CHEM 261 Fall 2024 September 19, 2024

RECALL:

Bond Energy

Example: Radicals Change in enthalpy = bond energy

$$H-CH_3 \rightleftharpoons H\bullet + \bullet CH_3$$

Bond	Bond Energy (kcal/mol)
H-C	99
H-O	111
C-C	83
C=O	179
O=O	119

At room temperature: there is an available energy of 15-20 kcal/mole

e.g.) Methane (CH_4)

$CH_4 + 2\ O_2 \xrightarrow{\Delta} CO_2 + 2\ H_2O$ – Exothermic reaction (releases Energy (E))

$\Delta E_{reaction} = \Delta E_{SM} - \Delta E_{pdt}$ (SM=starting material, pdt= product)

For CH_4:
4 x C-H bonds = 4 x 99 = 396 kcal/mol
2 x O=O = 2 x 119 = $\underline{238\text{ kcal/mol}}$
ΔE_{SM} = 634 kcal/mol

ΔE_{SM} = sum of bonds broken (enthalpy)

For products:
2 C=O = 2 x 179 = 358 kcal/mol
4 H-O = 4 x 111 = $\underline{444\text{ kcal/mol}}$
ΔE_{pdt} = 802 kcal/mol

ΔE_{pdt} = sum of bonds formed

$\Delta E_{reaction}$ = 634 kcal/mol – 802 kcal/mol = -168 kcal/mol (a negative energy result means it is an exothermic reaction, energy released). This is the enthalpy ΔH.

Acids and Bases

Bronsted – Lowry :

- An acid **donates proton (H^+)**
- A base **accepts a proton (H^+)**

Ex) $HCl + H_2O \quad H_3O^+ + Cl^-$

- Very fast reaction as HCl is a strong acid and NaOH is a strong base. NaCl is a weak base (weak conjugate base) and H_2O is a weak acid (weak conjugate acid).

$$HCl \longrightarrow H^+ + Cl^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

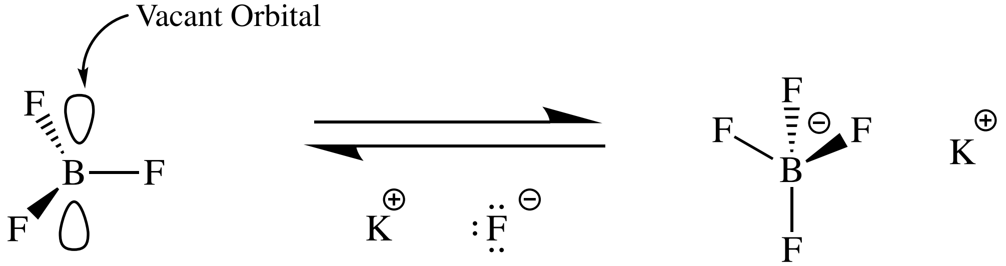
$$HCl + NaOH \longrightarrow NaCl + H\text{-}OH$$

Lewis Acid/Base:

- An **acid accepts a pair of electrons**
- A **base donates a pair of electrons**

e.g) BF_3

- Lewis Acid

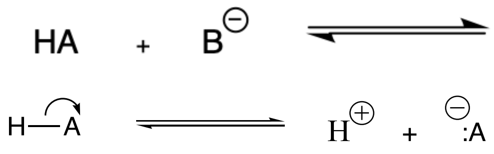


Boron trifluoride	Boron tetrafluoride
$-sp^2$	$-sp^3$
-Trigonal planar	-Tetrahedral
-120° bond angle	-109° bond angle

BF_3 can react with potassium fluoride (KF) to obtain an inert gas configuration. However, BF_4^- is unhappy with a formal negative charge, so the reaction is reversible.

- Every Bronsted-Lowry acid/base is also a Lewis acid/ base. The converse statement is not true; not all Lewis acids/bases can be classified as a Bronsted-Lowry acids/bases.

A general acid/base reaction:



$K_{eq} = K_a = \frac{[H^+][A^-]}{[HA]}$

K_a = acidity constant
$pK_a = -\log K_a$

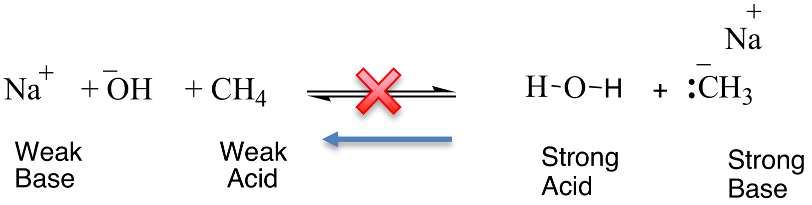
C-H > N-H > OH > F-H
Not acidic. Very acidic

Ex #1) Methane:

$H\text{-}CH_3 \rightleftharpoons H^+ + CH_3^-$

$K_a = \frac{[H^+][CH_3^-]}{[HCH_3]} = 10^{-46}$

$pK_a = -\log K_a = 46$



pK_a $CH_4 = 46$
pK_a $H_2O = 15.7$

The equilibrium above lies far (exclusively) to the left. Hydroxide will NOT deprotonate methane.

Ex #2) Ionization of HF

$HF \longrightarrow H^{\oplus} + F^{\ominus}$

$pK_a = -10$
$K_a = 10^{10}$

HF when solvated has a pKa of 3.5

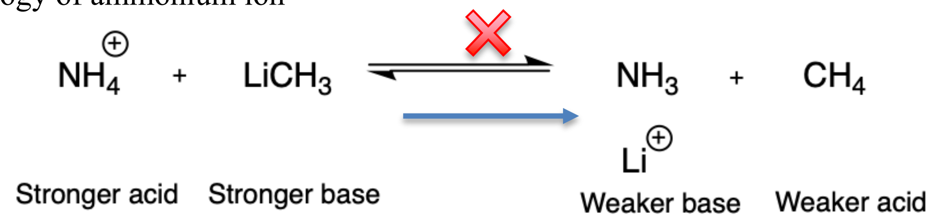
Ex # 3) Ammonia Gas:

$H\text{-}NH_2 \rightleftharpoons H^{\oplus} + {}^{\ominus}\!:\!\ddot{N}H_2$

$K_a = \frac{[H^+][^-NH_2]}{[NH_3]} = 10^{-36}$

$pK_a = 36$

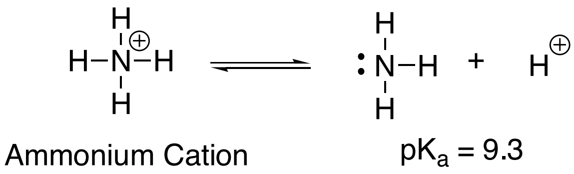
Biology of ammonium ion



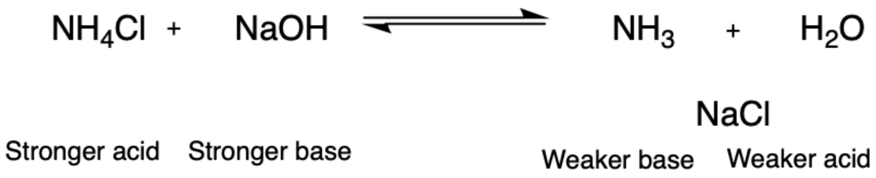
Ammonia gas is a better acid compared to methane (bigger K_a), because nitrogen is more electronegative than carbon. It can hold a negative charge easier than carbon.

NB: The lower the pK_a the more acidic

pK_a of "Ammonia" in biological system - ammonium cation pKa is 9.3

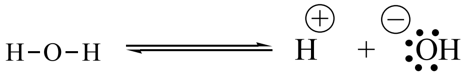


NB: Oxygen is more electronegative than nitrogen, which makes water more acidic than ammonia. Nitrogen more electronegative than carbon and that makes ammonia more acidic than methane.



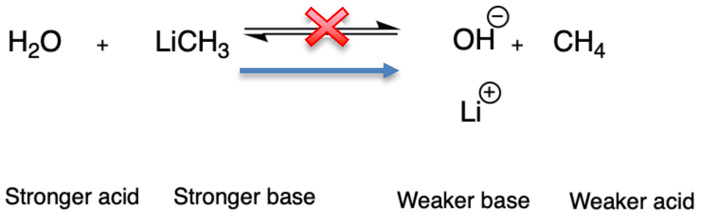
pK_a H_2O = 15.7 (weaker acid)
pK_a NH_4 = 9.3 (stronger acid)

Ex #4) Water:

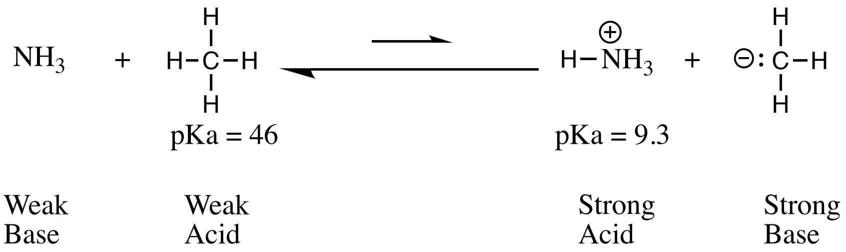


$$K_a = \frac{[H^+][^-OH]}{[HOH]} = 10^{-15.7}$$

$$pK_a = -\log K_a = 15.7$$



Ex #5) Strong acid/base



The reaction lies far (exclusively) to the left since ammonia is not a strong enough base to deprotonate methane

Another example:

$$LiNH_2 \quad + \quad H_2O \quad \rightarrow \quad LiOH \quad + \quad NH_3$$

pKa=15.7
stronger acid

pKa=36
Weaker acid

The lower the pK_a the more acidic the compound: reaction is far to right (LiOH and NH_3)

Examples of strong acids:

Acid	**pK_a**
HI	-10
HBr	-9
HCl	-7
HF	-10
H_3O^+	-1.75

→ Can go up to +3.17 in a diluted solution (in water)

Two factors that affect acidity of the above acids:

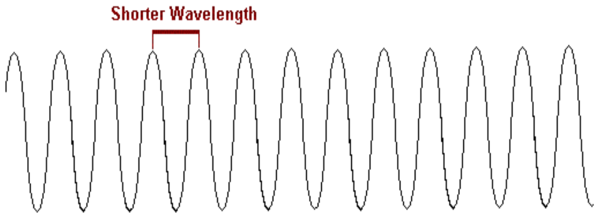
1) Electronegativity – the more electronegative the atom, the better it can hold a negative charge
2) Solvation – the larger the ion, the better solvated it can be and so the more acidic its conjugate acid will be - hence HI stronger than HCl as I^- is larger

Electromagnetic Radiation:

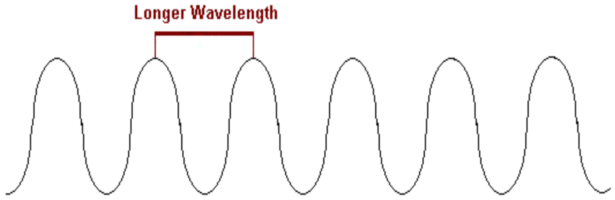
Infrared (IR) Spectroscopy – Background only:

$E = hc/\lambda = h\nu$, energy is quantized

E = Energy
h = Planck’s Constant= 6.6×10^{-34} joules/sec
ν = Frequency
λ = Wavelength
c = Speed of light = 3.0×10^{10} cm/sec



- ➢ Shorter Wavelength
- ➢ Higher Energy
- ➢ Higher Frequency

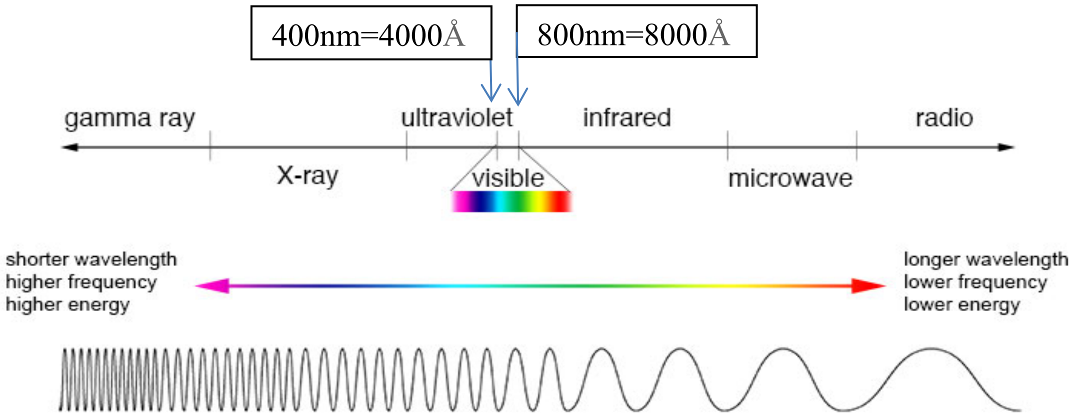


- ➢ Longer Wavelength
- ➢ Low Energy
- ➢ Low Frequency

NB: There is an inverse relationship between wavelength and frequency.

Electromagnetic Spectrum:

NB: 1nm = 10 angstrom



UV and visible light: conjugated double bond systems

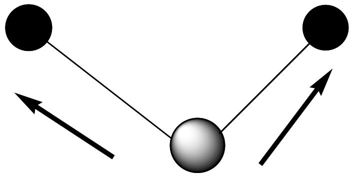
e.g. C=C bonds absorb UV light and some visible light

Infrared Radiation: bond stretching and bending modes

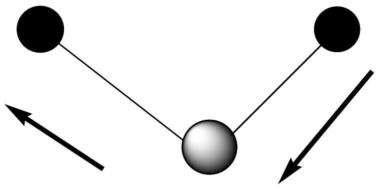
-Measured in wavenumbers (cm^{-1})

- Defined as cycles/second

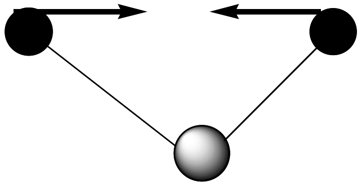
e.g. O-H bond can be seen around ~3400cm^{-1} in an IR spectrum



SYMMETRIC STRETCHING

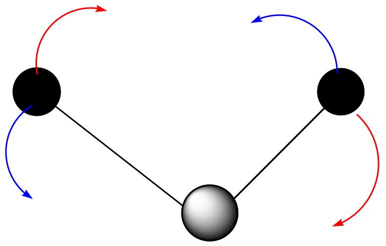


ASYMMETRIC STRETCHING



IN PLANE BENDING

(SCISSORING)



OUT OF PLANE BENDING

(TWISTING)

IR is Background Only - NOT on Midterm for Lecture Part

NEXT SECTION: Lecture Outline 2: ALKANES

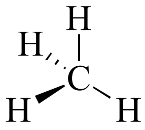
<u>Hydrocarbons</u> – Compounds that contain only C and H

- Alkanes contain only single bonds (C-H, C-C), sp^3
- Alkenes = contains C=C and has sp^2 hybridization (e.g. olefins)
- Alkynes = contains $C \equiv C$ and has sp hybridization (acetylenes)

<u>Alkanes</u>

- All carbons are sp^3 hybridized (optimal bond angle of 109°)
- Single bonds (σ bonds).
- Tetrahedral geometry at every carbon
- Held together by London (dispersion) forces

Ex #1) CH_4, methane

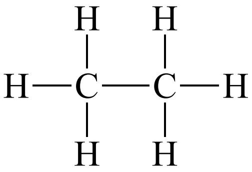


Bp = -161°C
(London
Forces)

BP = -164 °C

CH_4 H_4C CH_3-H

Ex #2) C_2H_6, ethane



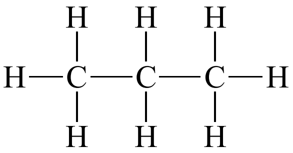
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Bp = -88°C

BP = -88 °C

C_2H_6 CH_3-CH_3 H_3C-CH_3

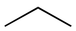
Ex #3) C_3H_8, propane

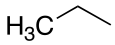


$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Bp = -42°C

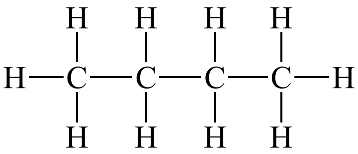
C_3H_8 $CH_3CH_2CH_3$



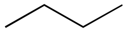


BP = -42 °C

Ex #4) C_4H_{10}, butane



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

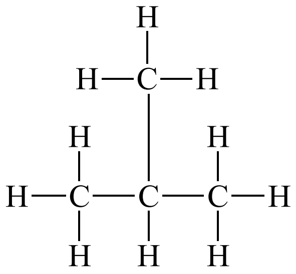


C_4H_{10}, $CH_3CH_2CH_2CH_3$

n-Butane: normal straight chain butane

NOTE: Propane has a boiling point of -42°*C, which is higher than methane because it's chain-like structure allows for more surface area for London dispersion forces to take effect.*

Ex #5) C_4H_{10} , isobutane or i-Butane



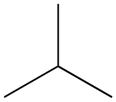
- Isomers are different compounds that have the same molecular formula and different structure. They have different physical properties (e.g. mp, bp, odour, biological effects)

\- iso - meros

same - parts

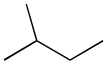
one type: structural (same as constitutional)

second type: stereoisomers (diastereomers and enantiomers) – will talk about more

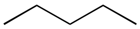


structural isomer = constitutional isomer

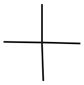
Ex #6) Pentane C_5H_{12}



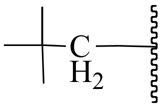
(isopentane or 2-methylbutane)



n - pentane



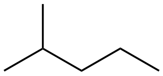
Neopentane



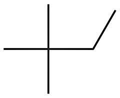
Neo Group

Ex #7) Hexane C_6H_{14}

n-hexane



Isohexane

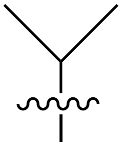


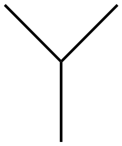
neohexane

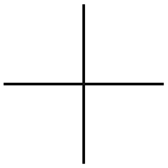
Systematic (IUPAC) Nomenclature

RULES:

1. Find the longest straight chain
2. Number from end of the chain, so that the 1st branch point has the lowest number
3. Name the chain, then add prefixes (for the groups attached) with number and name the groups attached
4. Separate numbers and names by dash







Common name:	isopropyl	isobutane	neopentane
Systematic name:		2-methylpropane	2,2-dimethylpropane

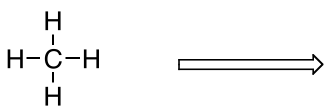
Note: iso = second-to-last carbon of the chain is disubstituted (2 methyl groups)
neo = second-to-last carbon of the chain is trisubstituted (3 methyl groups)

Prefixes for naming:
Di (2), Tri (3), Tetra (4), Penta (5), Hexa (6) etc.

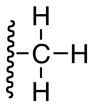
Groups (part of an alkane structure)

- In naming the particular group, drop the "ane" part and add "yl" to the name
- For example, methane → methyl

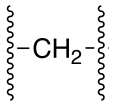
(i) Methyl group – CH_3



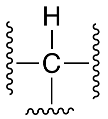
methane



methyl group

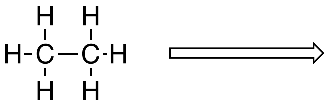


methylene

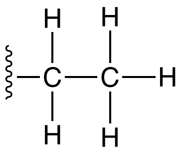


methine

(ii) Ethyl group – CH_2CH_3

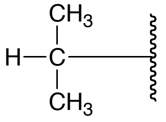


ethane

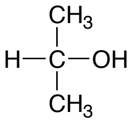


ethyl

(iii) Isopropyl group

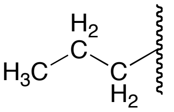


iso-propyl
group

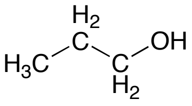


iso-propyl
alcohol

(iv) *n*-Propyl group

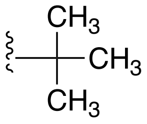


n-propyl chain

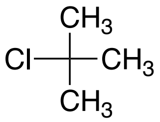


n-propyl alcohol

(v) *tert*-Butyl group (t-butyl)

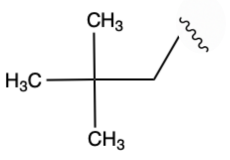


tert-Butyl chain

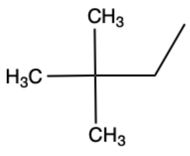


tert-Butyl chloride

(vi) neo group

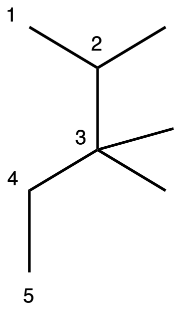


neo chain

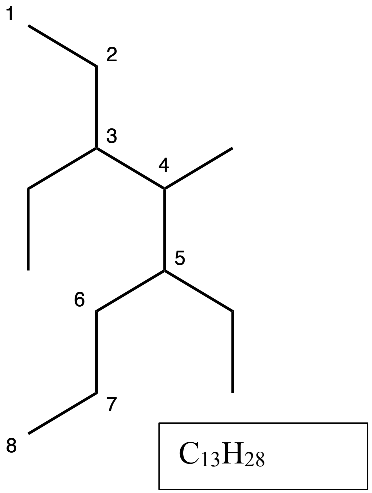


2,2-dimethylbutane

Naming Examples:



2,3,3-trimethylpentane



$C_{13}H_{28}$

3,5-diethyl-4-methyloctane

<u>Cycloalkanes</u>:

General Molecular Formula of Alkanes

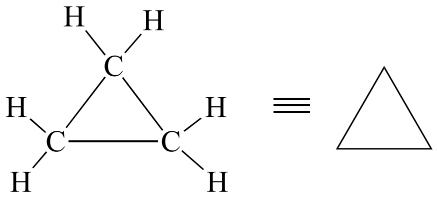
- Linear alkanes: general formula is $C_NH_{2N} + 2$
- Each **degree of unsaturation** "removes" 2 hydrogens from the $C_NH_{2N} +2$ formula
- (if there are no nitrogens in the molecule, there will always be an even # of hydrogens)
- Cylcoalkanes always have at least 1 degree of unsaturation

  e.g.
  - 1 Degree of unsaturation : C_NH_{2N} Alkanes with one ring or double bond
  - 2 Degrees of unsaturation : C_NH_{2N-2} Alkanes with two rings or double bonds, or one each

Note: Ring Structure Naming

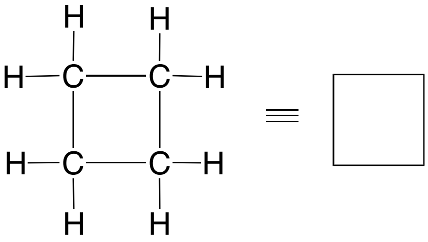
- Parent ring is the largest one
- Prefix with "cyclo"
- Start with numbering at point of maximum branching/most important functional group
- Number so as to give next branch/functional group lowest number

Cyclopropane, C_3H_6

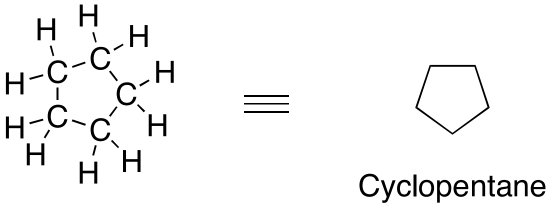


- One degree of unsaturation (*n*-propane is C_3H_8)
  - Not a structural isomer (different molecular formula)
- C-C-C bond angle (60°)
- Highly reactive due to ring strain (sp^3 carbons prefer to be 109°)

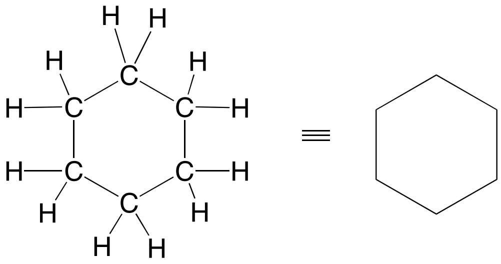
Cyclobutane, C_4H_8



Cyclopentane, C_5H_{10}

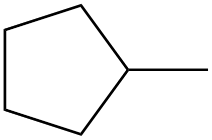


Cyclohexane, C_6H_{12}



Examples of Naming Cycloalkanes:

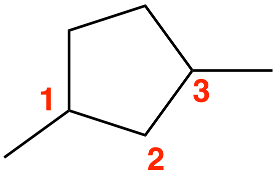
Ex #1) C_6H_{12}



Degree of Unsaturation= 1

1-methylcyclopentane (structural isomer of hexane)

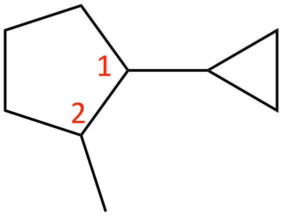
Ex #2) C_7H_{14}



Degree of Unsaturation= 1

1,3-dimethylcyclopentane

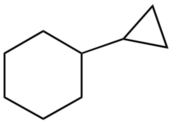
Ex #3) C_9H_{16}



1-cyclopropyl-2-methylcyclopentane

Degree of Unsaturation= 2

Ex #4) C_9H_{16}

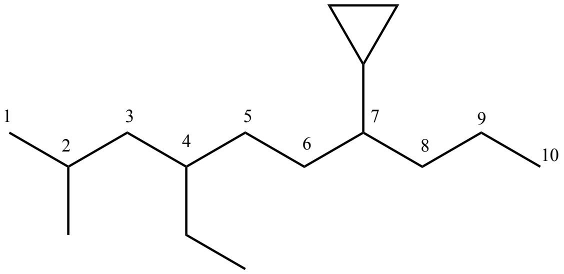


1-Cyclopropylcyclohexane

Degree of Unsaturation= 2

Example 3 and 4 both have the formula C_9H_{16} so they are structural isomers

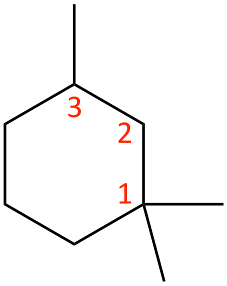
Ex #5) $C_{16}H_{32}$



7-cyclopropyl-4-ethyl-2-methyldecane

Degree of Unsaturation= 1

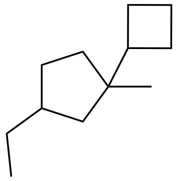
Ex #6) C_9H_{18}



1,1,3-trimethylcyclohexane

Degree of Unsaturation= 1

Ex #7) $C_{12}H_{22}$



Degree of Unsaturation= 2

1-Cyclobutyl-3-ethyl-1-methylcyclopentane