Organic chemistry

Contents

Organic chemistry

Organic chemistry as chemistry with the element Carbon!

Organic chemistry defines the structures, properties, and reactions of an enormous array of molecules (organic compounds - there are several types of organic compounds, but all have carbon as their principal constituent atom). The ability of the carbon atom to bind to four other atoms results in an amazing versatility among organic compounds and is also, among other factors, responsible for the importance of the organic compounds.

ChemComplete: What is Organic Chemistry?
<https://www.youtube.com/watch?v=DTKKSyooqyM> (youtube, 13m 34s)

Chemical bonding

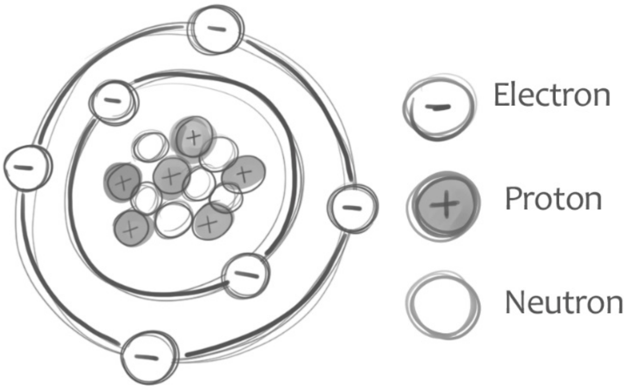
Atoms

Atoms: electrically neutral

Anion: negatively charged (addition of electrons)

Cation: positively charged (removal of electrons)

Isotope: atoms with equal numbers of protons and electrons but different numbers of neutrons.



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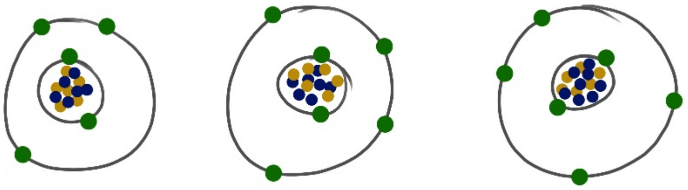
Carbon atom: Normally 6 protons and 6 neutrons in its core (atom number 12, ^{12}C).

- approx. 1% have an extra neutron (^{13}C)
- an even smaller amount have two extra neutrons (^{14}C)
- ^{14}C is unstable, radioactive and decay with a half-life of 5730 years.



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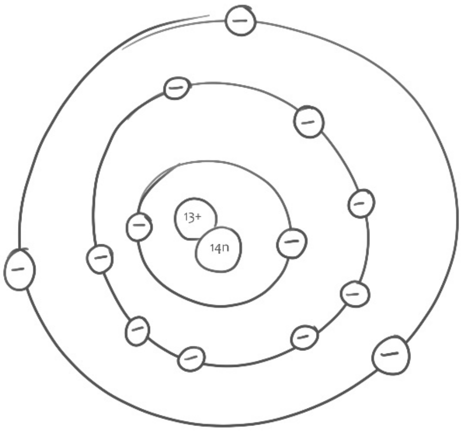
Electron shells

Electron shells: Energy intervals in which the electrons can move freely without losing their energy.

The electron shells are numbered according to: n = 1, 2, 3, 4…

Number of electrons within each shell = $2n^2$

FuseSchool: Drawing electron configuration diagrams.
<https://www.youtube.com/watch?v=hSkJzE2Vz_w> (youtube, 4m 58s)



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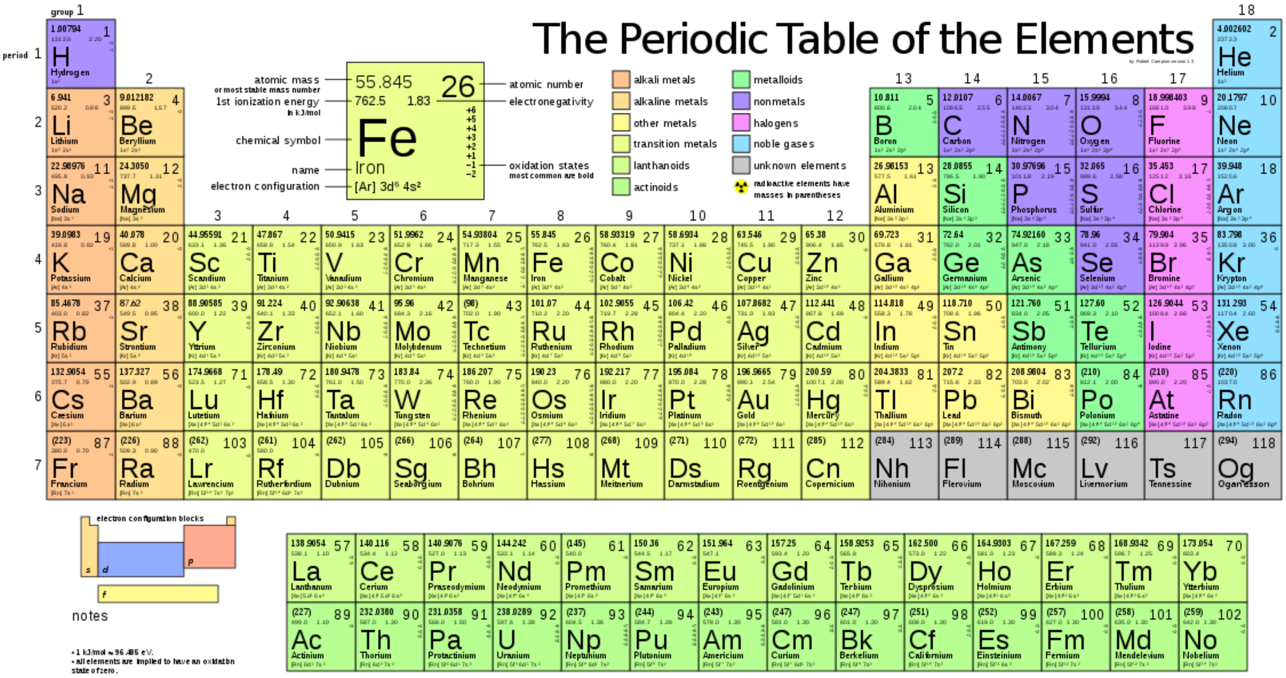
The periodic table of the elements



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Period (row): how many electron shells are being utilized.

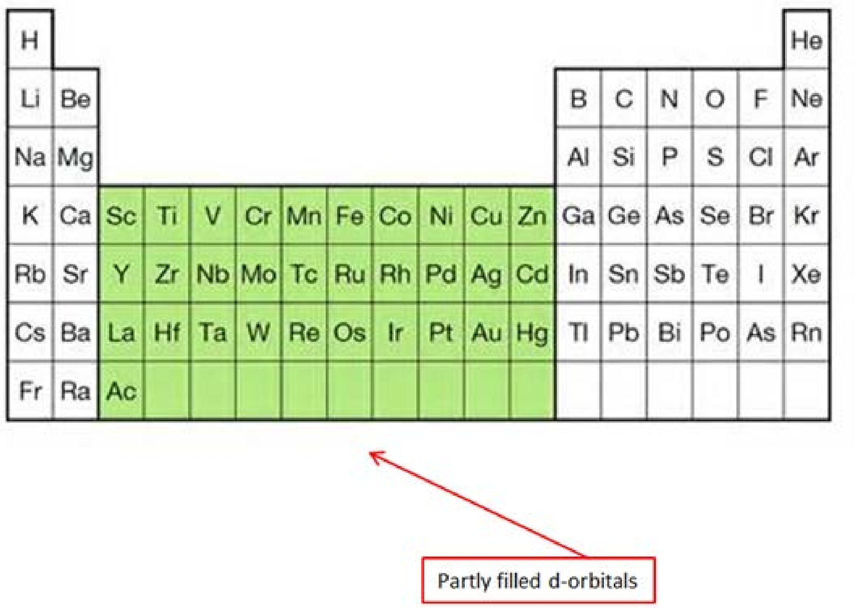
Group (column): how many electrons in the outer shell (He is exception).

The elements in period two:

- Inner (first) electron shell full
- Ne (Neon) has both the first and second shells full

Shell three: Is first filled with 8 electrons (Ar) (room for $2*3^2=18$ electrons)

- Before the remaining 10 are placed in shell three, shell four gets its first two electrons



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	As	Rn
Fr	Ra	Ac															

Partly filled d-orbitals

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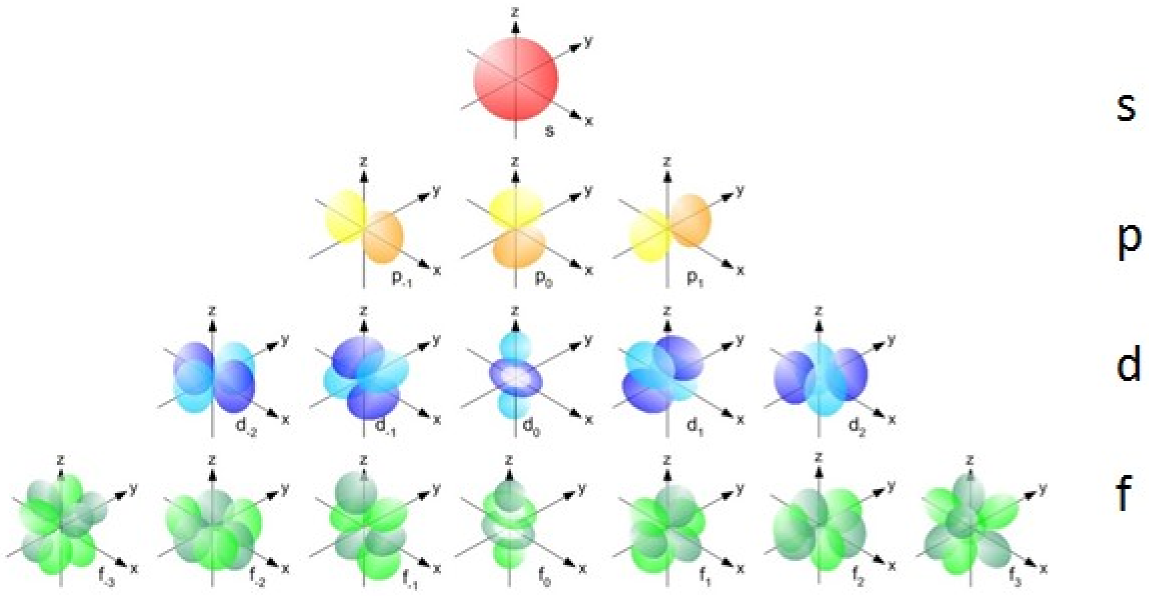
Orbitals

- A more advanced model than the electron shell model.
- Electrons are assigned to atomic orbitals that occupy different regions of space. The orbital is a theoretical volume where the electron exists 95 % of the time.
- The base orbitals are *s*, *p* and *d*.



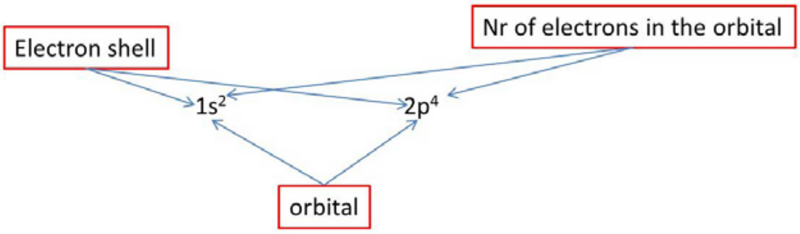
Atomic Orbitals:

In every electron shell: 1 s-orbital

From, and including, shell 2: 3 p-orbitals

From, and including, shell 3: 5 d-orbitals

Max 2 electrons in each orbital!!



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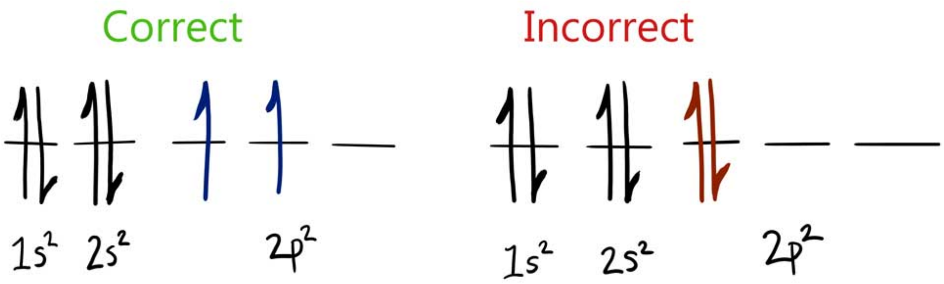
How to fill the orbitals with electrons

When all have one electron we start to fill the orbitals with the second electron.



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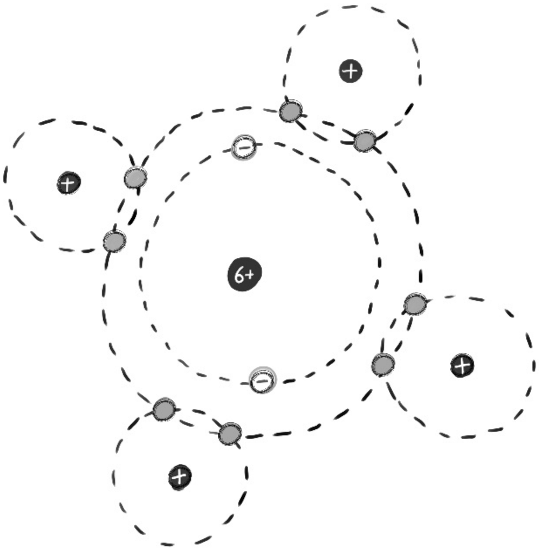
Atomic orbitals

The outer shell is the most interesting since it is the electrons in this shell that form chemical bonds (valence electrons).

Noble gas structure (filled s- and p-orbitals in the valence shell):



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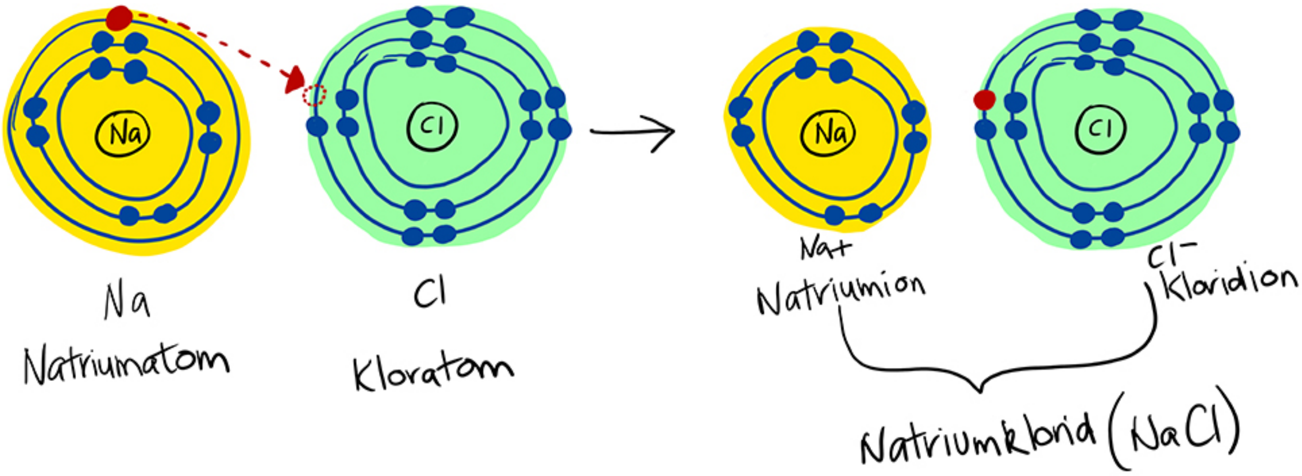
High stability/ Low energy

To achieve high stability and low energy is a fundamental driving force for the formation of chemical bonds!!!

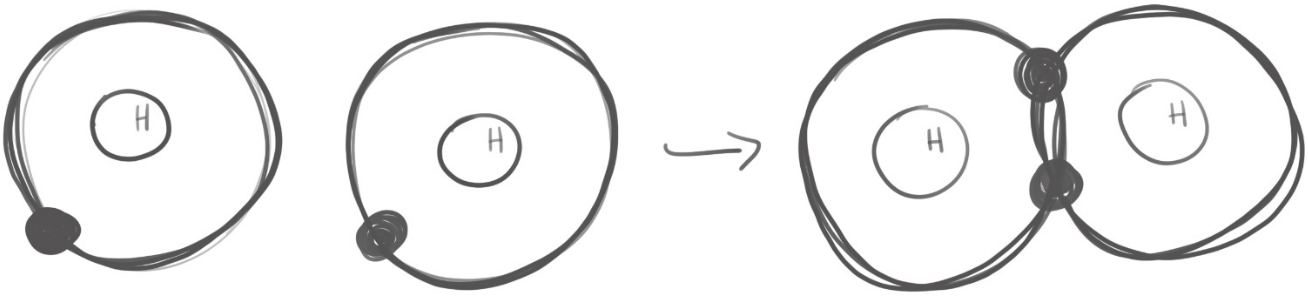
Covalent bonding – Ionic bonding

Two principally different ways to achieve noble gas structure, actually no sharp border between these two types of bonding.

Ionic bonding

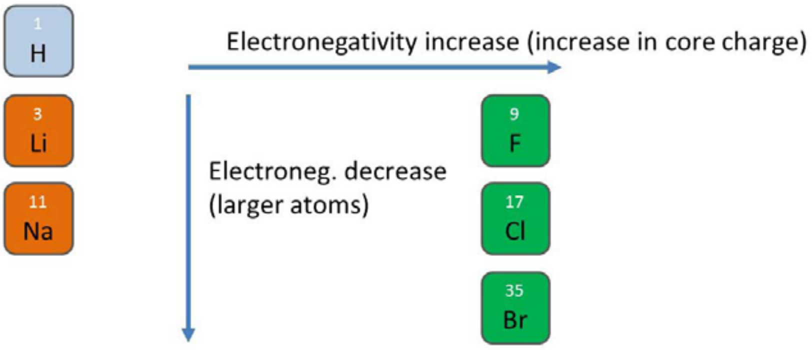


Covalent bonding



Difference in electronegativity::

≤ 0.5 nonpolar covalent bond
0.5 < 1.9 polar covalent bond
≥ 1.9 ionic bond



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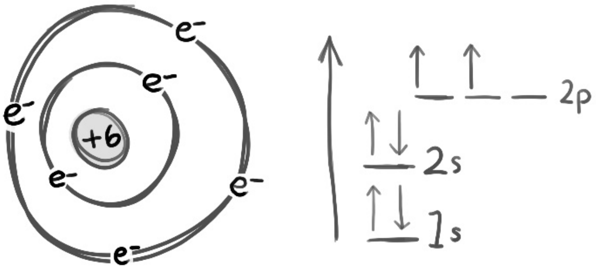
Covalent bonding

The carbon atom: 4 valence electrons



This should result in 2 bonds with certain character and 2 bonds with another type of character (s- and p- orbitals)

ChemComplete: Polar Covalent Bonds and Polarity
<https://www.youtube.com/watch?v=DTKKSyooqyM> (youtube)

However, carbon can form 4 identical bonds!!! How? The solution is hybridization!!

Hybridization

Introduction

Atoms can mix the base orbitals and create hybrid orbitals.

1 s-orbital + 3 p-orbitals

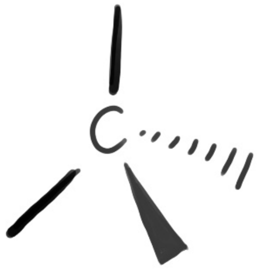
4 sp3-orbitals
(the carbon is sp^3-hybridized)

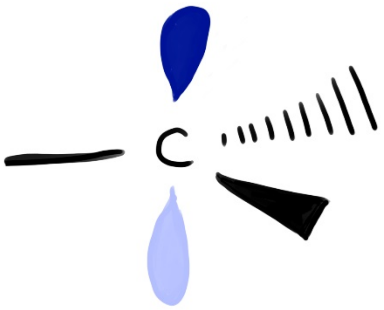
1 s-orbital + 2 p-orbitals

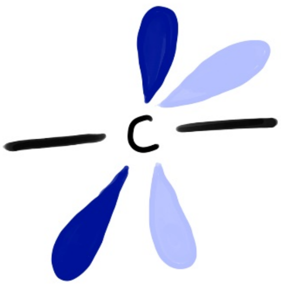
3 sp^2-orbitals
(the carbon is sp^2-hybridized)

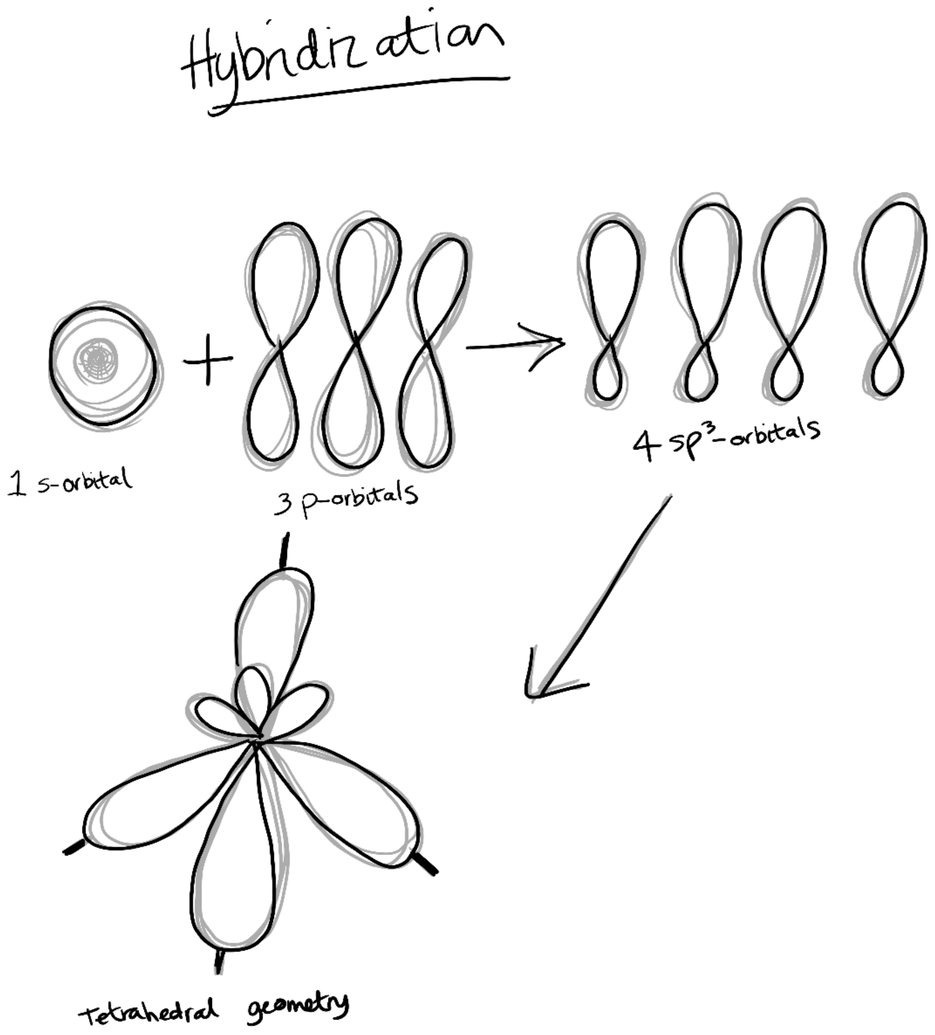
1 s-orbital + 1 p-orbital

2 sp-orbitals
(the carbon is sp-hybridized)



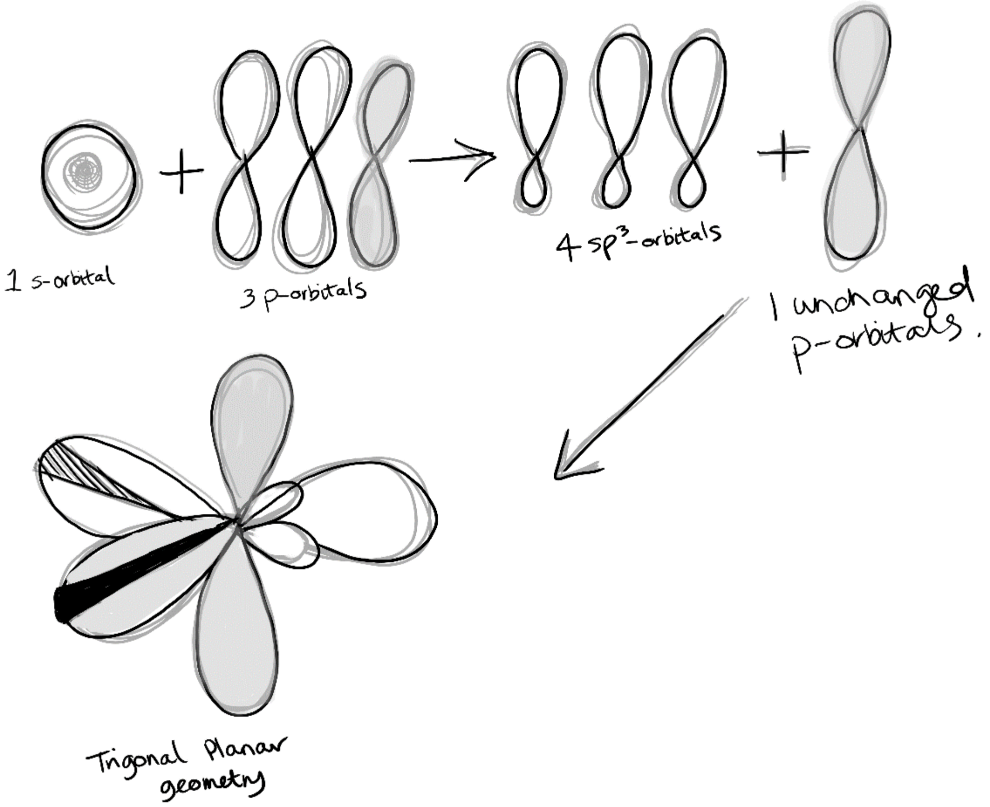




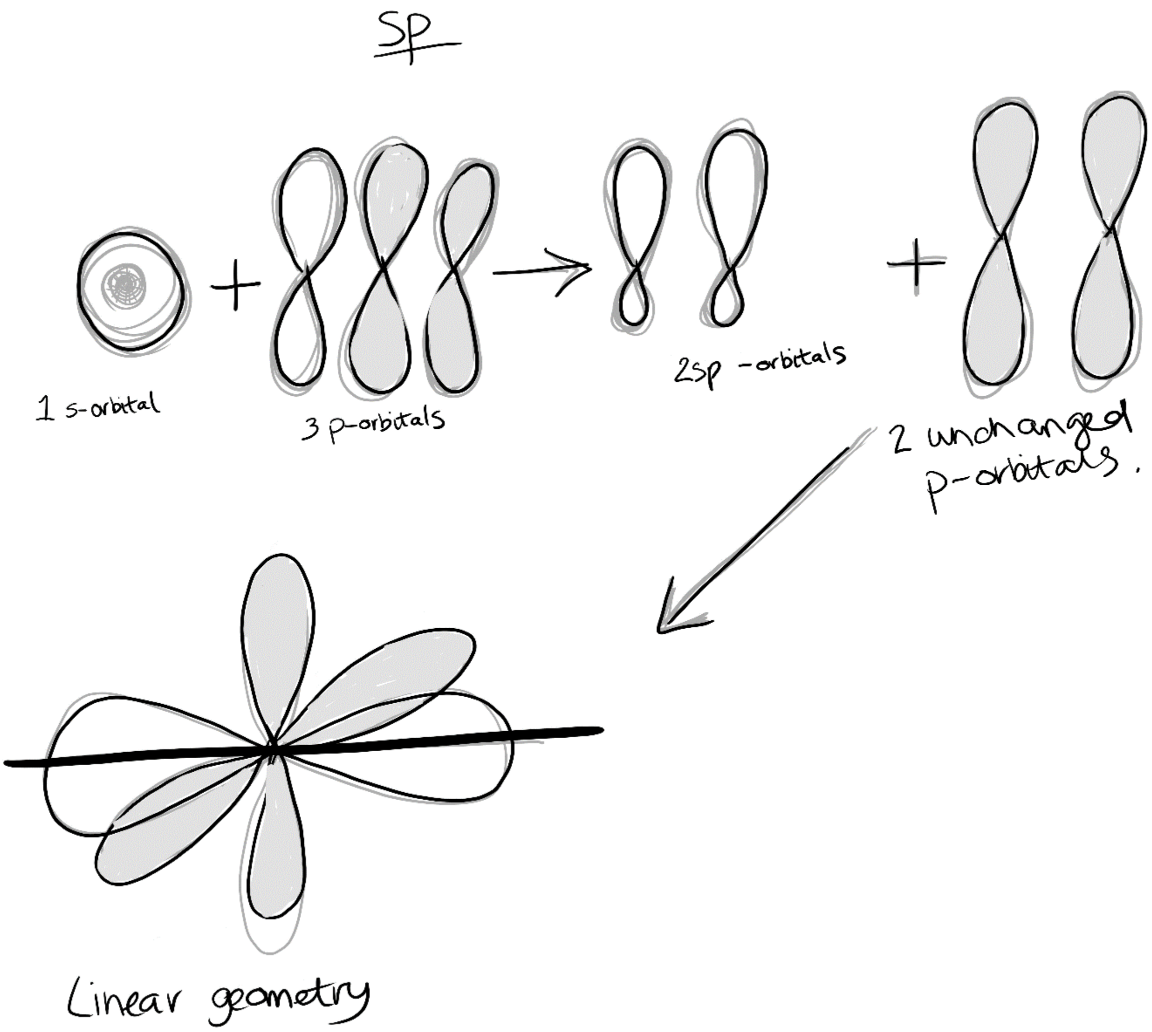


$$\left.\begin{array}{l}\mathrm{sp^3{-}sp^3\text{: single bond}}\\ \mathrm{sp^3{-}s\text{: single bond}}\end{array}\right\{\ \sigma\text{-bond}$$

Sp^2



$$\left.\begin{array}{c} sp^2-sp^2\text{: double bond} \\ sp^2-s\text{: single bond} \end{array}\right\{ \text{2p - 2p: } \pi\text{-bond}$$



$$\left.\begin{array}{l}\text{sp}-\text{sp: triple bond}\\ \text{sp}-\text{s: single bond}\end{array}\right\{\ 2\ \pi\text{-bonds}$$

Links

[ChemComplete: Carbon Hybridization](https://www.youtube.com/watch?v=DTKKSyooqyM)
<https://www.youtube.com/watch?v=DTKKSyooqyM> (youtube)

Khanacademy - sp^2 hybridization. <https://www.youtube.com/watch?v=DTKKSyooqyM>

Questions

Please complete the questions in the online version of this resource.

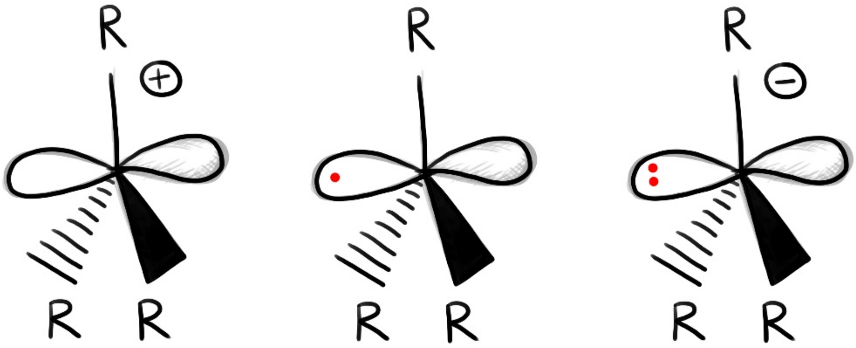
Reaction intermediates

Carbocation: An organic molecule with a positive charge on a carbon atom.

- The carbon atom has only 6 electrons in its valence shell.
- The carbocation is formed by heterolytic bond cleavage.

Carbanion: Has a free pair of electrons on a carbon atom that already has three bonds.

Radicals: Molecule with one or more unpaired electrons (an orbital with only one electron – high energy)
Formed e.g. through oxidation, reduction or by homolytic bond cleavage.



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Acid and base

Acid according to Brønsted: A compound that can donate protons (H^+)

Base according to Brønsted: A compound that can accept protons (H^+)

Acid according to Lewis (Lewis acid): A compound that can accept an electron pair

Base according to Lewis (Lewis base): A compound that can ‘donate’ an electron pair

Carbocations are strong Lewis acids.

Carbanions are strong bases (both Lewis and Brønsted).

Carbocations, carbanions and carbon radicals are reactive and participate in chemical reactions.

ChemComplete: Acids and Bases Part 1 - pKa and Acids
<https://www.youtube.com/watch?v=E2fVNc4VcGY> (youtube)

ChemComplete: Acids and Bases Part 2 - Lewis Acids and Bases
<https://www.youtube.com/watch?v=cyK6ul3wW1c> (youtube)

Amphoteric compound

An amphoteric substance is a molecule or ion that can react both as an acid as well as a base.

Hydrocarbons

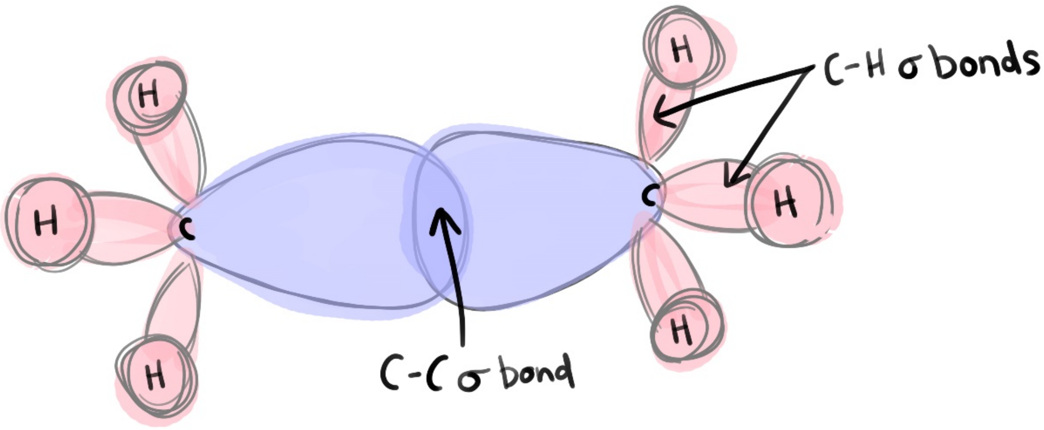
The access to crude oil makes hydrocarbons available in huge quantities. Hydrocarbons (contain only C and H atoms) can be categorized as aliphatic or aromatic.

- **Aliphatic** = no aromatic structure
- **Aromatic** = contains an aromatic structure

Saturated aliphatic hydrocarbons

Saturated aliphatic hydrocarbons = alkanes

Saturated means that the carbons are sp^3 hybridized and binds to each other or to hydrogen atoms (single bonds only) (we call them saturated since maximum nr. Of hydrogens are attached).



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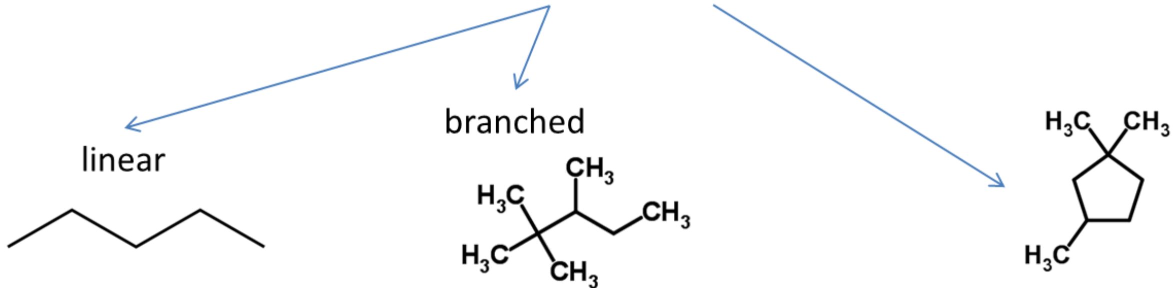
Aliphatic hydrocarbons can either be open or cyclic.



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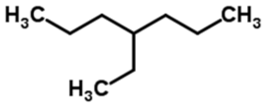
A little bit of nomenclature.

Alkanes are named after the **longest carbon chain** or the **biggest ring system**. When an alkane-chain is a substituent in a larger molecule it is called an alkyl group.

E.g.



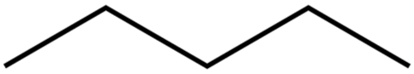
4-ethylheptane

Main	Alkyl-group	Nr of carbons
Methane	Methyl	1
Ethane	Ethyl	2
Propane	Propyl	3
Butane	Butyl	4
Pentane	Pentyl	5
Hexane	Hexyl	6
Heptane	Heptyl	7
Octane	Octyl	8
Nonane	Nonyl	9
Decane	Decyl	10

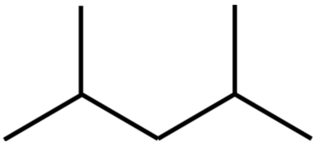
-ane is exchanged for -yl

- The alkyl groups should get as low numbers as possible (when numbering the longest chain).
- When we have more than one of a specific substituent we also add di, tri, tetra … before the alkyl group name.

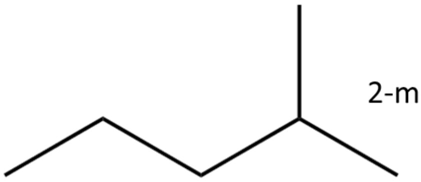
Examples of alkanes:



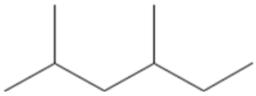
pentane (n-pentane)



2,4-dimethylpentane



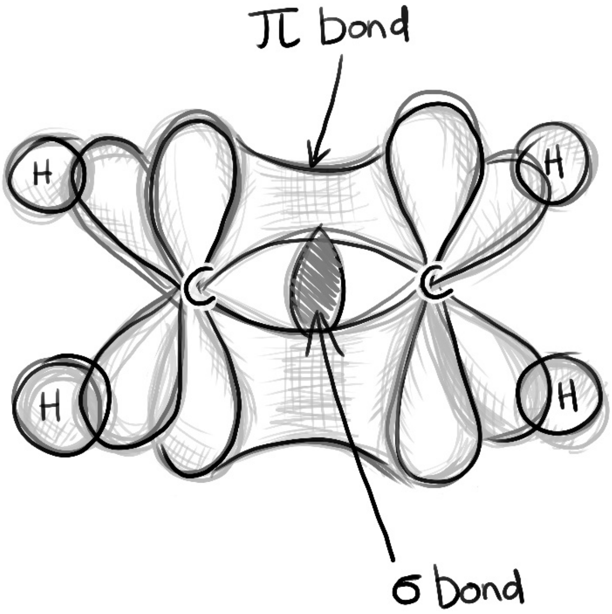
2-methylpentane



2,4-dimethylhexane

Unsaturated hydrocarbons

Introduction



Alkenes: carbon-carbon double bond (σ + π-bond).

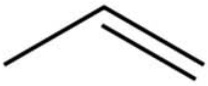
Alkynes: carbon-carbon triple bond (σ + 2 π-bonds).

Base of name will be the chain with the most unsaturation.

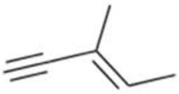
The double bond has priority over the triple bond and will form the base of the name.

The root chain is numbered from the end nearest a double bond carbon atom.

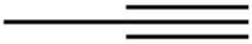
Examples of unsaturated hydrocarbons



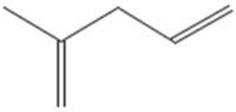
Propene



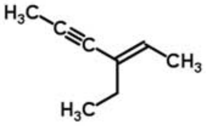
3-methyl-3-pentene-1-yne



Propyne



2-methyl-1,4-pentadien



3-ethyl-2-hexene-4-yne

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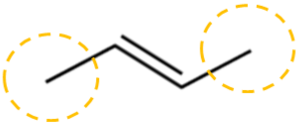
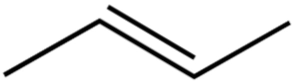
Isomerism

Alkenes where the double bond has more than one substituent can exist in conformers with different geometries. This is called isomerism.

One substituent (CH_3CH_2) – no isomers!!



Two substituents – isomers exist!!



Substituents on opposite side

Substituents on same side

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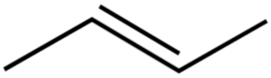
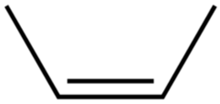


Substituents on opposite side

(E)-2-butene

(E) = Entgegen (opposite/contrary to)



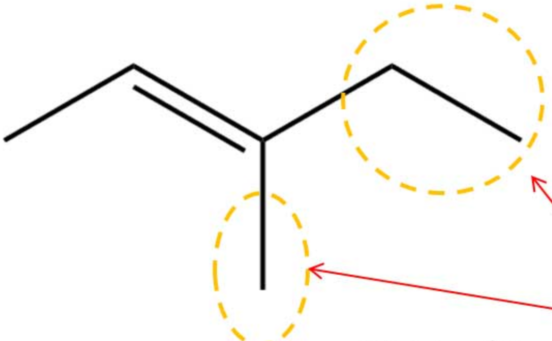
Substituents on same side

(Z)-2-butene

(Z) = Zusammen (together)

How about this structure?

Is it (E)-3-methyl-2-pentene or (Z)-3-methyl-2-pentene?



Which of these two substituents shall we consider?

Which group has the highest priority? The substituents look like this:

- $= C - CH_2 - CH_3$
- $= C - CH_3$

First atom attached to the double bonded C is C for both groups.

Second atom in the sequence is C in the first case and H in the second case

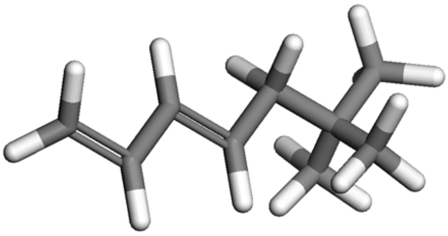
C has higher priority than H and the ethyl group is consequently the dominating group.

Rules for determining priority

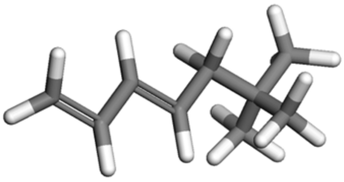
Rules for determining priority:

- Look at atoms directly bonded to the double-bonded carbons – rank according to atomic number (the higher number the higher priority).
- If the directly bonded atoms are the same look at the second, third and fourth atoms away from the double bonded carbon until first difference is found.
- Multiple-bonded atoms are equivalent to the same number of single bonded atoms.

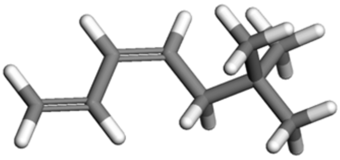
How shall we draw 3-hexyl-6,6-dimethyl-1,3-heptadien?



6,6-dimethyl-1,3-heptadien



or



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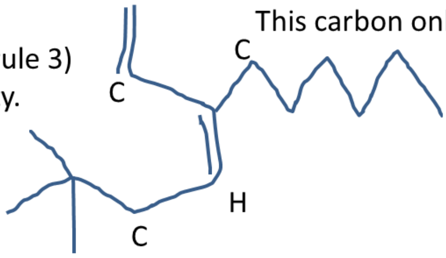
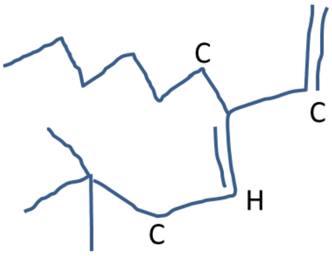


This carbon is considered to
bind to two other carbons (rule 3)
This group has higher priority.

This carbon only binds to one other carbon

This structure is (3Z)-3-hexyl-6,6-dimethyl-1,3-heptadien



This structure is (3E)-3-hexyl-6,6-dimethyl-1,3-heptadien

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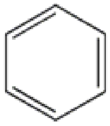
Aromatic hydrocarbons

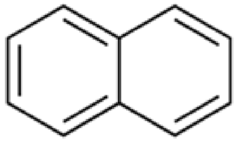
Introduction

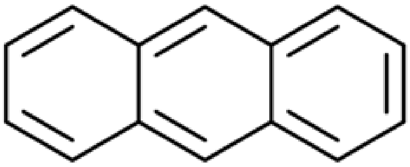
Seems to be part of the unsaturated hydrocarbons (double bonds) but they have so different properties that they form their own group.

Often have strong smell which has given them their names. Their nomenclature is based on a number of base structures: benzene, naphthalene, anthracene etc.



Benzene – the simplest and
the most frequently occurring.
Benzene is however cancerogenic.





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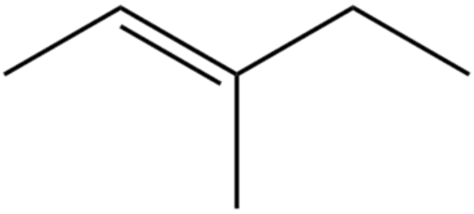

(E)-3-methyl-2-pentene

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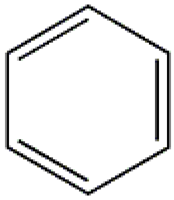
Benzine



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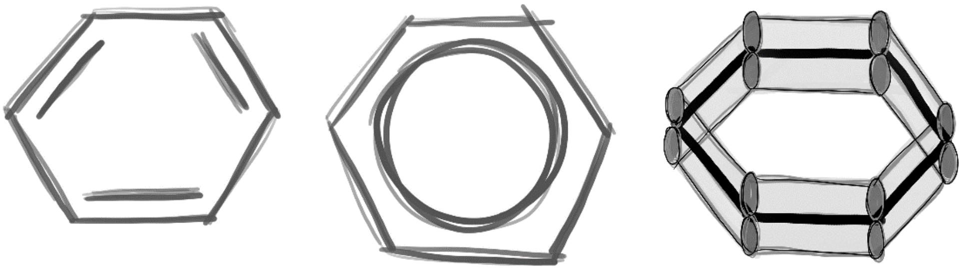
- Benzene as a substituent = phenyl.
- The benzene ring consists of 6 carbon atoms and three double bonds.
- The double bonds are not locked in position so all six bonds in the ring are.
- Identical (this is called aromaticity – not only for carbon).
- This yields a stable molecule.



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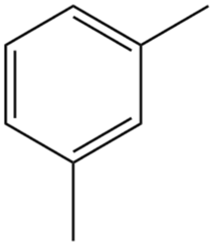
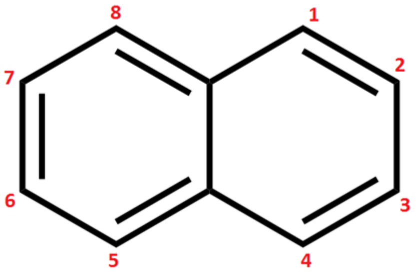
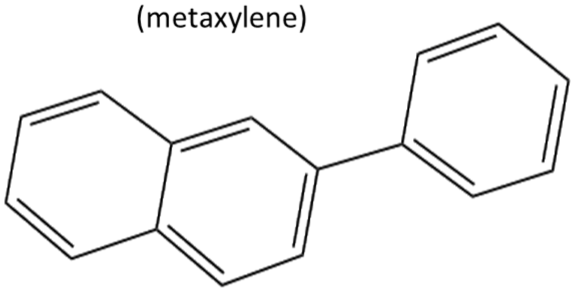
Numbering carbon atoms

Numbering of the carbon atoms in aromatic systems:

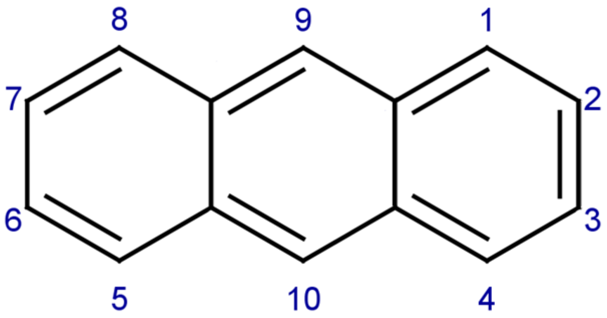


1,3-dimethyl benzene
(metaxylene)





2-phenyl naphtalene



Properties of hydrocarbons

Forces between molecules

Intramolecular forces:

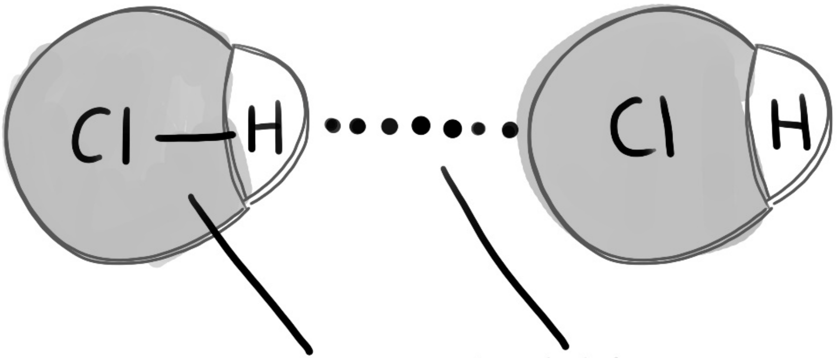
- The forces holding molecules together within a molecule are called intermolecular forces.

Types of intramolecular forces of attraction

- Ionic bond (Cations to anions)
- Covalent bond:
    - Nonpolar covalent bond (Nuclei to shared electrons)
    - Polar covalent bond (Partially charged cation to partially charged anion)
- Metallic bonding (Metal cations to delocalized electrons)

Intermolecular forces:

- Intermolecular forces are forces that exist between molecules.



Types of intermolecular forces

- Dipole-dipole interactions (Partially oppositely charged ions)
- Hydrogen bonding (H atom and O, N or F atom)
- London dispersion forces (Temporary or induced dipoles/van der Waals force)

Questions

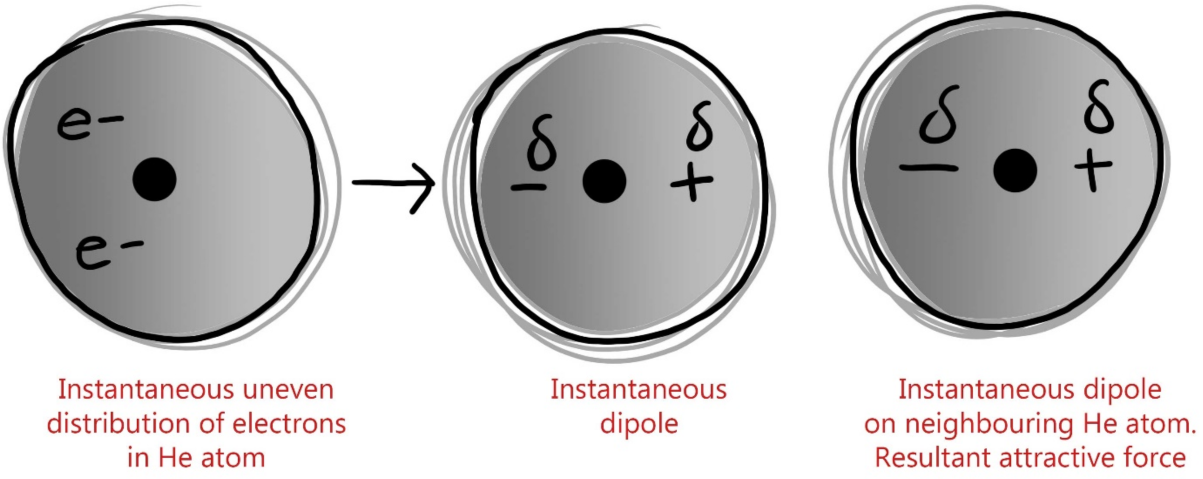
Please complete the questions in the online version of this resource.

Different forces between hydrocarbons

Non-polar covalent bonds in carbohydrates → weak electrostatic forces.

Electrostatic forces are weak between hydrocarbons since they are built up with non-polar covalent bonds

Always present are the London dispersion forces:



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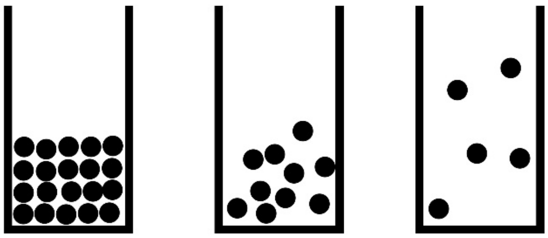
The bigger the molecule the larger surface area and the more induced dipoles can be formed.

- Many physical properties are determined by the intermolecular forces.

Melt temperature T_m: energy required to break the dispersion forces that connect the molecules in solid phase.

Melt temperature T_{bp}: energy required to break the dispersion forces that connect the molecules in the liquid phase.

The dispersion forces in the solid phase are strong since the molecules are arranged like bricks.



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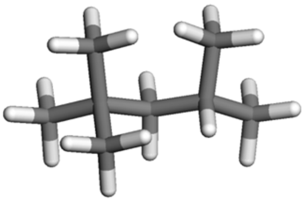
T_m varies with how well the molecules can be packed.

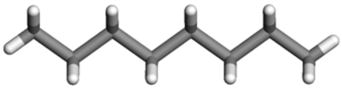
T_{bp} varies with molecular surface.



2,2,4-trimethyl pentane

Irregular shape – hard to pack
T_m is low (-107°C)

Somewhat spherical
Low surface area, T_{bp} = 99°C



Octane

Flexible, streched form can
easily be packed, T_m = -57°C

Not spherical
Large surface area, T_{bp}= 125°C

2,2,3,3-tetramethyl butane

Highly symmetric, easily packed
T_m is high (101°C)

Somewhat sperical
Low surface area, T_{bp}= 106°C

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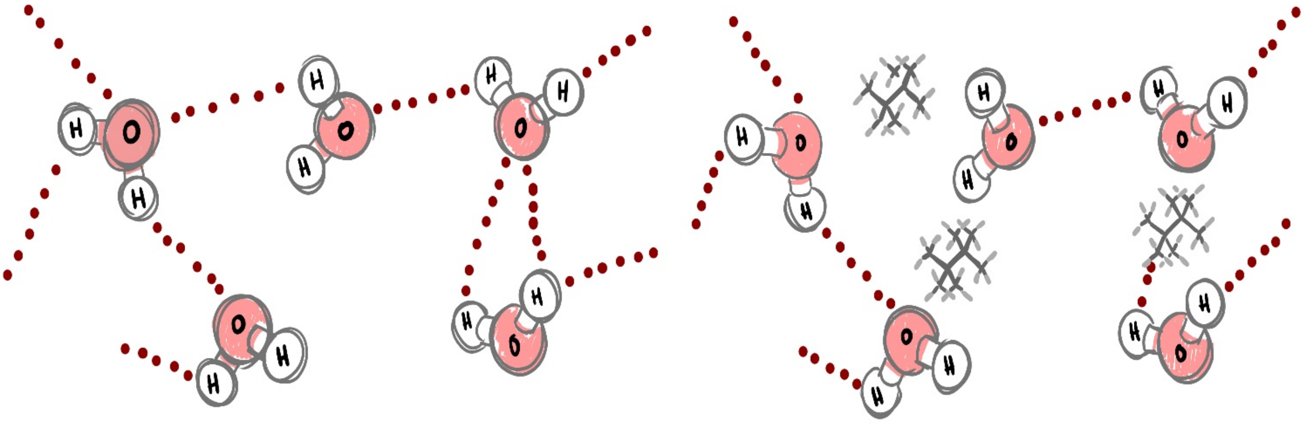
Hydrocarbons in water

Hydrocarbons are insoluble in water.

To dissolve strong intermolecular forces between water molecules need to be broken.

Removing bonds increase the systems energy – not favourable. Formation of bonds decreases the systems energy (favourable but the bonds formed between hydrocarbon and water molecules are very weak).



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All molecules containing H(ydrogens) can function as an acid.

- According to Brønsted's definition an acid is a substance that can release protons (Hydrogen atoms without electrons).
- A base is according to the same man a substance that can receive and bind protons.

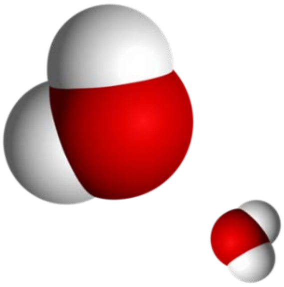
Hydrocarbons are full of hydrogens. We can therefore discuss their acid and base properties. (The acid strength can however be 10^{30} – 10^{40} times weaker than e.g. HCl or H_2SO_4)

Question

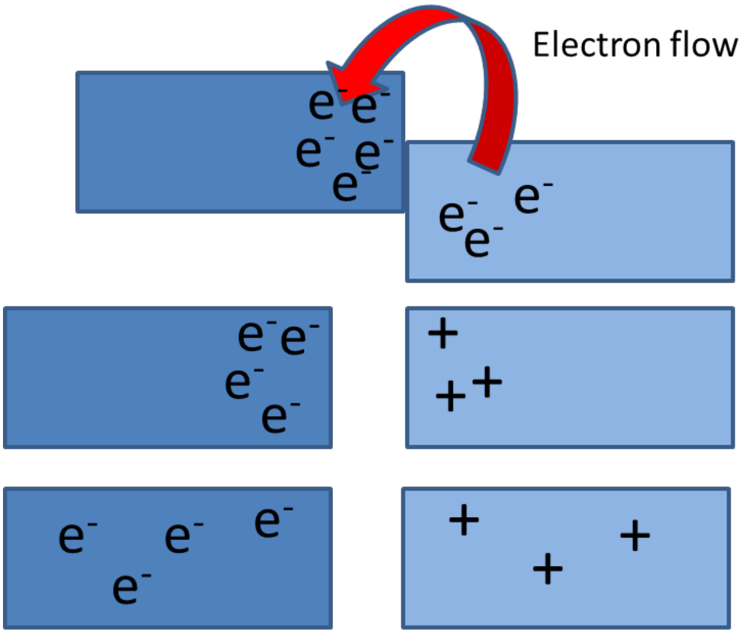
Please complete the question in the online version of this resource

Hydrophilicity

- Polymer should have polar groups/moieties
- These groups attracts water molecules
- Hydrophilicity results in comfortable feel
- Hydrophilicity also prevents charge build-up (static electricity)
- Static electricity is discharged by the water molecules to the surroundings.
- Static electricity:
    1. Dirt particle attraction
    2. Discomfort (ballooning, clinging)



Water molecules
wikimedia/ public domain



Instantaneous dissipation for conductive materials

- Electric charge generated by frictional forces is called triboelectrification.
- One can order materials and fibres in a series (triboelectric series).
- A material will be positively charged when rubbed against another material below it in the series.

Fibre type

Positive end of series	Negative end of series
Glass, Wool, Nylon 6, Nylon 6,6 Rayon, Cotton, Acetate, Hemp, Silk, Polyester, Acrylic, Modacrylic Polyethylene, Polypropylene	Polytetrafluorethylene

The greater the distance between the materials in the series the greater the electric charge.

Energy

Energy: Ability to do work

Types of energy:

1. Kinetic energy
2. Potential energy

Energy conversions

The energy of object can be converted from one to another.

$\Delta U = Q - W$

Change in internal energy = Heat added **to** the system – work done **by** the system

First law of thermodynamics

Energy cannot be created or destroyed (never lost) but can be converted from one form to another.
The total quantity of energy in the universe stays the same.

Khan Academy: First Law of Thermodynamics introduction
<https://www.khanacademy.org/science/biology/energy-and-enzymes/the-laws-of-thermodynamics/v/first-law-of-thermodynamics-introduction>

Second law of thermodynamics

The entropy (disorder) of the universe is constantly increasing.

Khan Academy: Second Law of Thermodynamics
<https://www.khanacademy.org/science/biology/energy-and-enzymes/the-laws-of-thermodynamics/v/the-second-law-of-thermodynamics>

Entropy

Entropy is a measure of disorder or randomness of a system (S).

- The higher entropy the more disorder

  $S_{Solid} < S_{Liquid} < S_{Gas}$ $\Delta S = S_{product} - S_{reactants}$

- Increase in entropy will be observed when:
  - A larger molecule is broken into smaller molecular fragments during the reaction
  - The moles of gas in the product will be increase during reaction.
  - A solid changes to a liquid or gas or a liquid changes to a gas in a process.

Khan Academy: Introduction to entropy
<https://www.khanacademy.org/science/biology/energy-and-enzymes/the-laws-of-thermodynamics/v/introduction-to-entropy>

Enthalpy

Enthalpy (H) is the total kinetic and potential energy of a system at a constant pressure.

The enthalpy of a reaction is a measure of how much heat is absorbed or given off when a chemical reaction occurs.

Change in enthalpy (ΔH): change in heat of system

$\Delta H = H_{final} - H_{initial}$

$\Delta H = H_{product} - H_{reactants}$

- If ΔH is negative: Exothermic reaction
- If ΔH is positive: Endothermic reaction

Gibbs free energy

Gibbs free energy is a quantity used to measure the amount of available energy (to do work) that a chemical reaction provides.

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

Where:

ΔG is Gibbs free energy (kJ), H is enthalpy (kJ), T is temperature (K) and S is entropy (kJ/K).

- A reaction will occur spontaneously if $\Delta G < 0$
- A reaction will not occur spontaneously if $\Delta G > 0$

Khan Academy: Gibbs free energy and spontaneity Key points <https://www.khanacademy.org/science/chemistry/thermodynamics-chemistry/gibbs-free-energy/a/gibbs-free-energy-and-spontaneity>

Khan Academy: Gibbs free energy and spontaneity (video) <https://www.khanacademy.org/science/chemistry/thermodynamics-chemistry/gibbs-free-energy/v/gibbs-free-energy-and-spontaneity>

Surface tension

Tensides

- Tensides are common textile chemicals.
- Tensides are the active component of detergents, emulsifying agents, dispersing agents and wetting agents.

- Tensides are surface active molecules, they enrich at interfaces (i.e. the boundary between two different phases for example water and oil).
- When enriched at the interface the tensides decrease the surface tension.

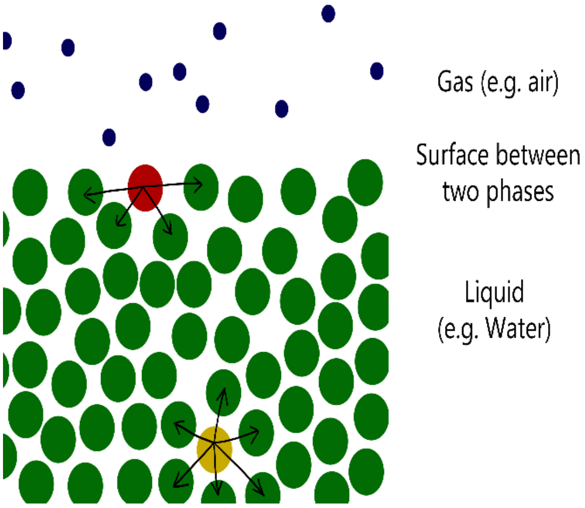
Molecules in the bulk of the liquid are attracted to its neighbours equally in all directions. At the interface molecules are not surrounded by neighbours in all directions. This results in an attractive force directed downwards (into the bulk).

Or expressed in another way: it is more energetically favourable for molecules to be in the bulk than at the surface.

Moving molecules from bulk to interface (i.e. creating new surface area) cost energy. As little surface area as possible is energetically favourable and this is why water droplets are spherical (smallest possible surface area).

Surface tension

It requires energy to create a surface between two phases.



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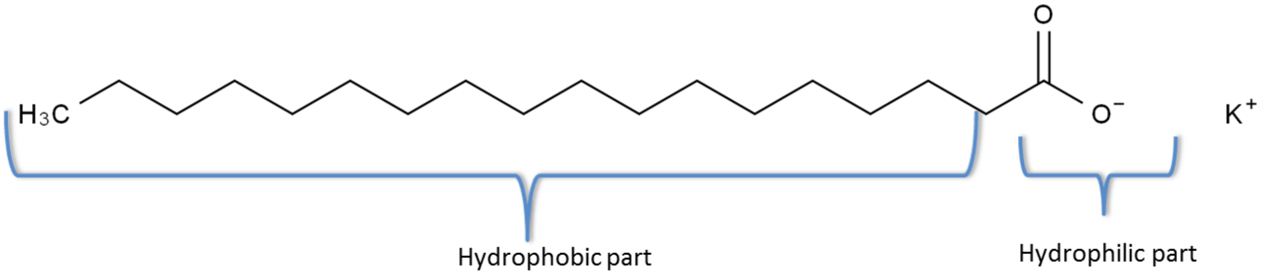
Definition:	Surface tension is the energy required per unit surface area to create a new interface isothermally and reversibly. (Energy required to overcome the opposing force and bring molecules to the surface).
Unit:	J/m^2
Alternative definition:	Surface tension is the force per unit length that acts perpendicularly to every line that can be drawn on the surface.
Unit:	N/m

The tensides molecular structure causes them to have an affinity for interfaces which reduces the surface tension. Tensides consist of a hydrophilic (water loving) part and a hydrophobic (water hating) part. Potassium stearate is one example (used in washing soap).

$C_{17}H_{35}COO^{-} K^{+}$



General depiction of a tenside with a hydrophilic head and a hydrophobic tail.

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Tenside molecular structure

The hydrophobic tail is not water soluble by itself, but together with the hydrophilic head a certain degree of water solubility is obtained.

Properties of tensides

Tensides enrich at interfaces or surfaces:

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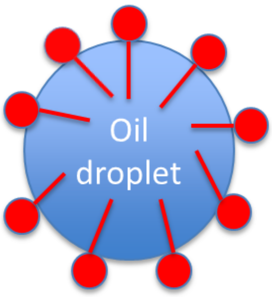
- Surface tension is reduced
    - The surface is wetted (spreading of the water droplet) more easily.
- For an oil and water mixture:
    - Shaking an oil and water mixture will form temporary oil droplets spread out in the water. These droplets adhere and soon the oil and water will form a two-phase system.



The ”head” is charged, this leads to repulsion between the oil droplets.
This repulsion prevents the aggregation of the droplets into one continuous phase.

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With tensides added, the tensides enrich at the oil and water interface, reducing the energy needed to create small droplets. These droplets can be stable for a long time – an emulsion is formed.

This ability to emulgate oil is critical for the washing properties of tenside molecules. Oil and dirt particles (dirt particles are often attached by a thin layer of oil) can be removed and rinsed away during laundering.

Colloids

Colloids are homogenous mixtures containing small particles that will stay suspended. For example, gel is the colloids which consist of gelatine particles suspended in water.

Khan Academy: Suspensions, colloids and solutions
<https://www.khanacademy.org/science/chemistry/states-of-matter-and-intermolecular-forces/mixtures-and-solutions/v/suspensions-colloids-and-solutions>

Summary

Summary

You should now be able to:

- Describe the intermolecular interactions or chemical bonding
- Describe that molecules interact with each other and these interactions influence many physical properties
- Describe the differences in boiling point, melting point, hydrophilicity and hydrophobicity of different substances and materials
- Explain the principal chemical processes that occur during common textile finishing processes

Further reading

- Zumdahl, Steven S., and Donald J. DeCoste. *Chemical Principles*. Pacific Grove, Calif. : Andover: Pacific Grove, Calif. : Brooks/Cole ; Andover : Cengage Learning distributor, 2012.
- Or equivalent general chemistry textbook