Alkanes

Chapters 3, 4, 10.2, 10.4
Organic Chemistry, 8th Edition
John E. McMurry

Hydrocarbons

- **Aliphatic** (*áleiphar* = Ointment (unguento)).
  - Alkanes (saturated hydrocarbons): hydrocarbons having only single C−C and C−H bonds.
    - Linear (*normal* alkanes, *n*-alkanes)
    - Branched
    - Cyclic
  - Alkenes (olefins): hydrocarbons having double bonds.
  - Alkynes: hydrocarbons having triple bonds.

- **Aromatic**

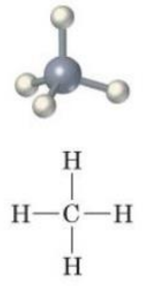
Alkanes

Number of C-atoms	Molecular formula	Name (*n*-alkane)
1	CH_4	methane
2	C_2H_6	ethane
3	C_3H_8	propane
4	C_4H_{10}	butane
5	C_5H_{12}	pentane
6	C_6H_{14}	hexane
7	C_7H_{16}	heptane
8	C_8H_{18}	octane
9	C_9H_{20}	nonane
10	$C_{10}H_{22}$	decane
20	$C_{20}H_{42}$	eicosane

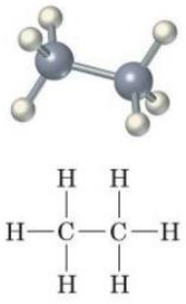
Empirical formula: C_nH_{2n+2}

Alkanes

Carbon in alkanes always has a sp^3 hybridization and only single bonds are present, so the carbon geometry is tetrahedral.

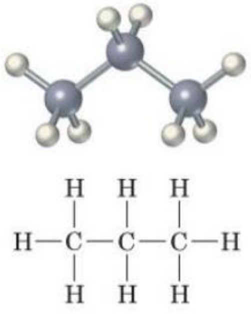


Metano, CH_4



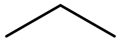
Etano, C_2H_6

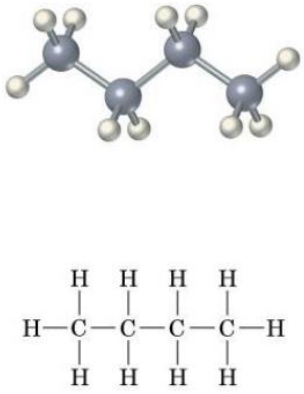
CH_3CH_2



Propano, C_3H_8

$CH_3CH_2CH_3$

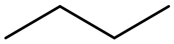




Butano

$CH_3CH_2CH_2CH_3$

$CH_3(CH_2)_2CH_3$

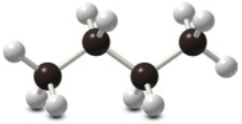


Alkanes – Structural Isomerism

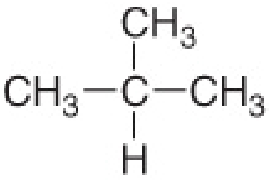
- There are two hydrocarbons with empirical formula C_4H_{10}: butane and isobutane.
- Butane and isobutane are structural isomers: they have the same composition but different physico-chemical properties.

$CH_3CH_2CH_2CH_3$

butane

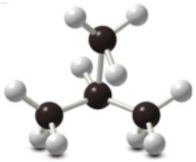


Linear Alkane



$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

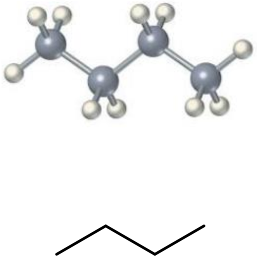
isobutane



Branched Alkane

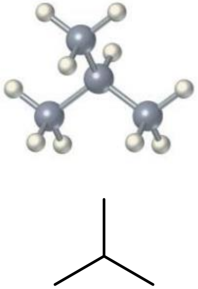
Alkanes – Structural Isomerism

C_4H_{10}



n-butane

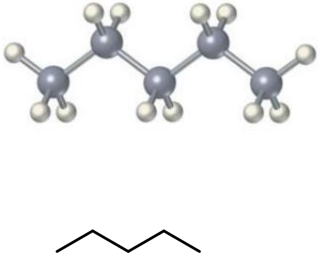
linear alkane



iso-butane
2-Methylpropan2

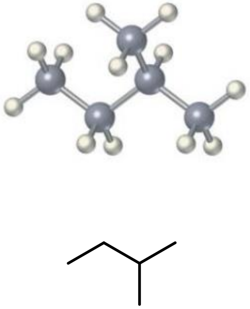
branched alkane

C_5H_{12}

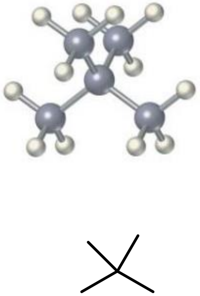


pentan2

linear alkane

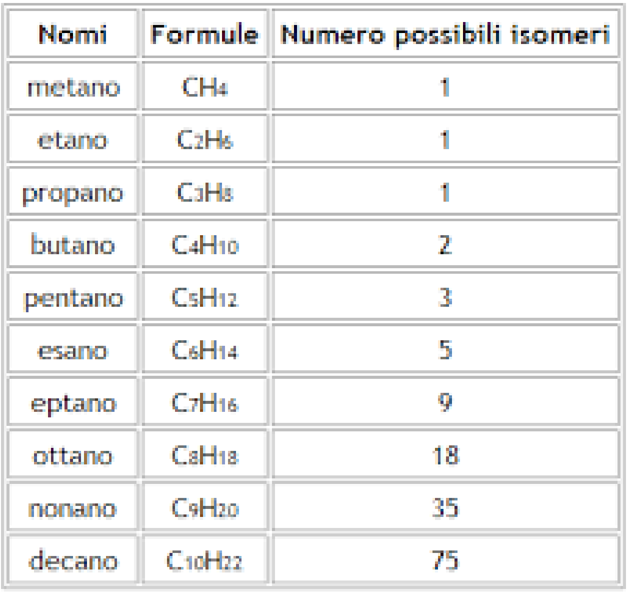


2-metilbutano



2,2-dimetilpropano

branched alkane



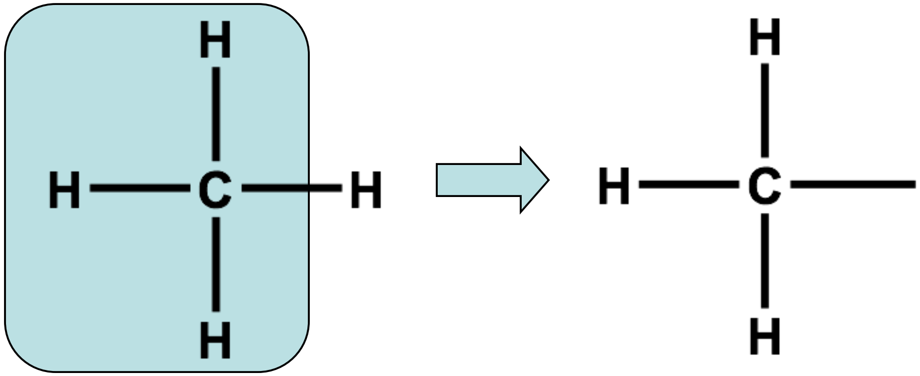
Nomi	Formule	Numero possibili isomeri
metano	CH_4	1
etano	C_2H_6	1
propano	C_3H_8	1
butano	C_4H_{10}	2
pentano	C_5H_{12}	3
esano	C_6H_{14}	5
eptano	C_7H_{16}	9
ottano	C_8H_{18}	18
nonano	C_9H_{20}	35
decano	$C_{10}H_{22}$	75

Alkyl Groups

In branched alkanes a main chain (the longest) is identified; the groups attached to the main chain are considered substitutes for the main chain and are called **alkyl groups.**

In general terms the alkyl substituent is referred to as **-R**.

Root-Suffix (= yl)



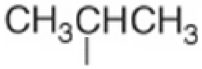
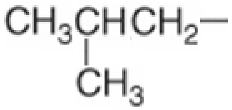
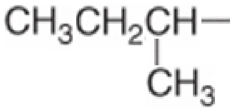
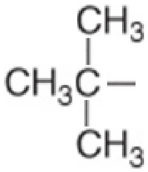
Free valence

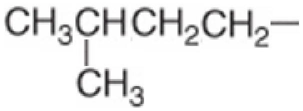
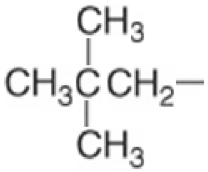
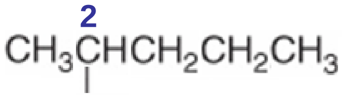
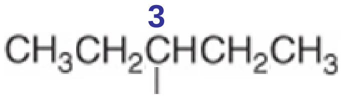
$= CH_3-$ **methyl**

$CH_3-CH_2- = C_2H_5-$ **ethyl**

$CH_3-CH_2-CH_2- = C_3H_7-$ **propyl**

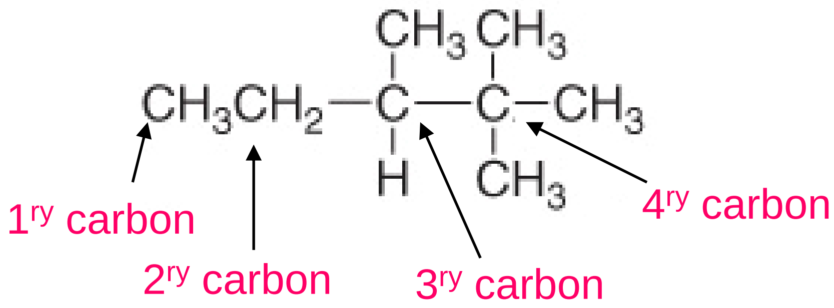
Alkyl Groups

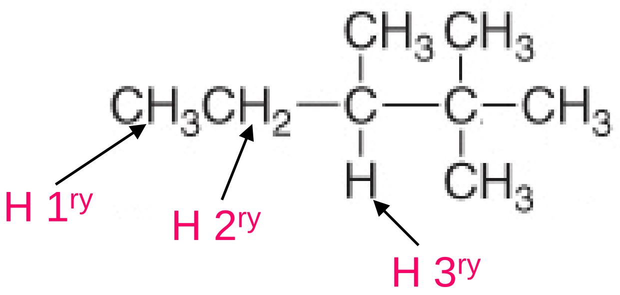
C-Atoms	Structure	Name
1	CH_3-	**methyl**
	$-CH_2-$	**methylene**
	 $-\overset{|}{C}H-$	**methine**
2	CH_3CH_2-	**ethyl**
3	$CH_3CH_2CH_2-$	***n*-propyl**
	 $CH_3\underset{|}{C}HCH_3$	**isopropyl**
4	$CH_3CH_2CH_2CH_2-$	***n*-butyl**
	 $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2-$	**isobutyl**
	 $CH_3CH_2\underset{\underset{CH_3}{|}}{C}H-$	***sec*-butyl**
	 $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$	***tert*-butyl**

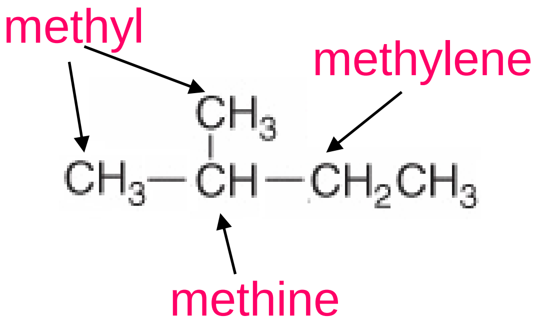
C-Atoms	Structure	Name
5	$CH_3CH_2CH_2CH_2CH_2-$	***n*-pentyl**
	 $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2-$	**isopentyl**
	 $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2-$	**neopentyl**
	 $CH_3\overset{2}{\underset{|}{C}}HCH_2CH_2CH_3$  $CH_3CH_2\overset{3}{\underset{|}{C}}HCH_2CH_3$	***sec*-pentyl**

Classification of carbon atoms

Carbon atoms are classified according to the number of carbon atoms to which they are bound. Hydrogen atoms are also classified in analogy.


$$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$


$$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$


$$CH_3-\overset{CH_3}{CH}-CH_2CH_3$$

Nomenclatura IUPAC

Costruzione del nome

prefisso + infisso + suffisso

a) numero di carboni (but-, pent- ecc.)

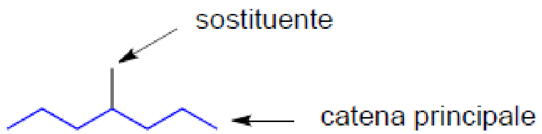
b) presenza di doppi o tripli legami (an-, en-, in-)

c) classe chimica (-o, -e, -olo, -ale, -one, ecc.)

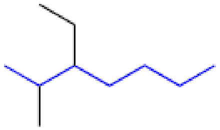
et-an-o
et-en-e
et-in-o

1. Agli alcani lineari il nome è assegnato in base al numero degli atomi di carbonio presenti:
   Metano, etano, propano, butano, pentano, esano, eptano, ottano, nonano, decano, undecano, dodecano, …

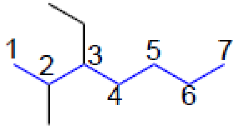
2. Per alcani contenenti catene di carbonio ramificate, si individua la catena principale:



3. Se due o più catene, nell'ambito della struttura, hanno la stessa lunghezza, si deve scegliere, come catena principale, quella con il numero maggiore di ramificazioni:

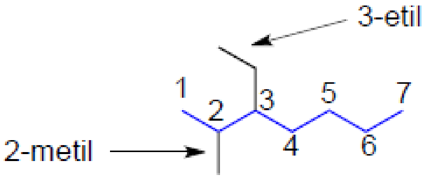


4. Si numerano consecutivamente i carboni della catena principale da una parte all'altra, nella direzione che attribuisce il numero più basso al primo punto di ramificazione:

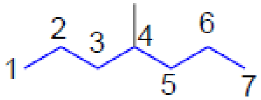


Nomenclatura IUPAC

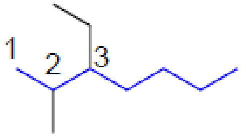
5. Si assegna il nome a ciascuna ramificazione e si identifica il numero del carbonio della catena principale sul quale essa si trova. (ricorda: isopropile, isobutile, sec-butile, t-butile, neopentile):



6. Costruisci il nome scrivendo il numero del carbonio della catena principale cui è legato il sostituente, un trattino, il nome del sostituente e il nome dell'alcano corrispondente alla catena principale:

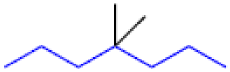


4-metileptano



3-etil-2-metilheptane

7. Se la catena principale contiene più sostituenti dello stesso tipo, ognuno di essi riceve il proprio numero. Si utilizzano i prefissi di, tri, tetra e così via, per indicare il numero dei sostituenti uguali:

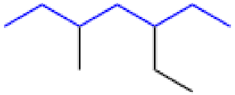


4,4-dimetileptano

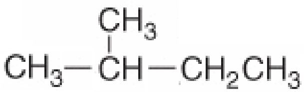
Nomenclatura IUPAC

9. I gruppi sostituenti sono citati nel nome in ordine alfabetico, senza tener conto della loro posizione nella catena principale. Nello stabilire quest'ordine alfabetico, i prefissi numerici di, tri, tetra e così via, così come i prefissi uniti con un trattino t- e sec- sono ignorati, a differenza dei prefissi iso, neo e ciclo che vanno invece considerati.

10. Se la scelta della numerazione dei gruppi differenti non può essere effettuata sulla base delle regole precedenti, al gruppo citato per primo viene attribuito il numero più basso:

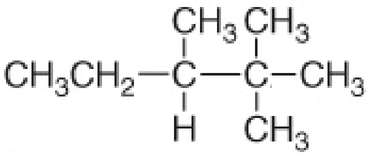


3-etil-5-metileptano
e non 5-etil-3-metileptano



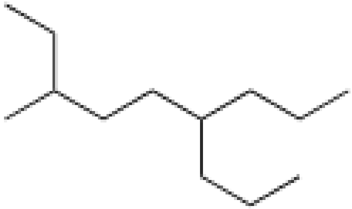
$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2CH_3$

2-metilbutano

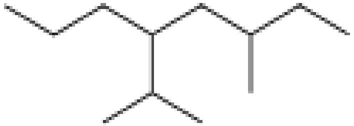


$CH_3CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

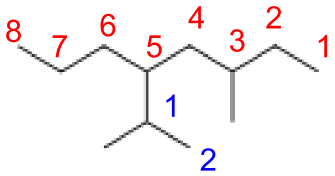
2,2,3-trimetilpentano



3-metill-6-propilnonano

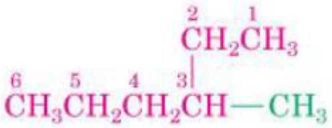


5-isopropil-3-metilottano

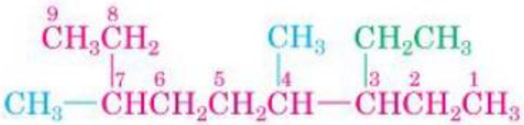


5-(1-metiletil)-3-metilottano

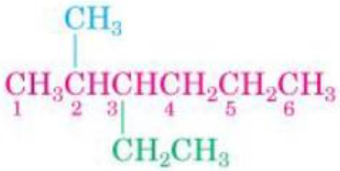
Nomenclatura IUPAC



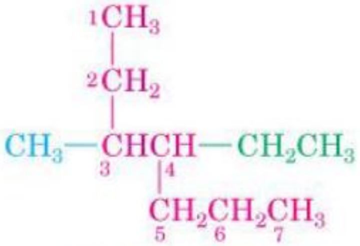
3-Metilesano



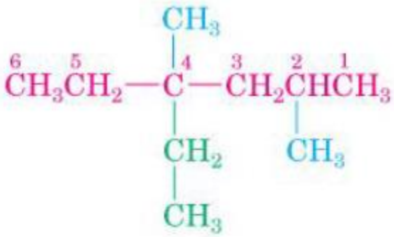
3-Etil-4,7-dimetilnonano



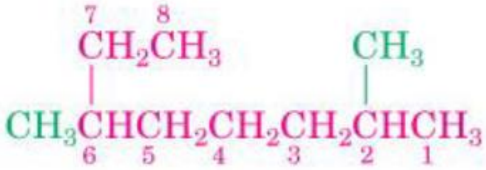
3-Etil-2-metilesano



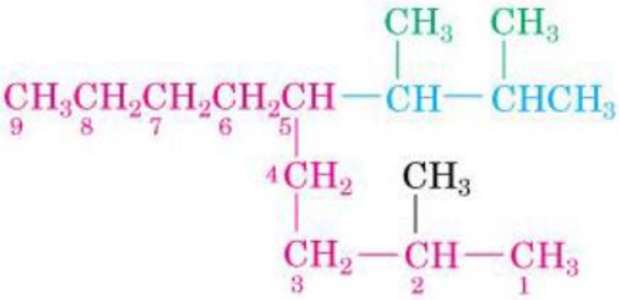
4-Etil-3-metileptano



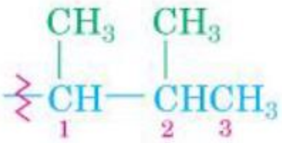
4-Etil-2,4-dimetilesano



2,6-Dimetilottano

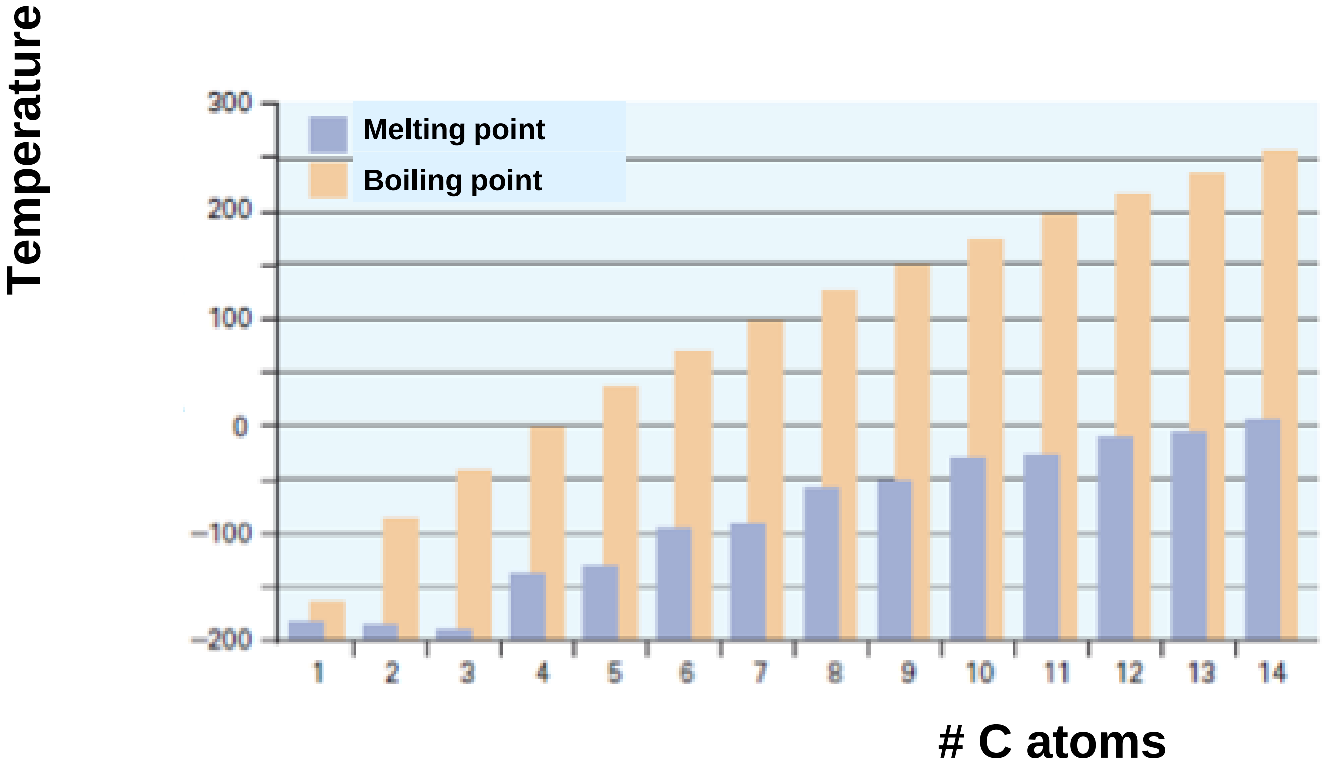


5-(1,2-Dimetilpropil)-2-metilnonano



5-(1,2-Dimetilpropil)-

Physical Properties



Physical Properties

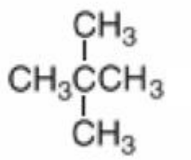
b.p.

$CH_3CH_2CH_2CH_3$
0 °C

$CH_3CH_2CH_2CH_2CH_3$
36 °C

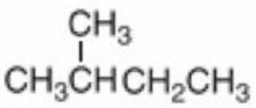
$CH_3CH_2CH_2CH_2CH_2CH_3$
69 °C

Surface area increases with C-atoms



$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3}$

10 °C



$\mathrm{CH_3\overset{CH_3}{C}HCH_2CH_3}$

30 °C

$CH_3CH_2CH_2CH_2CH_3$

36 °C

Surface area decreases with branching

m.p.

$CH_3CH_2CH_2CH_3$
–138 °C

$CH_3CH_2CH_2CH_2CH_2CH_3$
–95 °C

Surface area increases with C-atoms

$CH_3CH_2CH(CH_3)_2$
–160°C

$(CH_3)_4C$
–17 °C

Increases with symmetry

Physical Properties

Physical state:	C1-C4	gas /b.p.	-160°-0°
	C5-C17	liq./m.p.	-130°-20°
	>C17	solid	

Solubility:

soluble in organic solvents (apolar)

insoluble in water

Natural Sources

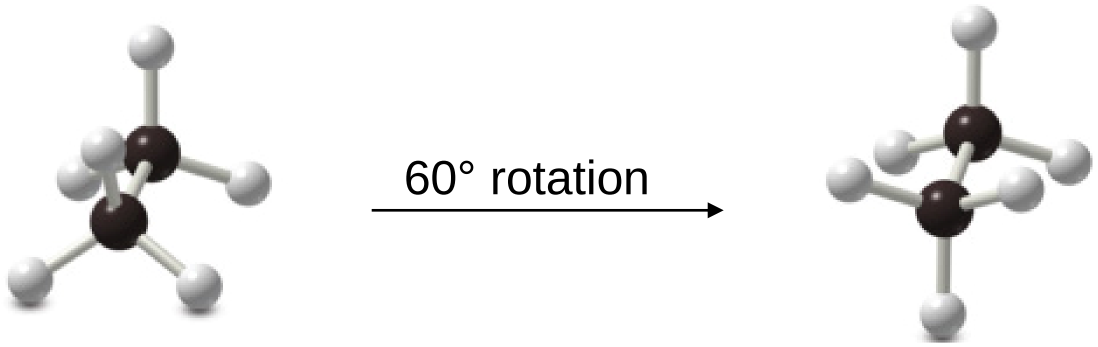
Natural sources of alkanes are natural gas and oil.

Natural gas contains mainly methane: minor components are ethane, propane and butane.

Oil is a complex mixture of, mainly, C_1-C_{40} hydrocarbons. Distillation of crude oil (refining) separates oil in fractions with different boiling point. The main fractions are:
gasoline: C_5H_{12} – $C_{12}H_{26}$
kerosene: $C_{12}H_{26}$ – $C_{16}H_{34}$
diesel oil: $C_{15}H_{32}$ – $C_{18}H_{38}$

Conformational Isomerism

Ethane



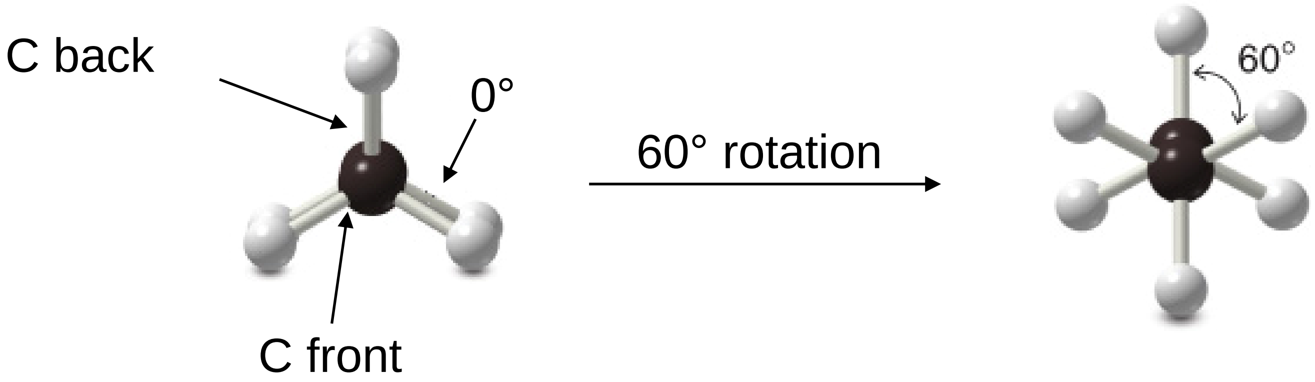
eclipsed **staggered**

- In the eclipsed conformation, all C−H bonds are alligned.
- In the staggered conformation, C−H bonds on each carbon bisect the H−C−H angles on the other carbon.

Ethane Conformations

- The H−C−C−H angle is called dihedral angle (0° in the eclipsed and 60° in the staggered conformation).

View along the C–C bond



Eclipsed conformation

Staggered conformation

The front C-H bonds bisect the H−C−H angles on the carbon atom at the back

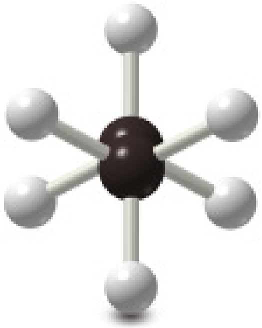
Newman Projection

- How to draw a Newman projection

  [1] Look along the C-C bond and draw a circle (the back C atom) with a dot in the centre (the front C atom).

  [2] Draw the bonds

  [3] Add the atoms



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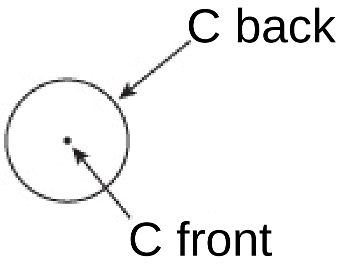
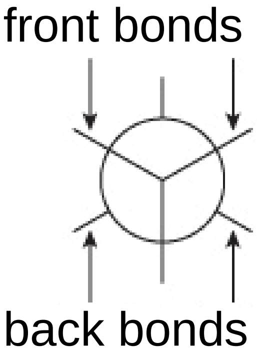
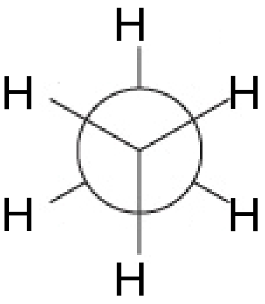




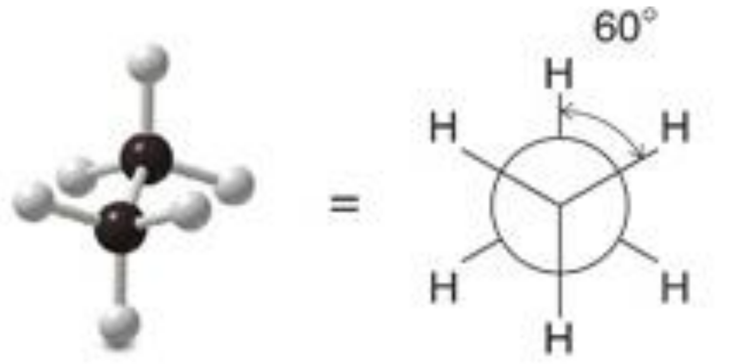


Newman Projections of Ethane

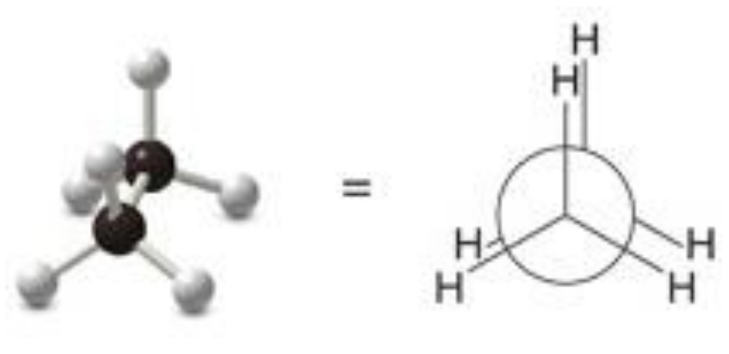
staggered conformation

eclipsed conformation

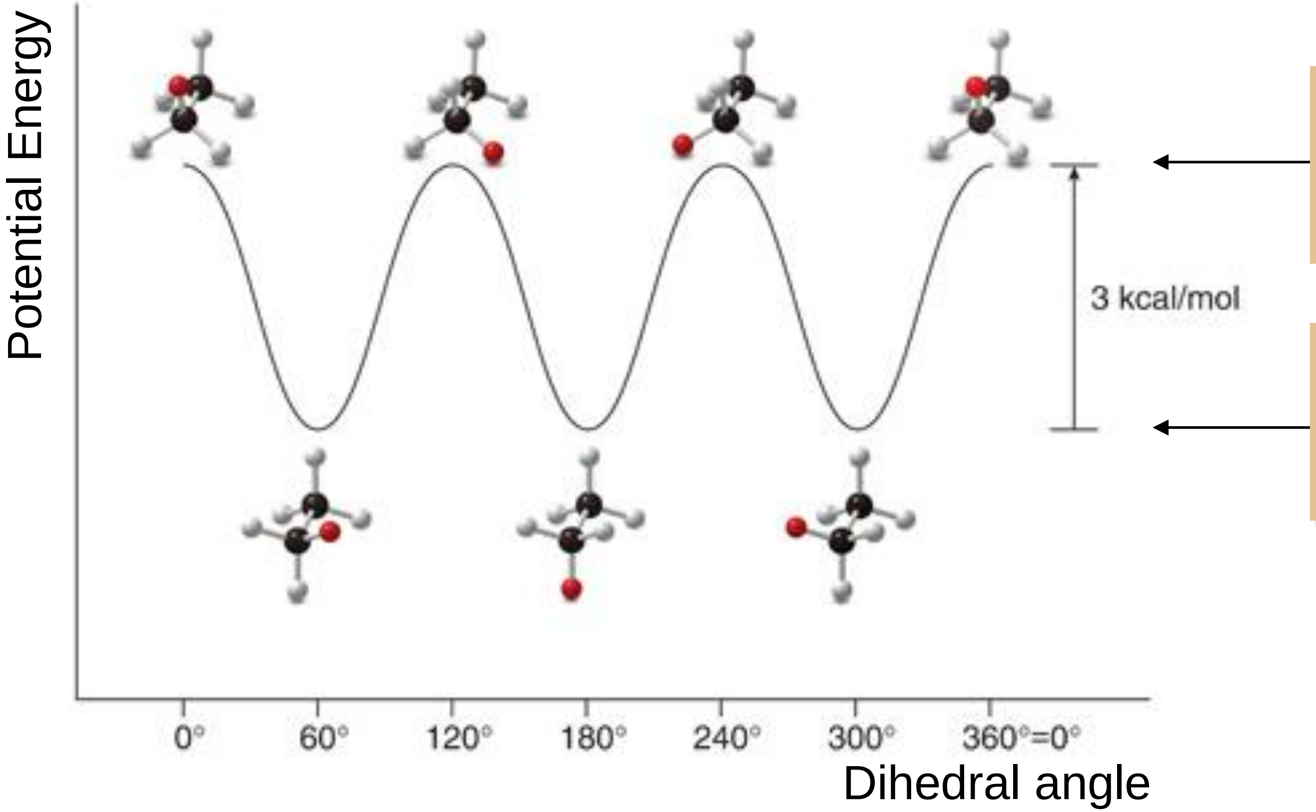
dihedral angle



Dihedral angle
0°



Conformations of Ethane

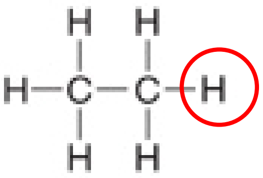


eclipsed
energy
maximum

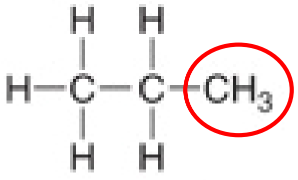
staggered
energy
minimum

Torsional Strain 3.0 kcal/mole

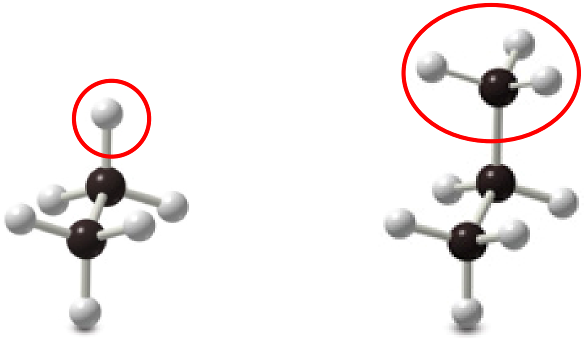
Conformations of Propane

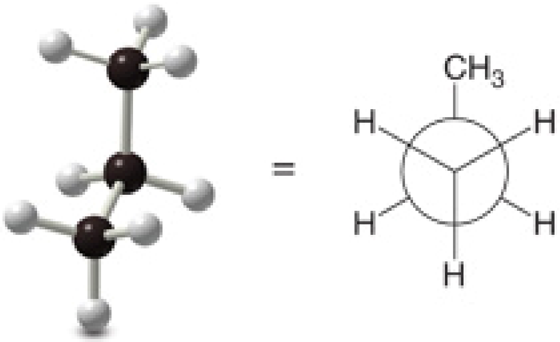


ethane

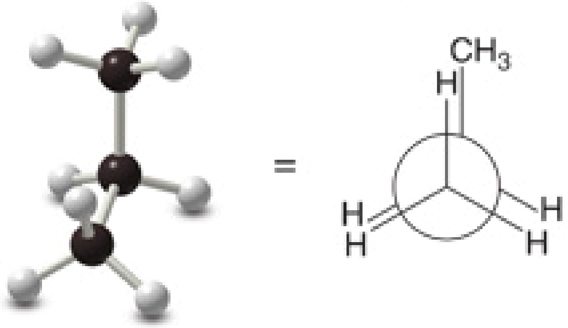


propane



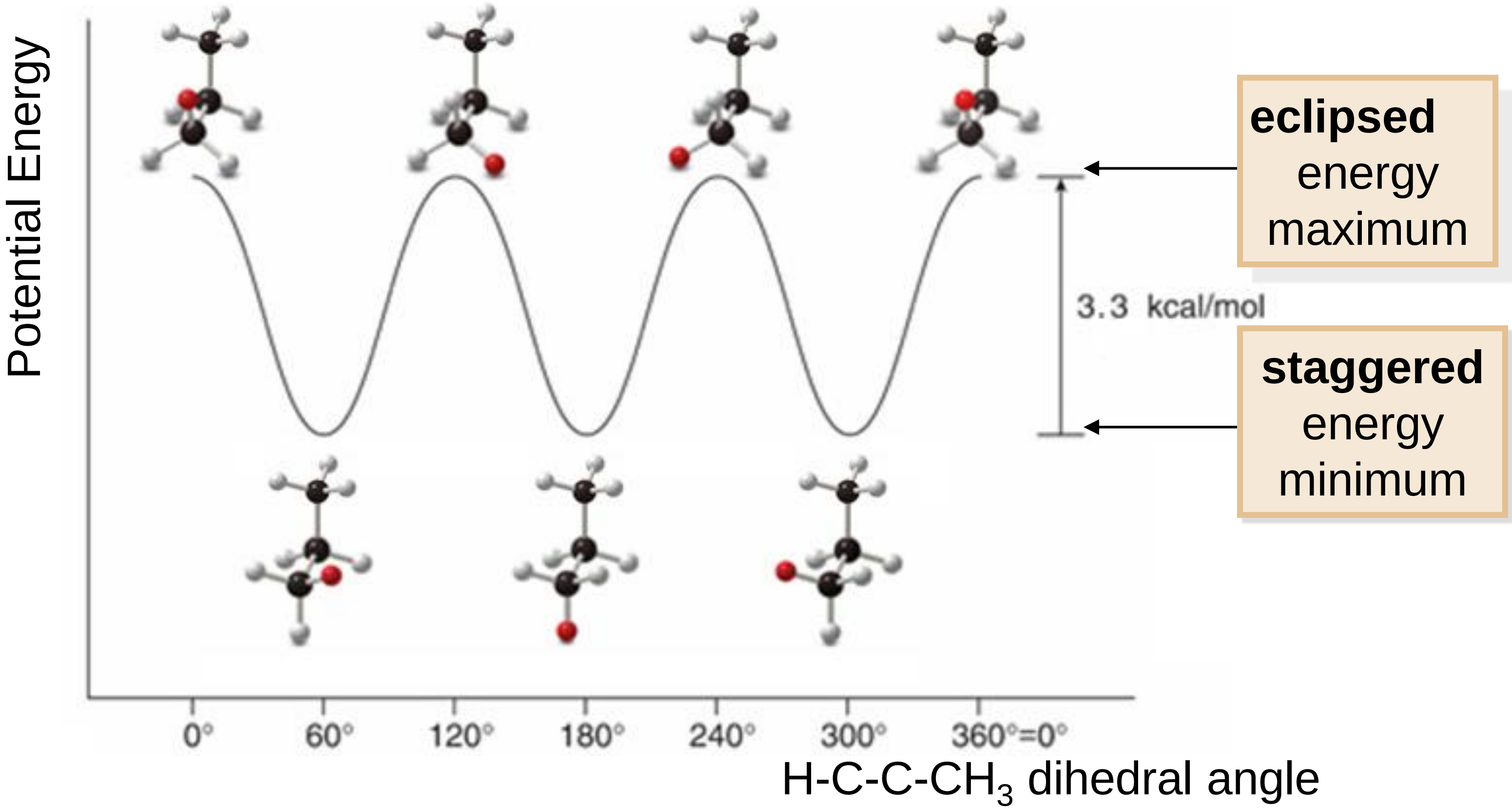


staggered conformation



eclipsed conformation

Conformations of Propane

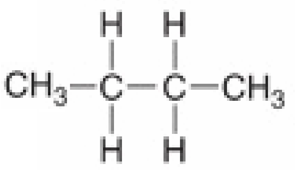


eclipsed energy maximum

staggered energy minimum

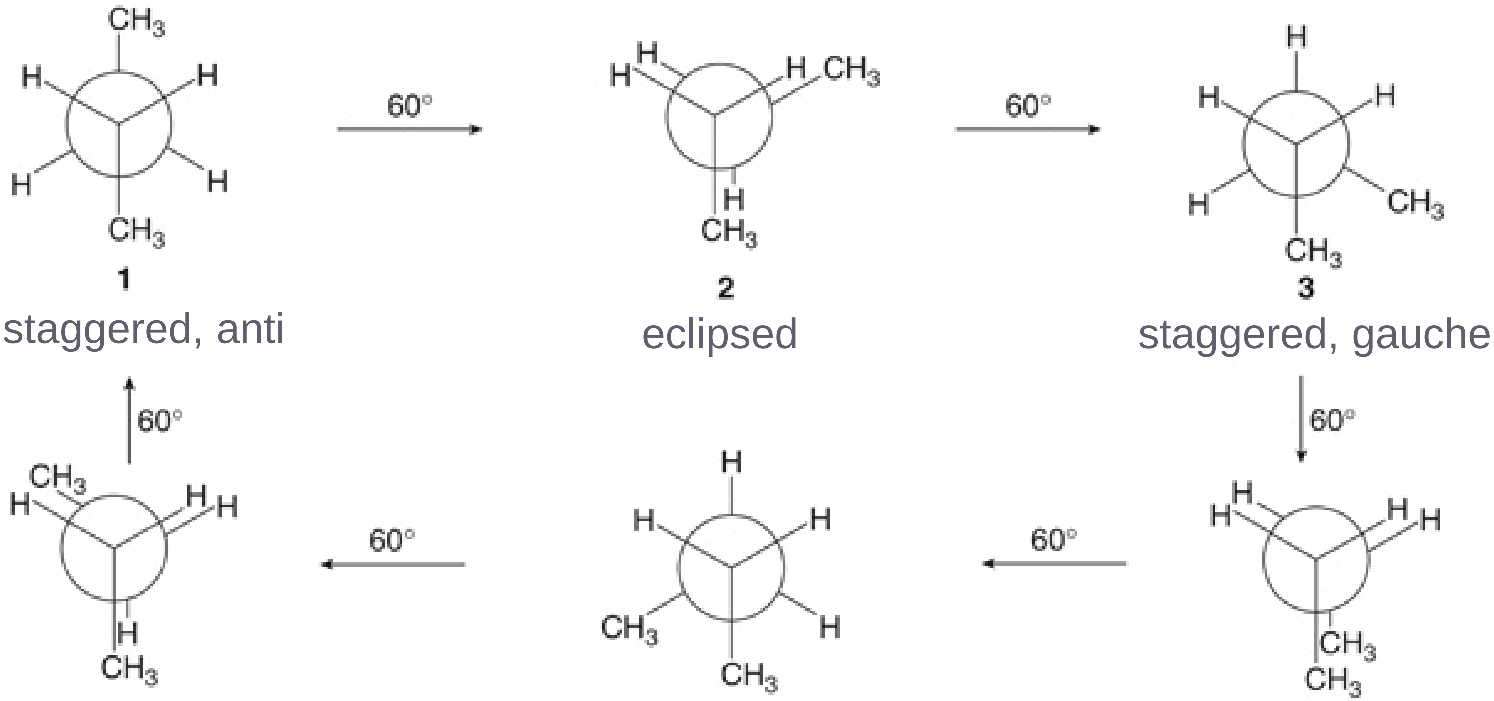
Torsional Strain (3.3 kcal/mole) is higher than in ethane. The methyl group is bulkier than a hydrogen atom

Conformations of Butane



$$CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_3$$

6 different conformations



1 staggered, anti

2 eclipsed

3 staggered, gauche

4 eclipsed

5 staggered, gauche

6 eclipsed

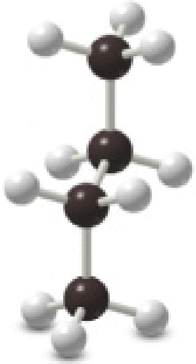
Conformations of Butane

A staggered conformation with two large groups at 180° is called *anti*

A staggered conformation with two large groups at 60° is called *gauche*.

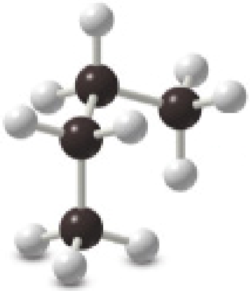
anti conformation

The CH_3 are at 180°



1

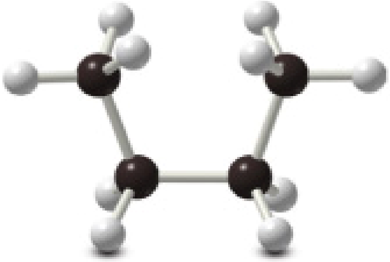
conformazione gauche



3

The CH_3 are at 60°
steric strain

Eclipsed conformation

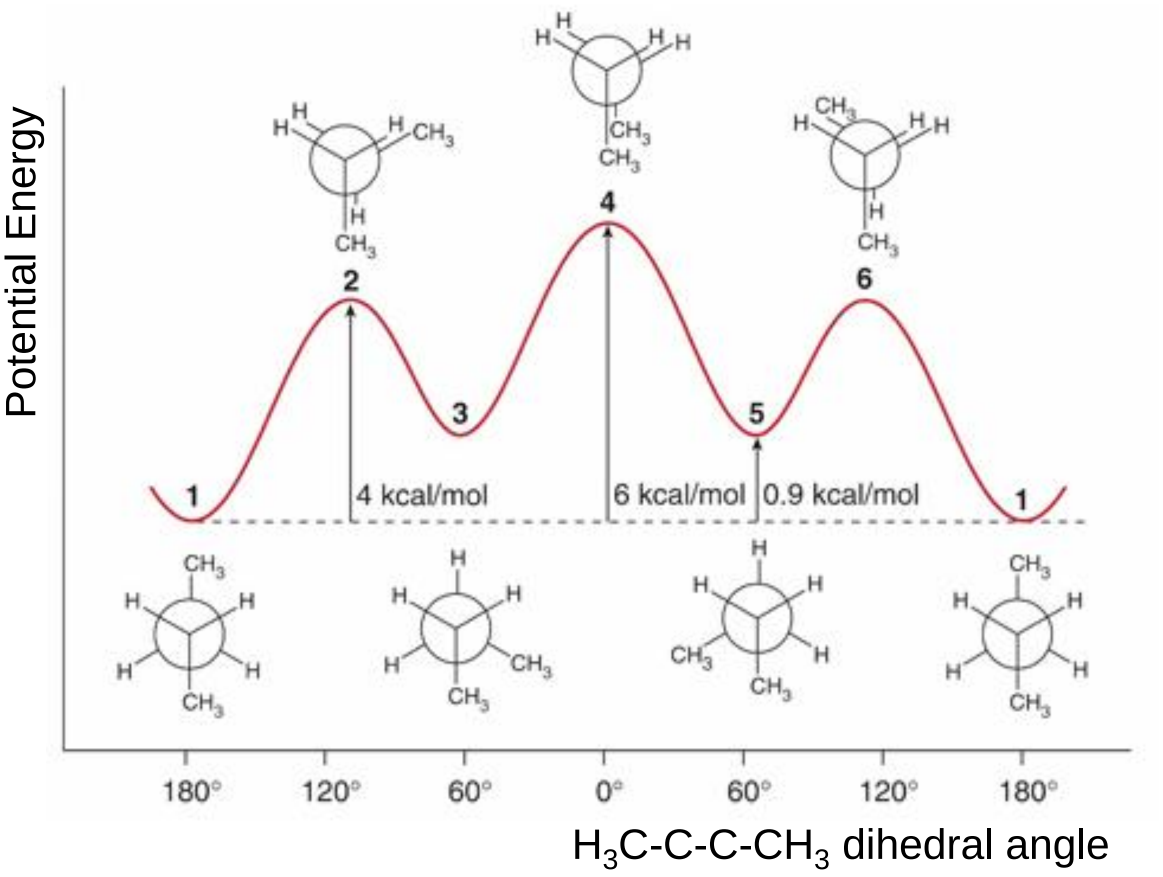


4

The CH_3 are at 0°
steric strain

Conformations of Butane

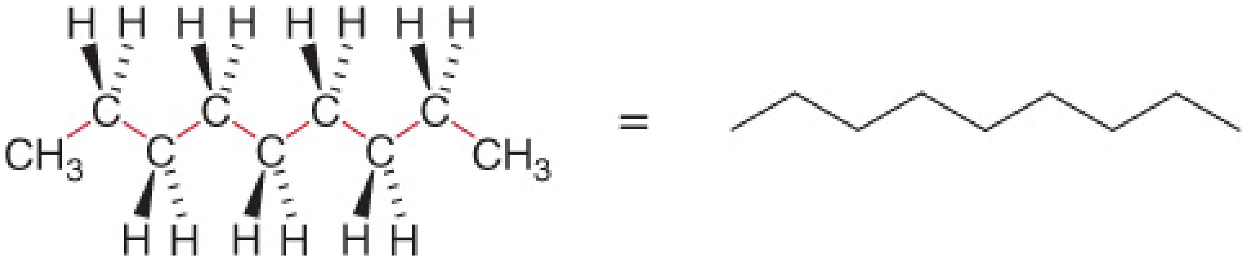
- *Staggered conformations*:
  - **1** (anti) is the absolute minimum
  - **3,5** (gauche) are relative minima
- *Eclipsed conformations:*
  - **4** is the absolute maximum (CH_3 eclipsed)
  - **2,6** are relative maxima



Torsional Strain in Linear Alkanes

Interaction	Energy (kcal/mole)
Eclipsing H,H	1
Eclipsing H,CH_3	1.5
Eclipsing CH_3,CH_3	4
Gauche CH_3,CH_3	0.9

- A rotational barrier is the energy difference between two minima.
- The most stable conformation of linear hydrocarbons is staggered with the bulky groups in anti. Thus long chains are usually drawn with a zigzag.



Cycloalkanes

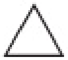
Cycloalkanes

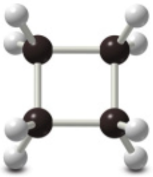
- Cycloalkanes have empirical formula $\mathbf{C_nH_{2n}}$ and contain carbon atoms arranged in a cyclic chain

- Nomenclature: cyclo + name of the corresponding alkane

cyclopropane

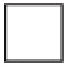
C_3H_6

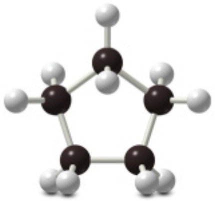




cyclobutane

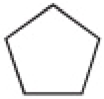
C_4H_8

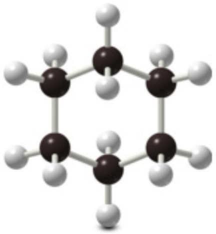




cyclopentane

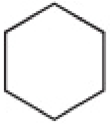
C_5H_{10}





cyclohexane

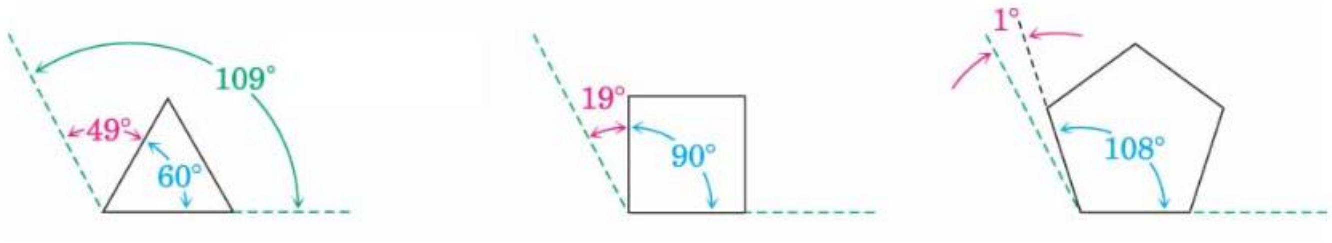
C_6H_{12}



Stability: Angular Strain (Baeyer's Strain)

- Baeyer (1885): as carbon prefers 109° bond angles, rings other than five or six membered may be too strained to exist.

- Cycloalkanes from C_3 to C_{30} do exist, but some of them are strained because of distorted bond angles and other interactions.



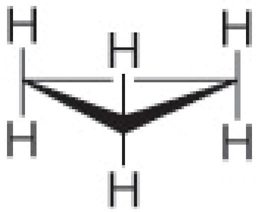
Ring Strain

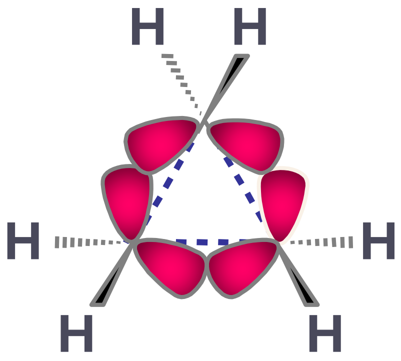
Stability of cycloalkanes depend on ring strain:

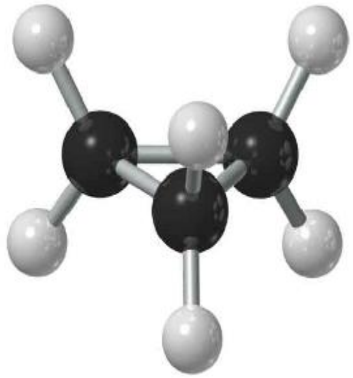
- angle strain: distorted bond angles.
- torsional strain: eclipsing of C-H bonds.
- VdW or steric strain: repulsions between non bonded atoms.

Cyclopropane C_3H_6

- Planar.
- Angle strain: 60° CCC angles.
- Torsional strain: all H are eclipsed.
- May be described as sp^3 hybridized with banana bonds.







Cyclobutane C_4H_8

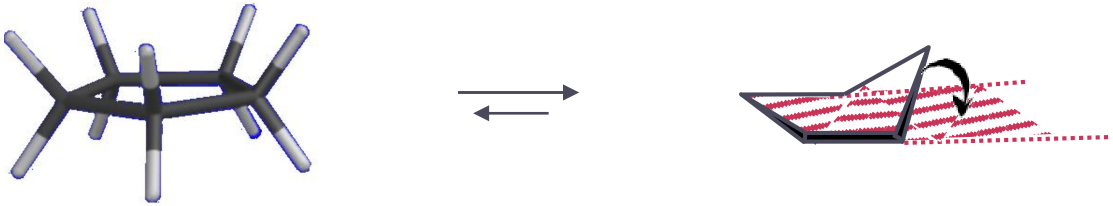
- In planar cyclobutane all hydrogens would be eclipsed.
- To relieve torsional strain, cyclobutane is puckered by about 25°.
- In doing so the CCC bond angles decrease to 88° and hydrogens on opposite carbons become closer.

25°
puckering
angle

Planar
angle strain
torsional strain

Puckered
slightly higher angle strain
lower torsional strain
some VdW strain

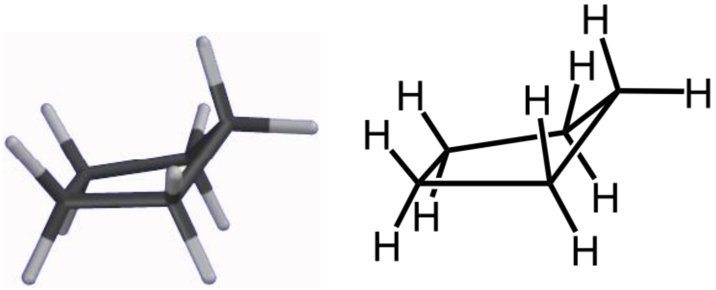
Cyclopentane C_5H_{10}



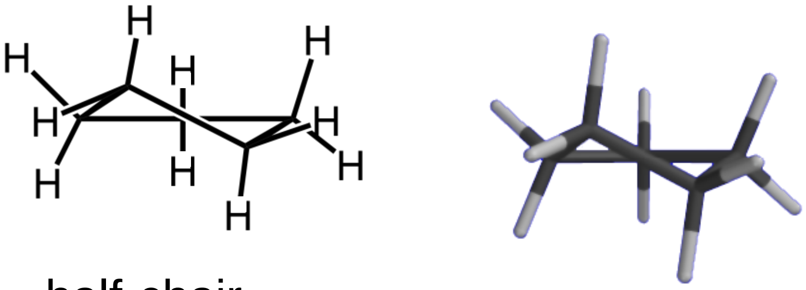
25°
puckering angle

angle strain
torsional strain

“envelope” conformation
eclipsing is partially relieved



envelope



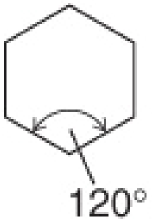
half-chair

envelope and *half-chair* conformations have similar energies and rapidly interconvert into one another

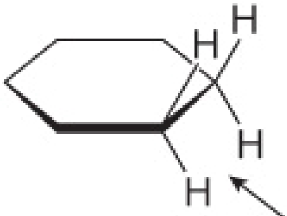
Cyclohexane C_6H_{12}

- Planar cyclohexane.

angle strain



CCC > 109.5°

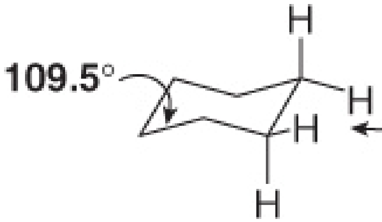


torsional strain

all H are eclipsed

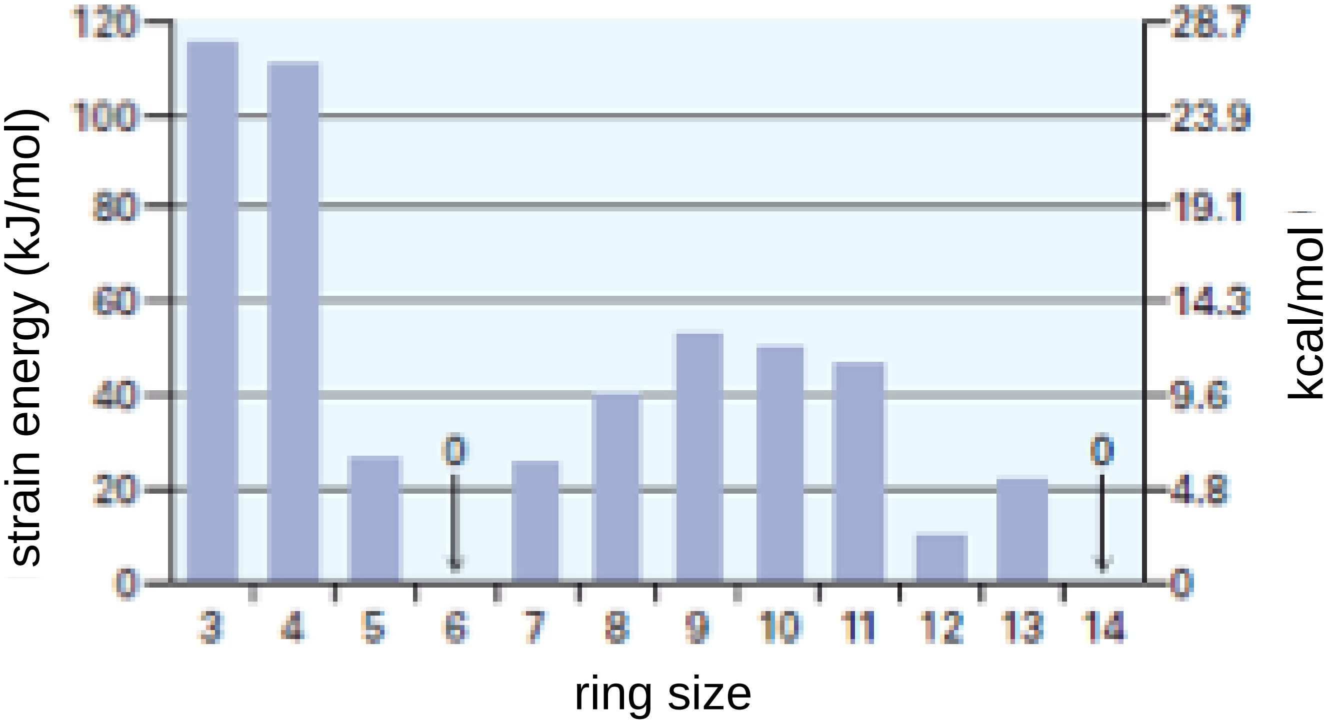
- *Chair* conformation.

strainless



H are staggered

Strain Energies of Cycloalkanes

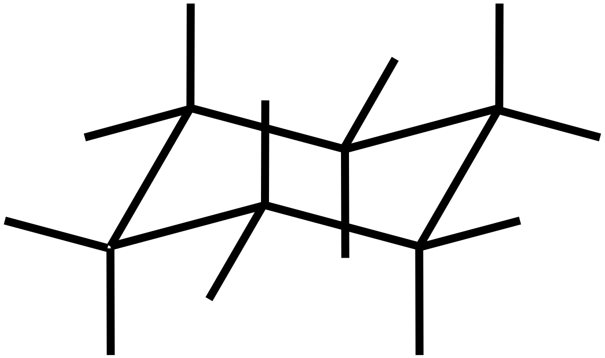


Strain Energies of Cycloalkanes

- Heats of combustion are used to calculate strain energies of cycloalkanes.
- Heats of combustion increase with the number of C atoms.
- Cyclohexane is taken as reference (Strain = 0).

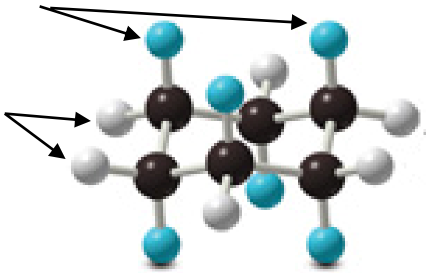
kJ/mol	2091	2724	3290	3910	4599	5264
Per CH_2	697	681	658	653	657	658
Strain	132	112	25	0	28	40

How to Draw Chair Cyclohexane



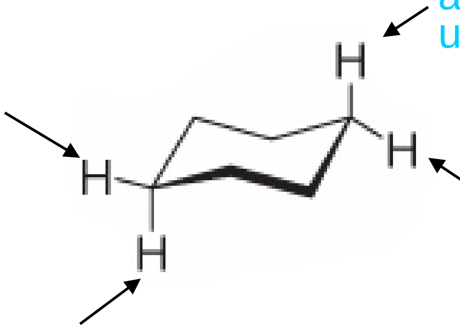
Chair Conformation of Cyclohexane

- There are two types of hydrogens:
  - Axial: perpendicular to the ring’s mid-plane, above and below the ring.
  - Equatorial: in the ring’s mid-plane, all around the ring.



H axial

H equatorial



equatorial upward

axial upward

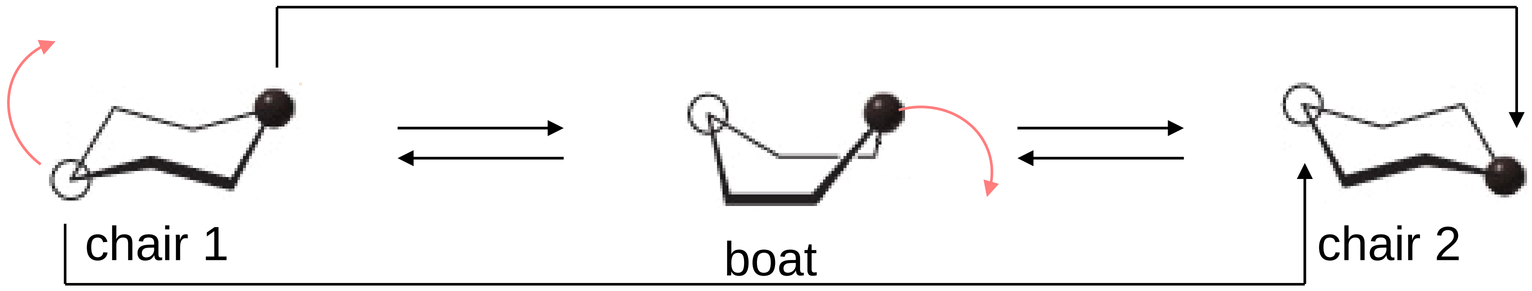
equatorial downward

axial downward

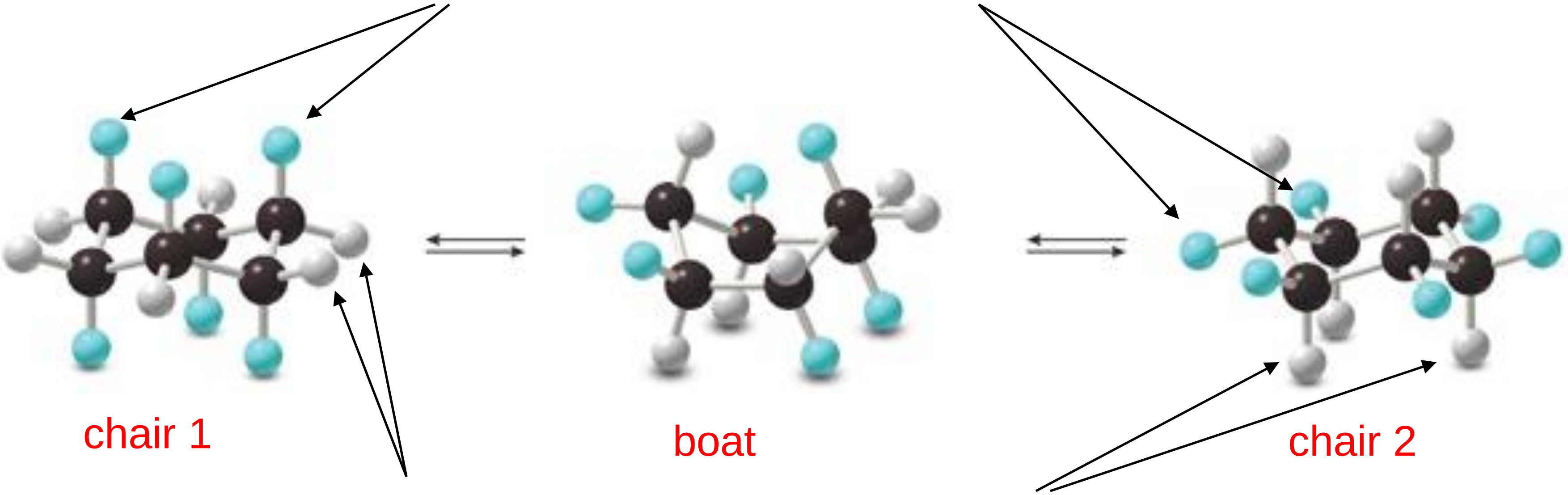
- There are 6 axial and 6 equatorial hydrogens in cyclohexane.

Ring Flipping

- Ring flipping is the interconversion between two chair conformations of cyclohexane.
- Upwards C become dawnwards and viceversa.
- Axial H become equatorial and viceversa.



Ring Flipping



axial H become equatorial

chair 1

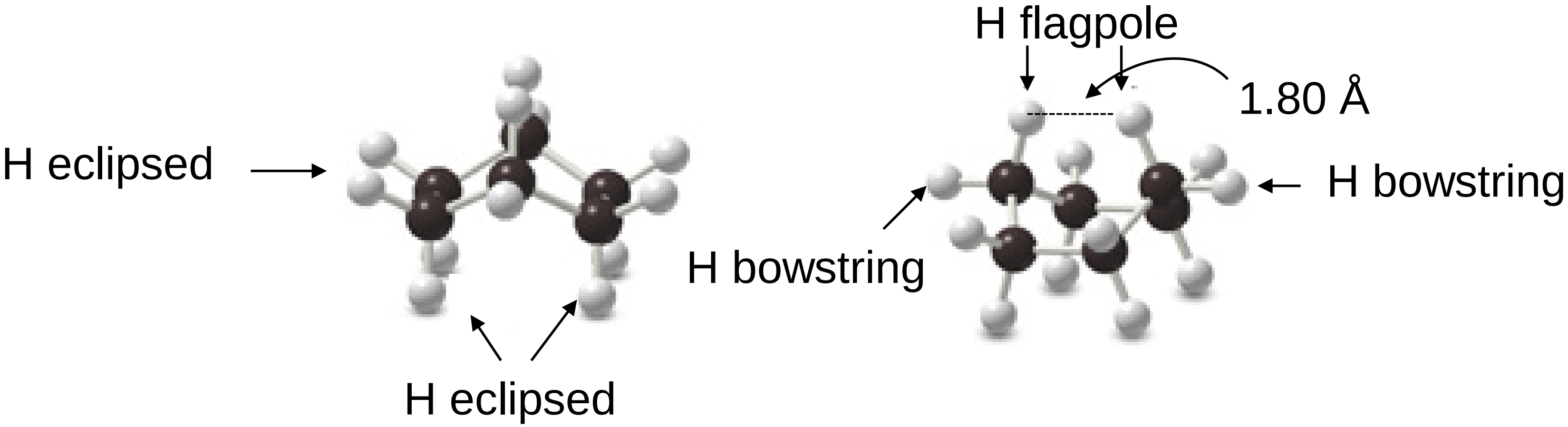
boat

chair 2

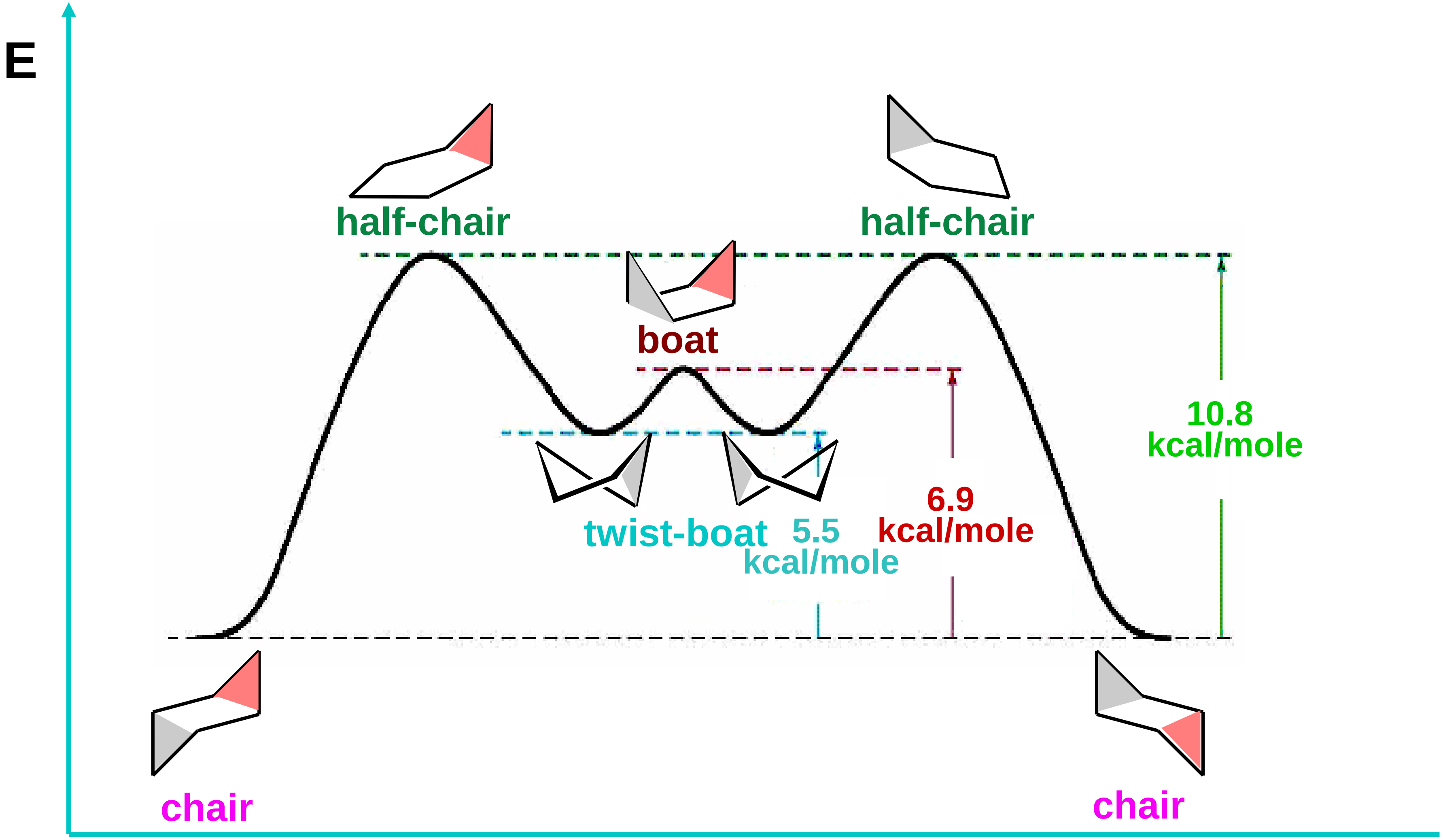
equatorial H become axial

Conformations of Cyclohexane

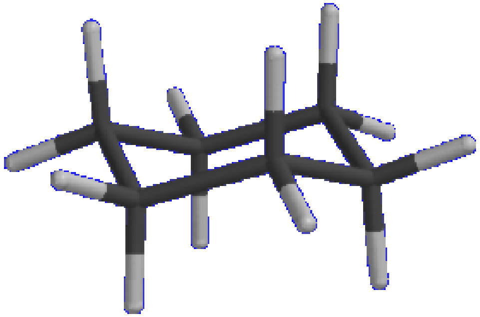
- Chair conformations are 7 kcal/mol more stable than boat conformations.
- Torsional strain. In the boat conformation the H on the base are eclipsed.
- Steric strain. Flag pole H are forced in close proximity.



Conformations of Cyclohexane



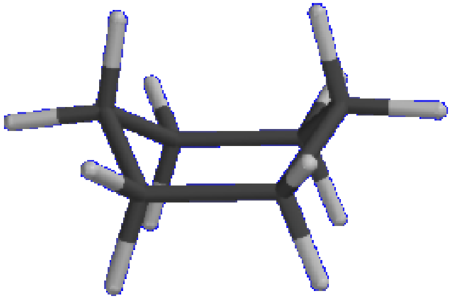
Conformations of Cyclohexane



chair

no ring strain

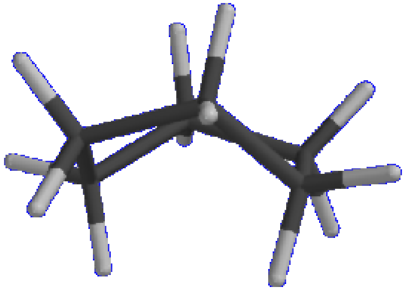
(99.99% at 25°C)



boat

- torsional strain
- steric strain

ring strain: ~ 7 kcal



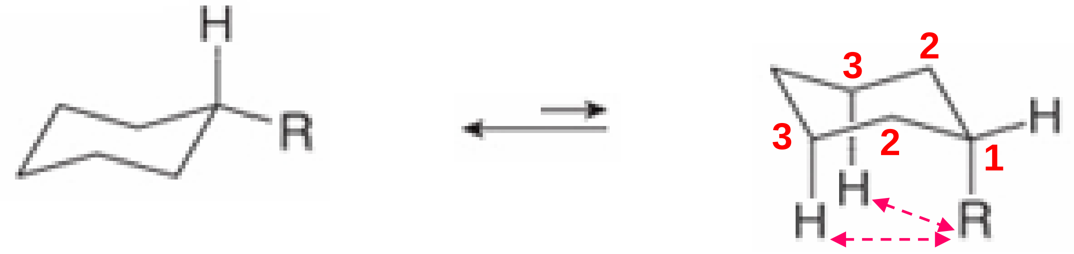
twist-boat

~ 1.5 kcal more stable than the boat

(0.01% at 25°C)

Substitued Cyclohexanes

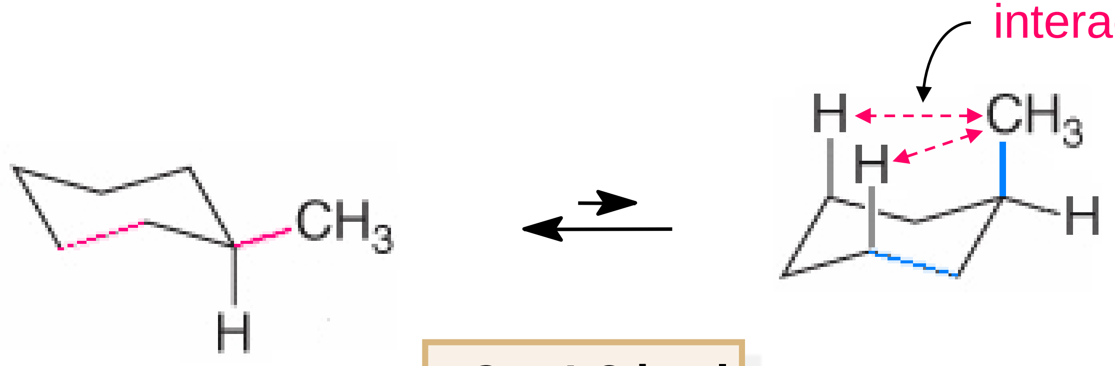
- The chair conformations are no longer equivalent: they have different energies.



- The axial conformer is destabilized by 1,3-diaxial interactions (VdW interactions) between the substituent and axial hydrogens.
- The larger the substituent, the less stable the axial conformation.

Methylcyclohexane

equatorial
(95%)
no steric strain



1,3-diaxial
interactions

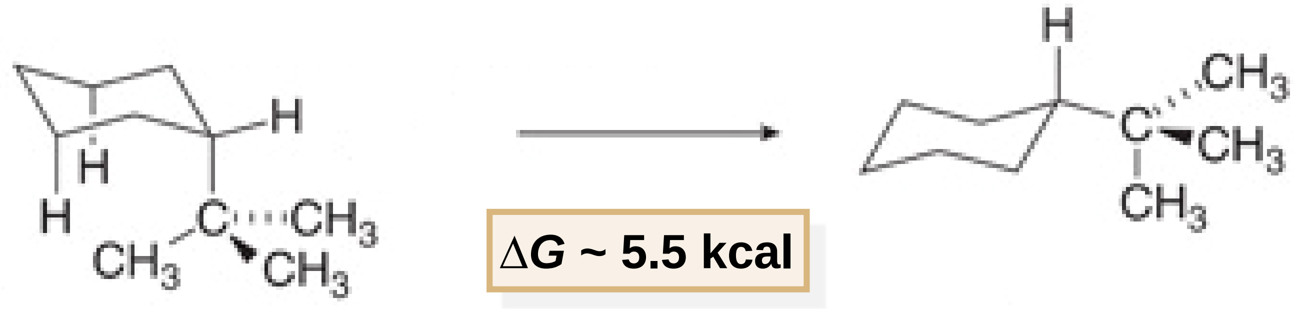
axial
(5%)
steric
repulsion

ΔG ~ 1.8 kcal

Each CH_3 / H interaction destabilizes the axial conformer by 0.9 kcal/mol

tert-Butylcyclohexane

- The *tert*-butyl group is so bulky that there is no axial conformer at the equilibrium.



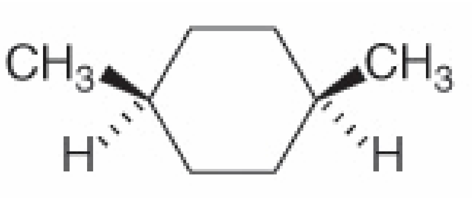
ΔG ~ 5.5 kcal

< 0.01% **> 99.99%**

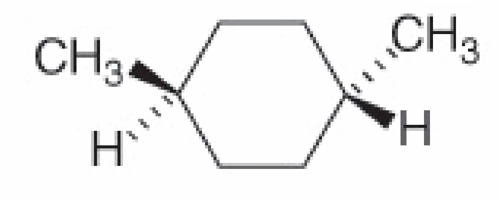
The *tert*-butyl group freezes the conformational equilibrium.

Disubstitued Cyclohexanes. Geometrical Stereoisomerism

- There are two isomers of 1,4-dimethylcyclohexane.



cis

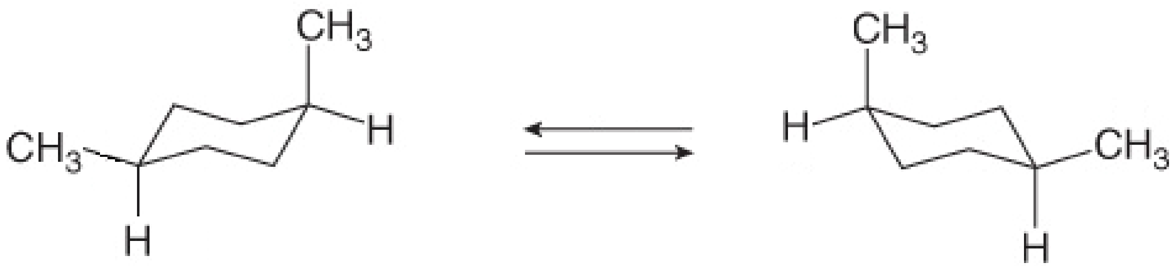


trans

- Each geometrical isomer has two possible chair conformations.

1,4-Dimethylcyclohexane

cis

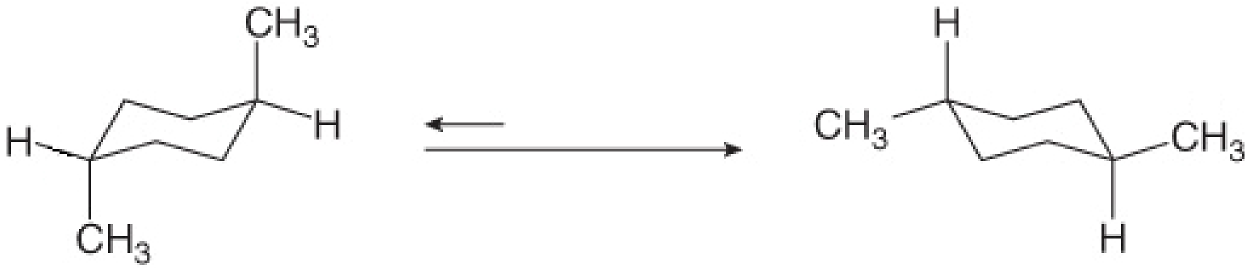


equatorial-axial
2 1,3-diaxial interactions
2 x 0.9 = 1.8 kcal

axial-equatorial
2 1,3-diaxial interactions
2 x 0.9 = 1.8 kcal

Δ*G* = 0 kcal

trans



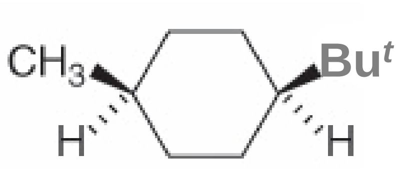
bisaxial
4 1,3-diaxial interactions
4 x 0.9 = 3.6 kcal

bisequatorial
no repulsions

Δ*G* ~ 3.6 kcal

cis-1-*t*-Butyl-4-methylcyclohexane

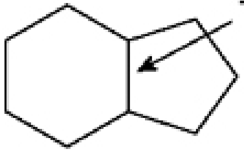
- The conformational equilibrium is frozen by the bulky t-butyl group.



5.5 kcal/mol 1.8 kcal/mole **ΔG ~ 3.7 kcal**

Polycyclic compounds

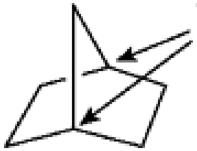
A fused bicyclic system



This C–C bond is **shared** by both rings.

- One bond is shared by two rings.
- The shared C's are adjacent.

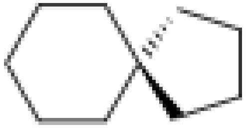
A bridged bicyclic system



These C's are **shared** by two rings.

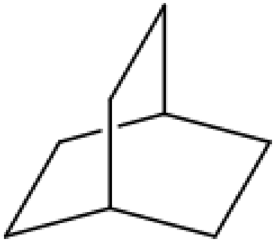
- Two non-adjacent atoms are shared by both rings.

A spiro bicyclic system

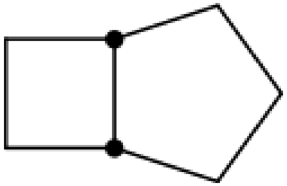


- One atom is shared by two rings

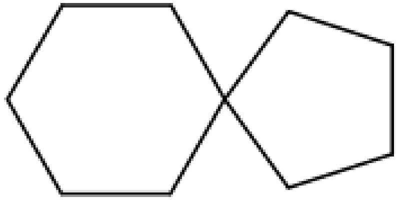
Polycyclic compounds



bicyclo[2.2.2]octane



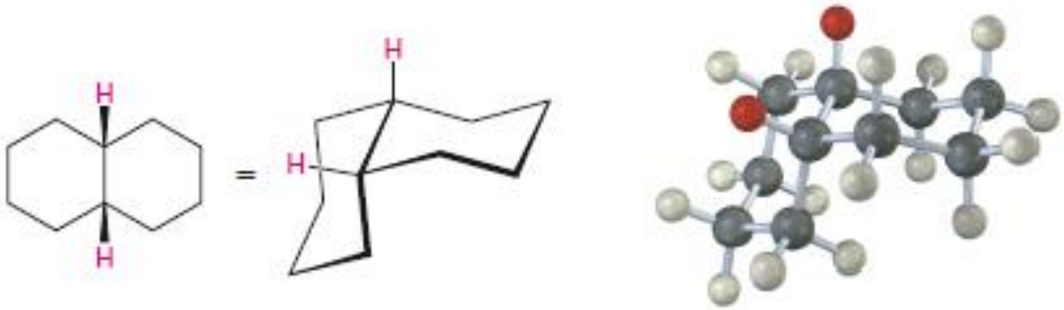
bicyclo[3.2.0]heptane



spiro[4,5]decane

Polycyclic Hydrocarbons

less stable
(1 axial substituent)

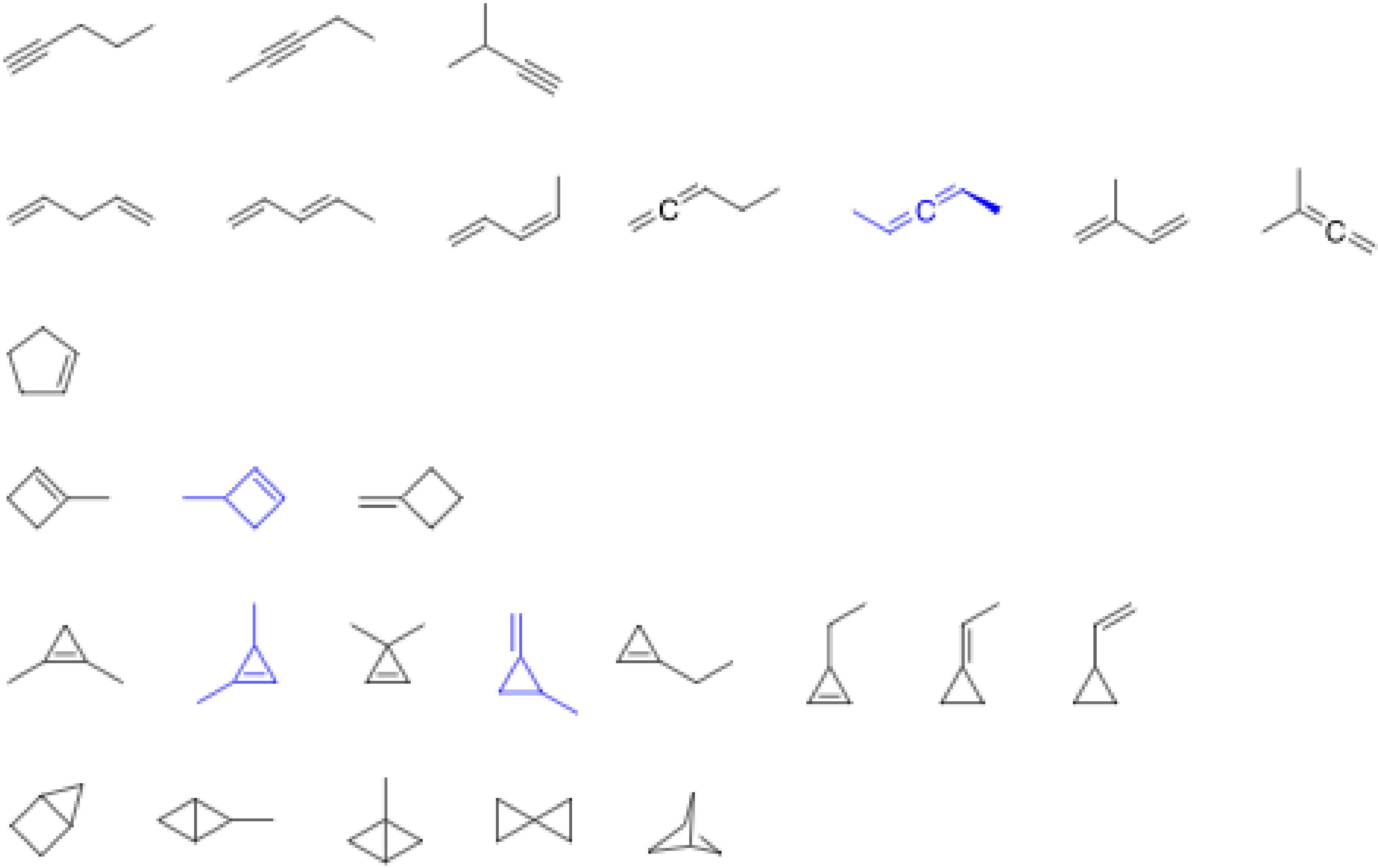


cis-decaline

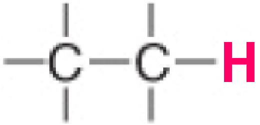
more stable
(equatorial substituents)

trans-decaline

C5H8 Isomers



Reactions of Alkanes



- no lone pairs
- no π bonds
- no heteroatoms
- not nucleophilic
- not electrophilic
- strong, not polar C–C, C–H bonds

Alkanes react only at high temperatures, with radical mechanisms.

Halogenation of Alkanes

Chapt. 10 Organic Chemistry, 8th Edition
John E. McMurry

Halogenation of Alkanes

- In the presence of heat or light, alkanes react with halogens, with a radical mechanism, to give alkyl halides.

$$R{-}H + X_2 \xrightarrow{\Delta \text{ or } h\nu} R{-}X + HX$$

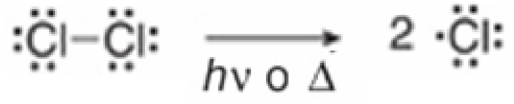
radical substitution

- Halogenation of alkanes is carried out with Cl_2 o Br_2. The reaction with F_2 is too violent and the reaction with I_2 is too slow.

Halogenation of Methane

Initiation

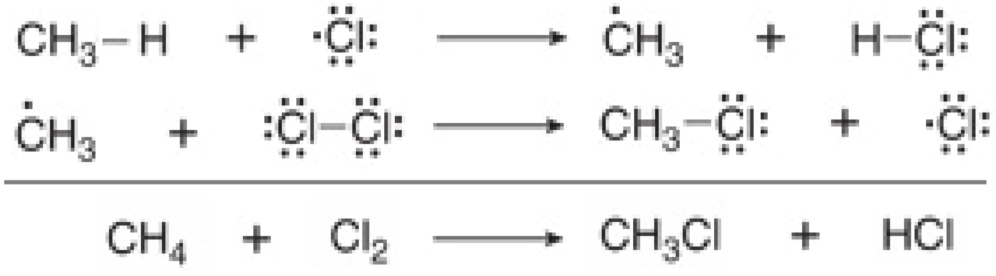
Stage [1]: formation of Cl· radicals



$$\mathrm{:\ddot{Cl}-\ddot{Cl}:} \xrightarrow[h\nu \text{ o } \Delta]{} 2\ \cdot\mathrm{\ddot{Cl}:}$$

Propagation

Stages [2] and [3]: A new radical is formed for each reacting radical

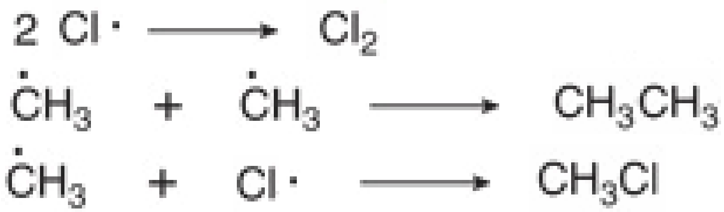


$$\mathrm{CH_3-H} + \cdot\mathrm{\ddot{Cl}:} \longrightarrow \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{H-\ddot{Cl}:}$$
$$\dot{\mathrm{C}}\mathrm{H_3} + \mathrm{:\ddot{Cl}-\ddot{Cl}:} \longrightarrow \mathrm{CH_3-\ddot{Cl}:} + \cdot\mathrm{\ddot{Cl}:}$$
$$\mathrm{CH_4} + \mathrm{Cl_2} \longrightarrow \mathrm{CH_3Cl} + \mathrm{HCl}$$

thousands of cycles.
Chain reaction

Termination

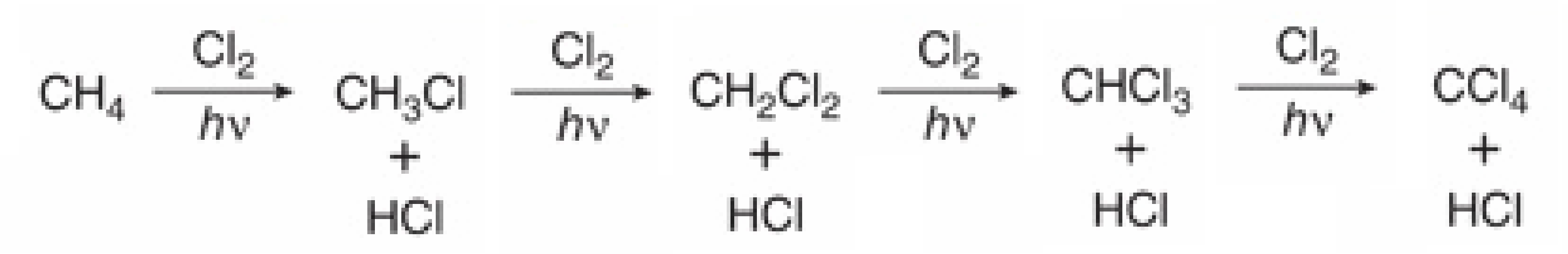
Stage [4]: Two radicals recombine forming a σ bond.



$$2\ \mathrm{Cl}\cdot \longrightarrow \mathrm{Cl_2}$$
$$\dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{C}}\mathrm{H_3} \longrightarrow \mathrm{CH_3CH_3}$$
$$\dot{\mathrm{C}}\mathrm{H_3} + \mathrm{Cl}\cdot \longrightarrow \mathrm{CH_3Cl}$$

Halogenation of Alkanes

- Monohalogenation is only possible with an excess of substrate, otherwise polyhalogenation predominates.

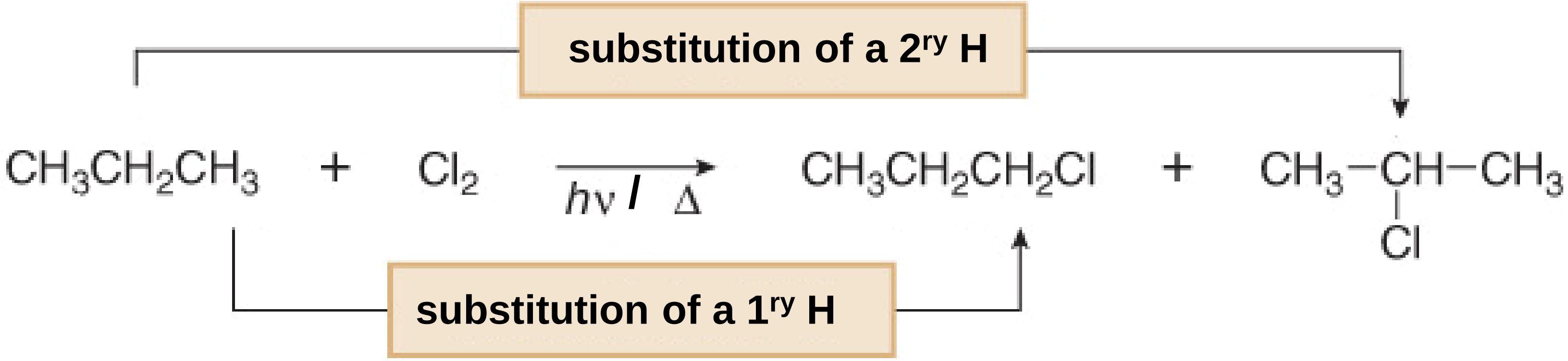


$$CH_4 \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\underset{+}{CH_3Cl}} \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\underset{+}{CH_2Cl_2}} \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\underset{+}{CHCl_3}} \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\underset{+}{CCl_4}}$$

- Problem: mixture of halogenated products.
- Solution: CH_4 in large excess and recycled.

Regioselectivity

- Isomers are formed in the halogenation of propane and higher hydrocarbons:



substitution of a 2ry H

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[h\nu\ /\ \Delta]{} CH_3CH_2CH_2Cl + CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

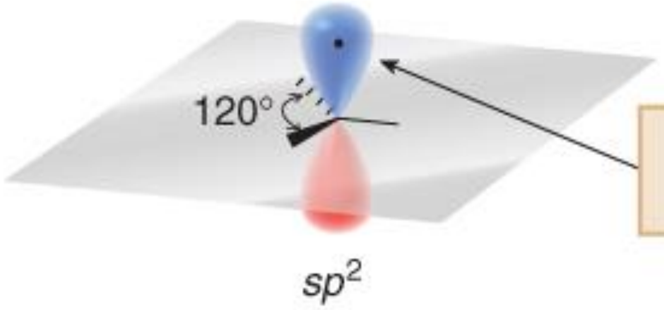
substitution of a 1ry H

statistical ratio	3	:	1
observed ratio	1	:	1

Structure of Radicals

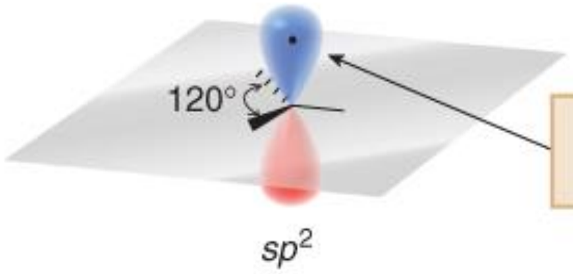
- Alkyl radicals are *sp*^{2} hybridized with a trigonal planar geometry.
- The p orbital contains an unpaired electron.

$\dot{C}H_3$	$R\dot{C}H_2$	$R_2\dot{C}H$	$R_3\dot{C}$
methyl radical	**1^{ry} radical**	**2^{ry} radical**	**3^{ry} radical**



a single electron in the p orbital

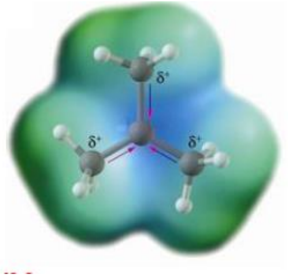
Stabilità dei radicali



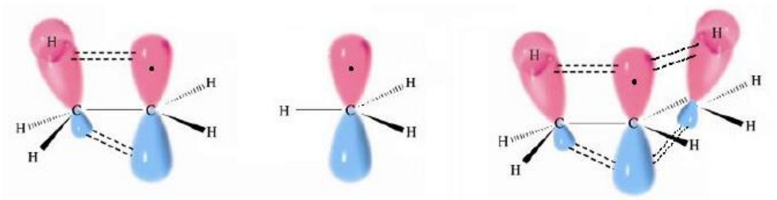
1 solo elettrone in un orbitale π

$\dot{C}H_3$	$R\dot{C}H_2$	$R_2\dot{C}H$	$R_3\dot{C}$
Radicale metile	**1ry**	**2ry**	**3ry**

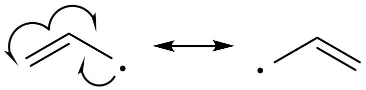
I gruppi alchilici hanno un effetto elettrondonatore e stabilizzano il radicale



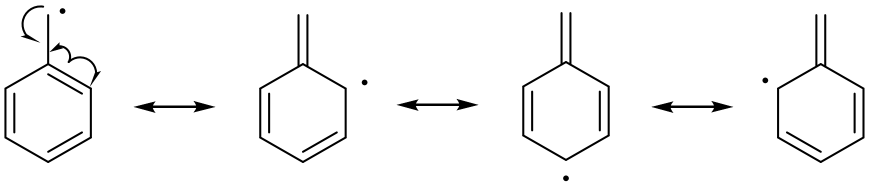
effetto induttivo



iperconiugazione



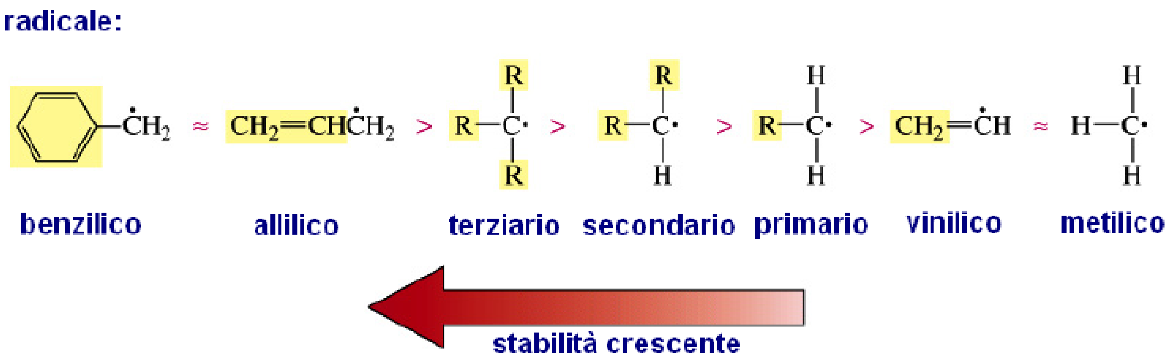
radicale allilico

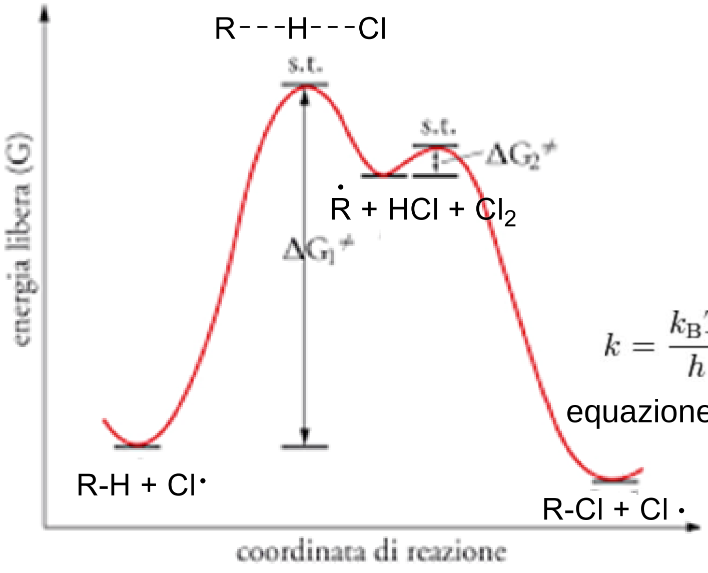


radicale benzilico

risonanza

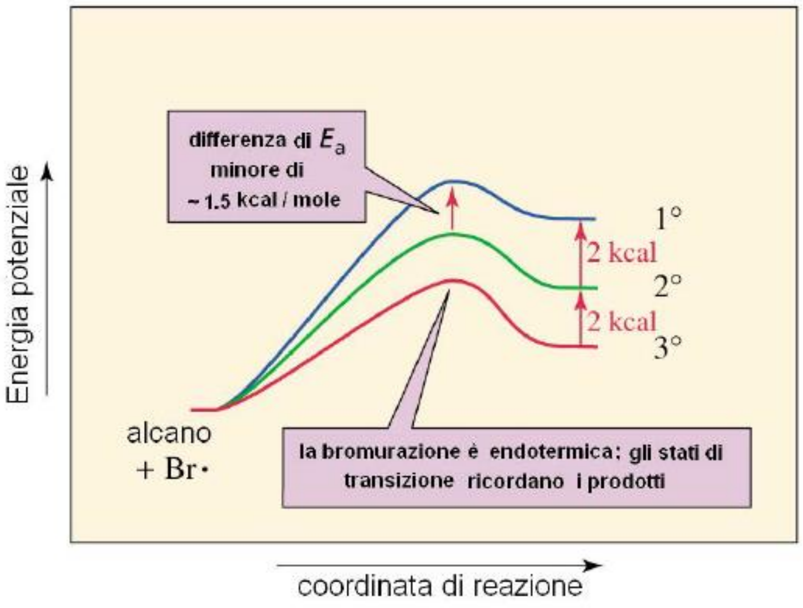
Stabilità dei radicali





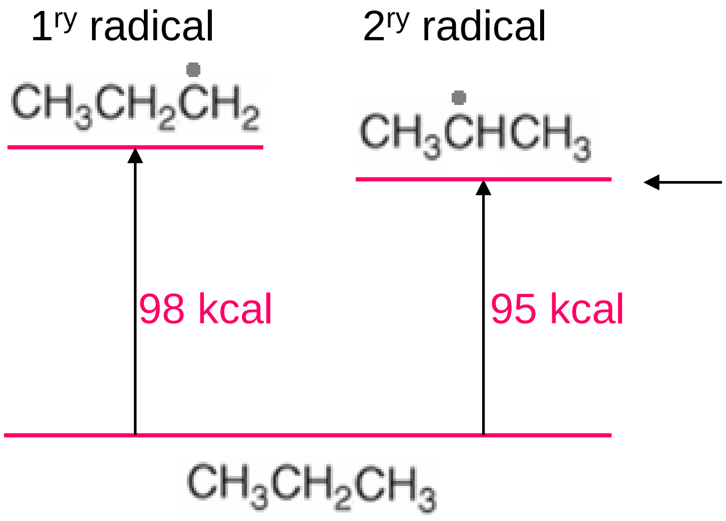
$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

equazione di Eyring



Si forma più velocemente il radicale più stabile e quindi il prodotto che deriva da quel radicale.

Regioselectivity



1^{ry} radical

$CH_3CH_2\dot{C}H_2$

2^{ry} radical

$CH_3\dot{C}HCH_3$

98 kcal

95 kcal

$CH_3CH_2CH_3$

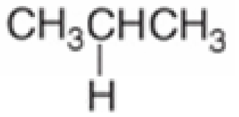
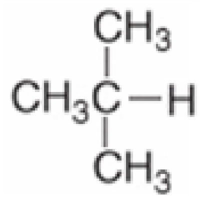
Lower energy, more stable, weaker C-H bond.

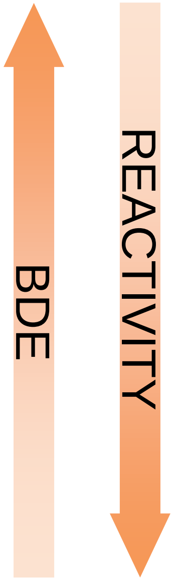
- Radical stability: $3^{ry} > 2^{ry} > 1^{ry}$.
- Strength of C-H bonds: $3^{ry} < 2^{ry} < 1^{ry}$.

C−H Bond Dissociation Energies

R−H → R• + H•

D*H* = BDE bond dissociation energy

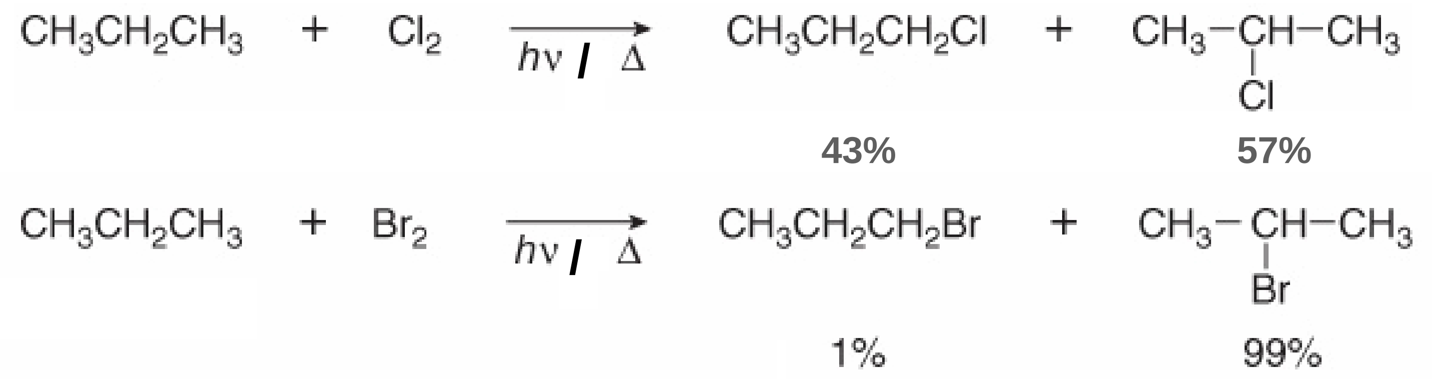
CH_3-H	**104 kcal/mole**	
CH_3CH_2-H	**98 kcal/mole**	
$CH_3CH_2CH_2-H$	**98 kcal/mole**	**(1ry C-H)**
 $CH_3\underset{\displaystyle H}{\underset{\vert}{C}}HCH_3$	**95 kcal/mole**	**(2ry C-H)**
 $CH_3\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-H$	**91 kcal/mole**	**(3ry C-H)**



Reactivity of C−H bonds:
$3^{ry} > 2^{ry} > 1^{ry} > CH_3-H$

Reactivity and Selectivity

- Chlorination of alkanes is faster than bromination.
- Bromination of alkanes is more selective.



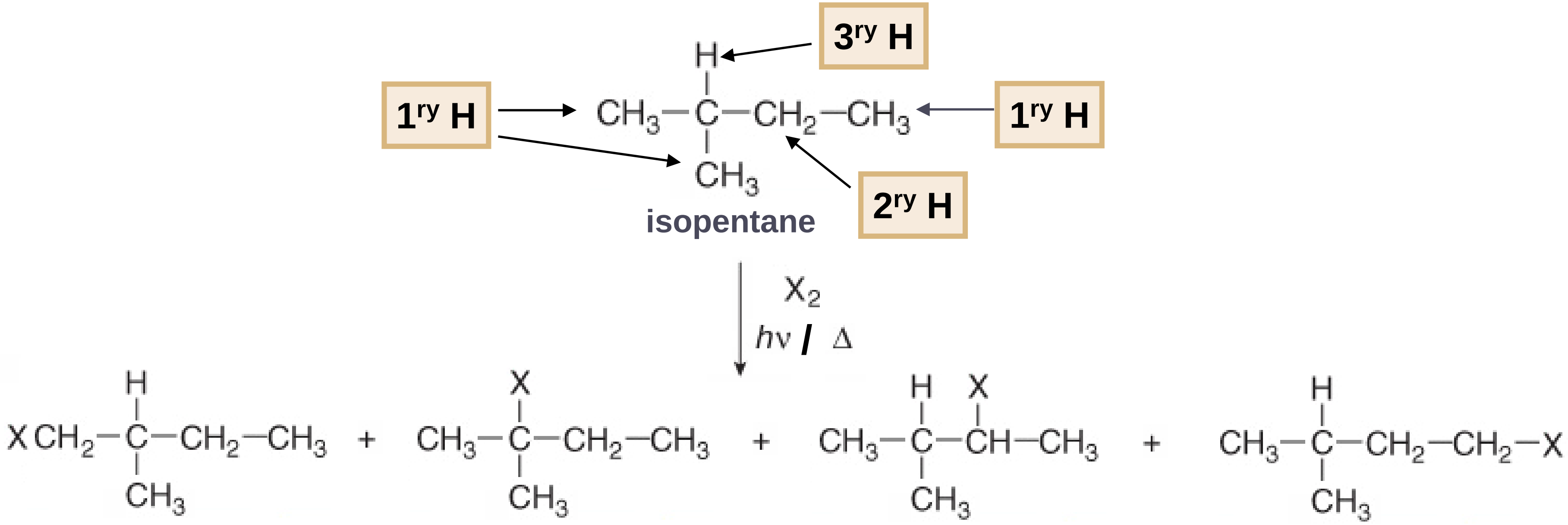
$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[h\nu\ /\ \Delta]{} CH_3CH_2CH_2Cl + CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$$

43% 57%

$$CH_3CH_2CH_3 + Br_2 \xrightarrow[h\nu\ /\ \Delta]{} CH_3CH_2CH_2Br + CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$$

1% 99%

Regioselectivity



Cl_2:	28%	23%	35%	14%
Br_2:	~0%	90%	9%	~0%

C-H relative reactivity	3ry	2ry	1ry
with Cl_2	5.2	3.9	1
with Br_2	1640	82	1

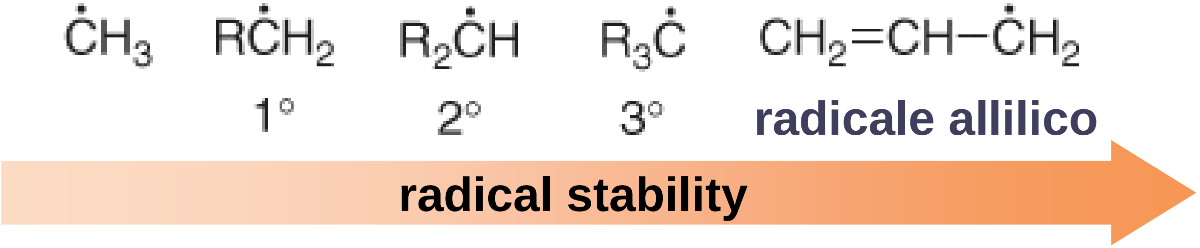
Halogenation of Allylic Carbons

- Allylic carbons are *sp*^{3} carbons adjacent to a double bond.
- A resonance-stabilized allylic radical is obtained by omolysis of an allylic C−H bond.

$$CH_2{=}CH{-}CH_2{-}H \longrightarrow CH_2{=}CH{-}\dot{C}H_2 \quad + \quad \cdot H \qquad \Delta H^\circ = +87\ \text{kcal/mol}$$

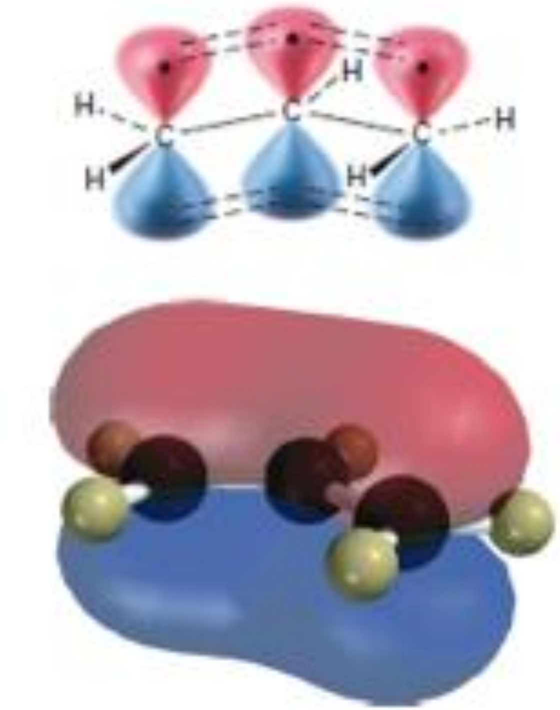
allylic radical

- BDEs of allylic C−H bonds are approximately 4 kcal/mol lower than BDE for 3ry C−H bonds.
- The delocalized allylic radical is more stable than a 3ry radical.

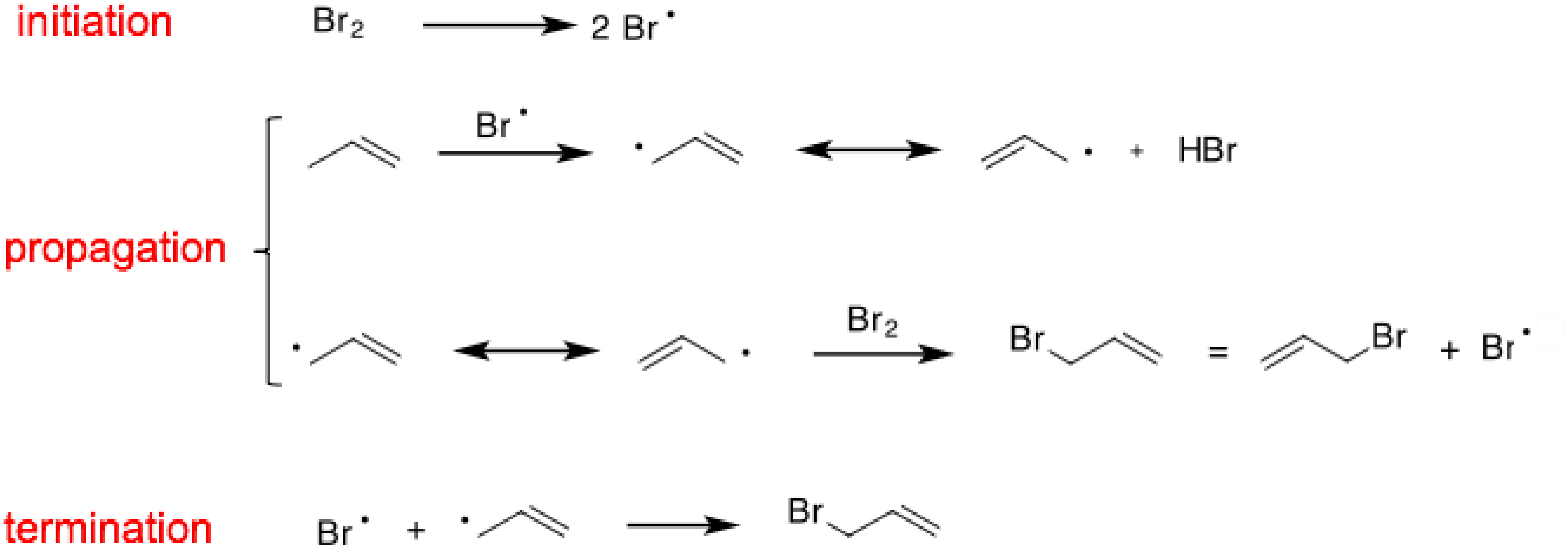


$\dot{C}H_3$ $\quad R\dot{C}H_2$ $\quad R_2\dot{C}H$ $\quad R_3\dot{C}$ $\quad CH_2{=}CH{-}\dot{C}H_2$

The Allylic Radical

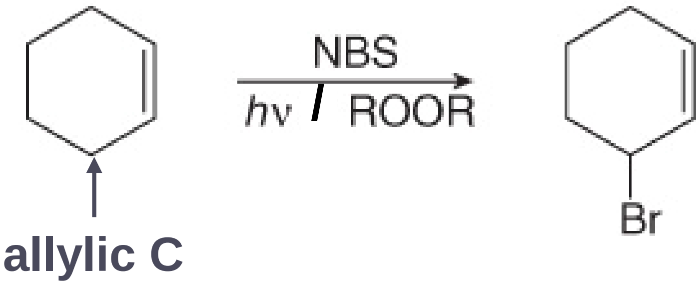


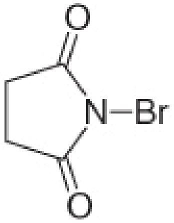
Halogenation of Allylic Carbons



Halogenation of Allylic Carbons

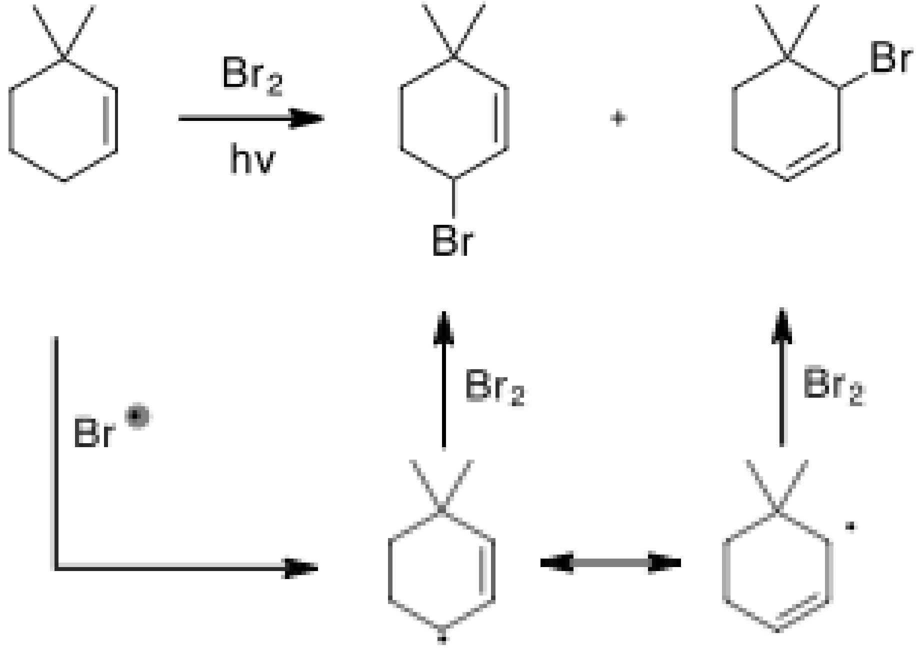
- Allylic carbons can be selectively brominated with NBS and UV irradiation or a radical initiator.
- Breaking of the weak N-Br bond of NBS initiates the radical chain reaction.





N-bromosuccinimide
NBS

Halogenation of Allylic Carbons



Combustion

- Combustion is a redox reaction. C is oxidized and O is reduced.
- All hydrocarbons burn giving carbon dioxide, water and heat ($\Delta H < 0$).
- C−C e C−H bonds are converted into C-O and H-O bonds.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \text{heat}$$

$$(CH_3)_3CCH_2CH(CH_3)_2 + (25/2)\,O_2 \longrightarrow 8\,CO_2 + 9\,H_2O + \text{heat}$$

isoottano

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \longrightarrow n\,CO_2 + (n+1)H_2O + \text{heat}$$

Every C atom is converted into CO_2

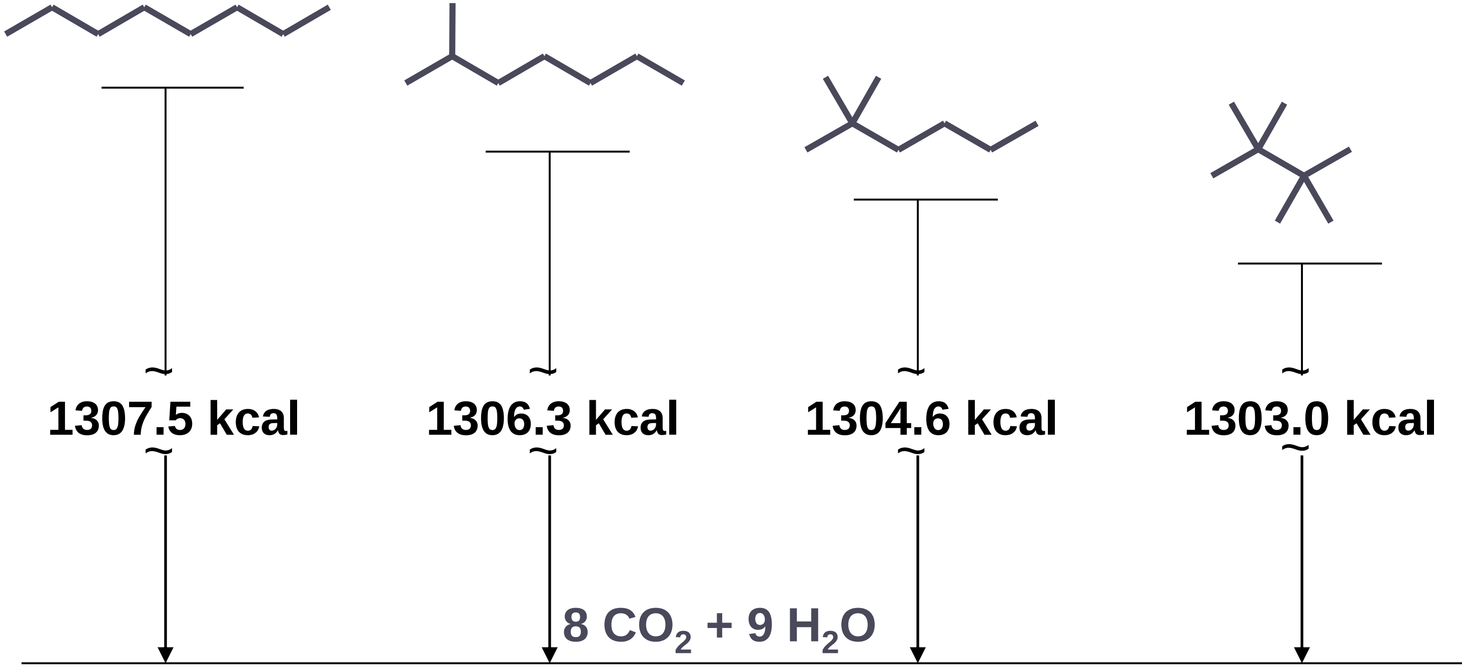
Strain Energies of Cycloalkanes

- Heats of combustion are used to calculate strain energies of cycloalkanes.
- Heats of combustion increase with the number of C atoms.
- Cyclohexane is taken as reference (Strain = 0).

kJ/mol	2091	2724	3290	3910	4599	5264
Per CH_2	697	681	658	653	657	658
Strain	132	112	25	0	28	40

Stability of Isomers

- Heats of combustion are used to compare the stability of isomers. E.g.: C_8H_{18}



1307.5 kcal **1306.3 kcal** **1304.6 kcal** **1303.0 kcal**

$8\ CO_2 + 9\ H_2O$

Branched isomers are more stable than linear ones.