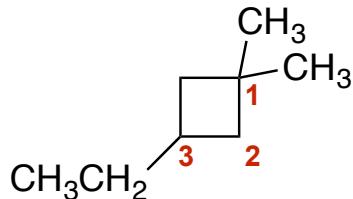
methyl



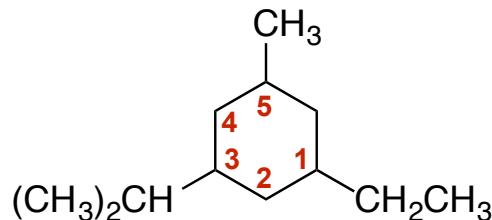
1-ethyl-2-methylcyclopentane



2-ethyl-1,4-dimethylcycloheptane



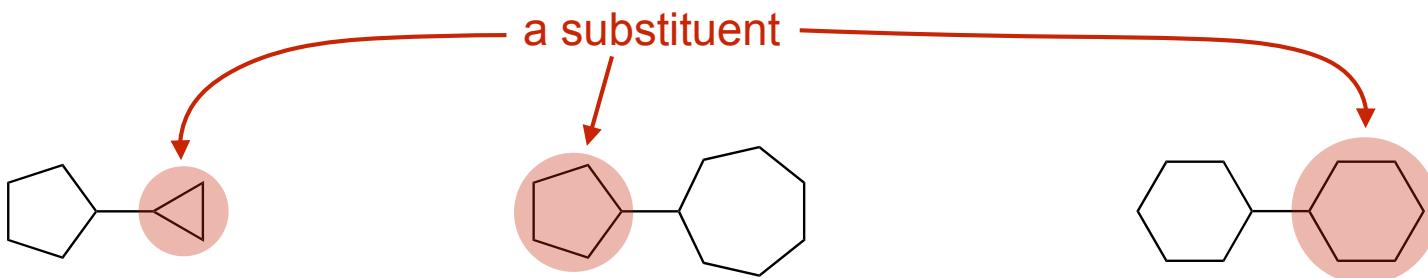
3-ethyl-1,1-dimethylcyclobutane



1-ethyl-3-isopropyl-5-methylcyclohexane

4. Name smaller rings as **cycloalkyl** substituents when bonded to larger parent rings

Ex:



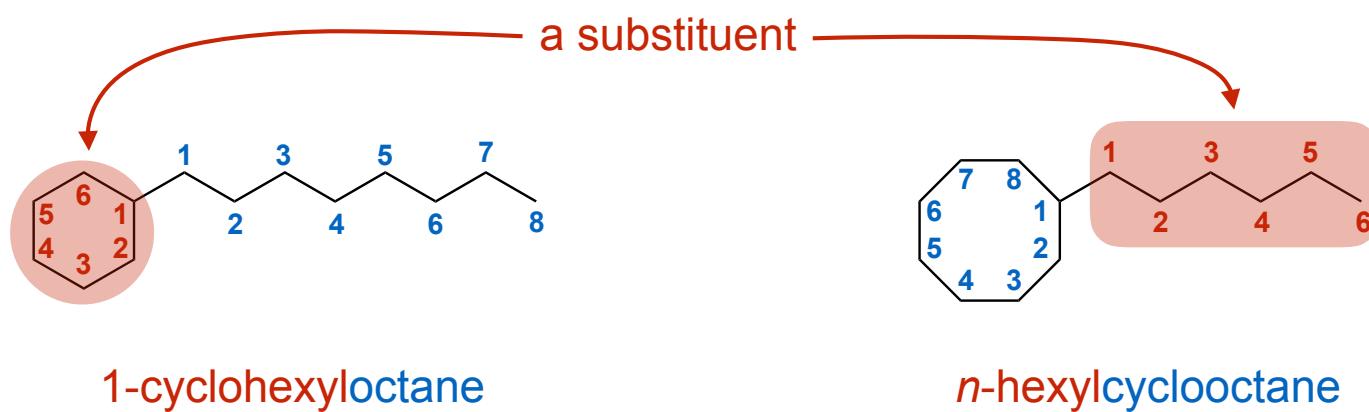
cyclopropylcyclopentane

cyclopentylcycloheptane

cyclohexylcyclohexane

5. Naming the parent as an alkane or a cycloalkane is determined based on whether the acyclic group (longest continuous carbon chain) or the ring **has the greater number of carbon atoms**.

Ex:



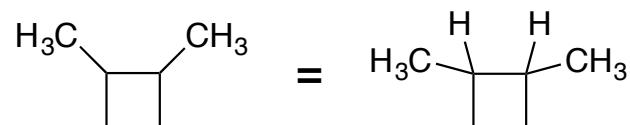
1-cyclohexyloctane

n-hexylcyclooctane

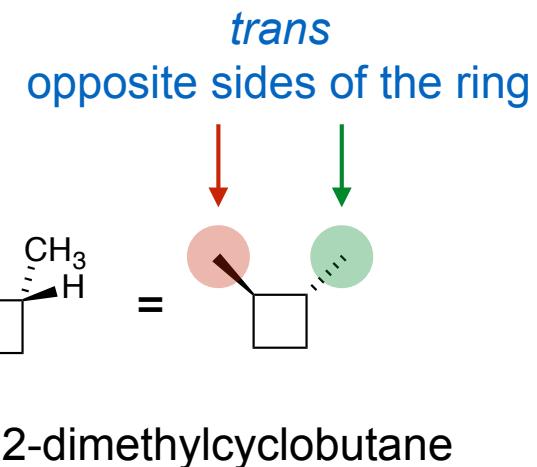
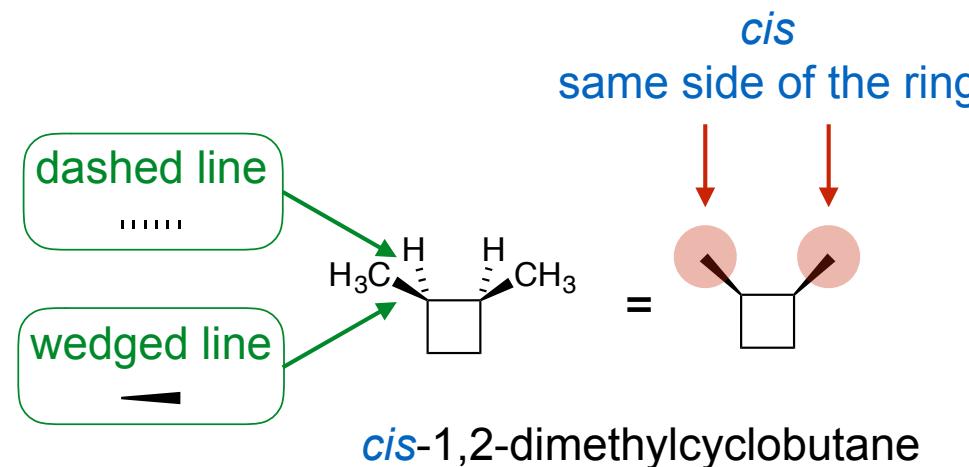
## Cis-trans Isomerism in Cycloalkanes (3-11)

Cycloalkanes with two or more substituents can form **geometric isomers (stereoisomers)**

Ex: 1,2-dimethylcyclobutane

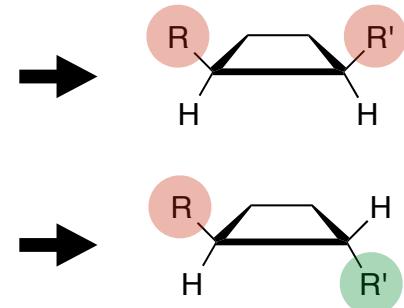


**Q:** What is the 3-D structure?

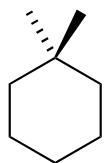


### Definitions:

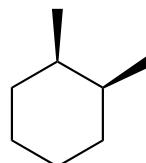
- **Cis:** two substituents on the same side (face) of a ring
- **Trans:** two substituents on opposite sides (faces) of a ring



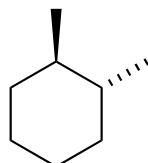
Ex: Draw all possible constitutional and geometric isomers of dimethylcyclohexane



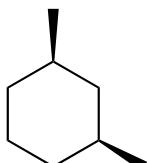
1,1-



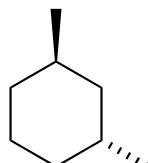
*cis*-1,2-



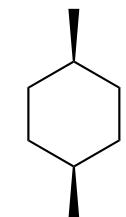
*trans*-1,2-



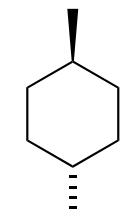
*cis*-1,3-



*trans*-1,3-



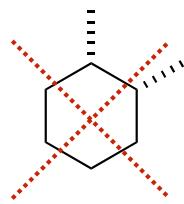
*cis*-1,4-



*trans*-1,4-

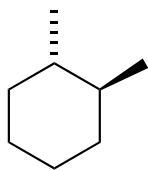
Q: How about these structures? Are they unique from the ones above?

Make  
Molecular  
Models!



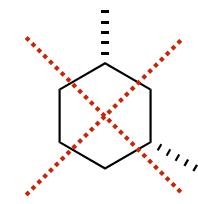
*cis*-1,2-

identical  
flip over



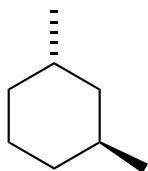
*trans*-1,2-

unique!  
stereoisomer  
Ch. 5: Chirality



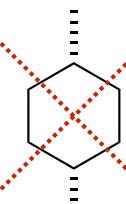
*cis*-1,3-

identical  
flip over



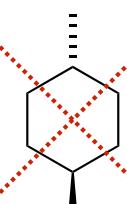
*trans*-1,3-

unique!  
stereoisomer  
Ch. 5: Chirality



*cis*-1,4-

identical  
flip over



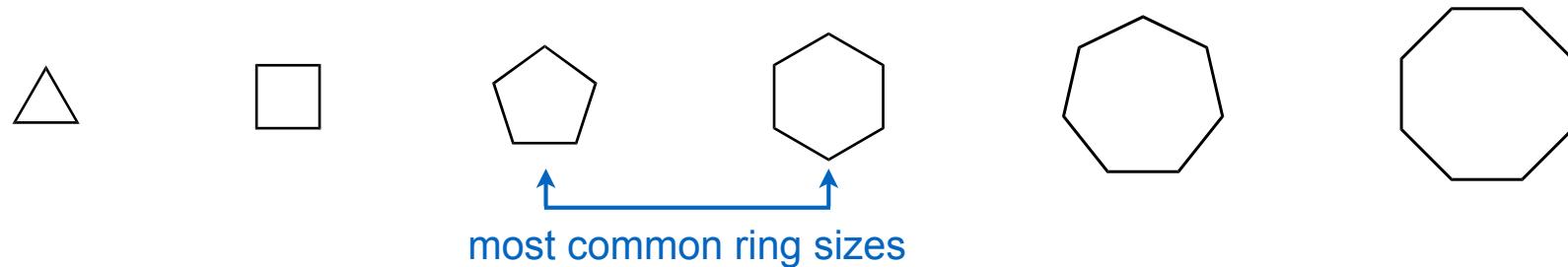
identical  
flip over  
or rotate



Nine compounds with distinctly different structures, shapes, reactivities!!!

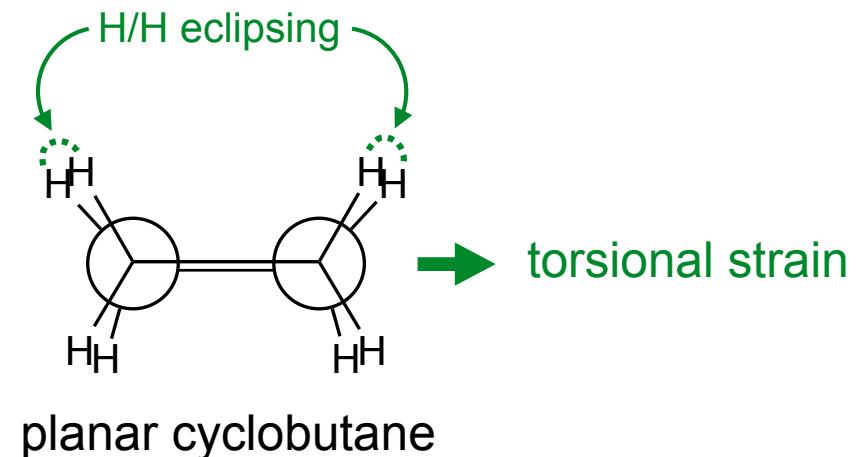
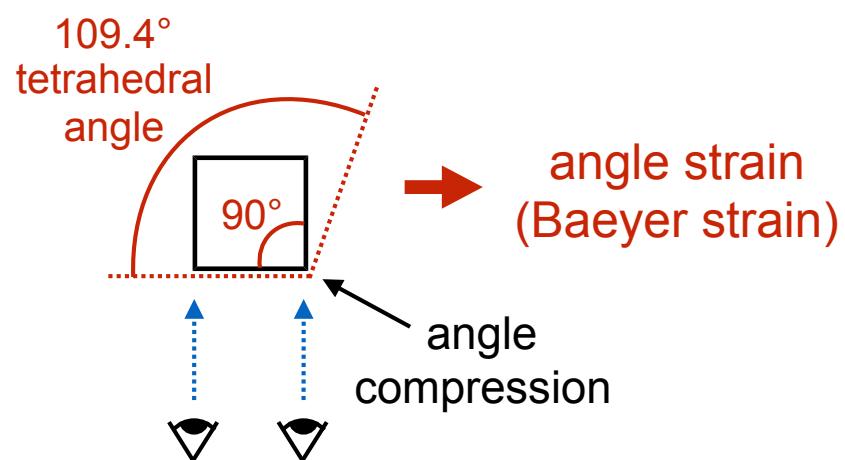
Q: Why is knowing this important?

## Stabilities and Conformations of Cycloalkanes (3-12)



Q: Conformations? Are the rings flat? Bond angles? Strain?

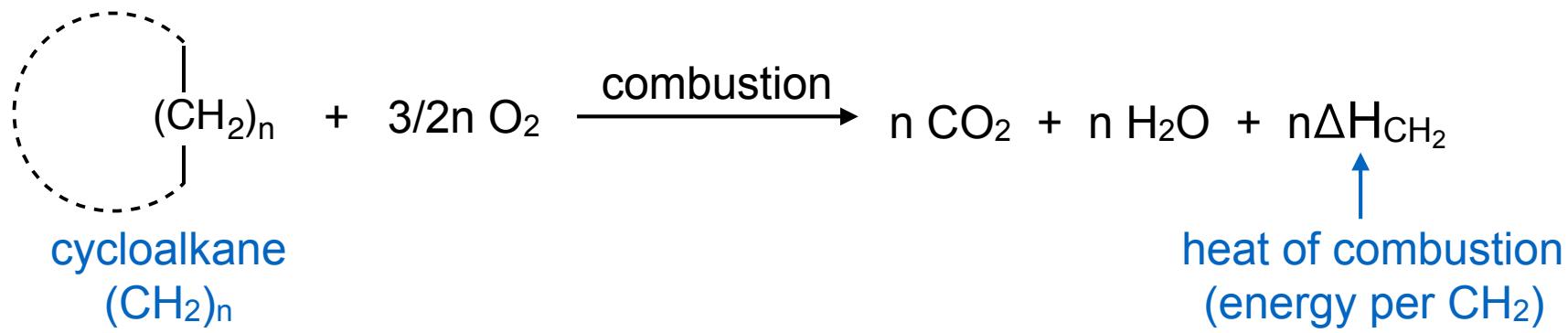
Ex: Cyclobutane



$$\text{Ring Strain} = \text{angle strain} + \text{torsional strain}$$

Q: How is ring strain measured?

→ Heats of combustion!



$$\text{Ring strain energy} = [\Delta H_{\text{CH}_2(\text{strained})} - \Delta H_{\text{CH}_2(\text{unstrained})}]_n$$

↑                      ↑                      ↑  
cycloalkane        acyclic alkane    #  $\text{CH}_2$  groups

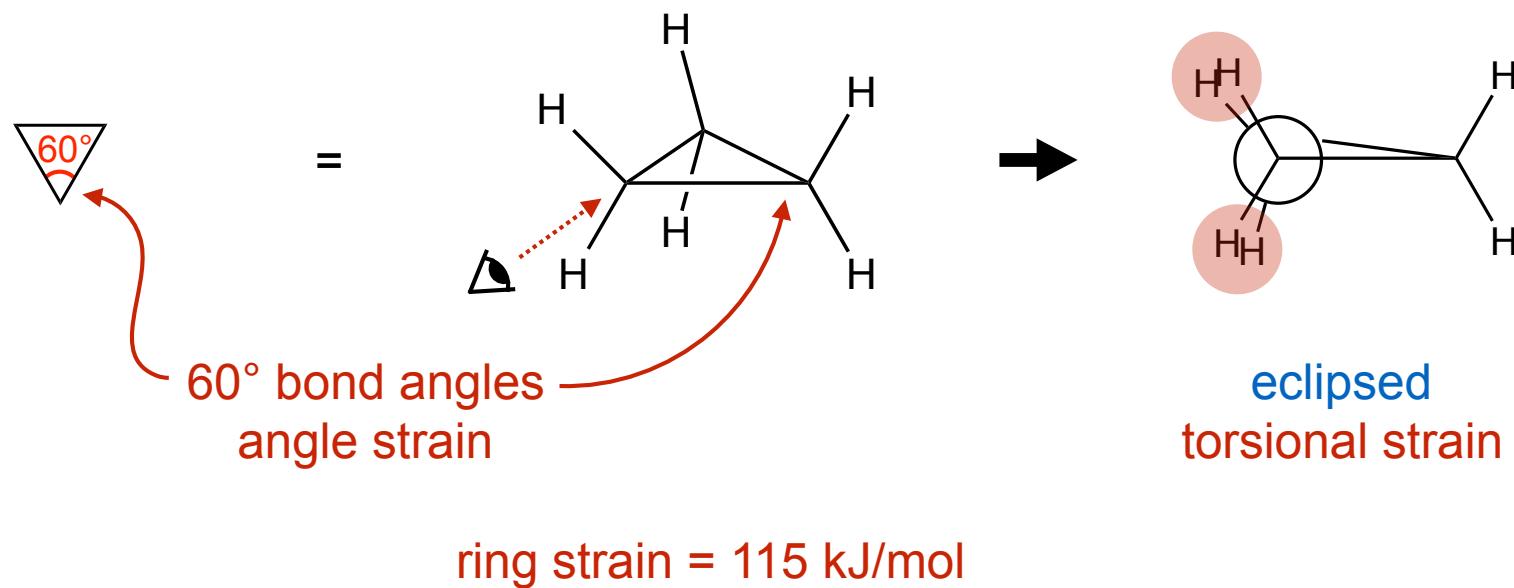
Note: reference  $\Delta H_{\text{CH}_2(\text{unstrained})} = 659 \text{ kJ/mol}$  →  $\text{CH}_2$  in *n*-alkanes

**TABLE 3-5** Heats of Combustion (per Mole) for Some Simple Cycloalkanes

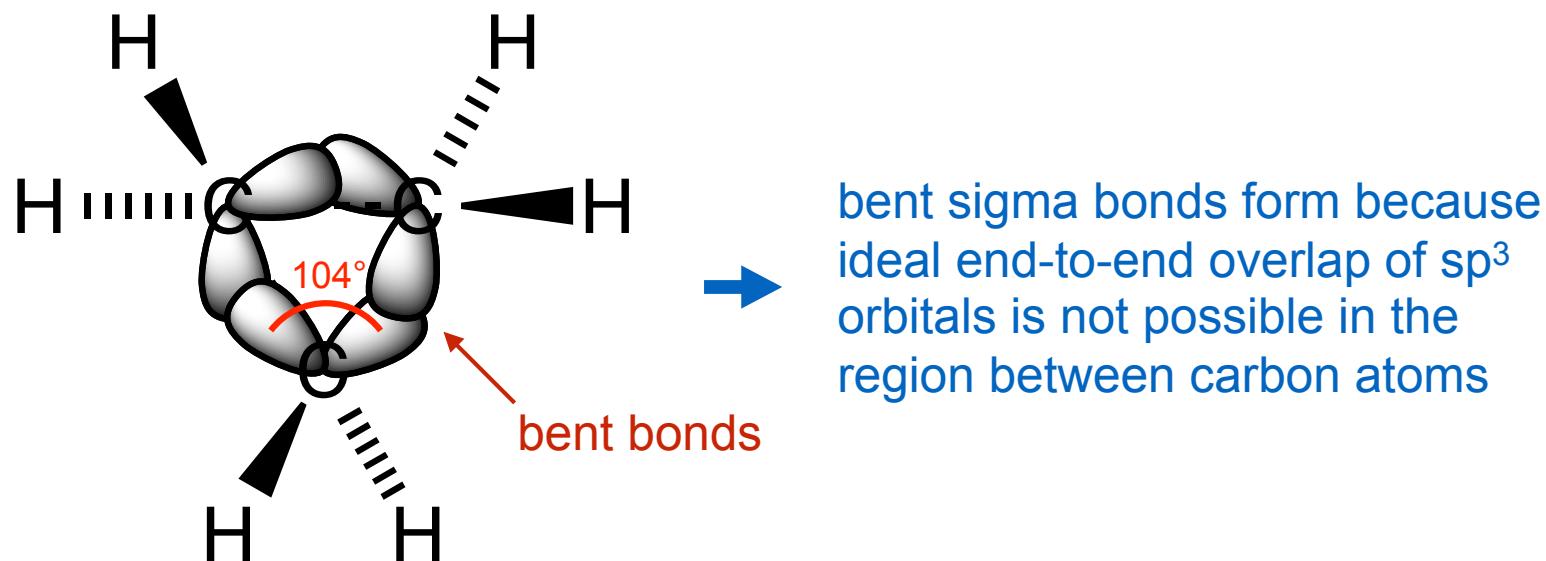
Ring Size	Cycloalkane	Molar Heat of Combustion	Heat of Combustion per CH <sub>2</sub> Group	Ring Strain per CH <sub>2</sub> Group	Total Ring Strain
3	cyclopropane	2091 kJ	697.1 kJ	38.5 kJ	115 kJ (27.6 kcal)
4	cyclobutane	2744 kJ	686.1 kJ	27.5 kJ	110 kJ (26.3 kcal)
5	cyclopentane	3320 kJ	664.0 kJ	5.4 kJ	27 kJ (6.5 kcal)
6	cyclohexane	3951 kJ	658.6 kJ	0.0 kJ	0.0 kJ (0.0 kcal)
7	cycloheptane	4637 kJ	662.4 kJ	3.8 kJ	27 kJ (6.4 kcal)
8	cyclooctane	5309 kJ	663.6 kJ	5.1 kJ	41 kJ (9.7 kcal)
reference: long-chain alkane					
			658.6 kJ	0.0 kJ	0.0 kJ (0.0 kcal)



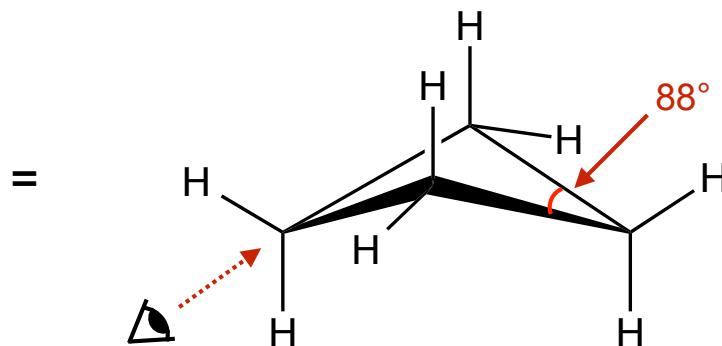
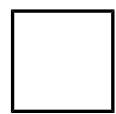
## Cyclopropane



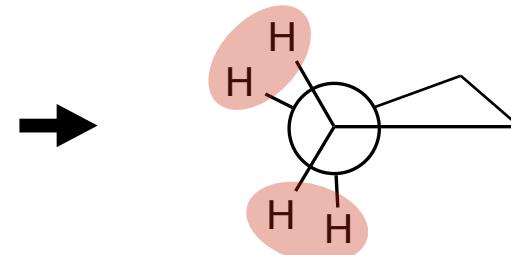
### orbital picture



## Cyclobutane

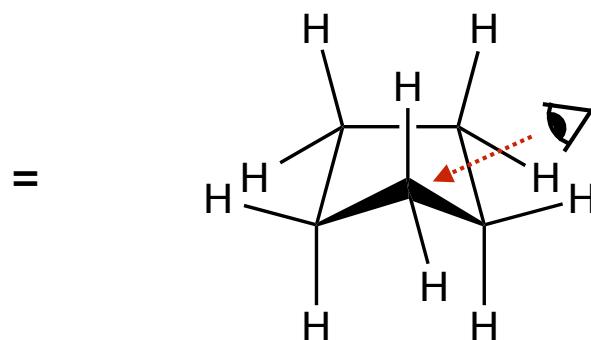
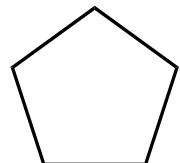


folded slightly  
to relieve eclipsing  
ring strain = 110 kJ/mol

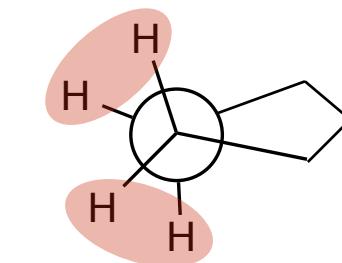


skew conformation  
(between eclipsed & staggered)  
some torsional strain

## Cyclopentane



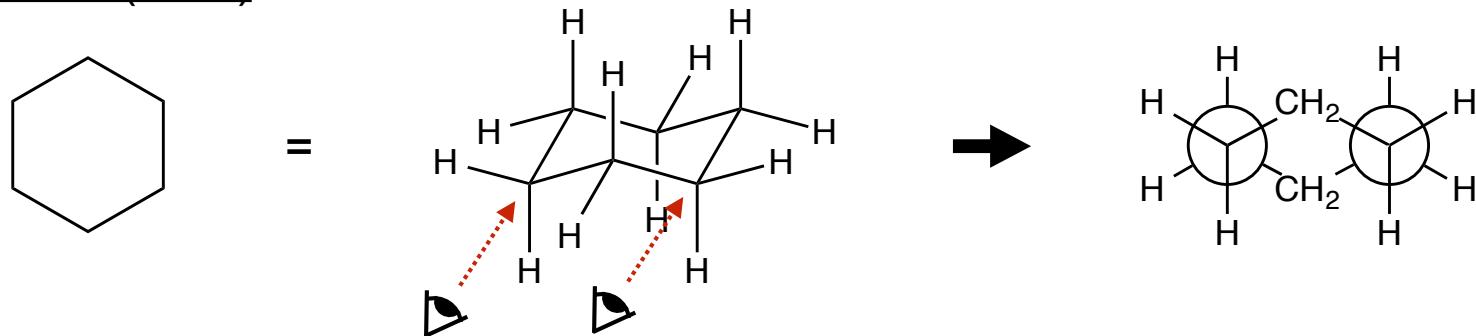
envelope conformation  
flap folded up  
ring strain = 27 kJ/mol



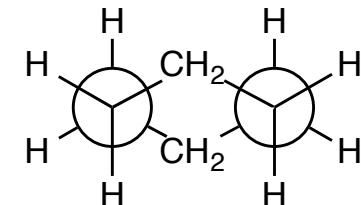
close to staggered  
minor torsional strain



## Cyclohexane (3-13)

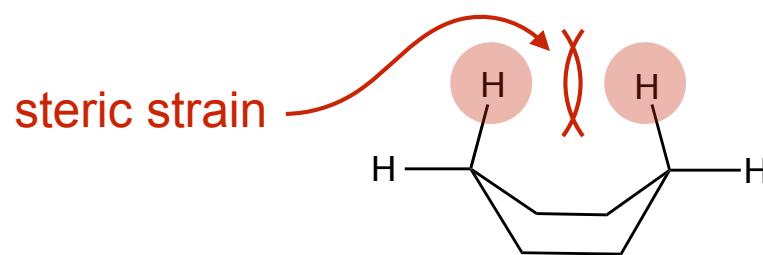


ring strain = 0 kJ/mol

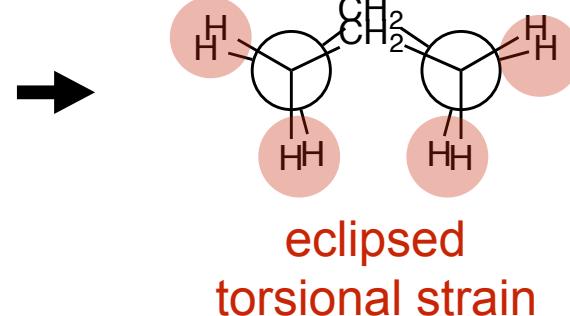


staggered  
idealized tetrahedral geometry

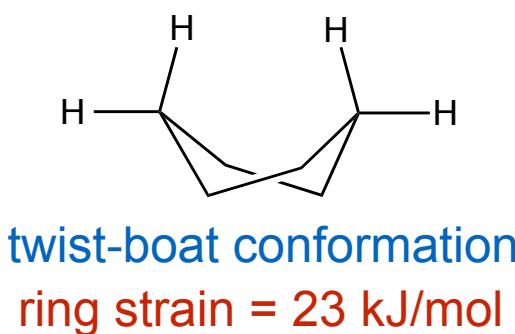
Note: cyclohexane has two other conformations that are higher in energy due to strain



boat conformation  
ring strain = 29 kJ/mol



eclipsed  
torsional strain

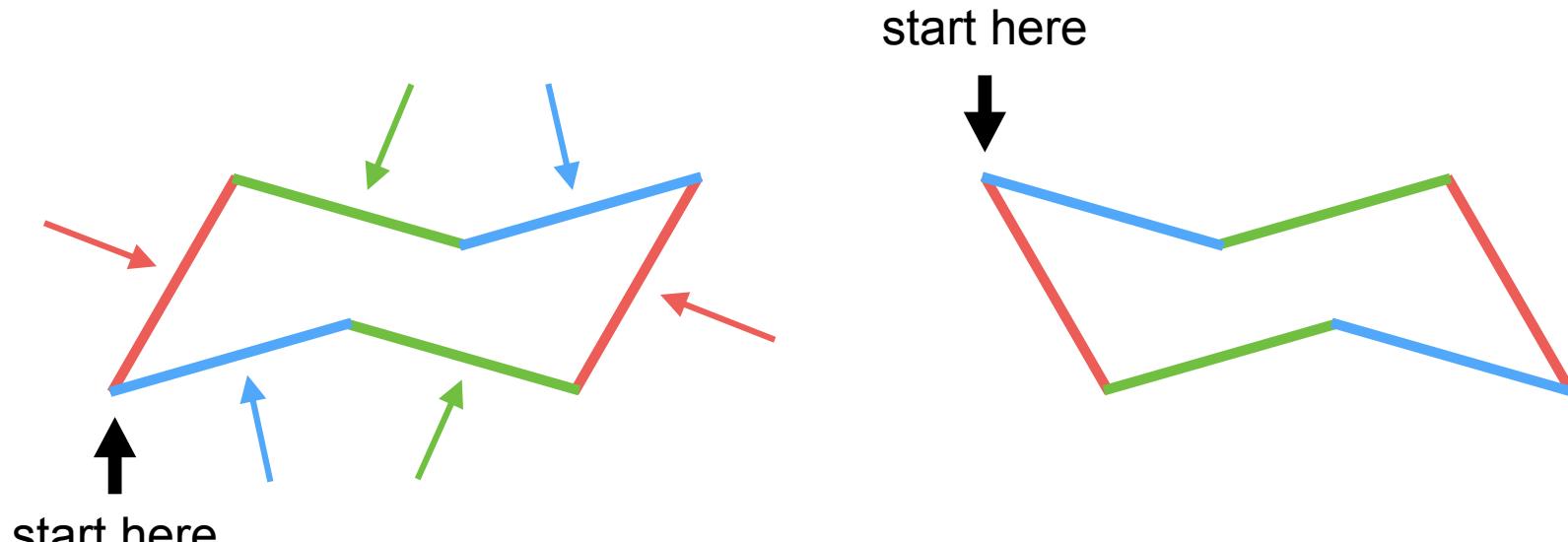


twist-boat conformation  
ring strain = 23 kJ/mol

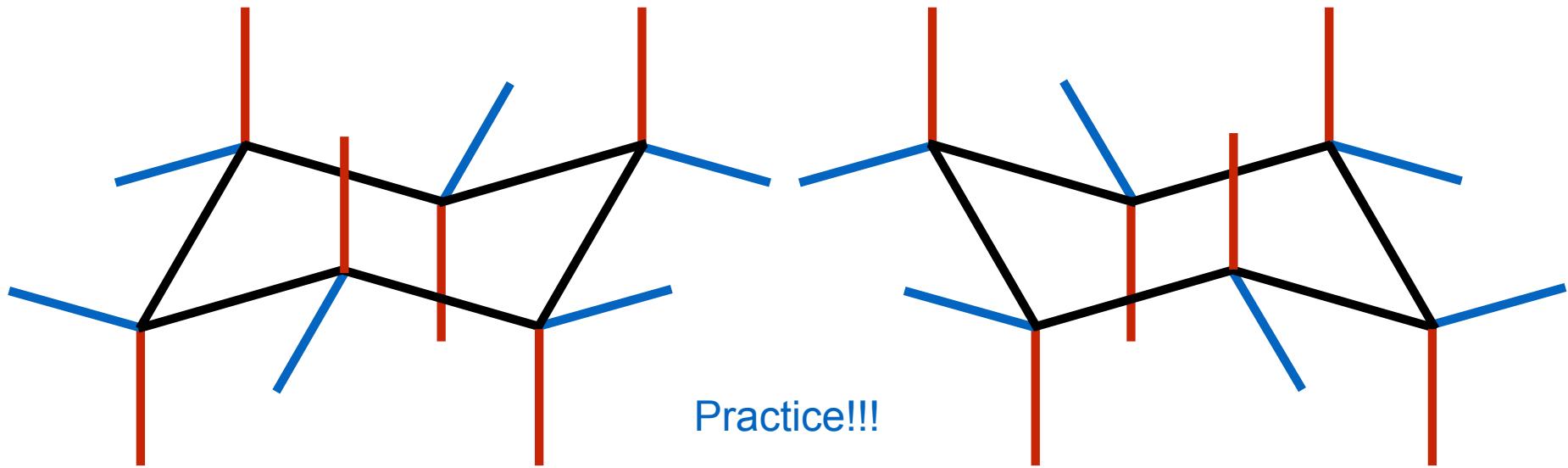
→ twisting relieves some  
steric and torsional strain

## How to Draw the Chair Conformation of Cyclohexane

Visualize the chair as three pairs of parallel lines that are offset

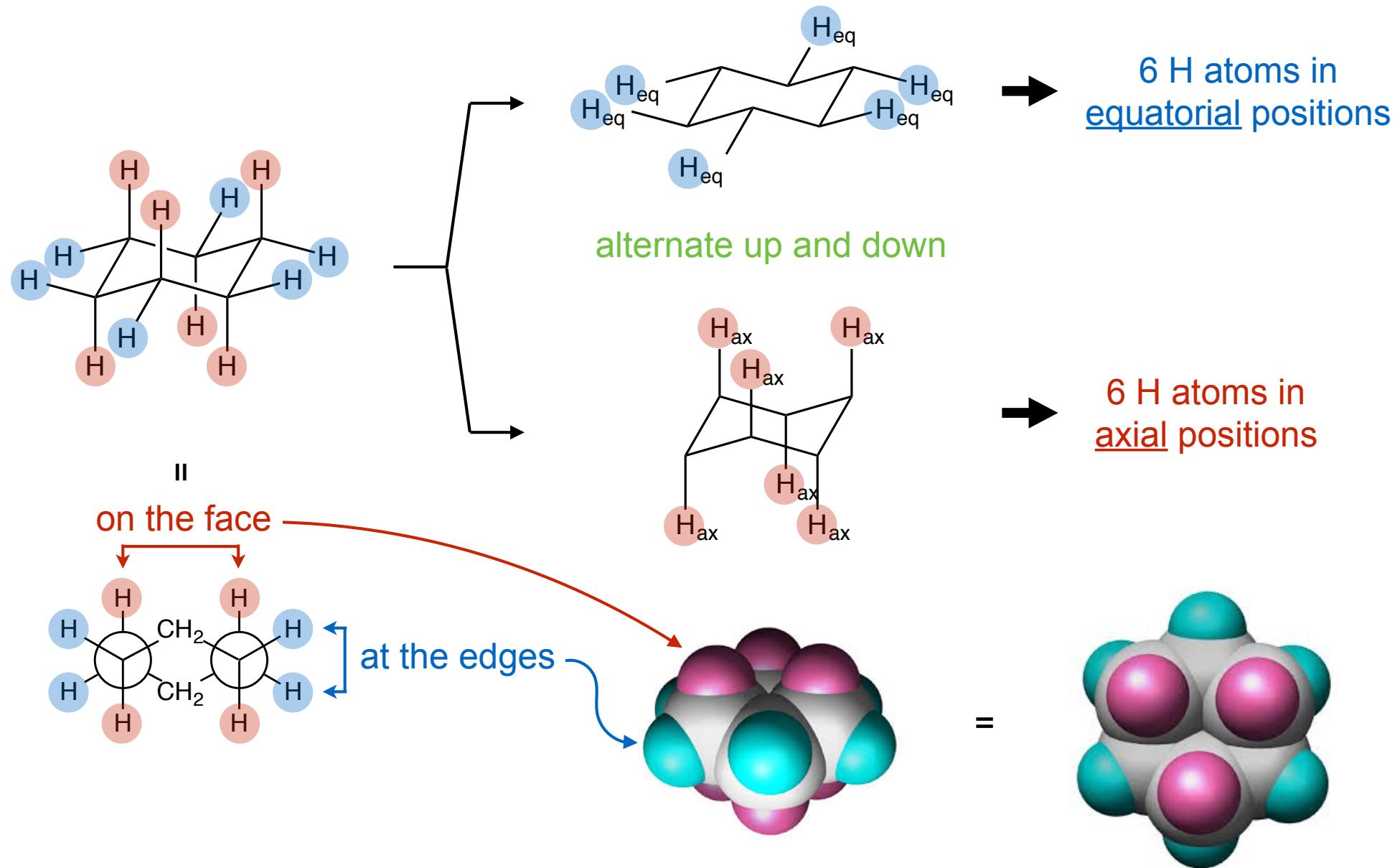


add hydrogens/substituents if needed



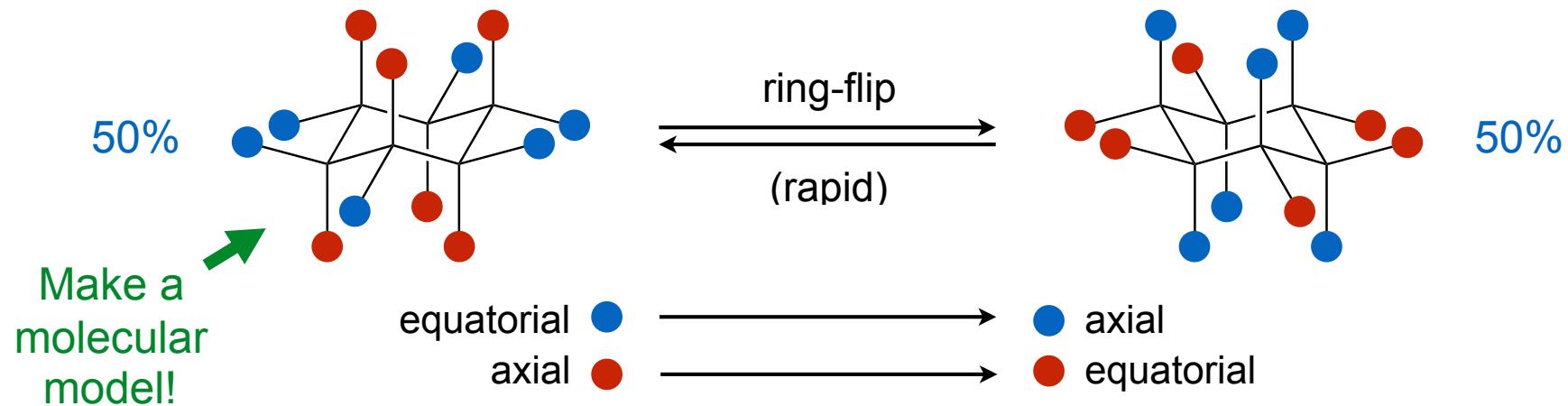
Practice!!!

## Equatorial vs. Axial Positions



Q: Why make the distinction between equatorial and axial positions?

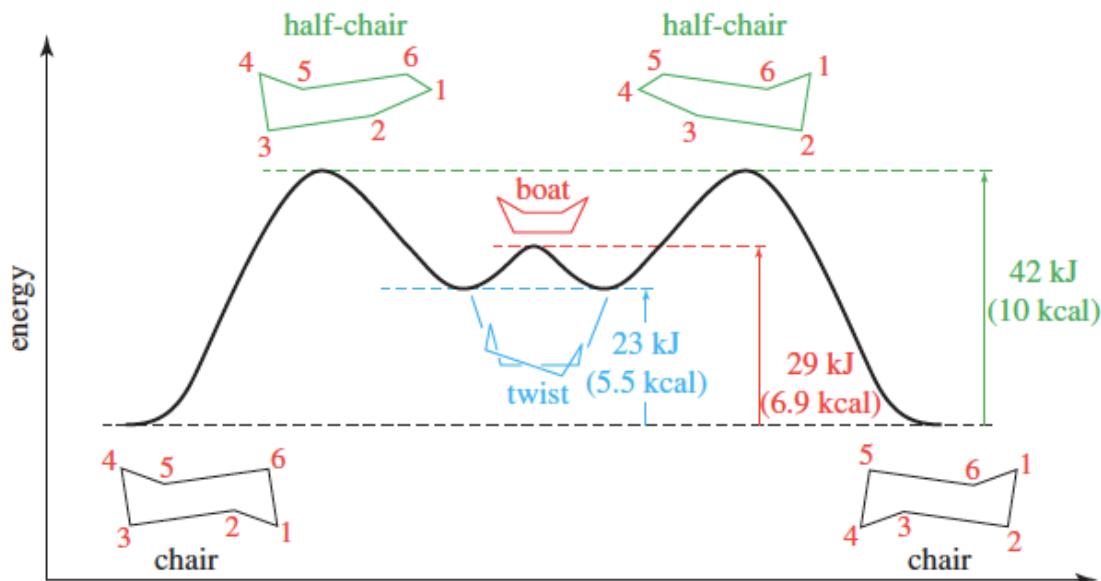
## Ring-Flip in Cyclohexane



Cyclohexane undergoes rapid conformational ring-flip at room temperature

**Ring-flip causes equatorial and axial substituents to switch positions!**

Ring-flip proceeds via boat and twist-boat conformations

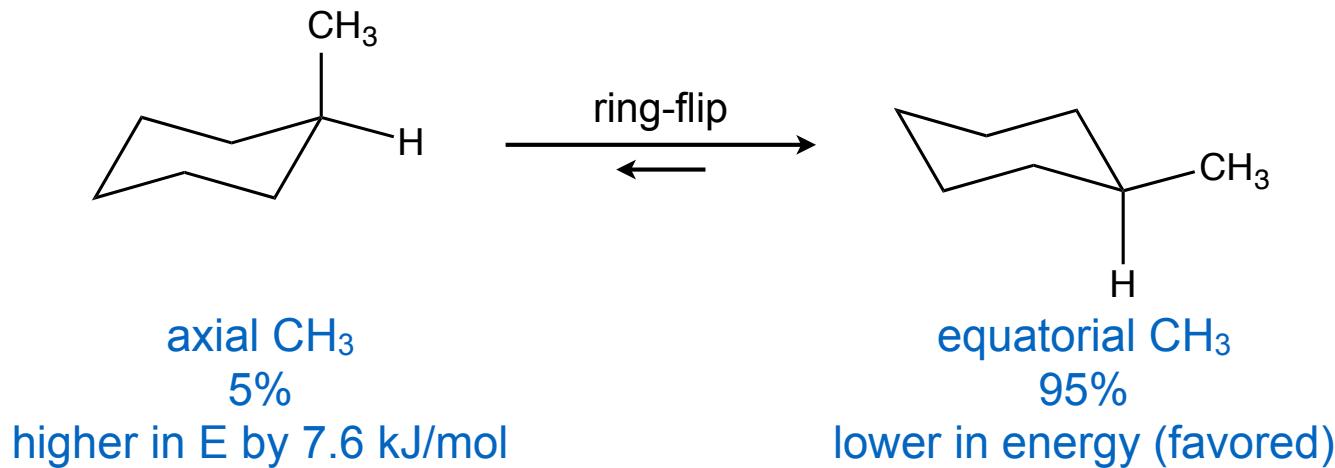


**Q: Consequences of ring-flip?**

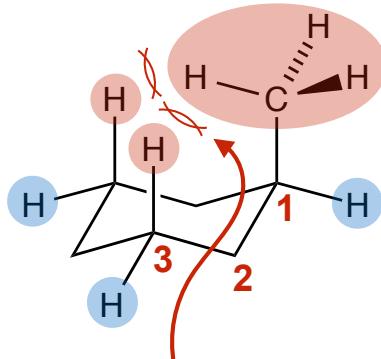
## Conformations of Mono-Substituted Cyclohexanes (3-14)

Q: What impact does ring-flip have on the distribution of conformations of cyclohexanes with one substituent?

Ex: methylcyclohexane

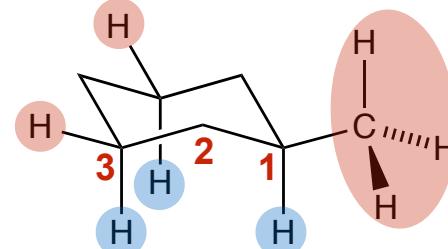


Q: Why is the conformer with the CH<sub>3</sub> group axial higher in energy?

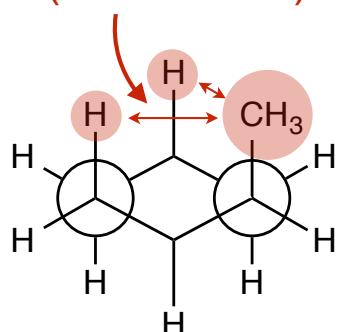


1,3-diaxial interactions with CH<sub>3</sub>  
(steric strain)

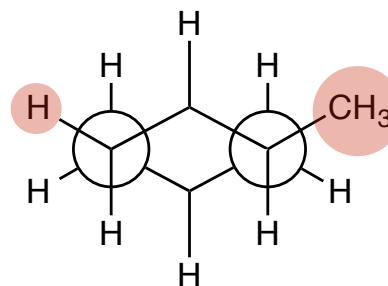
ring-flip



no 1,3-diaxial interactions with CH<sub>3</sub>  
(lower E)

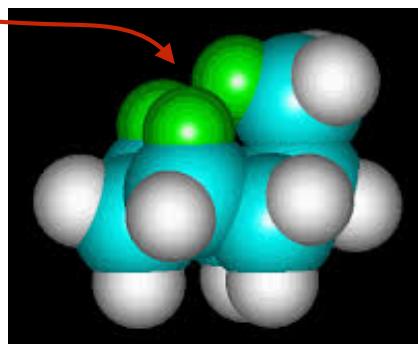


axial CH<sub>3</sub>

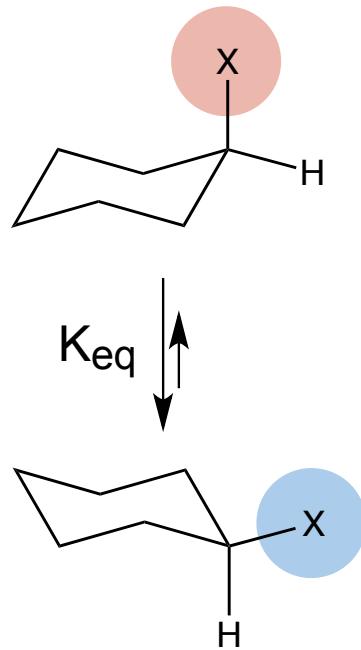


equatorial CH<sub>3</sub>

1,3-diaxial interactions: steric interactions between axial substituents that unfavorably raise energy due to electronic repulsion

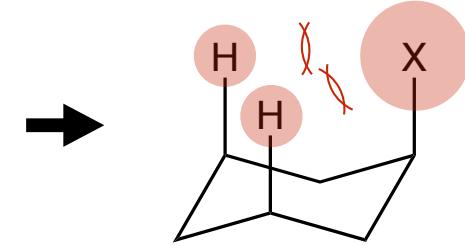


## Difference in Energy between Axial & Equatorial Conformations



Substituent ( $X$ )	1,3-Diaxial Strain Energy (kJ/mol)
-H	0
-F	0.8
-CN	0.8
-Cl	2.1
-Br	2.5
-OH	4.1
-CO <sub>2</sub> H	5.9
-CH <sub>3</sub>	7.6
-CH <sub>2</sub> CH <sub>3</sub>	7.9
-CH(CH <sub>3</sub> ) <sub>2</sub>	8.8
-C(CH <sub>3</sub> ) <sub>3</sub>	23

↓ increasing size ↓

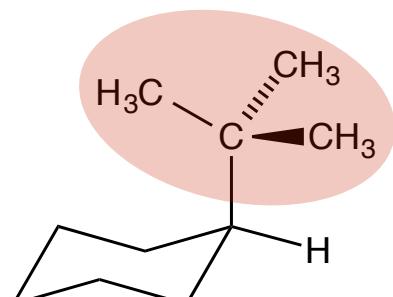


Make models!

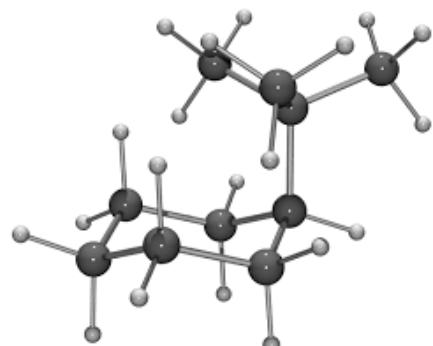
Note: Energy increases as the size (steric bulk) of substituents increases

Q: How much does 1,3-diaxial strain energy affect ring-flip conformations?

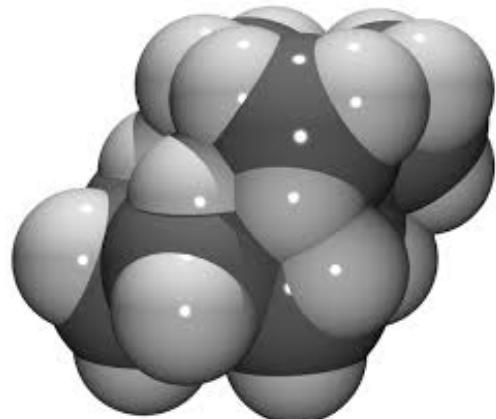
## Ex: *t*-butylcyclohexane



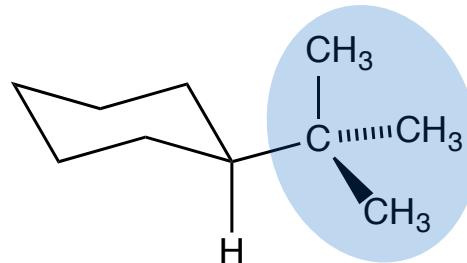
II



II



$$K_{\text{eq}} \rightleftharpoons$$



$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT}$$

$$K_{\text{eq}} = e^{-\Delta G^\circ/RT}$$

$$K_{\text{eq}} = e^{-(23 \text{ kJ/mol})/(0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1})(298\text{K})}$$

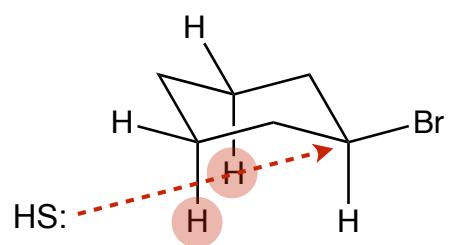
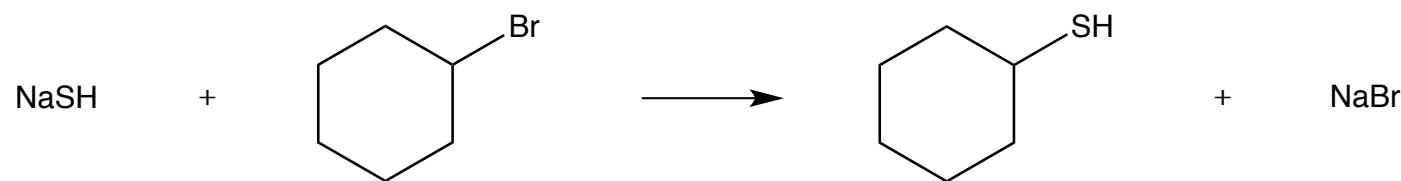
$$K_{\text{eq}} = 5.6 \times 10^{26} = \frac{[\text{P}]}{[\text{R}]} = \frac{[\text{equatorial}]}{[\text{axial}]}$$



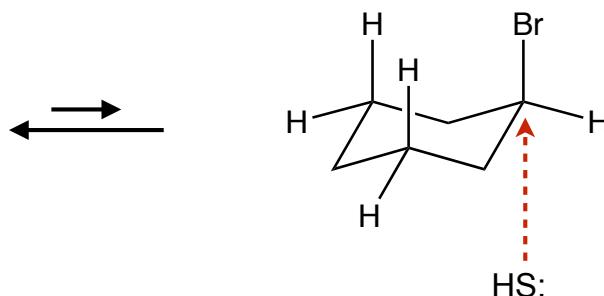
effectively eliminates ring-flip!

Q: How does 1,3-diaxial strain affect reactivity?

Ex: Synthesis of thiols



favored conformation  
approach is hindered sterically  
(no reaction or rate of reaction is slow)

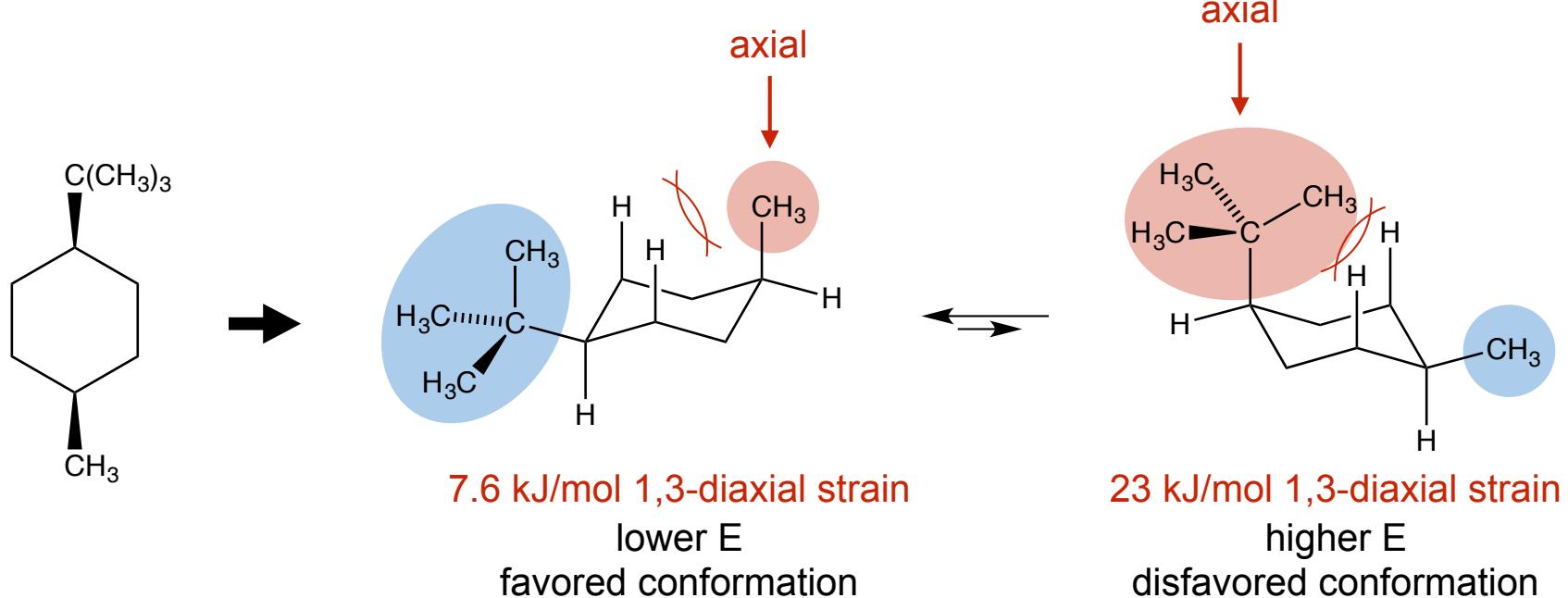


disfavored conformation  
approach is significantly less hindered  
(rate of reaction is faster)

## Conformations of Cyclohexanes with Two or More Substituents (3-15)

Ex: *cis*-1-*t*-butyl-4-methylcyclohexane

Q: Which conformation is lowest in energy?



Q: By how much is the lower-energy conformer favored?

$$\Delta G^\circ = (\Delta G_{\text{prod}} - \Delta G_{\text{react}}) = 23 \text{ kJ/mol} - 7.6 \text{ kJ/mol} = 15.4 \text{ kJ/mol}$$

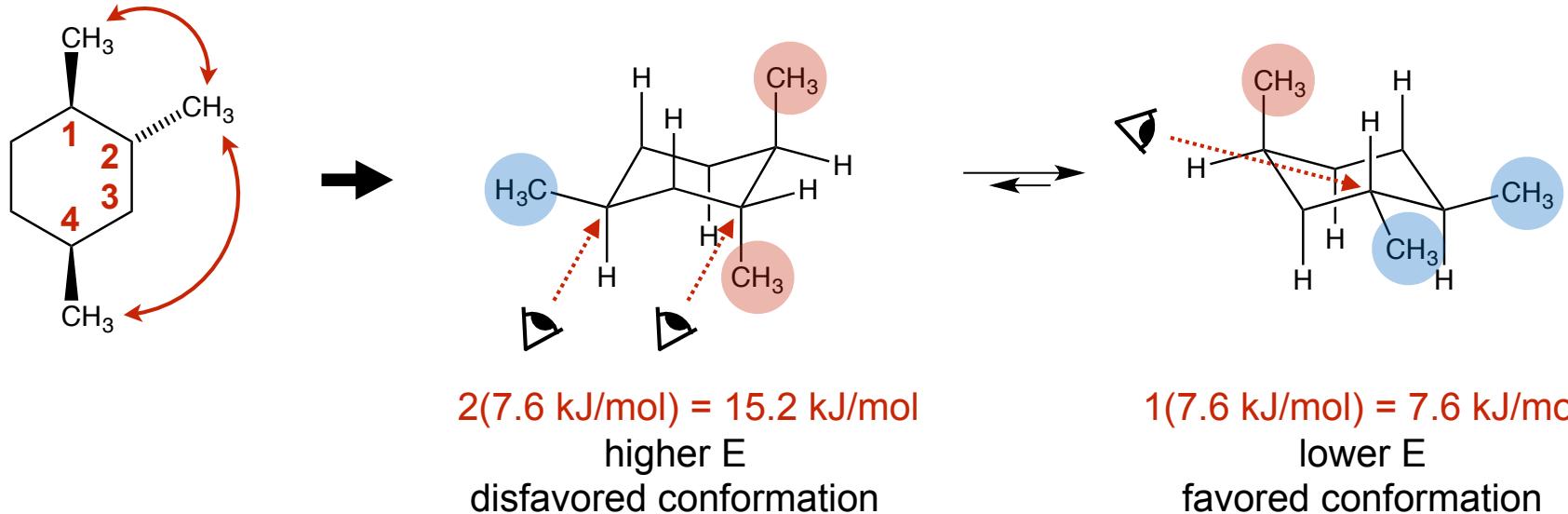
$$K_{\text{eq}} = e^{-\Delta G^\circ/RT} = e^{-(15.4 \text{ kJ/mol})/(0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1})(298\text{K})}$$

$$K_{\text{eq}} = 6.14 \times 10^{-17} = \frac{[\text{P}]}{[\text{R}]} = \frac{1}{1.63 \times 10^{16}}$$

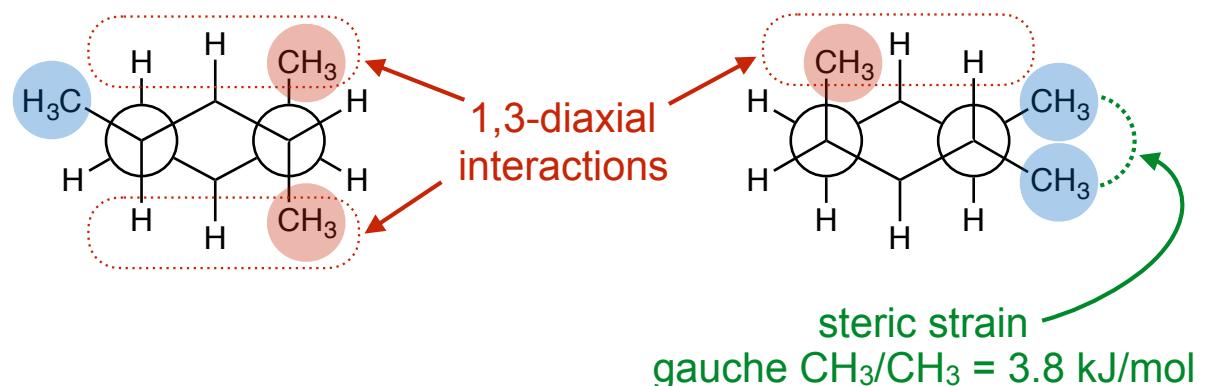
heavily favors conformer  
with *t*-Bu equatorial!

Ex: trans,trans-1,2,4-trimethylcyclohexane

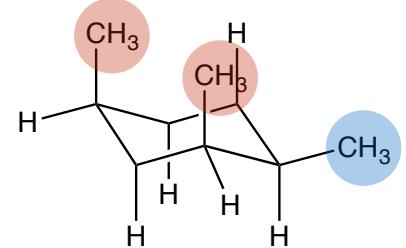
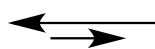
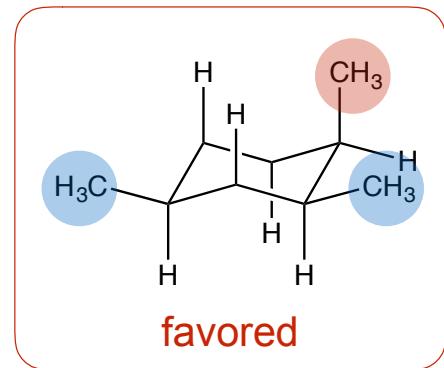
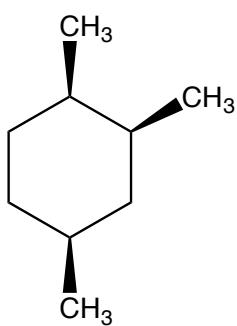
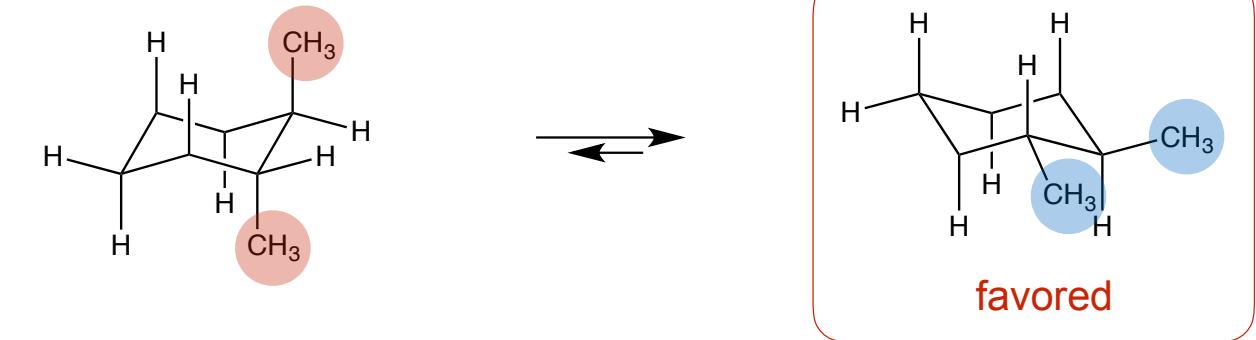
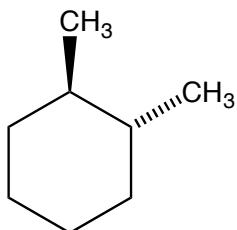
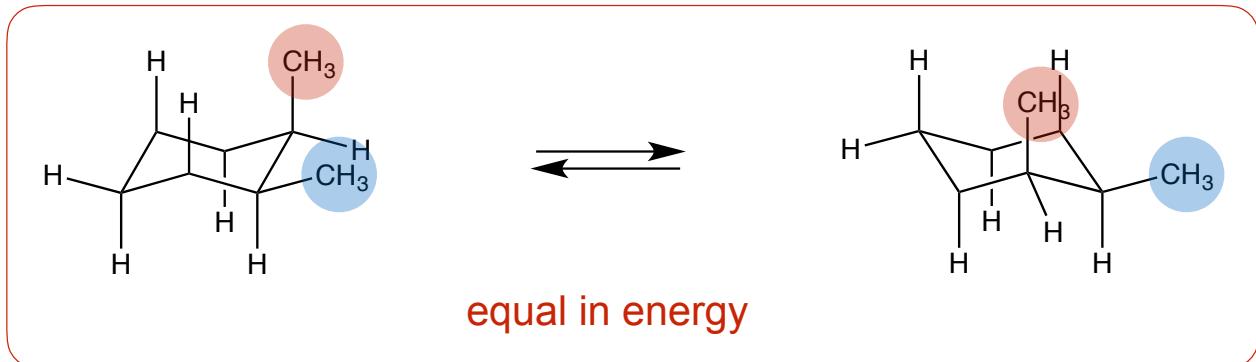
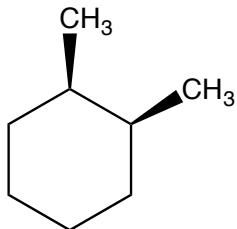
Q: Which conformation is lowest in energy?



Q: Any other strain that hasn't been taken into account?

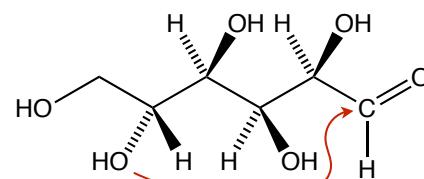


Ex: Determine the lowest-energy conformation of the following compounds



Q: Does conformational analysis of cycloalkanes translate to other cyclic compounds?

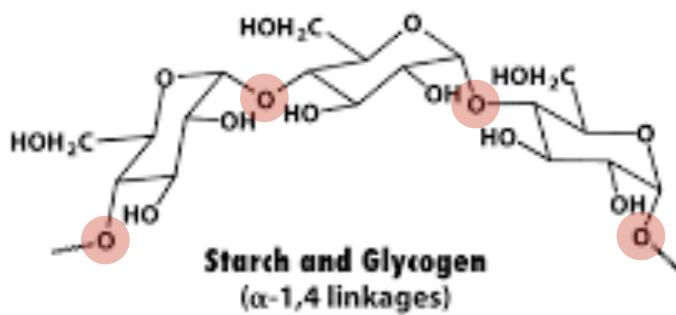
Sugars!



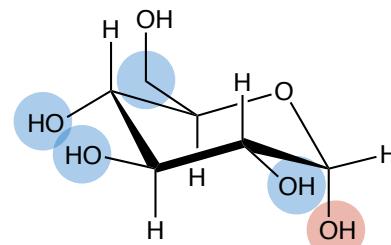
D-glucose (acyclic form)

cyclization

Q: Structures of ring-flip conformers?  
Q: Energies of ring-flip conformers?

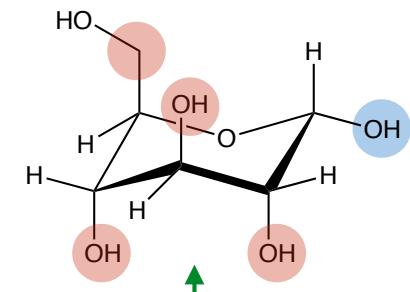


Starch and Glycogen  
( $\alpha$ -1,4 linkages)



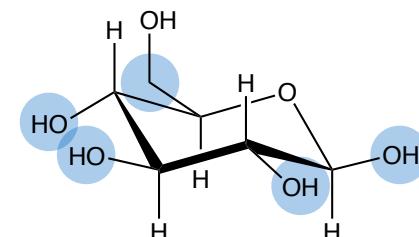
$\alpha$ -D-glucose (chair form)

ring-flip



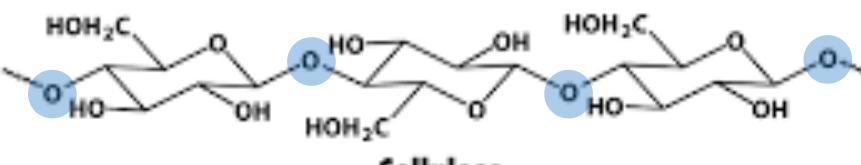
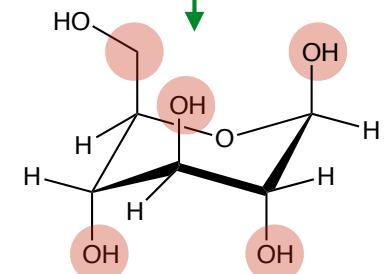
higher energy due to  
1,3-diaxial interactions

or



$\beta$ -D-glucose (chair form)

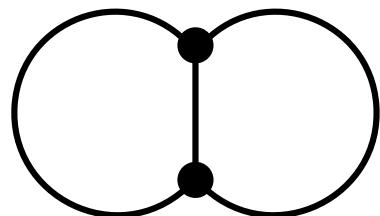
ring-flip



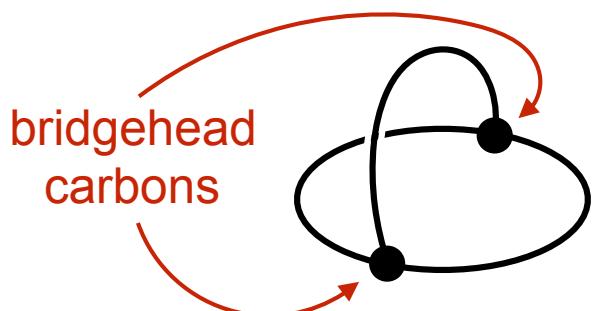
Cellulose  
( $\beta$ -1,4 linkages)

## Bicyclic and Polycyclic Alkanes (3-16)

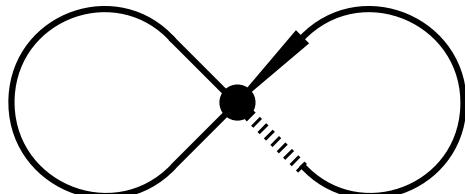
- Two or more rings can be joined to form bicyclic or polycyclic ring systems
- Rings can be joined together in three different ways:



Fused Rings - share two adjacent carbons

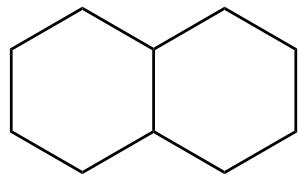


Bicyclic Rings - share two non-adjacent carbons

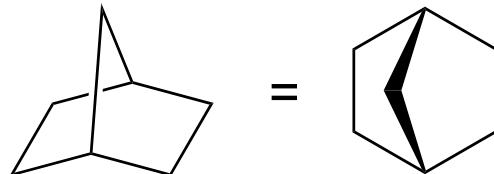


Spirocyclic Rings - share one carbon

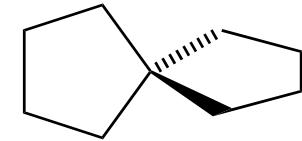
Ex: Some common bicyclic alkanes



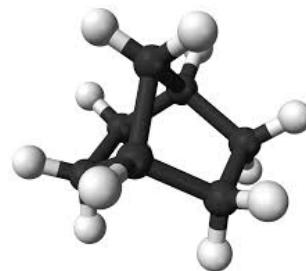
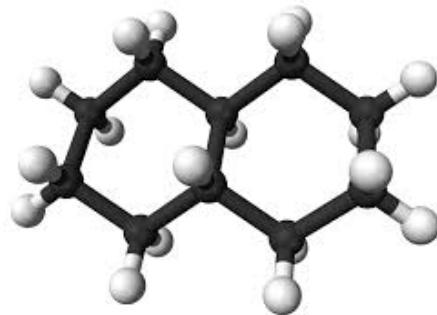
bicyclo[4.4.0]decane  
(decalin)



bicyclo[2.2.1]heptane  
(norbornane)

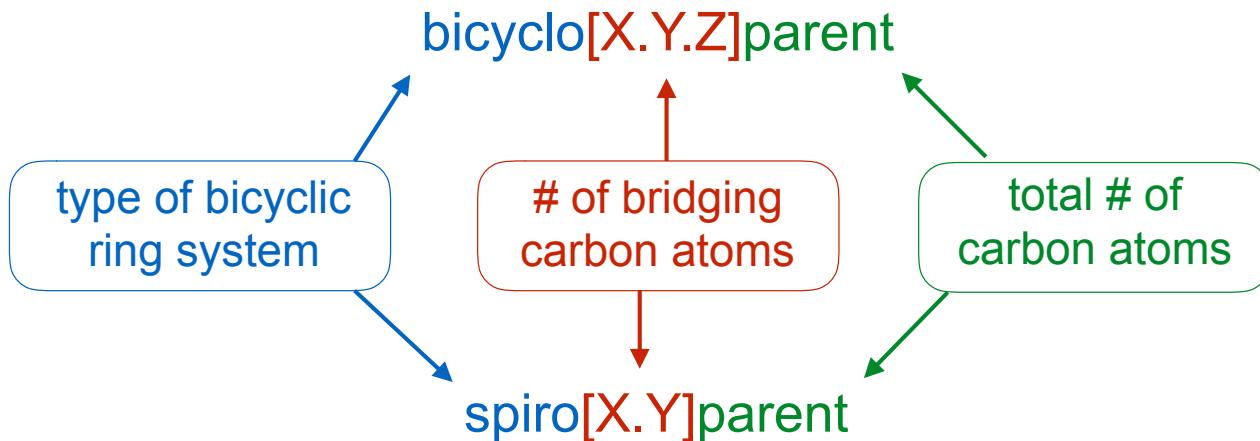


spiro[4.4]nonane

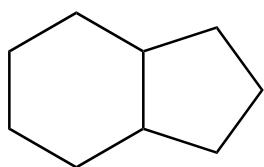


Q: What's up with those funky names?

## Nomenclature of Bicyclic Alkanes

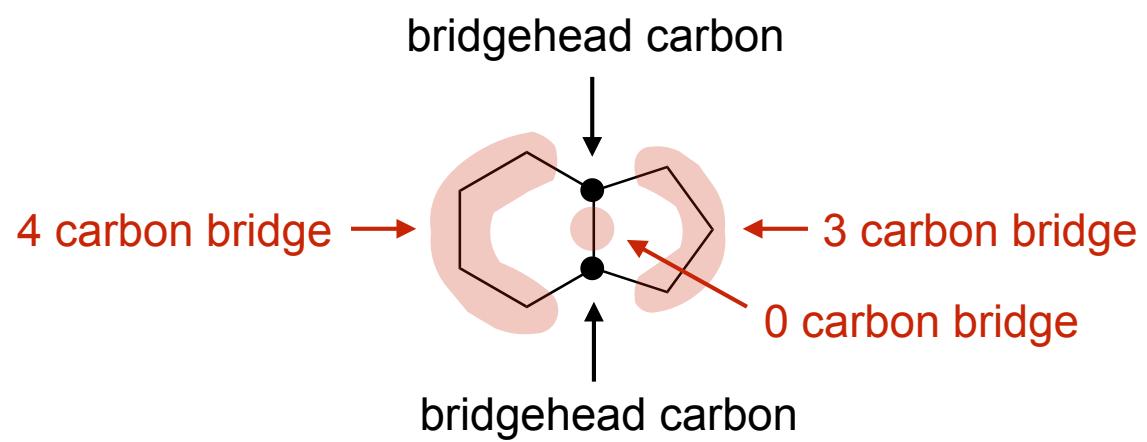


Ex:

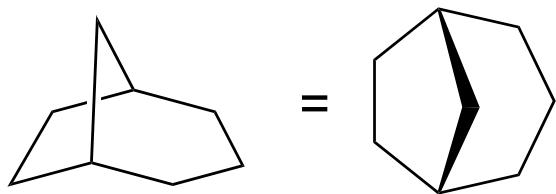


bicyclo[4.3.0]nonane

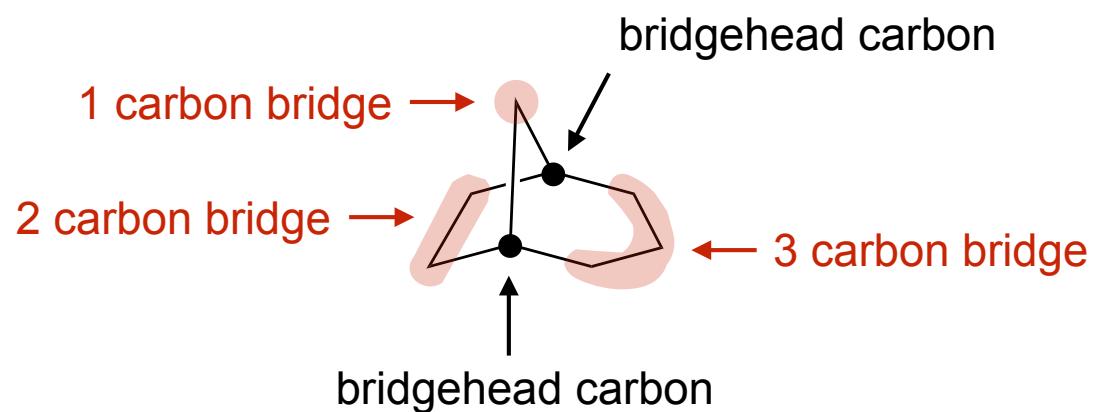
list from largest to smallest bridge



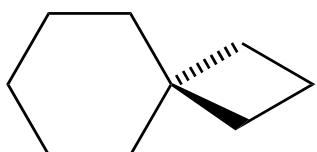
Ex:



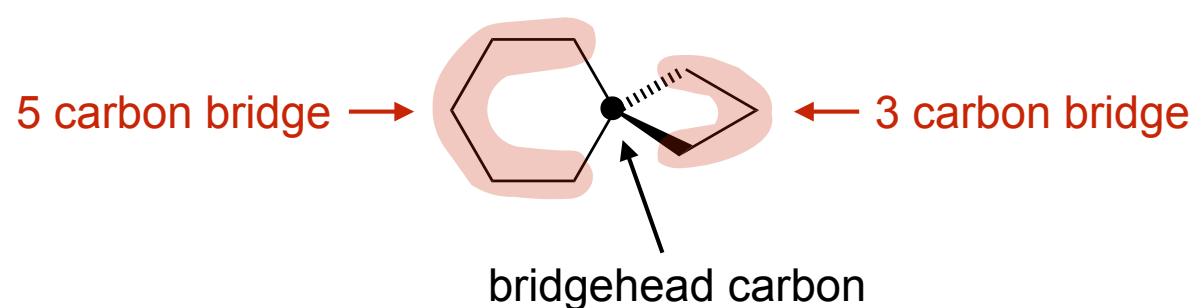
bicyclo[3.2.1]octane



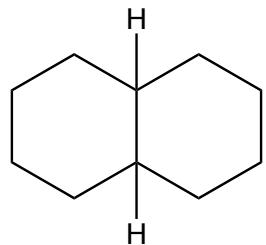
Ex:



spiro[5.3]nonane

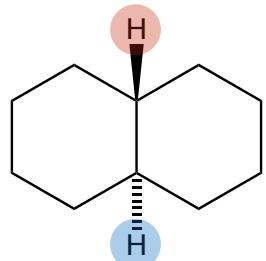


## Conformations of *trans*- and *cis*-decalin



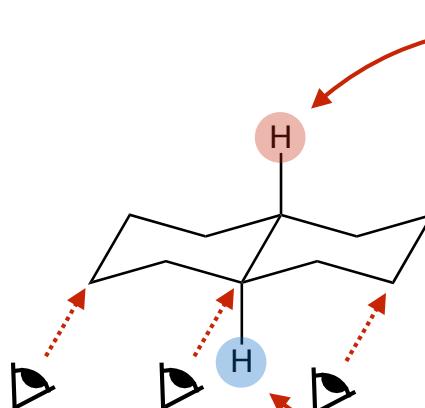
H atoms on bridgehead carbons can be *trans* or *cis*

bicyclo[4.4.0]decane  
(decalin)

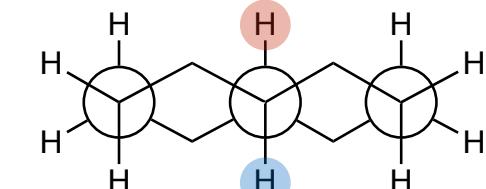


*trans*-decalin

=



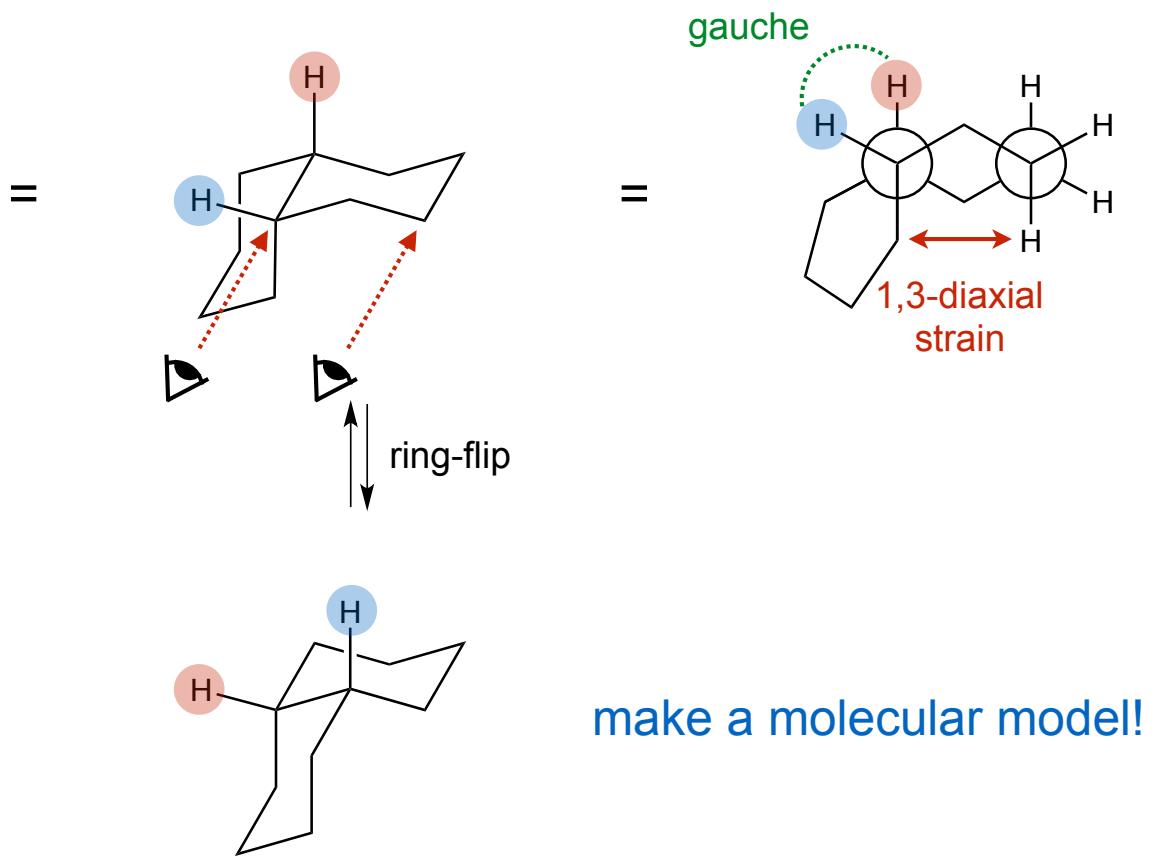
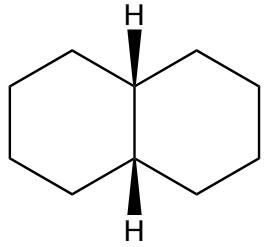
=



axial

Note: *trans*-decalin is conformationally rigid and cannot undergo ring-flip

Q: Why?



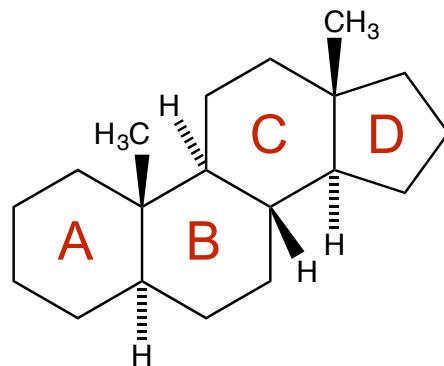
Note: *cis*-decalin is conformationally flexible and undergoes ring-flip

Q: Why?

## Polycyclic Ring Systems in Nature

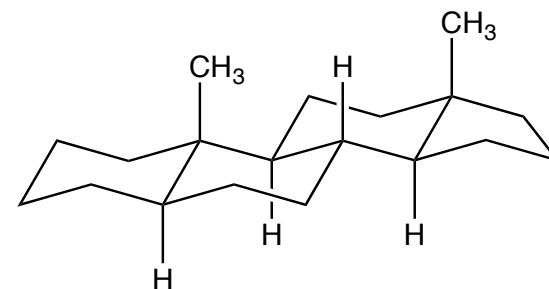
Ex: Steroids

- used by humans and other organisms as hormones to control sexual development, fertility and other functions

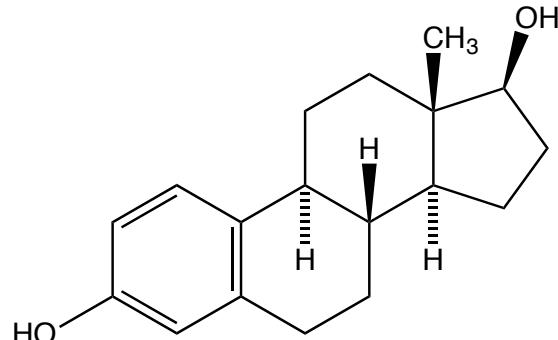


base steroid ring structure

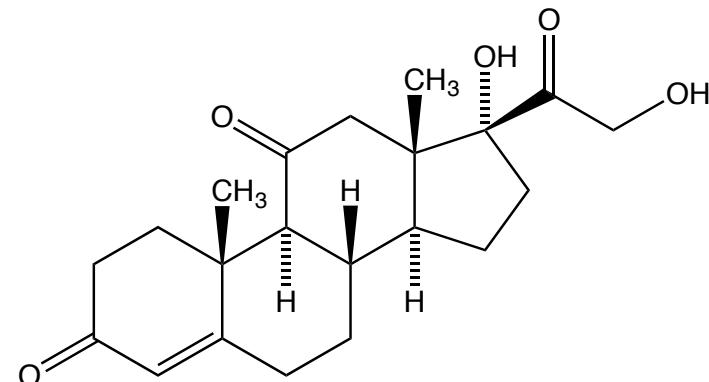
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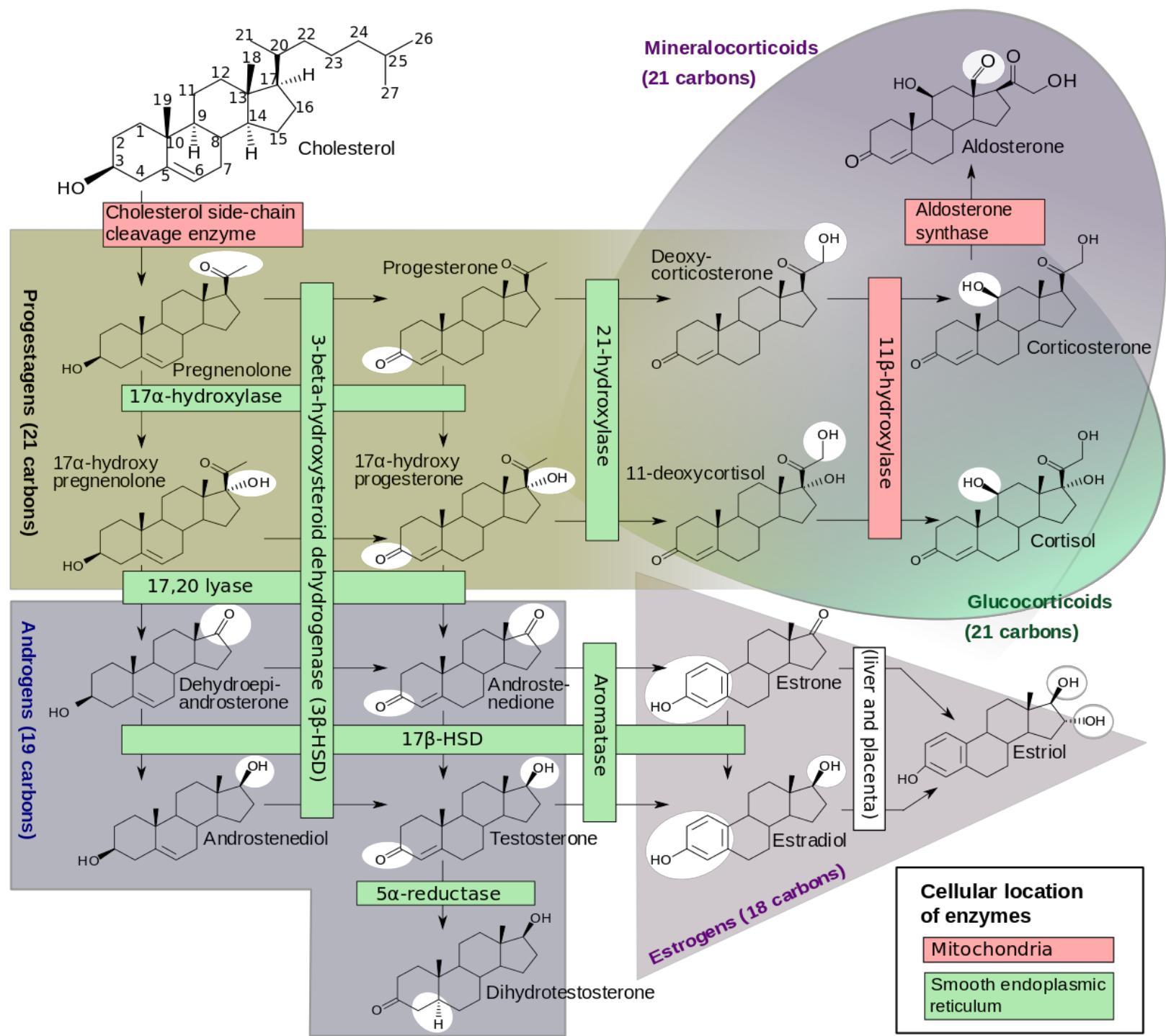
conformationally rigid scaffold  
(similar to *trans*-decalin)



estradiol (estrogen)



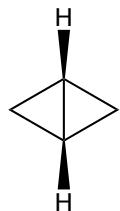
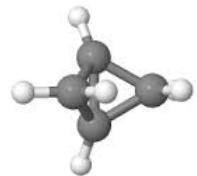
cortisone



## Unusual Cycloalkanes

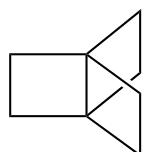
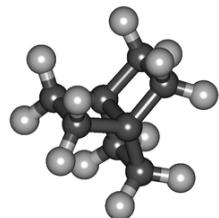
all are highly strained

strain energy (kJ/mol)



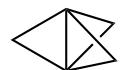
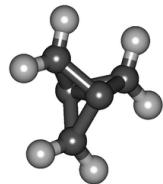
bicyclo[1.1.0]butane (1965)

276



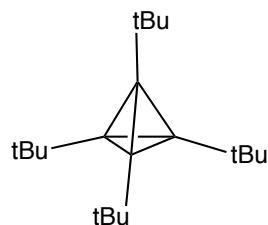
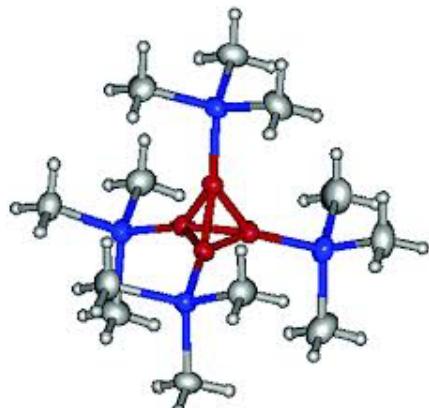
[2.2.2]propellane (1973)

405



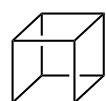
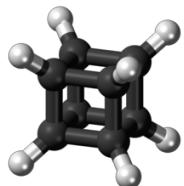
[1.1.1]propellane (1982)

431



tetrakis(*t*-butyl)tetrahedrane (1978)

539



cubane (1964)

656