CHEM 261 September 21,2021

Acids and Bases

Bronsted – Lowry :

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

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

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

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

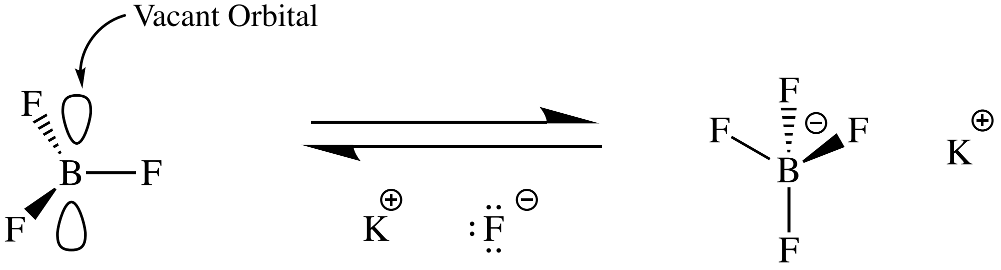
- Very fast reaction as HCl is a strong acid and NaOH is a strong base. NaCl is a weak base (weak conjugate base) and H_2O is a weak acid (weak conjugate acid).

Lewis Acid/Base:

- An **acid accepts a pair of electrons** (e.g. HCl, H_2SO_4)
- A **base donates a pair of electrons**

e.g) BF_3

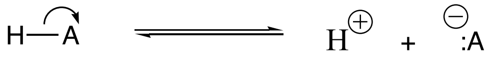
- Lewis Acid



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.



$$H{-}A \rightleftharpoons H^{\oplus} + :A^{\ominus}$$

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

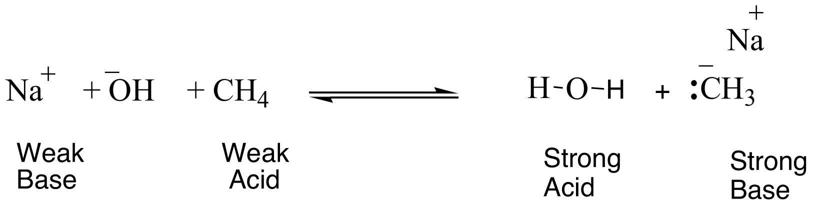
K_a = acidity constant
$pK_a = -\log K_a$

Ex #1) Water:

$$H{-}O{-}H \rightleftharpoons H^{\oplus} + :\ddot{O}H^{\ominus}$$

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

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



$$Na^+ + {}^-OH + CH_4 \rightleftharpoons H{-}O{-}H + :\overset{-}{C}H_3 \; Na^+$$

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

Ex # 2) Ammonia Gas:

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

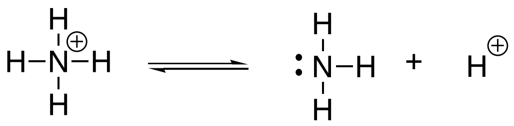
$$K_a = \frac{[H^+][^-NH_2]}{[NH_3]} = 10^{-36}$$

$$pK_a = 36$$

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 pKa the more acidic

pKa of "Ammonia" in biological system



Ammonium Cation

$pK_a = 9.3$

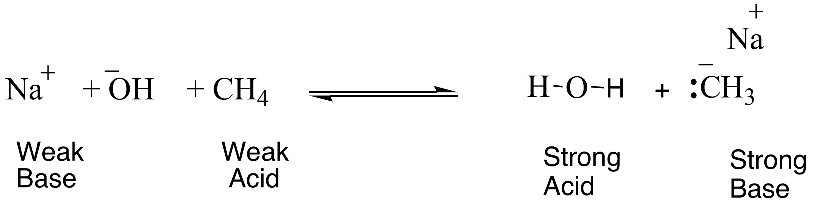
Ex #3) Methane:

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

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

$$pK_a = -\log K_a = 46 \text{ (NOT an acid)}$$

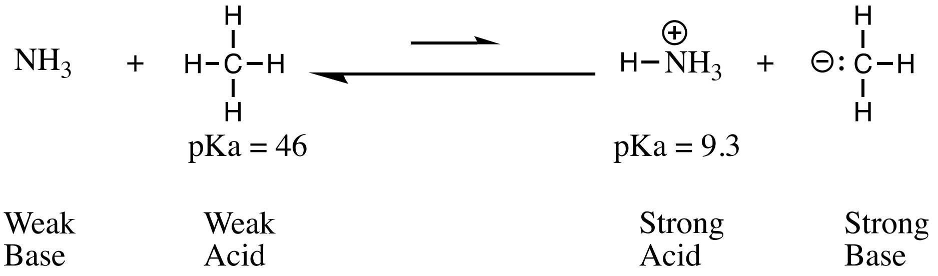
NB: Oxygen is more electronegative than nitrogen, which makes water more acidic than ammonia. Nitrogen more electronegative than carbon and that makes ammonia more acidic than methane.



$$Na^+ + {}^-OH + CH_4 \rightleftharpoons H\text{-}O\text{-}H + {:}CH_3^-\ Na^+$$

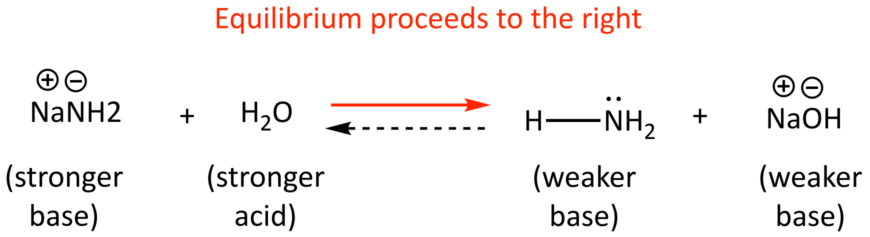
The equilibrium above lies far (exclusively) to the left. Hydroxide will NOT deprotonate methane.

Ex #4) Strong acid/base



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

E.g.



Recall:
The lower the pKa the more acidic the compound

Examples of strong acids:

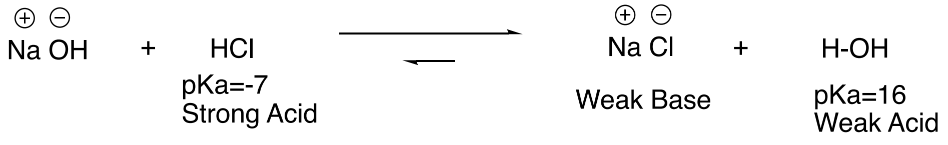
Acid	pKa
HI	-10
HBr	-9
HCl	-7
HF	-10
H_3O^+	-1.74

→ Can go up to +3.17 in a diluted sol'n (in water)

Two factors that affect acidity of the above acids:

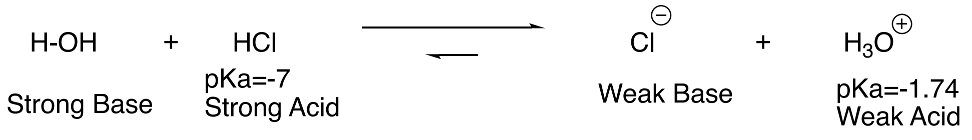
1) Electronegativity – the more electronegative the atom, the better it can hold a negative charge
2) Solvation – the larger the ion, the better solvated it can be and so the more acidic it's conjugate acid will be

Ex #1)



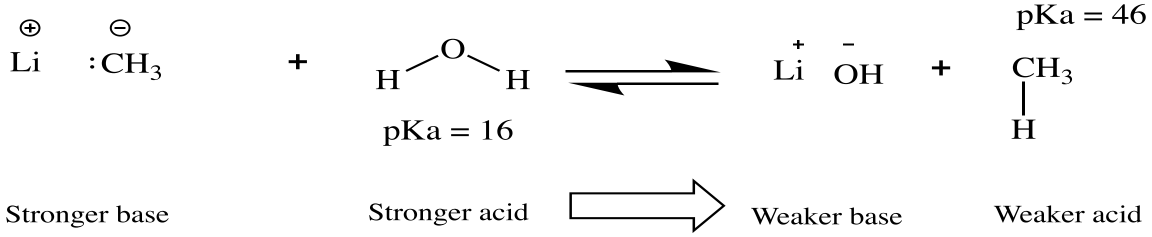
A strong acid and a strong base will quickly react with each other to drive the reaction to the weak acid and the weak base.

Ex #2)

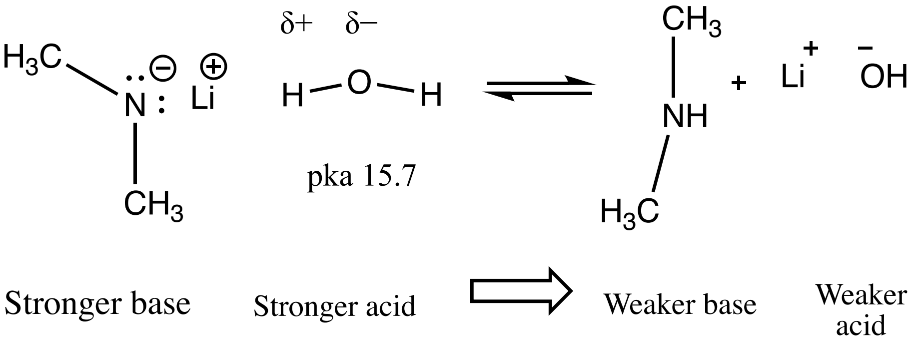


While water is not actually a strong base, it is in comparison to C^-. HCl is the strong acid, and so the equilibrium lies to the right. Hence H_3O^+ is the strongest acid that will exist in an aqueous solution of HCl.

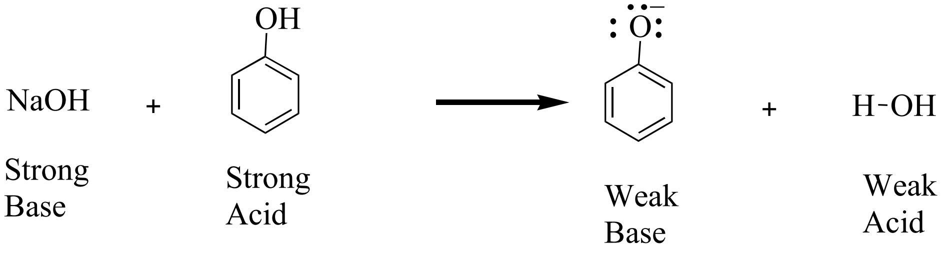
Ex #3)



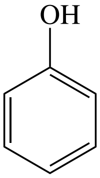
Ex #4)



Ex #5)



NB: Oxygen is more electron withdrawing than Carbon and can stabilize negative charge so removing a proton from the oxygen is preferable than from the Carbon on the phenol compound



Phenol

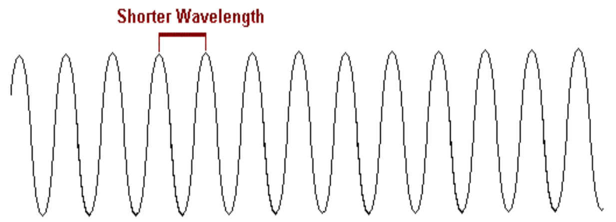
Phenol pKa = 10

Electromagnetic Radiation:

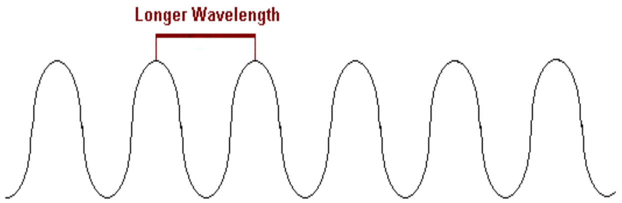
Infrared (IR) Spectroscopy – Background only:

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

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



- Shorter Wavelength
- Higher Energy
- Higher Frequency



- Longer Wavelength
- Low Energy
- Low Frequency

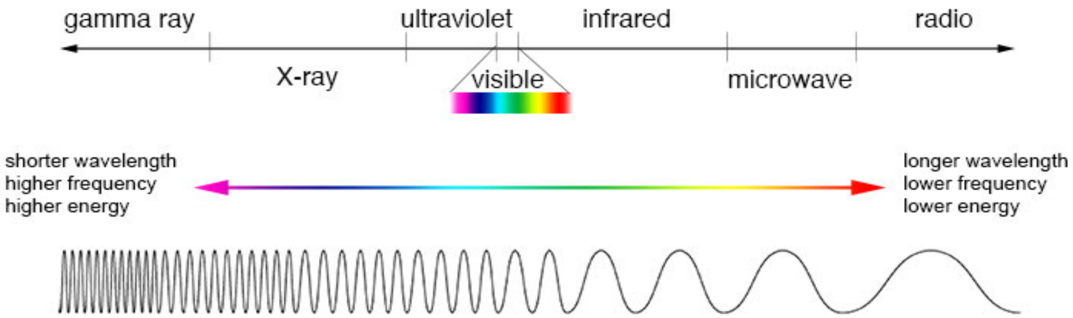
NB: There is an inverse relationship between wavelength and frequency.

Electromagnetic Spectrum:

NB: 1nm = 10 angstrom

400nm=4000Å

800nm=8000Å



UV and visible light: conjugated double bond systems

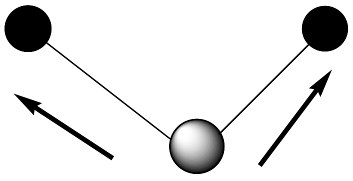
e.g. C=C bonds absorb UV light and some visible light

Infrared Radiation: bond stretching and bending modes

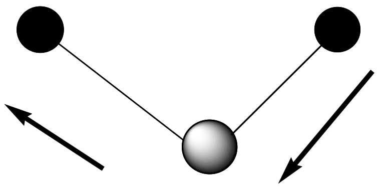
-Measured in wavenumbers (cm^{-1})

- Defined as cycles/second

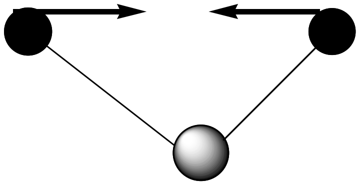
e.g. O-H bond can be seen around ~3400cm^{-1} in an IR spectrum



SYMMETRIC STRETCHING

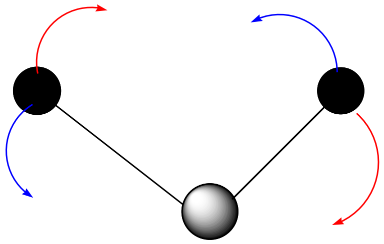


ASYMMETRIC STRETCHING



IN PLANE BENDING

(SCISSORING)



OUT OF PLANE BENDING

(TWISTING)

NEXT SECTION: Lecture Outline 2: ALKANES

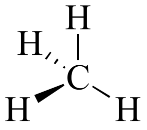
<u>Hydrocarbons</u> – Compounds that contain only C and H

- Alkanes contain only single bonds (C-H, C-C)
- Alkenes = Olefins (C=C)
- Alkynes =Acetylenes ($C\equiv C$)

<u>Alkanes</u>

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

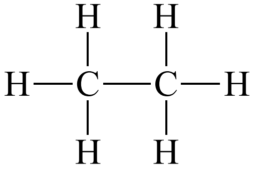
Ex #1) CH_4, methane



Bp = -161°C
(London
Forces)

CH_4 H_4C CH_3-H

Ex #2) C_2H_6, ethane

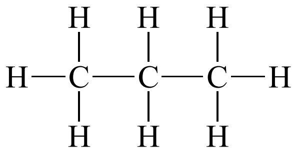


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Bp = -88°C

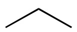
C_2H_6 CH_3-CH_3 H_3C-CH_3

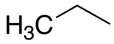
Ex #3) C_3H_8, propane



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

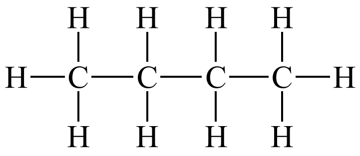
Bp = -42°C



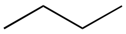


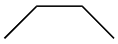
C_3H_8 $CH_3CH_2CH_3$

Ex #4) C_4H_{10}, butane



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$



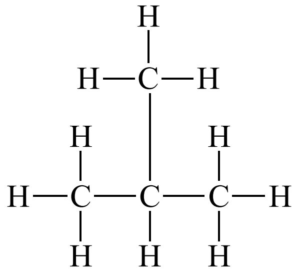


C_4H_{10}, $CH_3CH_2CH_2CH_3$

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.*

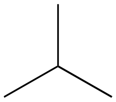
Ex #5) C_4H_{10} , isobutene or i-Butane



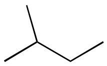
- Isomers are different compounds that have the same molecular formula and different structure. They have different physical properties (e.g. mp, bp, odour, biological effects)

- iso - meros
same - parts

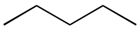
one type: structural (same as constitutional)



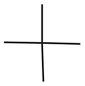
structural isomer = constitutional isomer



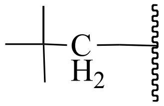
(isopentane or 2-methylbutane)



n - pentane



Neopentane

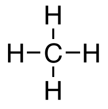


Neo Group

Groups (part of an alkane structure)

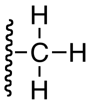
- In naming the particular group, drop the "ane" part and add "yl" to the name
- For example, methane → methyl

(i) Methyl group – CH_3

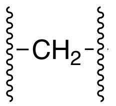


methane

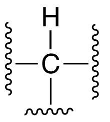
⟹



methyl group

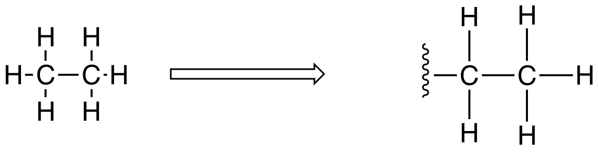


methylene



methine

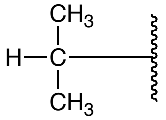
(ii) Ethyl group – CH_2CH_3



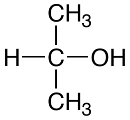
ethane

ethyl

(iii) Isopropyl group

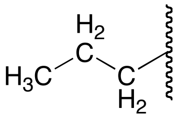


iso-propyl
group

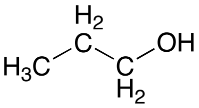


iso-propyl
alcohol

(iv) *n*-Propyl group

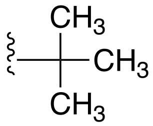


n-propyl chain

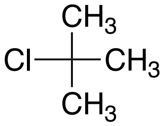


n-propyl alcohol

(v) *tert*-Butyl group



tert-Butyl chain



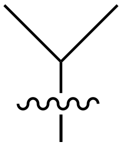
tert-Butyl chloride

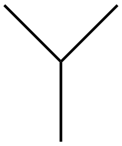
<u>Systematic Nomenclature</u>

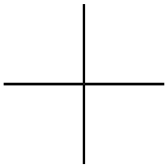
RULES:

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


isopropyl

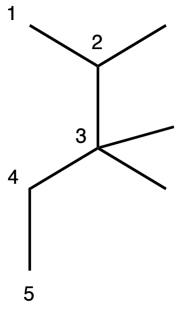

isobutane
2-methylpropane


neopentane
2,2-dimethylpropane

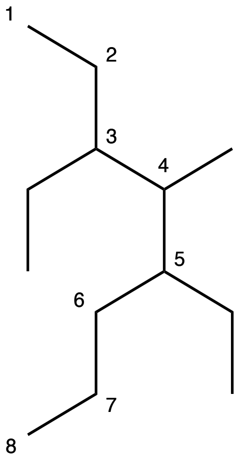
Note: iso = second-to-last carbon of the chain is disubstituted (2 methyl groups)
neo = second-to-last carbon of the chain is trisubstituted (3 methyl groups)

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

Naming Examples:



2,3,3-trimethylpentane



3,5-diethyl-4-methyloctane

Cycloalkanes:

General Molecular Formula of Alkanes

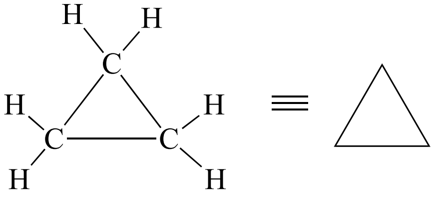
- No rings: general formula is C_NH_{2N+2}
- Each deviation of 2 hydrogens from the C_NH_{2N+2} formula is a **degree of unsaturation**

- 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

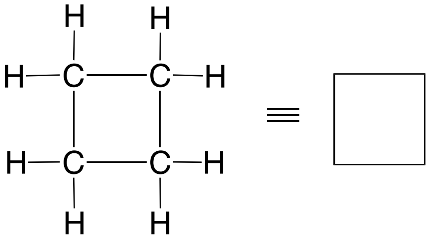
Note: Ring Structure Naming
- Prefix with "cyclo"
- Start with numbering at point of maximum branching/most important functional group
- Number so as to give next branch/functional group lowest number

Cyclopropane, C_3H_6

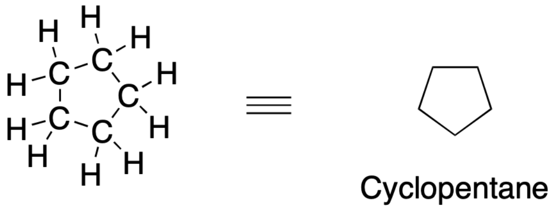


- One degree of unsaturation (*n*-propane is C_3H_8)
  - Not a structural isomer (different molecular formula)
- C-C-C bond angle (60 °)
- Highly reactive due to ring strain

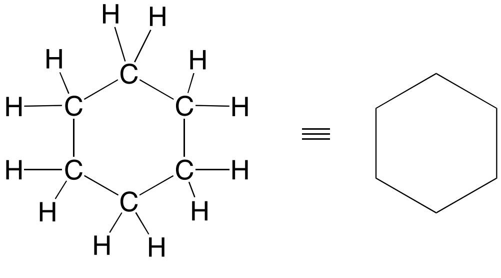
Cyclobutane, C_4H_8

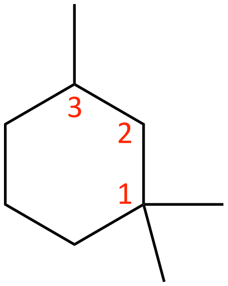


Cyclopentane, C_5H_{10}

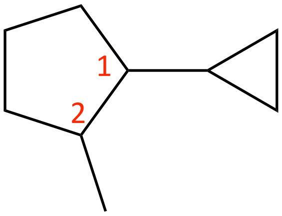


Cyclohexane, C_6H_{12}





1,1,3-trimethylcyclohexane



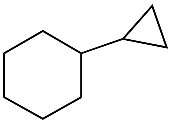
1-cyclopropyl-2-methylcyclopentane

General Molecular Formula of Alkanes

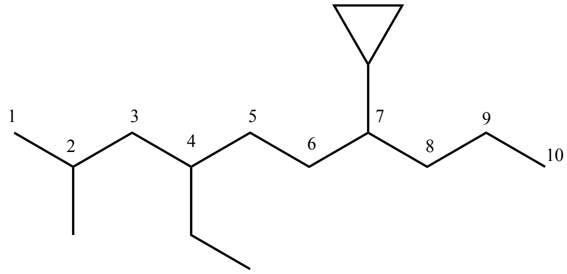
- No rings: general formula is C_NH_{2N+2}
- Each deviation of 2 hydrogens from the C_NH_{2N+2} formula is a **degree of unsaturation**
- 1 Degree of unsaturation : C_NH_{2N} Alkanes with one ring or double bond
- 2 Degrees of unsaturation : C_NH_{2N-2} Alkanes with two rings or double bonds, or one each

Examples of Naming Cycloalkanes:

Degree of Unsaturation= 2

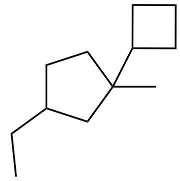


1-Cyclopropylcyclohexane



7-cyclopropyl-4-ethyl-2-methyldecane

Degree of Unsaturation= 1



1-Cyclobutyl-3-ethyl-1-methylcyclopentane

Degree of Unsaturation= 2

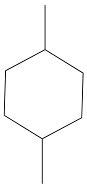
ISOMERS

Structural (Constitutional) Isomers

Share the same molecular formula but have the atomic bonds in different places

C_8H_{16}

1,1-dimethylcyclohexane

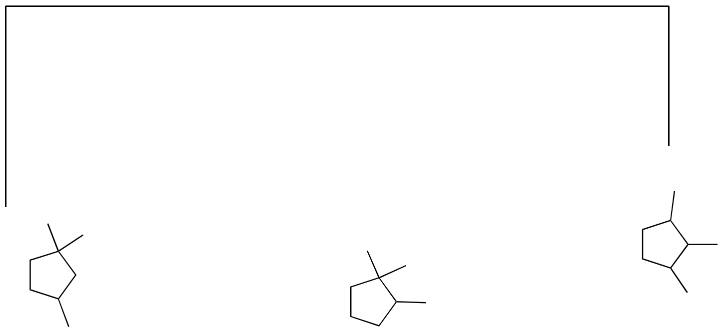


C_8H_{16}

1,4-dimethylcyclohexane

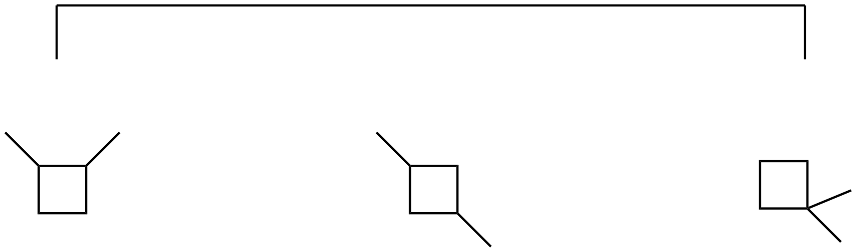
The above two compounds are structural (also known as constitutional) isomers

Structural or constitutional isomers



1,1,3-trimethylcyclopentane 1,1,2-trimethylcyclopentane 1,2,3-trimethylcyclopentae

Structural or constitutional isomers



1,2-dimethylcyclobutane 1,3-dimethylcyclobutane 1,1-dimethylcyclobutane

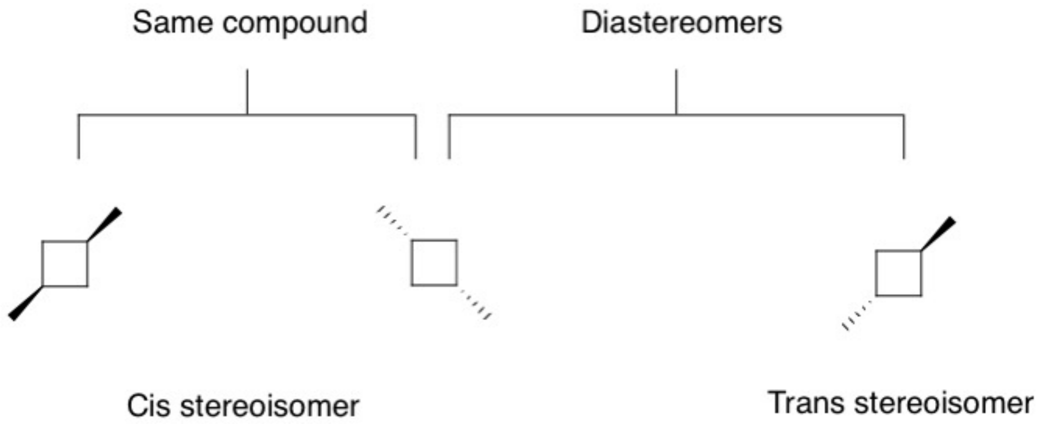
Stereoisomers

Compounds with the same molecular formula, same order of connection (base name) but connection of atoms that differ in 3D geometry

Two Types:

1. Diastereomers - stereoisomers that are not mirror images
2. Enantiomers - stereoisomers that are non-superposable mirror images of each other

Example: 1,3 dimethylcyclobutane

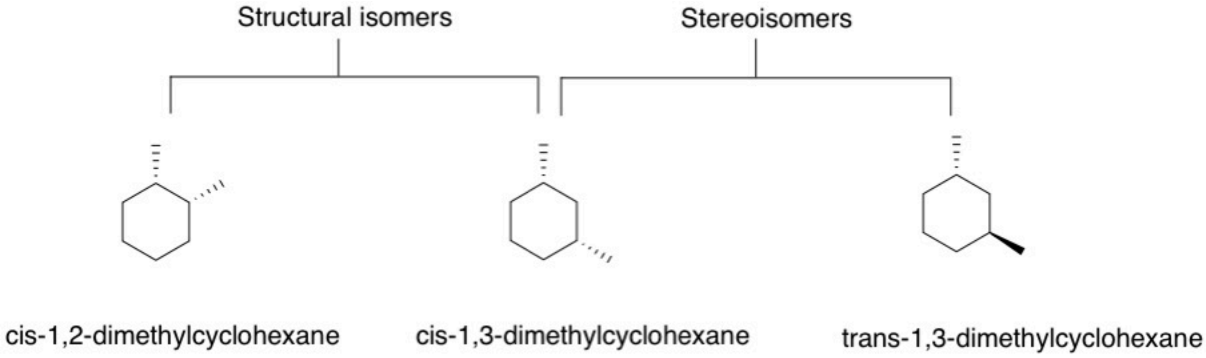


The first and second compounds are the same compound rotated in 3D space. The third compound has different geometry at one center, making it a stereoisomer, specifically a diastereomer.

Cis - the substituents are on the same side of the ring

Trans - the substituents are on opposite sides of the ring

Example: 1,2-dimethylcyclohexane and 1,3-dimethylcyclohexane



The second two compounds are diastereomers of each other.