HYDROCARBONS

Hydrocarbons are organic compounds composed of only two elements: carbon (C) and hydrogen (H). These elements have almost the same electronegativity (carbon 2.5, hydrogen 2.2) which makes their electronegativity difference of 0.3 only. If the electronegativity difference of two elements bound together is lower than 0.4 the bond between these elements is classified as nonpolar covalent bond. It follows from this that all bonds in molecules of hydrocarbons are of this nature: bonding electrons are shared almost equally by neighboring atoms (in C-H and also in C-C bonds) and this is why there are no partial charges found within these molecules - hydrocarbons are not polar ones. Compounds which are not polar are referred to as nonpolar or hydrophobic and they are insoluble in polar solvent (e.g. water). If you mix a hydrocarbon with water two phases will appear. Densities of hydrocarbons are lower than the density of water (1 g/cm$^3$) and so hydrocarbons flow on the surface of water if mixed together.

Because „similar solvent dissolves similar solute“ hydrocarbons are soluble in nonpolar solvents, e.g. petrol or many other organic liquids.

Hydrocarbons in which carbons are connected by a simple covalent bonds are called saturated hydrocarbons (all bonds of each carbon atom are saturated by hydrogen atoms). These chemicals are colorless, tasteless and nearly odorless. Their boiling points increase with increasing molar mass (the smallest hydrocarbons, C1 - C4, are gases under the room temperature) and decrease with branching because of weaker interactions among branched molecules (less regular structure). Volatility of hydrocarbons decreases with molar mass: short hydrocarbons have narcotic effect (they evaporate under the room temperature easily). The narcotic effect as well as an irritant effect increase with molar mass up to nine carbons in a molecule (the most stronger: C5 - C9).

The main natural source of hydrocarbons is petroleum. Petroleum is a mixture of aliphatic, alicyclic, and polycyclic hydrocarbons containing from one to fifty carbons. Its composition varies with its location. The other important source of hydrocarbons is the nature gas. The nature gas is composed of methane (up to 97%), ethane and propane which are the simplest gaseous alkanes. Other components of the nature gas are carbon dioxide (CO$_2$) and nitrogen (N$_2$).

The smallest hydrocarbon is methane (CH$_4$) - the only one containing only one carbon. Other hydrocarbons are composed of two or more carbons bonded either in linear, branched or cyclic chains. These chains are referred to as hydrocarbon skeletons. The term linear chain means a hydrocarbon skeleton having two ends. Branched hydrocarbons include a parent chain (= the longest linear part of the hydrocarbon) and one ore more branches each containing one or more carbons. Cyclic hydrocarbons form cycles which are either planar (triangle, square, pentagon) or spatial ones (hexagon or other polygons). The cyclic hydrocarbons can be either monocyclic or polycyclic - more rings (polygons) fused together, e.g. cyclohexane and sterane:

Hydrocarbons called aliphatic are all ones which are not aromatic. For definition of aromatic hydrocarbons see below. The term alicyclic is the abbreviation for „aliphatic cyclic“ hydrocarbons. Atoms of both linear and branched hydrocarbons are not found in one plane - hydrocarbons have spatial arrangement:

These spatial models describe methane (C1), ethane (C2), hexane (C6) and 3-methylpentane (branched C6: C5+1) respectively; gray balls are carbons, red balls (smaller ones) are hydrogens.
CLASSIFICATION OF HYDROCARBONS

Hydrocarbons are classified according to the type of bonds found in their molecules:

1. **saturated hydrocarbons** include only single C-C bonds (called sigma bonds, σ)
2. **unsaturated hydrocarbons** include one or more multiple C-C bonds in which so called pi (π) electrons are involved (pi bonds); the multiple bond can be either double or triple bond
3. **aromatic hydrocarbons** also include double bonds like other unsaturated hydrocarbons but their physico-chemical properties differ from them; this is why they are included in a separate group

**Saturated hydrocarbons**

The group of saturated hydrocarbons includes **alkanes** and **cycloalkanes**.

**Alkanes** can be described by a molecular formula \( C_nH_{2n+2} \) where \( n \) = number of carbon atoms in a molecule. Because each carbon atom is tetravalent (it forms 4 bonds in organic compounds) and each hydrogen atom is monovalent (it forms only one bond) the **condensed structural formulas** of alkanes are:

\[
\begin{align*}
\text{CH}_4, \text{CH}_3\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3, \\
\text{and so on. In these formulas bonds of carbon skeleton can be also expressed:} \\
\text{CH}_4, \text{CH}_3\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{In all these cases the dash (-) describes carbon-carbon bond (C-C) and each carbon is fully saturated by hydrogen atoms. Molecular formulas of these four hydrocarbons are:} \\
\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{C}_4\text{H}_{10} \quad (\text{according to: } C_nH_{2n+2})
\end{align*}
\]

The **molecular formulae** are useful for calculating molar masses (number of carbons and hydrogens in molecules are summarized) but the **structure of a hydrocarbon is not seen from this formula**. Hydrocarbons containing four or more carbons can be either linear or branched, e.g. the molecular formula \( C_9H_{18} \) can describe two or more different structures (isomers):

\[
\text{The picture describes real angles between carbons. The most abbreviated formulae describe only bonds:}
\]

**Isomers** are molecules having the same molecular formulae but differing in their structures.

Formulae of long chain hydrocarbons can be also abbreviated, e.g.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 - \text{CH}_3\text{(CH}_3\text{)}_3\text{CH}_3
\]

**Chemical reactivity** of alkanes is low, they were formerly called **paraffins** - the name is derived from Latin words parum affinis meaning „little activity”. The most common reaction of alkanes is substitution which is a replacement of one or more hydrogen atoms by other atoms. One example of the substitution is a replacement of hydrogen by a halogen („halogenation”): methane \( \text{CH}_4 \) can be converted by this reaction to \( \text{CH}_3\text{Cl} \) and if more chlorine atoms are bound instead of hydrogen the other products are \( \text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{CCl}_4 \).

Other **important reaction** of alkanes as of many other organic compounds is an **oxidation**. If the whole carbon skeleton of a hydrocarbon is **completely oxidized** each carbon is converted up to \( \text{CO}_2 \). Hydrogens are bound to oxygen as well: the other product of the reaction is **water** (\( \text{H}_2\text{O} \)). Heat is produced as a form of liberating energy at this reaction. The process of oxidation of organic compounds is used by many organisms to obtain energy by metabolizing nutrients. Also burning organic fuels (coal, petrol) is commonly used as a source of energy.

The **effect of alkanes on human health** can vary according to the type of chemicals. In general alkanes are **hydrophobic** - water insoluble - compounds and when they enter a human body they can be dissolved in cellular membranes. It means that these chemicals can damage cells or they can be stored in body fat which is also a hydrophobic chemical. **Inhalation of alkane vapors** (e.g. petrol) causes severe damage to the lung tissue. Liquid alkanes can also **harm the skin** - long-term contact between **low molecular mass alkanes** and the skin causes removing skin oils and can cause soreness and blisters. By the other hand **high molecular mass alkanes** can be used to protect the skin: mixtures of \( \text{C}_{20} - \text{C}_{30} \) alkanes are used in skin and hair lotions to replace natural oils.

**Cycloalkanes** have a molecular formula \( C_nH_{2n} \) because the ring (polygon) is closed by removing two more hydrogens from linear alkanes. Properties of cycloalkanes are similar to alkanes, but small molecules \( \text{C}_3 \) and \( \text{C}_4 \) are highly reactive because of the ring strain (small angles). Polycyclic molecule called **sterane** is a parent structure of **steroids** (e.g. cholesterol, sex hormons, glucocorticoids, and mineralocorticoids).
Unsaturated hydrocarbons

The group of unsaturated hydrocarbons includes **alkenes, alkadienes and alkynes**. The term "unsaturated" means that these chemicals contain less hydrogens than fully saturated carbon chains as found in alkanes (i.e. "saturated by hydrogens").

**Alkenes** can be described by a molecular formula C_{n}H_{2n}, where n = number of carbon atoms in a molecule. It means that alkenes and cycloalkanes have the same molecular formulae and thus their molecules of the same number of carbons are isomers.

*The simplest alkene* includes 2 carbons: CH_{2}=CH_{2} and it is called ethene. *In case of four or more carbon containing alkenes* the double bond can be found in *more than one position* in their molecule, so there are two or more alkenes having the same molecular formulae but different structures (= structural isomers). For example isomers of butene are:

\[(1^{st}) \text{CH}_{2}=\text{CH-CH}_{2}\text{-CH}_{3} \text{ and (2^{nd}) CH}_{3}\text{-CH=CH-CH}_{3}\]

The structure CH_{3}CH=CH_{2} (2^{nd}) is not the third isomer of butene - it is the same compound as the first one, because when numbering a hydrocarbon chain one must start from the end closer to a double bond. So the first and the third structural formulae describe the same molecule having the double bond at the position 1 (it means between the first and the second carbon) and it is called but-1-ene. The second isomer is called but-2-ene (a locant of the double bond is included in the name exactly before the suffix -ene expressing the presence of the double bond )

The alkene containing only 3 carbons can be thus written either as CH_{2}=CHCH_{3} or CH_{3}CH=CH_{2}

Both these formulae describe the same molecule called simply propene (a locant is not necessary).

**Abbreviated structural formulae are also used:**

\[\text{CH}_{3}\text{CH}!=\text{CHCH}_{2}\text{CH}_{3} \text{ or } \text{CH}_{3}\text{CHCH(}2\text{CH})\text{CH}_{3}\]

**Physico-chemical properties of alkenes** are similar to those of alkanes (nonpolar covalent bonds, hydrophobic character, insoluble in water) but **boiling points of alkenes are lower in comparison** with alkanes of the same length (C2 - C4 are gases). This property is related to **less regular structure of alkanes** because the double bond is **rigid** - there is no free rotation of carbon atoms around it like found in case of single bonds. This structure difference causes weaker intermolecular forces and so the energy needed for change of a liquid state to a gaseous one is slightly lower for alkenes than for alkanes (b.p. of ethene is -104 °C whereas the b.p. of ethane is -88 °C).

The double bond consists of one sigma (σ) and one pi (π) bond. π-electrons involved in the π-bond are more reactive because their spatial arrangement and this is why **alkenes are more reactive than alkanes**. Alkenes also have **higher biological effect than alkanes**, their narcotic effect and toxicity increase with molar mass and with number of other unsaturated bonds in a molecule.

A typical reaction of alkenes is an **addition**: alkene reacts with a small molecule and these two chemicals are joined together to form a compound containing all atoms present in the original chemicals. The double bond is transformed to a single bond:

\[\text{CH}_{2}=\text{CH}_{2}+ \text{Br}_{2} \rightarrow \text{Br}-\text{CH}_{2}\text{CH}_{2}-\text{Br}\]

\[\text{CH}_{2}=\text{CH}_{2}+ \text{HCl} \rightarrow \text{CH}_{3}\text{-CH}_{2}-\text{Cl}\]

\[\text{CH}_{2}=\text{CH}_{2}+ \text{H}_{2}O \rightarrow \text{CH}_{3}\text{-CH}_{2}-\text{OH}\]

\[\text{CH}_{2}=\text{CH}_{2}+ \text{H}_{2} \rightarrow \text{CH}_{3}\text{-CH}_{3}\]

The last above-mentioned reaction describes a **reduction of an alkene**: the unsaturated ethene is converted to the saturated alkane ethane. **The reverse reaction to an addition is called elimination**: whereas in addition an unsaturated hydrocarbon is converted to a saturated one in elimination a saturated hydrocarbon (or a hydrocarbon derivative, e.g. halogen derivative) is converted to an unsaturated hydrocarbon:

\[\text{CH}_{3}\text{-}2\text{CH}_{3} \rightarrow \text{CH}_{2}=\text{CH}_{2}+ \text{H}_{2}\]

\[\text{Br}-\text{CH}_{2}\text{-CH}_{2}-\text{Br} \rightarrow \text{CH}_{2}=\text{CH}_{2}+ \text{Br}_{2}\]

The first above-mentioned reaction describes an **oxidation of the saturated hydrocarbon** ethene, the unsaturated ethene is formed (hydrogens has been removed - the carbon chain is now unsaturated).

Other important reaction of alkenes is a **polymerization**: an unsaturated hydrocarbon serves as a **monomer** (= building block) from which a polymer (a macromolecule of high molecular mass) is formed. The polymerization can be described as **multiple addition** (n = nonspecified number of reacting alkene molecules):

\[\text{nCH}_{2}=\text{CH}_{2} \rightarrow (-\text{CH}_{2}-\text{CH}_{2})_{n} \text{ polyethylene (PE)}\]

Plastic materials are synthesized by this reaction, properties of polymers depend on the monomer used and the final molar mass of the polymer. The name of a polymer is often abbreviated, e.g. PE = polyethylene which is made from ethene monomers (the hydrocarbon rest -CH_{2}-CH_{2}- is called ethylene).
Alkadienes are unsaturated hydrocarbons including two carbon-carbon double bonds which are often separated from each other by one or more single bonds. The important alkadiene is isoprene:

![Isoprene structure]

Isoprene can be also used in polymerization reaction - the natural rubber is one of the naturally occurring polymers of isoprene. In human body other polymers of isoprene are found, e.g. cholesterol or steroid hormones are derivatives of isoprene.

Alkynes are unsaturated hydrocarbons including carbon-carbon triple bond in their molecules. The triple bond is shorter than the double bond (which is also shorter than the single bond) and it consists of one sigma and two pi bonds. Its reactivity is similar to that of the double bond of alkenes (addition reaction). The simplest alkyne is ethyne (its common - the alternative - name is acetylene): CHCH - all atoms of this molecule are found in a straight line. The molecular formula of alkynes is C_nH_{2n-2}.

Aromatic hydrocarbons

The group of aromatic hydrocarbons is a special kind of unsaturated hydrocarbons. They are classified separately because their properties differ from those of unsaturated hydrocarbons, (e.g. addition reaction is not common). The other group name of these compounds commonly used is arenes.

Arenes are cyclic planar molecules including alternating single and double bonds (= conjugated double bonds) in the ring (polygon). The simplest arene is benzene:

![Benzene structures]

All these structures describe the same molecule. The ring within a hexagon describes real structure of the arene: \( \pi \)-electrons involving in double bonds are delocalized above and below the ring plane. It means that in the real structures of arenes there is no alternation of single and double bonds but the bonds between neighboring carbons are equivalent.

An aromatic character can be checked by calculating the number of \( \pi \)-electrons in an aromatic ring equals \( 4n + 2 \) in which \( n \) is the whole number.

\[
\pi = 4n + 2 \quad \text{if} \quad n = 1, 2, 3, ...
\]

The calculation for benzene: the number of \( \pi \)-electrons is \( 6 \) (2 x 3 double bonds) so \( n \) calculated using the Hückel rule is 1 which is the whole number. It follows from this that benzene is an arene: Hückel rule fulfilled, benzene molecule is planar and it can be described by at least two resonance structures (those describing the same compound):

![Benzene resonance structures]

Aromatic compounds are called aromatic because their odour. They are either monocyclic or polycyclic and their names are not based on defined rules: arenes are called by common names only. Monocyclic arenes (benzene, toluene, xylene) are often used as laboratory solvents, they have narcotic and irritant effect:

![Aromatic compounds structures]

toluene, p-xylene, m-xylene, o-xylene respectively

Styrene (= vinyl benzene) is a monomer of polystyrene (PS) which is a commonly used polymer.

Polycyclic arenes are solid molecules often termed as polyaromatic hydrocarbons (PAH). If the polyaromatic hydrocarbons enter a human body they are metabolised and some intermediates of these biochemical reactions are highly toxic - they can damage DNA in cellular nucleus and give rise to tumors, e.g. benzopyrenes which are present in cigarette smoke:
Other important polyaromatic hydrocarbons are naphtalene (2 condensed benzene rings), anthracene and phenanthrene (3 rings) and pyrene (4 rings), pictured respectively:

![Naphtalene](image1)

![Anthracene](image2)

![Phenanthrene](image3)

![Pyrene](image4)

**NOMENCLATURE OF HYDROCARBONS**

Naming saturated and unsaturated hydrocarbons is based on the name of the longest unbranched part (linear hydrocarbon chain, parent chain) of their molecule. The number of carbons involved in the parent chain is expressed by a prefix, the type of a hydrocarbon (alkane, alkene, alkyne) is expressed by a suffix of the name:

- CH$_4$ is **methane** = C1, alkane
- CH$_3$CH$_3$ is **ethane** = C2, alkane
- CH$_2$CH$_2$ is **ethylene** = C2, alkene
- CHCH is **ethyne** = C2, alkyne

These names are termed as **systematic or IUPAC names** because if you know rules based on given prefixes and suffixes you are able to write a structural formula according to this name. All important prefixes are summarized at the end of this chapter.

Some compounds are also called by an alternative name termed as **common or trivial name**. This name is not based on regular rules and must be memorized in a relationship to a systematic name of the compound:

- CH$_2$CH$_2$ is „**ethylene**“ (common name) = ethene (systematic name)
- CHCH is „**acetylene**“ (common name) = ethyne (systematic name)

The most important common names you must know are summarized at the end of this chapter.

The term parent chain will be explained in naming branched hydrocarbons. Branches are called by names of hydrocarbon residues (= alkyls) attached to the parent chain:

![Isoprene](image5)

To call isoprene systematically one must find a longest unbranched (parent) chain of its molecule including all multiple bonds (= nomenclature rule). The parent chain of isoprene includes four carbons and two double bonds.

Then carbons of the parent chain has to be numbered from the end of a molecule which brings the lowest locants to multiple bonds as well as the lowest locants to all branches as possible. In case of isoprene the first carbon of its molecule is found on the left: then positions of double bonds are 1 and 3 and the position of its branch is 2.

The name of a branch (alkyl residue) is derived from the name of a hydrocarbon from which it was derived by removing one hydrogen:

- an alkyl CH$_3^-$ was derived from the molecule CH$_4$

Because CH$_4$ is called methane, the alkyl derived from it is called methyl: the suffix -ane was replaced by the suffix -yl which is the universal suffix for alkyl or aryl residues (hydrocarbon rests derived from arenes).

The systematic name of isoprene can be put together:

- locant of the branch: 2-
- branch name: **methyl**
- prefix describing the number of carbons: **but(a)**
- locants of double bonds: 1,3-
- multiple prefix: **di** (for 2 double bonds)
- suffix describing a type of a hydrocarbon: **-ene**
- resulting name: 2-methylbuta-1,3-diene

If two or more branches are present in a molecule, multiple prefixes must be included:

- CH$_3$CH$_2$CH$_2$CH$_3$ is **2,2-dimethylpropane**
- (prop = C3 in the parent chain)

In case of two or more different branches the alkyl names must be ordered **alphabetically**:

- CH$_3$CH$_2$CH$_2$CH$_3$ is **3-ethyl-2-methylpentane** (pent = C5 in the parent chain)
- (the numbering of this parent chain must start from the right end to obtain the lowest locants as possible for both branches)
### Important common names

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### Important nomenclature prefixes

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Prefixes summarized in the second row are used to express the **number of carbons** in an organic molecule, the prefixes in the third row are multiple ones used to describe **number of multiple bonds, branches or substituents** in a molecule.