

ORGANIC CHEMISTRY- PART 1 FUNDAMENTALS



Muhammad Arif Malik
Hampton University

Organic Chemistry -Part 1 Fundamentals

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (<https://LibreTexts.org>) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide an accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by [NICE CXone Expert](#) and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptations contact info@LibreTexts.org or visit our main website at <https://LibreTexts.org>.

This text was compiled on 08/22/2025

TABLE OF CONTENTS

Licensing

1: Bonding and structure

- 1.1: What is organic chemistry
- 1.2: Structure of an atom
- 1.3: Chemical bonds
- 1.4: Bonding theories and geometries of molecules
- 1.5: Polarity of bonds and molecules

2: Representing organic structures

- 2.1: Drawing organic structures
- 2.2: Resonance
- 2.3: Organic nomenclature -alkanes
- 2.4: Organic nomenclature -functional group containing compounds

3: Stereochemistry

- 3.1: Introduction to stereochemistry
- 3.2: Conformational analyses
- 3.3: Conformational analysis of cyclohexanes
- 3.4: Configurational stereoisomerism
- 3.5: Assigning R/S stereodescriptors to chirally center
- 3.6: Optical activity
- 3.7: Types of chiral molecules
- 3.8: Chirality related topics

4: Acids and bases

- 4.1: Importance of acids, bases and their reactions
- 4.2: Arrhenius Acids and Bases
- 4.3: Brønsted-Lowry Acids and Bases
- 4.4: Predicting the direction of acid-base reactions
- 4.5: Thermochemistry of acid-base reactions
- 4.6: Factors affecting the strength of an acid
- 4.7: Lewis acids and bases

5: Alkanes and Free radical reaction mechanisms

6: Alkenes, alkynes and electrophilic addition reactions

7: Alkyl halides and Nucleophilic substitutions and eliminations

8: Aromaticity and electrophilic aromatic substitution reactions

[Index](#)

[Glossary](#)

[Detailed Licensing](#)

[Detailed Licensing](#)

Licensing

A detailed breakdown of this resource's licensing can be found in [Back Matter/Detailed Licensing](#).

CHAPTER OVERVIEW

1: Bonding and structure

- [1.1: What is organic chemistry](#)
- [1.2: Structure of an atom](#)
- [1.3: Chemical bonds](#)
- [1.4: Bonding theories and geometries of molecules](#)
- [1.5: Polarity of bonds and molecules](#)

This page titled [1: Bonding and structure](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

1.1: What is organic chemistry

Chemistry

Chemistry is the study of the properties and behaviour of matter.

Pure matter can be classified as either an element or a compound. An element consists of only one type of atom. Currently, there are 118 known elements. A compound, on the other hand, is made up of more than one type of atom that are held together in fixed proportions by electrostatic attractive forces known as chemical bonds. Compounds can be categorized as either inorganic or organic. Inorganic compounds are generally defined as all compounds that do not contain covalently bonded carbon (C) and hydrogen (H).

Organic compounds

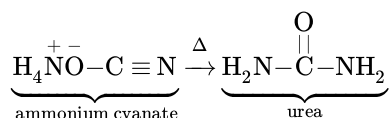
Organic compounds are compounds of C covalently bonded with H or sometimes with other elements, e.g., with oxygen (O), nitrogen (N), phosphorus (P), sulfur (S), etc.

This is not a comprehensive definition of organic compounds. The exceptions, include the oxides of carbon, like carbon dioxide CO_2 , carbon monoxide CO , salts of carbonates CO_3^{2-} , and cyanides CN^- , etc. Note that these exceptions are compounds of C without any covalent bond between a C and a H. Organic compounds have a C covalently bonded with a H with very few exceptions. Atoms other than C and H in an organic compound are called **heteroatoms**. For example, O's are heteroatoms in glucose $\text{C}_6\text{H}_{12}\text{O}_6$.

Organic Chemistry

Organic chemistry studies the synthesis, reactions, and other properties of organic compounds.

The importance of organic compounds lies in the fact that they are synthesized and utilized by living things. For example, glucose is synthesized during photosynthesis from CO_2 and H_2O at the expense of energy from sunlight. Glucose is then utilized to synthesize other organic compounds or to convert it back to CO_2 and H_2O , releasing the energy. In earlier times, it was hypothesized that a "vital force" present in living things was necessary to synthesize organic compounds. This hypothesis was debunked when Wöhler synthesized an organic compound called urea in the laboratory from an inorganic compound, ammonium cyanate, by the following chemical reaction.



Why nature has chosen C and H to constitute organic compounds

Considering the process of natural selection, i.e., the "survival of the fittest," when applied at the molecular level, the question arises why C and H have survived as the major constituents of organic compounds? Here are some plausible explanations based on what we know about elements at present. H is the lightest atom known, offering living things the advantage of carrying less weight. However, H is monovalent and needs another element to make larger molecules. Second row elements like C, N, O, etc., are the lightest multivalent elements. Among second row elements, C has the highest valency, i.e., tetravalent, making stronger covalent bonds with C, H, N, O, etc. Particularly, the ability of C to make stable bonds with C allows the synthesis of straight chains, branched chains, and cyclic structures that are the framework of a vast array of complex structures in organic compounds. C not only make single bonds, but can also make double and triple bonds, resulting in a more reactive variety of organic compounds. The ability of C to make polar single, double, and triple bonds, N, O, S, P, etc., adds an enormous variety of organic compounds containing reactive sites with various desirable properties.

H -the lightest monovalent atom, not only caps unused valencies of C, N, O, etc., it has several other functions essential for the processes of life. For example, polar covalent bonds between H and N or O allow attaching other molecules or parts of the same molecule through intramolecular forces called hydrogen bonding. The hydrogen bonding plays a crucial role in

establishing shapes, called the secondary structures of biomolecules, that are needed for their functions in biochemical processes. For example, an egg can be hatched to give birth to a chick, but boiling it breaks the hydrogen bonding, converting it into a non-fertile egg.

Usually, the C–H covalent bonds are formed by breaking C–O and O–H covalent bonds by absorbing energy, e.g., by capturing energy from sunlight in photosynthesis:



The process is gradually reversed during digestion, producing partially oxygenated intermediates and releasing the energy living things need. Complete oxidation reproduces CO_2 gas that is exhaled and H_2O liquid that adds to body mass and helps dissolve and excrete other waste products. Recall that H_2O constitutes 60% to 90% of the body mass of living things, acting as a medium for transportation and reactions of the biochemicals.

This page titled [1.1: What is organic chemistry](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

1.2: Structure of an atom

Model of an atom and the related terminologies

Subatomic particles

An atom is the smallest particle of an element that represents its properties. It comprises subatomic particles called electrons, protons, and neutrons. Electrons (e^-) carry a negative charge equal to the unit elementary charge (e), i.e., $-1e$, and have a mass equal to 9.11×10^{-31} kg. Protons (p^+) carry a positive charge equal to $+1e$ and a mass of 1.6726×10^{-27} kg. Neutrons (n^0) are neutral particles having a mass equal to 1.6749×10^{-27} kg. Electrons do not have substructures, but protons and neutrons are composed of elementary particles called quarks. However, the basic knowledge of subatomic particles, electrons, protons, and neutrons is sufficient for the purpose of this book.

Depicting an atom

According to the modern view of an atom, protons and neutrons are in the center of the atom, usually in a region called the nucleus, and the electron cloud is around the nucleus. Figure 1.2.1 illustrates a helium atom. The diameter of a nucleus varies in the range of about 2 femtometers (fm) to 10 fm ($1 \text{ fm} = 10^{-15} \text{ m}$). The diameter of an atom varies in the range of about 5 angstroms (Å) to 15 Å ($1 \text{ Å} = 10^{-10} \text{ m}$). It means the size of a nucleus is about one thousandth of the size of an atom, i.e., electrons occupy more than 99.999% of the space in an atom, and more than 99.999% of the atom's mass is in the nucleus.

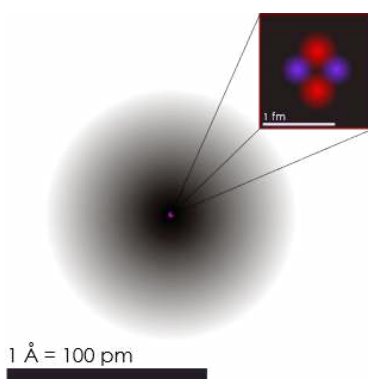


Figure 1.2.1: Illustration of a helium atom having a nucleus (pink) which is enlarged in the figure insert, consisting of two protons (red) and two neutrons (purple). The fuzzy cloud is the electron probability cloud. (Copyright; Yzmo, CC BY-SA 3.0, via Wikimedia Commons)

Atomic number

The number of protons in an atom is called its atomic number (Z). Atomic number defines the element, e.g., an atom with one proton is H, with six protons is C, with eight protons is O, and so on. In other words, the atomic number is implicit in the element's symbol or name.

Mass number

The number of protons + neutrons is called mass number (A). Atomic number is also shown as subscript and mass number as a superscript to left of the symbol of element, as ${}_Z^AX$, where X is the symbol of an element. For example, ${}_6^{12}\text{C}$ represents a carbon atom having 6 protons and 6 neutrons, i.e., atomic number 6 and mass number 12.

Atomic mass and relative atomic mass

Atomic mass (m_a) is the sum of the masses of protons, neutrons, and electrons in an atom. Atomic mass is slightly less than the sum of the masses of the atom's isolated protons, neutrons, and electrons. This difference, called the mass defect, arises because energy is released equal to the binding energy when protons and neutrons are bonded together in the nucleus. The binding energy is proportional to the loss of mass given by the formula $E = mc^2$ where E is the energy, m is the mass, and c is the speed of light. Consequently, the nuclear forces, stronger than electrostatic repulsive forces between positively charged protons, bind neutrons and protons. Energy equal to the binding energy is needed to break a proton or a neutron from the nucleus. Nuclear forces operate at short distances, comparable to the sizes of the nuclei. Electrons in an atom are at distances larger than the range of nuclear forces. Therefore, electrostatic attractive forces between electrons and oppositely charged protons in the nucleus hold electrons in an atom.

Atomic mass is usually measured in unified atomic mass unit u , which is exactly equal to $\frac{1}{12}$ th the mass of $^{12}_6\text{C}$ atom in its neutral state. Biologists usually use dalton (Da) in the place of u ($Da = u = 1.99264688270(62) \times 10^{-26} \text{ kg}$).

Relative atomic mass is the same as atomic mass but without any unit, i.e., a dimensionless unit. The unit is lost because it is a ratio of atomic mass to $\frac{1}{12}$ th the mass of $^{12}_6\text{C}$, i.e., the mass unit in numerator and denominator of the ratio cancel each other.

Isotopes

Isotopes are atoms of the same element having a different number of neutrons. For example, protium ^1_1H , deuterium ^2_1H , and tritium ^3_1H , are isotopes of hydrogen having zero, one, and two neutrons, respectively. Similarly, $^{12}_6\text{C}$, $^{13}_6\text{C}$, and $^{14}_6\text{C}$ are isotopes of carbon having six, seven, and eight neutrons, respectively.

Atomic weight

Atomic weight or standard atomic weight ($A_r^\circ(E)$ for element E) is the weighted average of relative atomic masses of all isotopes of that element in a natural sample.

The following formula calculates the atomic weight:

$$A_r^\circ(E) = \sum (\text{relative atomic mass of isotope}) \times (\text{fractional abundance of the isotope})$$

, where $\sum$ means summation over all isotopes of the element, the fractional abundance of the isotope is the % abundance divided by 100. For example, copper (Cu) has two isotopes in natural samples: $^{63}_{29}\text{Cu}$ having relative atomic mass 62.929 is 69% (fractional abundance = $\frac{69}{100} = 0.69$) and $^{65}_{29}\text{Cu}$ having relative atomic mass 64.927 is 31% (fractional abundance = $\frac{31}{100} = 0.31$). Standard atomic weight of copper ($A_r^\circ(_{29}\text{Cu})$) is calculated as shown below.

$$A_r^\circ(_{29}\text{Cu}) = 62.929 \times 0.69 + 64.927 \times 0.31 = 63.55 \quad (1.2.1)$$

Note that atomic weight is a dimensionless quantity because it is calculated from relative atomic masses, which are dimensionless.

Ions: cations and anions

The number of electrons in a neutral atom equals the number of protons in it. However, an atom may lose or gain one or more electrons and become an ion, a charged particle. The charge is shown as a superscript to the right of the element's symbol: a number followed by a sign (+/-). Loss of one or more electrons forms a particle with a positive charge, i.e., a cation. For example, $^{23}_{11}\text{Na}^+$ is a cation of sodium that has 11 protons but one less, i.e., 10 electrons with 1+ charge on it and $^{24}_{12}\text{Mg}^{2+}$ is a cation of magnesium having 12 protons but two less, i.e., 10 electrons and 2+ charge on it. Similarly, $^{19}_9\text{F}^-$ is an anion of fluorine having 9 protons but one more, i.e., 10 electrons with 1- charge on it and $^{16}_8\text{O}^{2-}$ is an anion of oxygen having 8 protons but two more, i.e., 10 electrons and 2- charge on it. Note that when the sign follows the number in the superscript and when the charge is ± 1 , the number is not shown, only the sign is shown, but when the charge is more than one, both the number and the sign are shown.

Electron configuration of an atom

Electron configuration is the arrangement of electrons around the nucleus, as illustrated in Figure 1.2.1 for a helium atom. To understand it, first recall the dual nature of radiation and matter. Electromagnetic radiation is a wave, but can also be treated as particles, i.e., packets of energy called photons. The energy E of a photon is related to the frequency ν and mass m by the following equations.

$$E = h\nu = mc^2$$

, where h is Planck's constant and c is the speed of light. De Broglie derived the following equation relating the wavelength λ of a wave associated with a matter particle to the mass m and speed v of a matter particle.

$$\lambda = \frac{h}{mv}$$

For matter particles that we see around have large masses that are associated with wavelengths too small to be characterized. Still, the wavelength of particles with a mass as small as an electron is comparable to that of electromagnetic radiation. It has been

experimentally characterized, e.g., electron diffraction has been observed like X-ray diffraction.

The Schrödinger equation is a mathematical equation that can predict the behaviour of an electron in an atom or a molecule, treating it as a wave. Solution of the Schrödinger equation yields a wavefunction, called psi ψ , that represents the probability amplitude of finding an electron at a given point in space around the nucleus. Recall that waves have amplitudes that vary along the wave and have phases: positive on the crest side and negative on the trough. The square of the wavefunction ψ^2 has physical meaning, i.e., the probability of finding an electron at the given point.

Electron quantum numbers in an atom

The analogy of the electron waves in an atom is that of the standing waves. Recall that standing waves are established only when the length is equal to $\frac{1}{2}\lambda$ or a multiple of it. Similarly, the electron wavefunction ψ takes three quantum numbers: principle n , angular momentum l , and magnetic l_m quantum number.

1. The n has integer values, i.e., 1, 2, 3, 4, etc. It determines the energy and the average distance of the electron from the nucleus, called the shell- the higher the n , the higher the energy and the longer the average distance.
2. The l has integer values from 0 to $l - 1$ and defines the shape of the regions around the nucleus where the electron is found, called a subshell within the shell. $l = 0$ is designated as s subshell, $l = 1$ is p , $l = 2$ is d , $l = 3$ is f and so on. The l also contributes to the energy along with n , i.e., the higher the $n + l$, the higher the energy of the orbital. When $n + l$ values are equal, the n breaks the tie, i.e., the higher the n , the higher the energy.
3. The m_l has integer values from $-l$ to 0 to $+l$. It defines the number and the orientation of a unique region around the nucleus where an electron may be found, called orbitals within a subshell. For example, $l = 0$ is s subshell that has only one value of $m_l = 0$, and has only one orbital in it, $l = 1$ is p subshell that has three values of $m_l = +1, 0$, and -1 , corresponding to three p orbitals. If one p orbital is oriented along x-axis, called p_x , the second is along y-axis, called p_y and the third is along z-axis, called p_z . The $l = 2$ is d subshell that has five orbitals corresponding to its five m_l values $+2, +1, 0, -1$, and -2 and $l = 3$ is f subshell that has seven orbitals corresponding to its seven m_l values $+3, +2, +1, 0, -1, -2$, and -3 .

The fourth quantum number, called the electron spin quantum number m_s , describes the angular momentum of an electron in an orbital. The angular momentum, called spin, can have two possible orientations, corresponding to two possible values of $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$.

Atomic orbital

An atomic orbital in an atom around the nucleus is defined by boundaries in which the probability of finding a given electron is higher, usually limited to 90% or 95%.

Orbital notations

Each orbital in an atom has a unique combination of the three quantum numbers, n , l , and l_m . Therefore, the number of orbitals in a shell n is equal to n^2 . For example, the first shell ($n = 1$) has only one orbital ($1^2 = 1$) having $n, l, l_m = 1, 0, 0$. It is designated as 1 s , where the number represents shell# and the letter represents subshell. Second shell ($n = 2$) has four orbitals ($2^2 = 4$). These are 2 s , and three $2p$ orbitals: $2p_x$, $2p_y$, and $2p_z$.

Shapes and orientations of s and p orbitals

Quantum number l defines the shape and orientations of an orbital. 1 s orbital has $l = 0$ and is the same on all orientations, i.e., spherically symmetrical, as illustrated in Figure 1.2.2. Recall that an electron is being treated as a wave; like a wave, it has phases and a variable amplitude. 1 s orbital has only one phase, + or -. The probability density is highest per unit volume close to the nucleus, represented by darker gray in the figure, decreasing as the distance from the nucleus increases, becoming lighter gray in the figure.

The 2 s orbital is spherically symmetrical but larger than 1 (s). The electron density is maximum at the center close to the nucleus, falls to zero, rises again to a maximum, and gradually decreases as the radius increases. This feature is evident from the onion shell-like structure of 2 s orbital: a dark gray inner sphere and a light gray outer shell with a white shell of zero electron probability separating the two. 2 s orbital has two phases, if the inner sphere is +, the outer will be - and vice versa.

Node in orbital

A region of zero electron density in an atomic orbital is called a node.

A node can be a sphere, as in the case of $2s$ orbital, or a plane representing a region where the wavefunction changes sign or phase. $2s$ orbital is larger than $1s$ with one node, $3s$ is larger than $2s$ with two nodes, and so on, as illustrated in Figure 1.2.2.

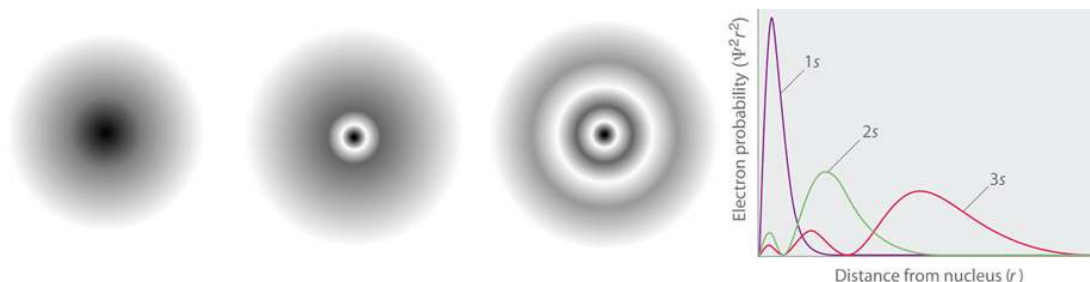


Figure 1.2.2: Illustration of a cross-section of $1s$, $2s$, and $3s$ orbitals (left) (Copyright; Koantum, CC BY-SA 3.0, via Wikimedia Commons) and radial electron probability distribution (Copyright: Public domain).

$2p$ orbital is dumbbell-shaped with two lobes of opposite polarity; if one is $+$, the other is $-$ phase. The nucleus is in the middle with a nodal plane passing it perpendicular to the two axes of the two lobes. There are three $2p$ orbitals corresponding to the quantum numbers n , l , and l_m . If one $p = 2, 2, +1$; $2, 2, 0$; and $2, 2, -1$, respectively. If one is oriented along the x -axis, called $2p_x$, the second is along the y -axis, called $2p_y$, and the third is along the z -axis, called $2p_z$, as illustrated in Figure 1.2.3.

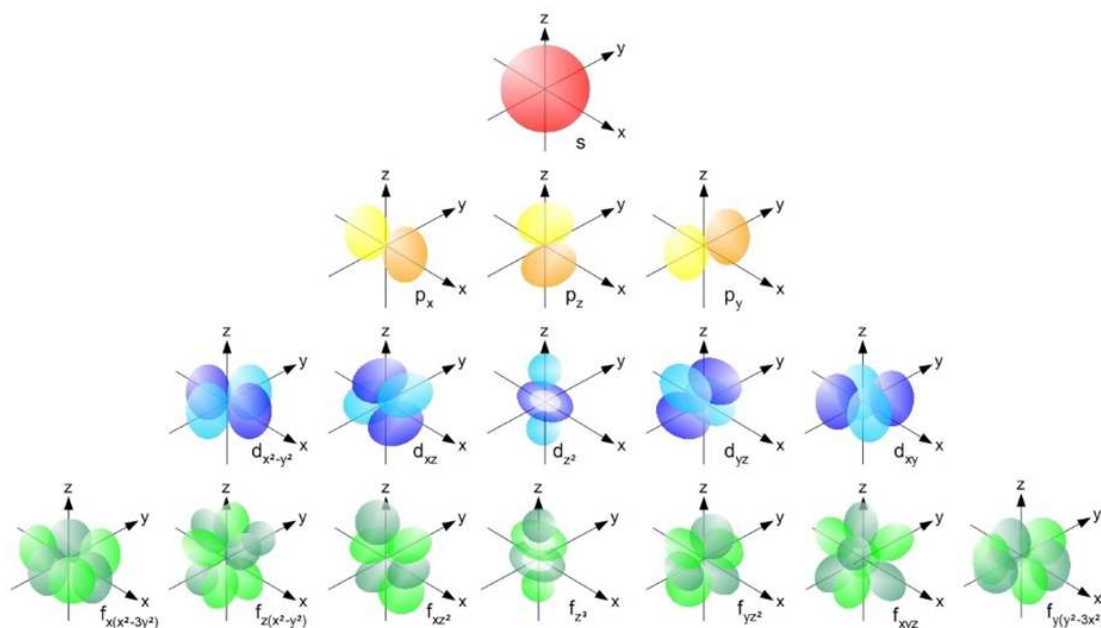


Figure 1.2.3: Illustration of $1s$ (top-row), $2p$ (2nd-row), $3d$ (3rd-row) and $4f$ (4th row) orbitals. Different colors represent different phases in the orbitals. (Copyright; haade, CC BY-SA 3.0 via Wikimedia Commons)

The shapes and orientations of d and f orbitals are shown in Figure 1.2.3. The details of s and p orbitals are described above because they are the most important in understanding organic chemistry, but those of d and f are not described as they are more complicated and not necessary for the purpose understanding organic chemistry described in this book.

Energy order of atomic orbitals

Each atomic orbital has a unique set of three quantum numbers n , l , and l_m . The energy of an orbital is determined by the combination of two quantum numbers $n + l$ -here, the $n + l$, the higher the energy, where n is the tie breaker. It results in the following order from the lowest to the highest energy: $1s$ $2s$ $2p$ $3s$ $3p$ $4s$ $3d$ $4p$ $5s$ $4d$ $5p$ $6s$ $4f$ $5d$ $6p$ $7s$ $5f$ $6d$ $7p$, as illustrated in Figure 1.2.4.

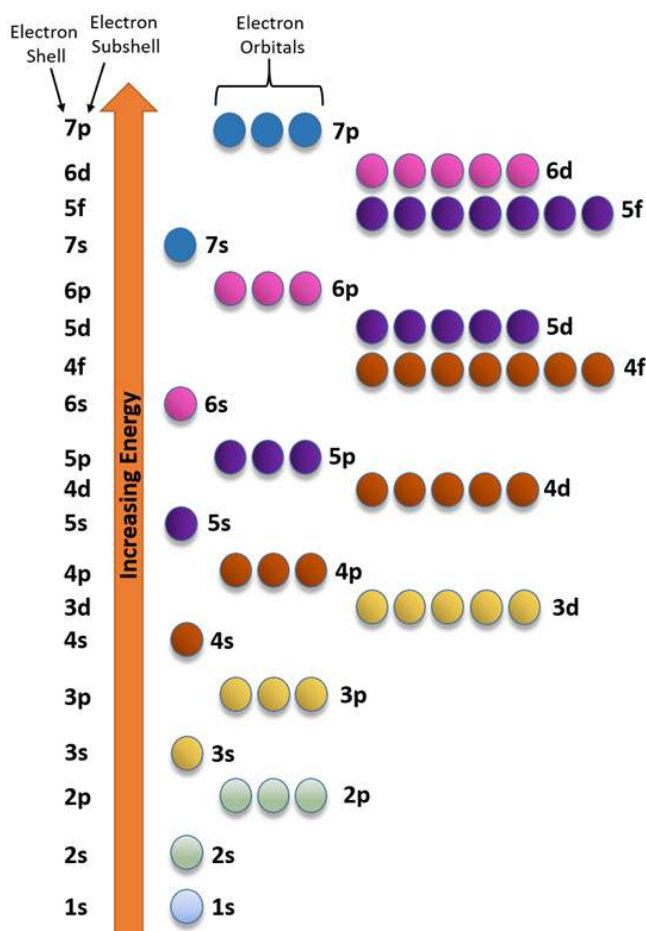


Figure 1.2.4: Relative energies of shells, subshells, and orbitals in multi-electron atoms. Source: <https://www.hiclipart.com/free-trans...yfbwx/download>

Note that if both the n and the l are the same, the energy of the orbitals is the same. For example, $2p_x$, $2p_y$, and $2p_z$ have same $n = 2$ and same $l = 1$, different in l_m , are of equal energy.

Degenerate orbitals

The atomic orbitals having the same energy level are called degenerate orbitals. For example, three $2p$: $2p_x$, $2p_y$, and $2p_z$ orbitals are degenerate.

Filling atomic orbitals with electrons

The number of electrons in a neutral atom is equal to the number of protons in the nucleus, i.e., equal to the atomic number. These electrons occupy the atomic orbitals by the following three rules.

1. The Aufbau Principle states that electron filling follows the energy order of the orbital, starting with the lowest energy $1s$ orbital and progressing to higher energy orbitals.
2. Pauli's exclusion principle states that each electron in an atom has a unique set of four quantum numbers. Since each atomic orbital has a unique set of three quantum numbers n , l , and l_m , it can take a maximum of two electrons: one with $m_s = +\frac{1}{2}$, called "up spin" and represented as $\uparrow$ or $\uparrow$ and the other with $m_s = -\frac{1}{2}$, called "down spin" and represented as $\downarrow$ or $\downarrow$.
3. Hund's rule states that when filling degenerate orbitals, the electrons occupy separate orbits with the same spins, usually represented as $\uparrow$ or $\uparrow$, until no degenerate orbital is left empty. Then the additional electron pairs up with one of the singly occupied orbitals.

Paired electrons and unpaired electron

Two electrons in the same orbital are called paired electrons and represented as $\uparrow\downarrow$ or $\downarrow\uparrow$.

One electron in a singly occupied orbital is called an unpaired electron and is usually represented as $\uparrow$ or $\downarrow$.

The simplest and most common way is that the number of electrons occupying a subshell is shown as a superscript to the letter s , p , d , or f . For example, the electron configuration of hydrogen, having one electron, is: $1s^1$. Similarly, the electron configuration of helium with two electrons is $1s^2$, lithium with three electrons is $1s^2 2s^1$, beryllium with four electrons is $1s^2 2s^2$, boron with five electrons is $1s^2 2s^2 2p^1$, and carbon with six electrons is $1s^2 2s^2 2p^2$. First shell has one orbital $1s$ and can take two electrons, second shell with four orbitals ($2s$ and three $2p$ orbitals) and can take eight electrons, third has nine orbitals ($3s$, three of $3p$ and five of $3d$) and can take eighteen electrons, and so on. Table 1.2.5 below shows the electron configuration of the first 18 elements.

Table 1.2.5: The electron configuration of the first eighteen elements in the periodic table (valence shells and valence electrons are shown in red fonts).

Group → Rows ↓	1	2	13	14	15	16	17	18
1	1H $1s^1$							2He $1s^2$
2	3Li $1s^2 2s^1$	4Be $1s^2 2s^2$	5B $1s^2 2s^2 2p^1$	6C $1s^2 2s^2 2p^2$	7N $1s^2 2s^2 2p^3$	8O $1s^2 2s^2 2p^4$	9F $1s^2 2s^2 2p^5$	10Ne $1s^2 2s^2 2p^6$
3	11Na $1s^2 2s^2 2p^6 3s^1$	12Mg $1s^2 2s^2 2p^6 3s^2$	13Al $1s^2 2s^2 2p^6 3s^2 3p^1$	14Si $1s^2 2s^2 2p^6 3s^2 3p^2$	15S $1s^2 2s^2 2p^6 3s^2 3p^3$	16P $1s^2 2s^2 2p^6 3s^2 3p^4$	17Cl $1s^2 2s^2 2p^6 3s^2 3p^5$	18Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

The electron configurations shown above are simple, but when degenerate orbitals are filled, the paired and unpaired electrons are not distinguished. For example, the electron configuration of ${}_6\text{C } 1s^2 2s^2 2p^2$, does not show the electrons in $2p$ orbital are unpaired. They are unpaired based on Hund's rule. To clarify, electron configurations are shown in a box diagram with boxes representing orbitals and electrons by an up arrow for unpaired electrons and a pair of up and down arrows for paired electrons. For example, the electron configuration of ${}_6\text{C}$ $\begin{array}{|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow \\ \hline 1s & 2s & 2p & \end{array}$; of ${}_7\text{N}$ $\begin{array}{|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow & \uparrow \\ \hline 1s & 2s & 2p & \end{array}$, and of ${}_8\text{O}$ $\begin{array}{|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow \\ \hline 1s & 2s & 2p & \end{array}$.

The electrons in the outermost shell that participate in chemical reactions are called **valence electrons**, and the rest in the inner orbitals that do not directly participate in chemical reactions are called **core electrons**. The shell containing the valence electrons is called the valence shell, and the rest of the inner shells are called core shells.

Table 1.2.5 shows valence electrons in red and core electrons in black. If the outermost shell is n , the $ns np$ shell of the main group elements is a partially filled valence shell. The valence shell of noble gases is completely filled and does not usually take part in chemical reactions. A filled shell is also called a **closed shell**. The valence shell of transition metals is $(n-1)d ns np$ because their $(n-1)d$ subshell is partially filled and takes part in chemical reactions. Similarly, the valence shell of inner transition metals is $(n-2)f (n-1)d ns np$.

Electron configuration of ions

1. First, the electron configuration of the corresponding neutral atom is written as described above.
2. Then, electrons are added or removed proportionate to the total charge;
 1. One electron is added to the outermost orbital for each negative charge, and
 2. one is removed for each positive charge in the following order: first from np , then from ns , then from $(n-1)d$, irrespective of their order of filling.

The following examples explain these steps.

- The electron configuration of ${}_6\text{O}$ is $1s^2 2s^2 2p^4$ and for the anion ${}_6\text{O}^{2-}$ two electrons are added for 2- charge, resulting in: $1s^2 2s^2 2p^6$.

- The electron configuration of $_{11}\text{Na}$ is $1s^2 2s^2 2p^6 3s^1$ and two electrons are removed for $2+$ charge resulting in: $_{11}\text{Na}^+$ is $1s^2 2s^2 2p^6$.
- The electron configuration of $_{26}\text{Fe}$ is filled in this order $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ but usually written following the order of n followed by l numbers, as: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$.
 - For $_{26}\text{Fe}^{2+}$ two electrons are removed from the ns resulting in: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$, and
 - for $_{26}\text{Fe}^{3+}$, three electrons are removed, two from the ns and one from $(n-1)d$, resulting in: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

Abbreviated electron configuration

The electron configuration is abbreviated by replacing core electrons with the symbol of the noble gas having the same electron configuration as the core electrons, followed by the valence shell. For example $_{26}\text{Fe}$ configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ is abbreviated as $[\text{Ar}] 3d^6 4s^2$. Note that the noble gas symbol is placed in square brackets.

Figure 1.2.6 shows electron configurations of all elements. Note: there are some anomalies in the electron configuration, especially when valence d or f orbitals are near half-filled or near filled, they may draw an electron from the next s orbital to become half-filled or filled. Further details of the anomalies are beyond the scope of this book.

Periodic table of the elements

Legend for Iron (Fe):

- oxidation states (the most common are in bold)
- 1^{st} ionization energy (in kJ/mol)
- electronegativity (Pauling)
- electron configuration
- electrons by energy level
- element name (gas, liquid or solid at 0°C and 101.3 kPa)
- atomic number
- chemical symbol
- relative atomic mass (or that of the most stable isotope)

Legend for element categories:

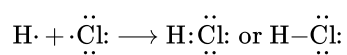
- Metals:** Alkali metals, Alkaline-earth metal, Lanthanides, Actinides, Transition metals, Post-transition metals.
- Metalloids:** (Elements between metals and nonmetals).
- Nonmetals:** Reactive nonmetals, Noble gases.
- Unknown chemical properties:** (Elements with no data).
- Origin (natural occurrence):** primordial, from decay, synthetic.

Figure 1.2.6: A periodic table of elements showing electron configurations and other properties. (Copyright; Michka B, CC BY-SA 4.0, via Wikimedia Commons)

Bonding in organic compounds

Group → Rows ↓	1	2	13	14	15	16	17	18
1	H·							He:
2	Li·	·Be·	·B·	·C·	·N·	·O·	·F·	·Ne:
3	Na·	·Mg·	·Al·	·Si·	·P·	·S·	·Cl:	·Ar:

Figure 1.2.7: Lewis dot structures of the first eighteen elements in the periodic table showing valence electrons as dots. (Copyright; Public domain)



This page titled [1.2: Structure of an atom](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [2.3: Atoms of elements](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

1.3: Chemical bonds

What is a chemical bond?

The observation that noble gases have filled valence shells and are usually inert in chemical reactions led to the theory of valency.

✎ Electron theory of valency

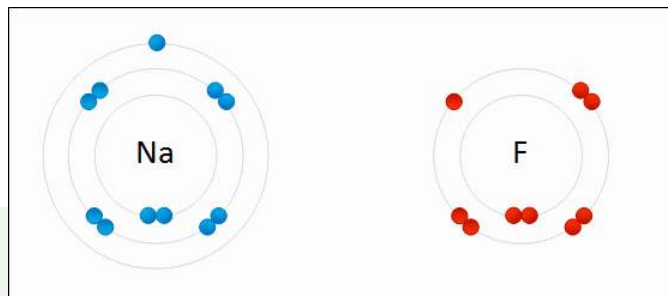
During chemical reactions, atoms gain, lose, or share valence electrons to acquire the nearest noble gas configuration.

A **chemical bond** is an electrostatic attraction developed by transferring or sharing valence electrons that hold the atoms together. An atom that can transfer or share one valence electron is monovalent, two is divalent, three is trivalent, and four is tetravalent.

Ionic bond

Metals, particularly those on the left side of the periodic table, tend to lose valence electrons, leaving the core shells with the nearest noble gas configuration. The loss of an electron leaves a positive charge on the atom, making it a cation. For example, sodium Na has six electrons in the first two core shells and one in the valence shell as depicted in the figure on the right (copyright; Wdcf, CC BY-SA 3.0, via Wikimedia Commons). It lose one electron becoming Na^+ when it reacts with fluorine F.

Nonmetals, particularly those on the right side of the periodic table, except noble gases, tend to gain electrons to achieve the electron configuration of the nearest noble gas. Gain of an electron creates a negative charge, making an anion. For example, F become anion F^- after gaining one electron.

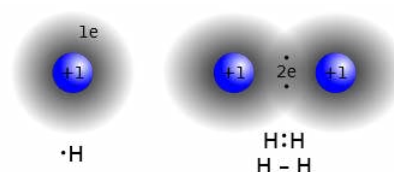


Cations, formed by losing electrons, and anions, formed by gaining electrons, are held together by electrostatic attractions, forming an **ionic bond**.

For example, Na^+F^- is an ionic compound held by ionic bonds. Atoms may lose or gain more than one electron in ionic bond formation. Still, the number of electrons lost by cations equals the electrons gained by anions, i.e., the positive charge is balanced by an equal negative charge in an ionic compound. For example, $\text{Mg}^{2+}\text{Cl}_2^-$, $\text{Ca}^{2+}\text{O}^{2-}$, $\text{Fe}^{3+}\text{Cl}_3^-$ are overall neutral ionic compounds with equal positive and negative charge.

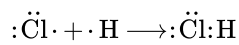
Covalent bond

Reacting atoms, especially nonmetal atoms, can share some of their valence electrons to achieve the electron configuration of the nearest noble gas. For example, two hydrogen atoms can share their valence electron, shown as dot on the symbol of the element, by the following reaction $\text{H}\cdot + \cdot\text{H} \rightarrow \text{H}:\text{H}$, as illustrated in the figure on the right (copyright; Jacek FH, CC BY-SA 3.0, via Wikimedia Commons).



A shared pair of valence electrons holding the two atoms together is a covalent bond.

The shared pair of electrons, shown as dots between the bonded atoms, is a **bonding pair**, e.g., two dots in $\text{H}:\text{H}$. Valence pairs of non-shared electrons are nonbonding or lone pairs in the molecule. For example, chlorine shares one of the seven electrons to make a covalent bond with hydrogen, leaving six valence electrons as three lone pairs in the molecule, as in the following reaction.



The covalent bond, i.e., the bonding pair is usually represented by a line between the nuclei to distinguish it from lone pairs, e.g., $\text{H}:\text{H}$ is usually written as $\text{H}-\text{H}$ showing one covalent bond and $:\ddot{\text{Cl}}:\text{H}$ is usually written as $:\ddot{\text{Cl}}-\text{H}$, showing one covalent bond and three lone pairs on chlorine.

Octet rule

Valence shell of main group elements is $ns\ np$ that can accommodate a maximum of eight electrons, two in ns and six in the three np orbitals. Noble gases have eight electrons in their valence shell, resulting in a stable electron configuration. A rule of thumb is formulated based on these observations, called the octet rule.

The **octet rule** states that main group elements tend to gain, lose, or share valence electrons so they have eight valence electrons, including the shared electrons.

Modifications of the octet rule

There are two modified forms of the octet rule.

1. First row elements have $1s$ valence shell and can take a maximum of two electrons, called the **duet rule**. The duet rule applies to H that makes one covalent bond, achieving the electron configuration of noble gas He.
2. Transition metals of $(n - 1)d\ ns\ np$ valence shell that can take eighteen electrons, called the **18-electron rule**.

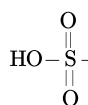
Exceptions to the octet rule

Exceptions to the octet rule include the following.

- **Odd-electron molecules:** In some compounds, the total number of valence electrons of the combining atoms is odd, while the octet is an even number. Such compounds will have odd-valence electrons in some atom. For example, N has seven valence electrons and O has six. If they combine to make NO, one of the two atoms must have odd-number valence electrons, e.g., $\cdot\dot{\text{N}}=\ddot{\text{O}}\cdot$

- **Incomplete octet:** Some elements have fewer than four valence electrons and may form stable compounds with fewer than eight valence electrons, called an incomplete octet. For example boron makes stable compound, like $\text{F}-\underset{\text{F}}{\text{B}}-\text{F}$ with three covalent bonds and no lone pair, i.e., incomplete valence shell with only six valence electrons. Similarly, beryllium forms $\text{H}-\text{Be}-\text{H}$ with two covalent bonds and no lone pair, i.e., an incomplete valence shell with only four valence electrons. Although such compounds exist, they are usually reactive and tend to gain more electrons to complete their octet.

- **Expanded octet:** Second-row elements, including C, N, O, etc., can not have more than eight valence electrons, but third-row and higher elements may do so. For example P in $\text{HO}-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}-\text{OH}$ has five covalent bonds, i.e., ten valence electrons and S in



has six covalent bonds, i.e., twelve valence electrons (note: two lone pairs on each oxygen in these two structures are omitted for simplicity). Atoms with more than octet valence electrons in compounds are called in a hypervalent state or expanded octet state. Although it is explained by the involvement of inner $(n - 1)d$ orbitals in the bonding, in addition to $ns\ np$ valence orbitals, it is controversial whether there is an expanded octet or whether such compounds still obey the octet rule. This debate will be discussed later.

In summary, the octet rule strictly applies to second row elements, including C, N, O, etc., and halogens.

Lewis structures

Lewis structures are a convenient way of writing covalent compounds based on valence electrons and the octet rule. They show shared pairs of electrons as lines and unused valence electrons as lone pairs (pairs of dots).

Lewis symbol of elements

Lewis's symbol of elements shows valence electrons as dots around the symbol, as shown in Table 1.3.1.

1. In any order, up to four valence electrons are shown as single dots on four sides (top, bottom, left, and right) of the element symbol. For example, one valence of hydrogen may be shown as $\cdot\text{H}$, $\text{H}\cdot$, $\overset{\cdot}{\text{H}}$, or $\underset{\cdot}{\text{H}}$ and $\cdot\dot{\text{C}}\cdot$ represents four valence electrons of carbon as dots.

2. Fifth to eighth valence electrons are paired, one each, with any of the single dots, in any order. For example, six valence electrons of oxygen may be shown as $\ddot{\text{O}}\cdot$, $\cdot\ddot{\text{O}}\cdot$, $\cdot\ddot{\text{O}}\cdot$, or $\ddot{\text{O}}\cdot$, etc. and $\text{:}\ddot{\text{Ne}}\text{:}$ represents eight valence electrons of neon.
3. Helium is an exception that has full valence shell with two electrons that are shown as a pair of dots.

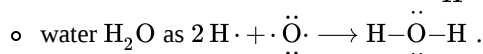
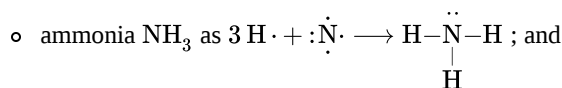
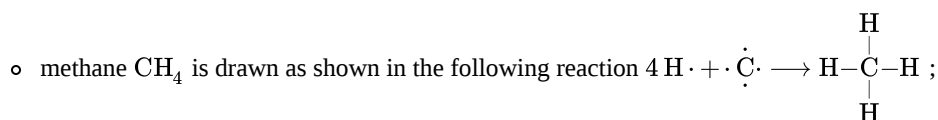
Group → Rows ↓	1	2	13	14	15	16	17	18
1	H·							He:
2	Li·	·Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
3	Na·	·Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·

Table 1.3.1: Lewis dot structures of the first eighteen elements in the periodic table showing valence electrons as dots. (Copyright: Public domain)

Lewis structures of simple molecules

The following steps can be used to draw Lewis structures of simple molecules.

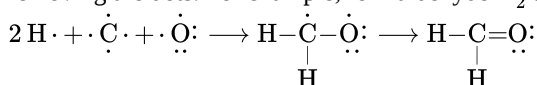
1. Place the most electropositive element in the middle and the others around it, add a line between atoms depicting a covalent bond, and remove one dot from each bonded atom. Count the shared electrons in both atoms' valence shells. If the octet of every atom is complete (duet for hydrogen), it is a correct Lewis structure. For example,



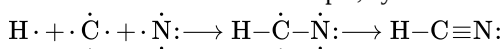
- Note the exception when hydrogen reacts with other atoms; it is never placed in the middle. Also note that the paired dots in the Lewis symbol remain as lone pairs on the respective atom in the molecule.

2. If the octet is incomplete on some atoms and

- There is a single dot (unpaired electron) on two adjacent atoms, making a second covalent bond (double bond) and removing the dots. For example, formaldehyde H_2CO is drawing as shown in the following reaction



- If there are two single dots on two adjacent atoms, make two more covalent bonds between them, resulting in a triple bond, and remove the dots. For example, cyanic acid HCN is drawn as in the following reaction



Drawing Lewis structures of relatively complex molecules and covalent-bonded ions

The following steps, explained with examples, can be used to draw the Lewis structures of relatively complex molecules and ionic species.

- Add valence electrons of all atoms in the molecule and adjust for the charge, i.e., remove one electron for each positive charge and add one for each negative charge. For example C_2H_6 has $4 \times 2 + 1 \times 6 = 14$ electrons; CO_2 has $4 + 2 \times 6 = 16$ electrons; $[\text{NH}_4]^+$ has $7 + 1 \times 4 - 1 = 10$ electrons, and $[\text{NO}_3]^-$ has $7 + 6 \times 3 + 1 = 24$ electrons.
- Note: valence electrons is equal to the first digit of group number in the periodic table, e.g., H is in group 1 has one valence electron, C in group 14 has 4, N in group 15 has 5, and O in group 16 has 6 valence electrons.

- Place the most electropositive atom in the middle (except H which is always peripheral) and the rest around it and join them by

a line representing a covalent bond, i.e., a pair of bonded electrons. For example C_2H_6 becomes $\begin{array}{c} H & H \\ | & | \\ H-C & -C-H \\ | & | \\ H & H \end{array}$; CO_2 become

$O-C-O$; $[NH_4]^+$ become $\left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array} \right]^+$, and $[NO_3]^-$ become $\left[\begin{array}{c} O \\ | \\ O-N-O \end{array} \right]^-$. Note: charged species are placed within square brackets, and the charge is shown as superscript to the right square bracket.

- Count the valence electrons consumed in the covalent bonds in the previous step, and distribute the remaining from the total, first to the peripheral atoms and then to the central atom to complete their octet (H is an exception that follows the duet rule).

For example C_2H_6 has no valence electrons left and remains the same $\begin{array}{c} H & H \\ | & | \\ H-C & -C-H \\ | & | \\ H & H \end{array}$; CO_2 become $:\ddot{O}-C-\ddot{O}:$ after

distributing 12 remaining electrons; $[NH_4]^+$ has no electrons left and remains the same $\left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array} \right]^+$, and $[NO_3]^-$ become

$\left[\begin{array}{c} :\ddot{O}: \\ | \\ :\ddot{O}-N-\ddot{O}: \end{array} \right]^-$ after distributing the remaining 18 electrons.

- If the octet of every atom (duet for hydrogen) is complete, it is a correct Lewis structure. For example, the following are the

correct Lewis structures at this stage: C_2H_6 is $\begin{array}{c} H & H \\ | & | \\ H-C & -C-H \\ | & | \\ H & H \end{array}$; and $[NH_4]^+$ is $\left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array} \right]^+$.

- If an octet is incomplete for an atom, convert a lone pair from its peripheral atom into a second covalent bond (double

bond). For example, octet of N is incomplete in $\left[\begin{array}{c} :\ddot{O}: \\ | \\ :\ddot{O}-N-\ddot{O}: \end{array} \right]^-$ and is completed by converting a lone pair from any O

into a double bond as in $\left[\begin{array}{c} :\ddot{O}: \\ | \\ :\ddot{O}-N=\ddot{O}: \end{array} \right]^-$. C in $:\ddot{O}-C-\ddot{O}:$ has octet in complete. Converting a lone pair from one of the O

into a double bond as $:\ddot{O}=C-\ddot{O}:$ still leaves the octet incomplete.

- If the octet remains incomplete after the previous step, convert another lone pair from the same peripheral atom into another covalent bond (triple bond) or from another peripheral atom to create a second double bond. For example, Converting a lone pair of the second oxygen in $:\ddot{O}=C-\ddot{O}:$ into a second double bond completes the Lewis structure with octet of all atoms completed as $:\ddot{O}=C=\ddot{O}:$

Formal charge

Formal charge F_c on an atom in a covalent compound is calculated as the difference in the valence electrons V_e of the isolated neutral atom and the valence electrons assigned to it in the compound, i.e., the sum of nonbonding electrons V_e of + half of the bonding electrons B_e , by using the following formula.

$$F_c = V_e - \left(N_b + \frac{B_e}{2} \right)$$

Each covalent bond is two bonding electrons. The total number of bonding electrons B_e is divided by two, assuming a covalent bond is an equally shared pair of electrons. The sum of the formal charges of all atoms in a species equals the overall charge on the species. A zero formal charge is not shown, but a nonzero formal charge is shown, usually as a superscript on the atom's symbol.

✓ Example 1.3.1

Calculate formal charge on H and N atoms in $\left[\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N}-\text{H} \\ | \\ \text{H} \end{array} \right]^+$ and show it on the structure.

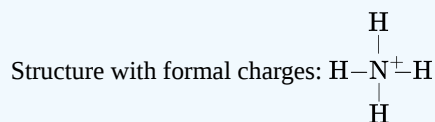
Solution

Given for every H:	$V_e = 1$	$N_b = 0$	$B_e = 2$	$F_c = ?$
--------------------	-----------	-----------	-----------	-----------

$$\text{Calculations: } F_c = V_e - \left(N_b + \frac{B_e}{2} \right) = 1 - \left(0 + \frac{2}{2} \right) = 0$$

Given for N:	$V_e = 5$	$N_b = 0$	$B_e = 8$	$F_c = ?$
--------------	-----------	-----------	-----------	-----------

$$\text{Calculations: } F_c = V_e - \left(N_b + \frac{B_e}{2} \right) = 5 - \left(0 + \frac{8}{2} \right) = +1$$



Note: zero formal charge is not shown, and the sum of formal charges on all atoms equals the overall charge on the given species.

✓ Example 1.3.2

Calculate formal charge on O labelled (I), (II) and (III) and N atoms in $\left[\begin{array}{c} :\ddot{\text{O}}:(\text{I}) \\ | \\ (\text{II}):\ddot{\text{O}}-\text{N}=\text{O}:(\text{III}) \\ | \\ :\ddot{\text{O}}: \end{array} \right]^-$ and show it on the structure.

Solution

Given for O labeled (I) and (II):	$V_e = 6$	$N_b = 6$	$B_e = 2$	$F_c = ?$
-----------------------------------	-----------	-----------	-----------	-----------

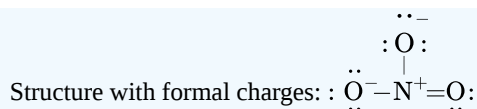
$$\text{Calculations: } F_c = V_e - \left(N_b + \frac{B_e}{2} \right) = 6 - \left(6 + \frac{2}{2} \right) = -1$$

Given for O labeled (III):	$V_e = 6$	$N_b = 4$	$B_e = 4$	$F_c = ?$
----------------------------	-----------	-----------	-----------	-----------

$$\text{Calculations: } F_c = V_e - \left(N_b + \frac{B_e}{2} \right) = 6 - \left(4 + \frac{4}{2} \right) = 0$$

Given for N:	$V_e = 5$	$N_b = 0$	$B_e = 8$	$F_c = ?$
--------------	-----------	-----------	-----------	-----------

$$\text{Calculations: } F_c = V_e - \left(N_b + \frac{B_e}{2} \right) = 5 - \left(0 + \frac{8}{2} \right) = +1$$



Note: zero formal charge is not shown, and the sum of formal charges on all atoms equals the overall charge on the given species.

Uses of formal charge

Charges on atoms are always destabilizing compared to the corresponding neutral atoms. Therefore, in situations where more than one correct Lewis structure can be drawn, the structure with zero or minimum formal charge is selected as the representative Lewis structure. For example, between the two structure of CO_2 : $\ddot{\text{O}}=\text{C}-\ddot{\text{O}}:$ and $:\ddot{\text{O}}^+ \equiv \text{C} - \ddot{\text{O}}^-:$ the first one with zero formal charges is selected while the second has two: a positive and a negative. Furthermore, in chemical reactions, electrons redistribute, and formal charges change. Tracking these changes helps one better comprehend the reactions. Table 1.3.2 lists the number of bonds and lone pairs expected in neutral atoms and atoms with formal charges of elements commonly found in organic compounds. This knowledge enables the quick determination of formal charges without calculations in most cases. It is essential to memorize this information because, often, the lone pairs are not shown in organic structures; they are understood.

Table 1.3.2: Pattern of number of bonds and lone pairs associated with the formal charges of elements commonly found in organic compounds. (Copyright; Public domain)

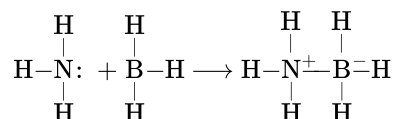
<i>Atom</i> ^{formal charge}	Number of covalent bonds	Number of lone pairs	Depiction
C	4	0	$\begin{array}{c} \\ -\text{C}- \\ \end{array}$
C ⁺	3	0	$\begin{array}{c} + \\ -\text{C}- \\ \end{array}$
C ⁻	3	1	$\begin{array}{c} \cdot\cdot \\ -\text{C}- \\ \end{array}$
N	3	1	$\begin{array}{c} \cdot\cdot \\ -\text{N}- \\ \end{array}$
N ⁺	4	0	$\begin{array}{c} \\ -\text{N}^+- \\ \end{array}$
N ⁻	2	2	$\begin{array}{c} \cdot\cdot \\ -\text{N}^- \\ \cdot\cdot \end{array}$
O	2	2	$\begin{array}{c} \cdot\cdot \\ -\text{O}- \\ \cdot\cdot \end{array}$
O ⁺	3	1	$\begin{array}{c} \cdot\cdot \\ -\text{O}^+ \\ \end{array}$
O ⁻	1	3	$\begin{array}{c} \cdot\cdot \\ -\text{O}^- \\ \cdot\cdot \end{array}$
Halogens X	1	3	$\begin{array}{c} \cdot\cdot \\ -\text{X}: \\ \cdot\cdot \end{array}$
Halide ions X ⁻	0	4	$\begin{array}{c} \cdot\cdot \\ :\text{X}: \\ \cdot\cdot \end{array}$
H	1	0	$-\text{H}$
H ⁻	0	1	$\begin{array}{c} \cdot\cdot \\ \text{H}^- \end{array}$

Formal charge is not real

As described in the next section, the bonding electrons are not equally shared when the bonded atoms are different. Therefore, the formal charge is not real because it is based on the assumption that the bonding electrons are equally shared. Still, the formal charge helps to locate the atom that is expected to carry the significant portion of the charge.

Dative covalent bonds

Both atoms donate one electron that becomes a shared pair of electrons, i.e., a covalent bond. However, there are situations in which one atom donates both the bonding electrons for its nonbinding lone pair to an atom that is electron-deficient, resulting in a bonded pair of electrons that is called a **dative covalent bond** or a **coordinate covalent bond**. The lone pair donor atom is called a donor, and the other is a receptor in the dative covalent bond. For example, N in $\text{H}_3\text{N:}$ donates a lone pair to make a bond with B has octet incomplete in BH_3 , making a dative covalent bond by the following reaction.



Note: the formal charge of the donor atom is increased by +1, and the formal charge of the recipient decreases by -1. The concept of formal charge is essential to understand, as it is often observed in chemical reactions.

This page titled [1.3: Chemical bonds](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

1.4: Bonding theories and geometries of molecules

Valence shell electron pair repulsion (VSEPR) theory

Lewis structures show bonds and lone pairs around atoms in a molecule, but they do not predict the angles between them. For example, Lewis structure of water may be written as $\text{H}-\ddot{\text{O}}:$ or $\text{H}-\ddot{\text{O}}-\text{H}$ both showing two bonds and two lone pairs around O

which correct, the first implies 180° angle between the bonds and second 90° , which are incorrect. The experimentally measured bond angle in water is 104.5° .

- **Valence shell electron pair repulsion (VSEPR)** predicts the geometry of atoms around a central atom in a molecule, based on repulsion between electron groups on the central atom.

- The **central atom** is an atom bonded to more than one atom in the molecule, e.g., O in $\text{H}-\ddot{\text{O}}:$
 H

✚ Electron groups

The electron groups are assigned to an atom in a molecule as follows.

1. an unpaired electron as on N in $:\dot{\text{N}}=\ddot{\text{O}}:$ is one electron group,
2. two electrons of a lone pair, as on N in $:\dot{\text{N}}=\ddot{\text{O}}:$ is one electron group (note: two lone pairs on O are two separate electron groups),
3. two bonded electrons in a single bond as on C in $\text{H}-\text{C}\equiv\text{N}:$ is one electron group,
4. four electrons in a double bond as on N in $:\dot{\text{N}}=\ddot{\text{O}}:$ is one electron group, and
5. six electrons in a triple bond as on C in $\text{H}-\text{C}\equiv\text{N}:$ is one electron group.

N in $:\dot{\text{N}}=\ddot{\text{O}}:$ has a total of three electron groups, an unpaired electron, a lone pair, and a double bond. O in $:\dot{\text{N}}=\ddot{\text{O}}:$ also has a total of three electron groups, two lone pairs and a double bond. C in $\text{H}-\text{C}\equiv\text{N}:$ has two electron groups, a single bond, and a triple bond.

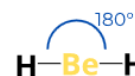
✚ Electron group geometry and molecular geometry

The geometry of electron groups surrounding the central atom in a molecule is referred to as **electron group geometry**. The electron groups may be bonding or nonbonding electrons. If electron groups are all bonding electron pairs, the electron group geometry is the same as the molecule geometry. However, if some electron groups are nonbonding, e.g., lone pairs, the geometry of atoms connected by bonds is called **molecular geometry**.

Diatomic molecules like $\text{H}-\text{H}$, $\text{H}-\text{Cl}$, and $\text{Cl}-\text{Cl}$ are always linear. The geometry of the molecule containing three or more atoms is determined by the number of electron groups around the central atom, as explained below.

Two electron groups

Two electron groups are farthest apart at 180° in a linear arrangement. Therefore, the electron group geometry and the molecular geometry are linear if the central atom has two electron groups, as: . For example, Be in $\text{H}-\text{Be}-\text{H}$ and C in $\text{H}-\text{C}\equiv\text{N}:$ and $:\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$ have two electron groups around the central C atom, resulting in a linear geometry of these molecules, as illustrated in the figures on the right. Examples of organic compounds are those that have a triple bond on C, e.g., $\text{H}-\text{C}\equiv\text{C}-\text{H}$. Note that this compound has two C atoms, both of which are central atoms with linear geometry, resulting in four atoms in a row on the line.



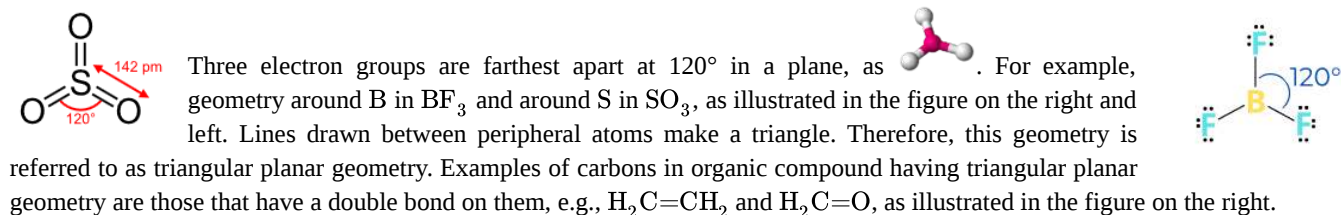
✎ Hydrocarbons

Organic compounds containing only C and H are called **hydrocarbons**.

Alkynes

Hydrocarbons having at least one $C \equiv C$ bond are called **alkyne**.

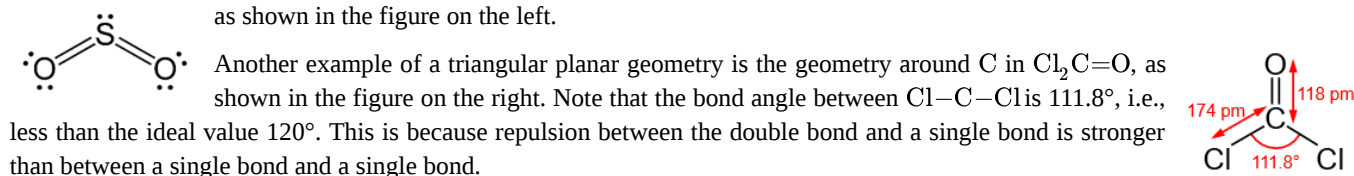
Three electron groups



Alkene

Hydrocarbons having at least one $C=C$ are called **alkenes**.

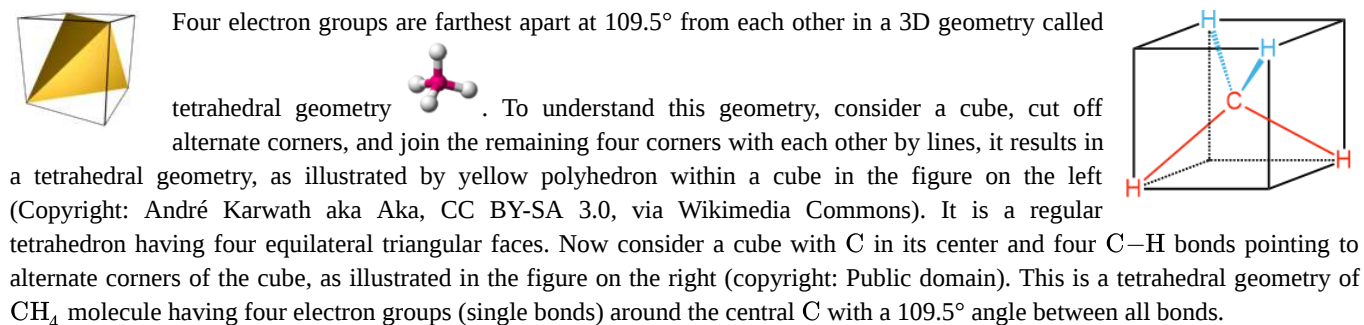
If one of the three electron groups is a lone pair, the electron group geometry is still triangular planar. Still, the molecule geometry, i.e., the geometry of atoms in the molecule around the central atom, is bent. For example, geometry around S in $:O=\ddot{S}=O:$ is bent, as shown in the figure on the left.



Order of repulsion force between electron groups

Repulsion force between different types of electron groups usually increases in the following order: single bond to single bond < single bond to double bond < single bond to lone pair < lone pair to lone pair.

Four electron groups



Perspective drawing of a tetrahedral C

Note that the tetrahedral CH_4 inserted in a cube, as shown in the figure on the right, is composed of two Vs of 109.5° internal angle joined at vortices and oriented perpendicular to each other. One V of $H-C-H$ bonds in the plane of the page is shown by solid lines in red. The other V of $H-C-H$ bonds shown in blue and viewed slightly from the top-right corner, has one C-H bond protruding out of the page towards the viewer is represented by a solid wedge, and the other C-H bond receding to the back of the page away from the viewer is represented by a hashed wedge. The red V in the plane of the page appears wider than the blue V perpendicular to the page. This is a conventional way of representing the perspective drawing of a 3D

tetrahedral molecular geometry. The wider V in the plane of the page may be shown pointing up, down, left, or right, as illustrated in Figure 1.4.1 and the interactive model of CH_4 molecule is presented in Figure 1.4.2.

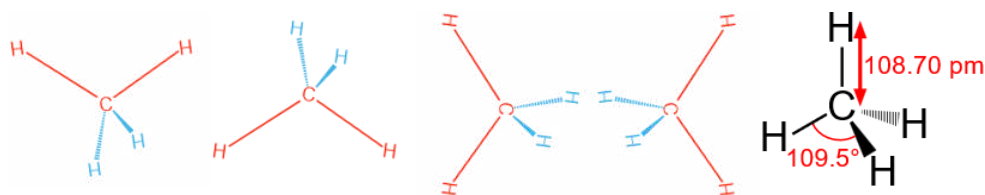


Figure 1.4.1: Perspective drawing of tetrahedral CH_4 molecule represented as two Vs of 109.5° internal angle joined at vortices and oriented perpendicular to each other. The V in the plane of the page (red) is shown pointing up, down, left, right, and top-right direction, from left to right (Copyright: Public domain).

Figure 1.4.2: Interactive model of CH_4 molecule. The model can be enlarged by two-finger gestures on the touchpad or by right-clicking and dragging, and rotated by swiping one finger in the image area or by left-clicking the mouse and dragging.

Organic compounds have multiple carbons. All carbons in the organic compound that have four single bonds have tetrahedral geometry. A perspective drawing of a chain of tetrahedral carbons can be represented by a zig-zag row of carbons, representing the Vs in the plane of the page and hydrogen as solid and hashed wedges on a V perpendicular to the page. For example, the figure on the right is a perspective drawing of the pentane C_5H_{12} molecule, and Figure 1.4.3 is its interactive model.

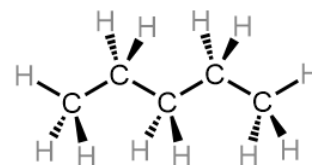
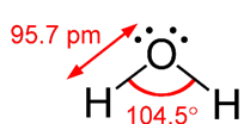
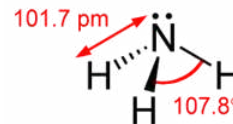


Figure 1.4.3: Interactive model of pentane C_5H_{12} molecule. The model can be enlarged by two-finger gestures on the touchpad or by right-clicking and dragging, and rotated by swiping one finger in the image area or by left-clicking the mouse and dragging.

If one of the four electron groups is a lone pair, the electron group geometry is tetrahedral, but the

molecule geometry is trigonal pyramidal, as . The name is based on the fact that connecting the three peripheral atoms makes a triangle, and the central atoms are raised in the middle, creating a trigonal pyramidal shape. For example, N in $H_3N:$ has a trigonal pyramidal shape, as shown in the figure on the right. Note that $H-N-H$ angle has been reduced from the perfect value of 109.5° to 107.8° because lone pair to bond pair repulsion is stronger than bond pair to bond pair repulsion.



If two of the four electron groups are lone pairs, the electron group geometry is tetrahedral, but the molecule geometry is bent, as . For example, O in $H_2O:$ is bent, as shown in the figure on the left. Note that $H-O-H$ angle has been reduced from the perfect value of 109.5° to 104.5° because lone pair to lone pair repulsion is stronger than bond pair to bond pair repulsion.

Valence bond theory

Lewis model of bonding predicts the number of bonds and the bond type: single, double, or triple, around an atom in a molecule. VSEPR theory predicts the bond angles and geometry around the central atom in a molecule. These two models are empirical and offer limited explanation. Still, they are used because they are simple. Two models, valence bond (VB) theory and molecular orbital theory (MO) theory, have been developed that take into account the orbitals of electrons. These are more complex, but not only predict the bonds and geometries, they can also predict additional properties, including bond strength, spectroscopic properties, and magnetic properties of the molecules. Among VB and MO theories, VB theory is relatively simple and more often used in organic chemistry. Although MO theory is more complex, it is still used because some of the chemical properties can be modeled better or exclusively by it. Here, a VB theory will be described, followed by a brief introduction to MO theory. Later in this course, a hybrid approach of VB and MO theories will be used to explain the chemical properties of organic molecules.

According to the valence bond theory, as atoms approach each other, their singly occupied valence orbitals overlap, resulting in the pairing of the two electrons in the overlapped orbital. Forces of attraction between both the nuclei and the two electrons in the overlapped orbitals primarily hold the two nuclei together, forming a covalent bond.

Mechanism of covalent bond formation

Atoms in the liquid or gas state move around due to thermal energy. Atoms have both positive-charge nuclei and negative-charge electrons. When two atoms approach each other, attractive forces between opposite charges and repulsive forces between the same charges develop. The two atoms move towards each other due to the attractive force, decreasing their potential energy until the minimum potential energy is reached. Decreasing the internuclear distance further from the optimum value increases repulsive forces more than attractive forces, as illustrated in Figure 1.4.4.

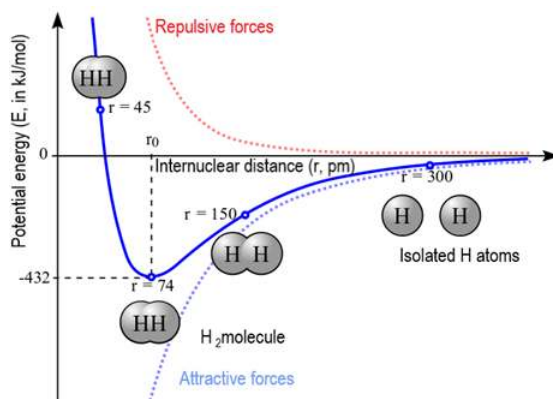


Figure 1.4.4: Illustration of potential energy vs. internuclear distance during a covalent bond formation between two H atoms. (Copyright; Public domain)

Bond length, bond energy, and the bond strength

- **Bond length** is the distance between the centers of the two atoms at the potential energy minimum in bond formation. For example, the bond distance in H–H is 74 pm.
- The difference in the energy of isolated atoms and the energy state at the bonding distance is the **bond energy**. For example, the bond energy of H–H is 432 kJ/mol as shown in Figure 1.4.4.
- Bond energy is always released when the bond is formed, and the same amount of energy is absorbed when the same bond is broken. **Stronger bonds** have higher bond energy, and **weaker bonds** have lower bond energy.

Sigma σ and pi π bonds

Sigma (σ) bond

A **sigma σ bond** is formed by head-on overlap of atomic orbitals such that the overlapped orbital places the electron density mostly between the two nuclei symmetrically on and around the bonding axis.

When an s orbital overlaps with an s orbital, a σ_{s-s} bond is formed, e.g., H–H is a σ_{1s-1s} bond. An s orbital overlaps with a p orbital by approaching it along the axis of the p orbital, forming an σ_{s-p} bond, e.g., H–F is a σ_{1s-2p} bond. When two p orbitals overlap by approaching each other along their axis, they make a σ_{p-p} bond, e.g., F–F is a σ_{2p-2p} bond. An s orbital is spherically symmetrical and it always makes a σ bond. A single bond is always a σ bond. Figure 1.4.5 illustrates the schematics of these σ bonds.

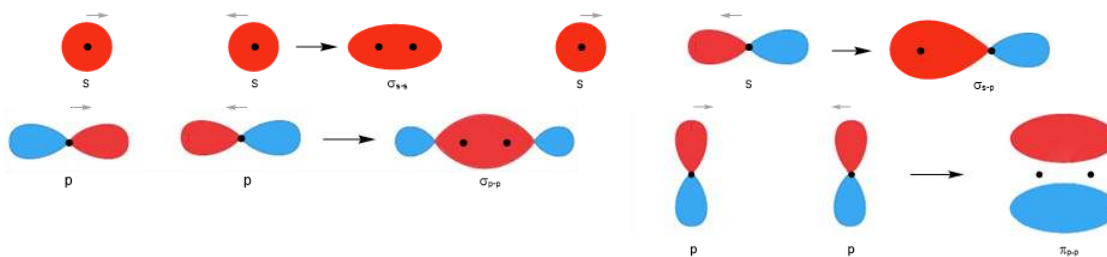


Figure 1.4.5: Schematics of σ_{s-s} , σ_{s-p} , σ_{p-p} , and π_{p-p} bonds. Black dots represent nuclei in these schematics (Copyright: Public domain).

Pi (π) bond

A π bond is formed when a lateral overlap happens between two lobes of an orbital on one atom with two lobes of the other orbital on the second atom, overlapping, placing electron density above and below the bond axis. There is a nodal plane passing through the bond axis, which is the common nodal plane of the two overlapping orbitals.

For example, when two p orbitals overlap by approaching each other with their axes parallel, they overlap sideways, forming a π_{p-p} bond. The π -bonding is not as effective an overlap as a σ bond, and, consequently, a π bond is weaker than a σ bond between the same orbitals. Usually, π bond is the second bond in a double bond or the second and the third bond in a triple bond because only one orbital in an atom can approach head-on, forming one σ bond with another atom. Figure 1.4.5 illustrates the schematics of a π_{p-p} bond.

Hybrid orbitals

The valence bond theory could not explain the geometry of several molecules. For example, the electron configuration of carbon is $1s^2 2s^2 2p^2$. It has two unpaired electrons and should form two bonds. It does not agree with four bonds to carbon in CH_4 .

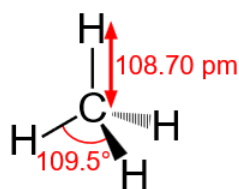
Assuming an electron is excited and jumps from $2s$ to $2p$ valence orbital resulting in the electron configuration $1s^2 2s^1 2p^3$.

Now it can make four bonds, releasing more energy than the energy consumed in the excitation of an electron. Still, it is expected to have three bonds from p orbitals at 90° angles and one from s orbital at any angle. It does not agree with the tetrahedral geometry around C in CH_4 with all bonds equal and all bond angles equal to 109.5° . This deficiency is addressed by introducing the concept of hybrid orbitals in the valence bond theory, which form bonds in molecules.

Orbital hybridization is a concept of mixing some valence orbitals, resulting in an equal number of hybrid orbitals, suitable for bond making, and of different energies and shapes than the constituent orbitals.

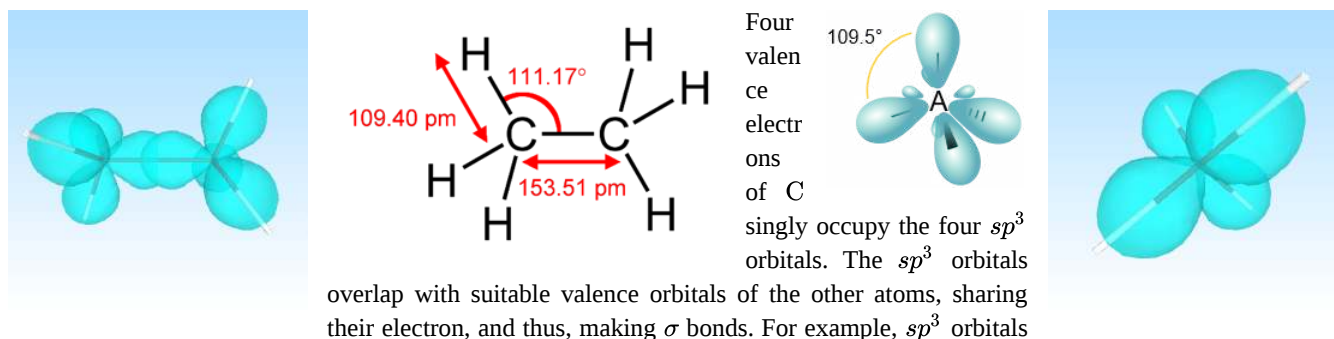
For example, one $2s$ orbital of C can mix with three $2p$ orbitals resulting in four equal hybrid orbitals, designated as sp^3 orbitals. Note that the superscript three does not represent electrons occupying the hybrid orbital; it tells the number of orbital types mixed to form the hybrid orbital, i.e., one $2s$ and three $2p$ orbitals. Similarly, one $2s$ orbital of C can mix with two $2p$ orbitals resulting in three equal hybrid orbitals, designated as sp^2 orbitals leaving one $2p$ orbital unchanged, and one $2s$ orbital can mix with one $2p$ orbitals resulting in two equal hybrid orbitals, designated as sp orbitals, leaving two $2p$ orbitals unchanged in the valence shell. The shapes and geometries of these hybrid orbitals are described next.

sp^3 Hybrid orbitals



An s orbital is spherically symmetrical, $\bullet$ and a p orbital is shaped with two lobes ∞ . One s and three p valence shell orbitals mix to form four equal sp^3 orbitals with one small and one large lobes ∞ that orient at 109.5° from each other in tetrahedral geometry, as illustrated in the figure on the right

(Copyright: Jfmeleiro, CC BY-SA 3.0, via Wikimedia Commons).



sp^2 Hybrid orbitals

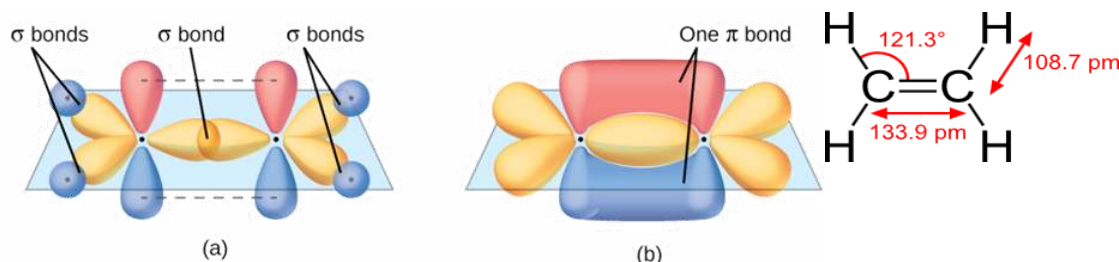
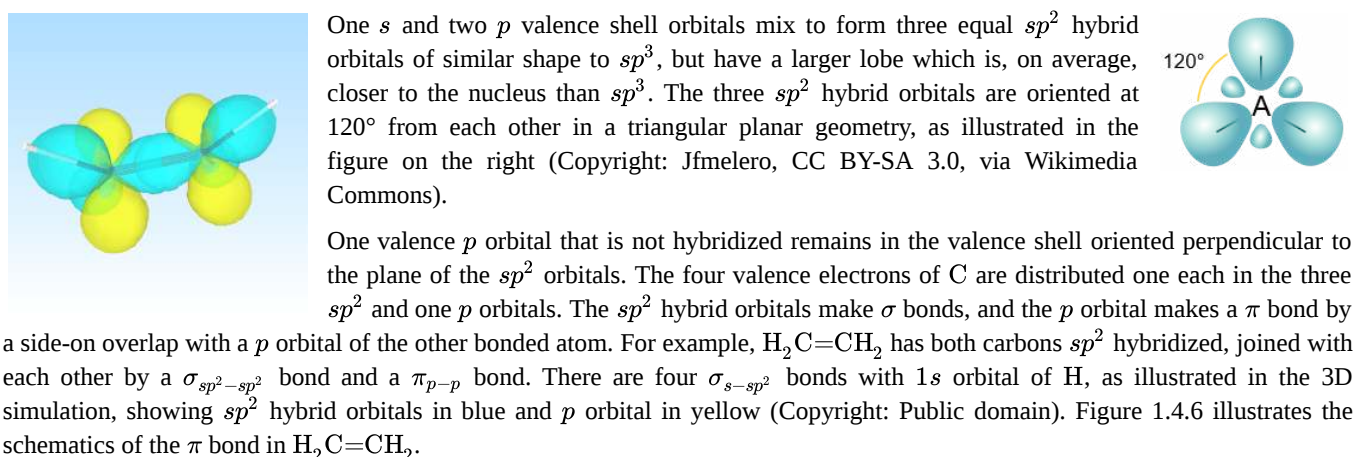
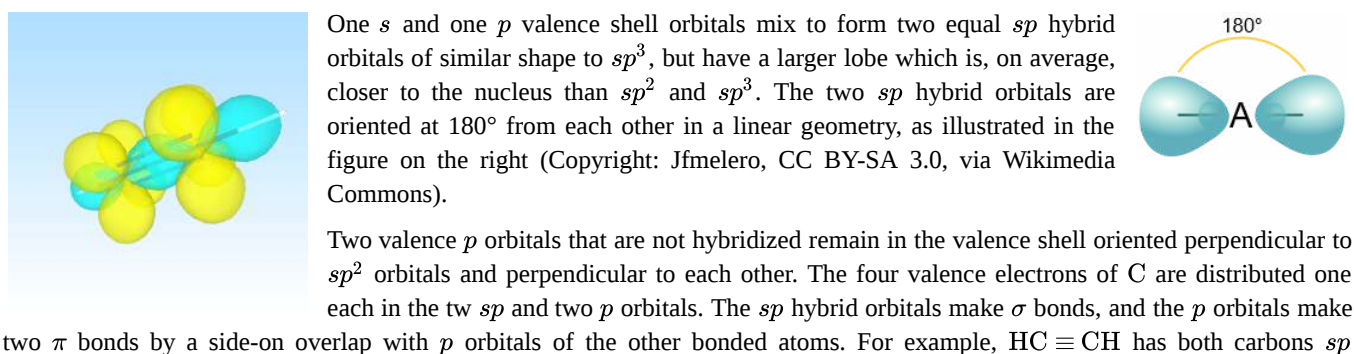


Figure 1.4.6: Illustration of bonds in $\text{H}_2\text{C}=\text{CH}_2$: a) one $\sigma_{sp^2-sp^2}$ and four σ_{s-sp^2} , b) one π_{p-p} bond (Copyright: https://it.wikibooks.org/wiki/Chimica:_orbitali_ibridi, CC BY 4.0, via Wikimedia Commons). Figure on the right is a perspective drawing of $\text{H}_2\text{C}=\text{CH}_2$ (Copyright: Public domain).

sp Hybrid orbitals



hybridized, joined with each other by a σ_{sp-sp} bond and two π_{p-p} bonds. There are two σ_{s-sp} bonds with $1s$ orbital of H, as illustrated in the 3D simulation, showing sp hybrid orbitals in blue and p orbitals in yellow (Copyright: Public domain). Figure 1.4.7 illustrates the schematics of the π bonds in $\text{HC} \equiv \text{CH}$.

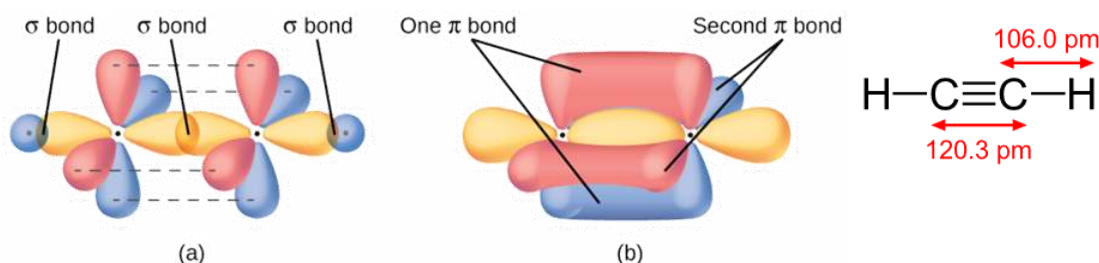


Figure 1.4.7: Illustration of bonds in $\text{HC} \equiv \text{CH}$: a) one σ_{sp-sp} , one σ_{s-sp} and two π_{p-p} bonds (Copyright: https://it.wikibooks.org/wiki/Chimic...rbitali_ibridi, CC BY 4.0, via Wikimedia Commons). Figure on the right is a perspective drawing of $\text{HC} \equiv \text{CH}$ (Copyright: Public domain).

Hybridization in atoms other than C

The concept of valence orbital hybridization is not limited to C, it applies to other atoms as well. The difference is in the number of valence electrons, resulting in a different number of bonds and lone pairs. For example, N has five valence electrons. When N makes all single bonds, it is sp^3 hybridized with three sp^3 orbitals singly occupied that make three single bonds with other atoms, and the fourth sp^3 orbital is filled with two electrons that remains non-bonded as a lone pair. For example, N in H_3N is sp^3 hybridized with three σ_{s-sp^3} bonds with H and one lone pair occupying the fourth sp^3 orbital, and trigonal pyramidal molecular geometry, as illustrated in the figure on the right. The H-N-H angles are 107.8° , a little less than ideal 109.5° , due to stronger lone pair-to-bond pair repulsion than bond pair-to-bond pair repulsion. $[\text{NH}_4]^+$ has one less valence electron and it has tetrahedral geometry with four σ_{s-sp^3} bond with H and no lone pair, like CH_4 , as illustrated in the figure on the left. $\text{H}_3\text{C}-\ddot{\text{N}}\text{H}_2$ is an example of sp^3 hybridized N in organic compound. P is in the same group with N having five valence electrons. In some compounds, like Cl_3P : is sp^3 hybridized with three σ_{s-sp^3} bonds with Cl and one lone pair occupying the fourth sp^3 orbital in a trigonal pyramidal geometry, as illustrated in the figure on the left.

Like C, when N has one double bond, it is sp^2 hybridized and when it has a triple bond it is sp hybridized. $\text{H}_2\text{C}=\ddot{\text{N}}\text{H}$ is an example of sp^2 hybridized N with the lone pair in an sp^2 orbital and $\text{CH}_3-\text{C} \equiv \text{N}$: is an example of sp hybridized N in organic compound with a lone pair in an sp orbital.

O has six valence electrons. When O has all single bonds, it is sp^3 hybridized with two σ bonds and two lone pairs in sp^3 orbitals. For example, O in $\text{H}_2\ddot{\text{O}}$ is sp^3 hybridized with two σ_{s-sp^3} orbitals and two lone pairs in sp^3 orbitals in a bent molecular geometry, as illustrated in Figure on the left. $\text{CH}_3-\ddot{\text{O}}-\text{H}$ is an example of sp^3 hybridized O in an organic compound. When there is one double bond on O it is sp^2 hybridized with two σ bonds, a π bond, and two lone pairs in sp^2 orbitals, as in $\text{CH}_2=\ddot{\text{O}}$, illustrated in the figure on the right. S is in the same group with O and its compounds can have similar hybridization as O. For example, S is sp^3 hybridized in $\text{CH}_3-\ddot{\text{S}}-\text{H}$ and sp^2 hybridized in $\text{CH}_2=\ddot{\text{S}}$ similar to oxygen compounds.

🔑 Quickly recognizing the hybridization and geometries of atoms in molecules

- When C, N, and O have octet complements in molecules with only single bonds, they are sp^3 hybridized, e.g., C in CH_4 , N in H_3N ., and O in $\text{H}_2\ddot{\text{O}}$: is sp^3 .
 - When they have one π bond (a double bond), they are sp^2 hybridized, e.g., C and \(\text{O}\) in $\text{CH}_2=\ddot{\text{O}}$, and C and N in $\text{H}_2\text{C}=\ddot{\text{N}}\text{H}$.

- When they have two π bonds (a triple bond or two double bonds), they are sp hybridized, e.g. C in $O=C=O$ and C and N in $CH_3-C \equiv N$:
- When a sp^3 hybridized atom has no lone pair, it has a tetrahedral molecular geometry, e.g. C in CH_4 .
 - When there is one lone pair, it has trigonal pyramidal geometry, e.g., N in H_3N :
 - When it has two lone pairs, it has bent geometry, e.g., O in $H_2\ddot{O}$: is sp^3 .
- When an sp^2 hybridized atom has no lone pair, it has a triangular planar geometry, e.g. C in $CH_2=\ddot{O}$.
 - When there is one lone pair, it has bent geometry, e.g., N in $H_2C=\ddot{N}H$.
 - When it has two lone pairs, it has linear geometry, e.g., O in $CH_2=\ddot{O}$.
- sp hybridized atoms always have linear geometry around them, e.g. C and N in C and N in $CH_3-C \equiv N$:

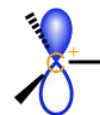
Structures of these examples are illustrated in this and the previous section.

Reactive intermediates

In addition to the stable form C commonly found in organic compounds that has four covalent bonds and may be sp^3 , sp^2 , or sp -hybridized, several reactive intermediates are high energy reactive and short-lived species, formed during chemical reactions and quickly convert into more stable species. Geometry and hybridization of some of these are described here.

Carbocation

Carbocation, more specifically, carbenium ion, is an sp^2 -hybridized C with +1 formal charge, three covalent bonds and an empty p -orbital, as illustrated on the right. Its examples include tertiary butyl cation $(CH_3)_3C^+$, triphenylmethyl cation $(C_6H_5)_3C^+$, etc. Its structure is trigonal planar with an empty p orbital perpendicular to the trigonal plane. The C in a carbenium ion has six valence electrons, i.e., octet incomplete. It is highly reactive and tends to complete its octet during chemical reactions.

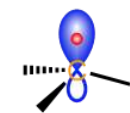


Carbanion

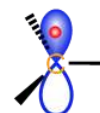


A carbanion is an anion with a lone pair on a tetravalent carbon, as illustrated in the figure on the left. Its examples include ethanide $CH_3CH_2^-$, t -butanide $(CH_3)_3C^-$, triphenylmethanide $(C_6H_5)_3C^-$, etc. It is usually sp^3 -hybridized with lone pair in one sp^3 -orbital, resulting in a trigonal pyramidal geometry, like that of ammonia. It has eight valence electrons, is still reactive because of the negative charge, and tends to react and convert into neutral, more stable species in chemical reactions.

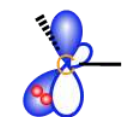
Carbon radical



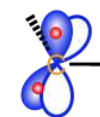
Carbon radical is a molecule containing a C with zero formal charge and an unpaired electron. Its examples include methyl radical $\dot{C}H_3$, t -butyl radical $(CH_3)_3\dot{C}$, triphenylmethyl radical $(C_6H_5)_3\dot{C}$, etc. It is usually sp^2 hybridized with an unpaired electron in p -orbital, as illustrated in the figure on the right. Still, pyramidal geometries are also observed in some cases, as illustrated in the figure on the left. Since the radical C has an incomplete octet with seven valence electrons, it is highly reactive and tends to make covalent bonds to complete its octet in chemical reactions.



Carbene

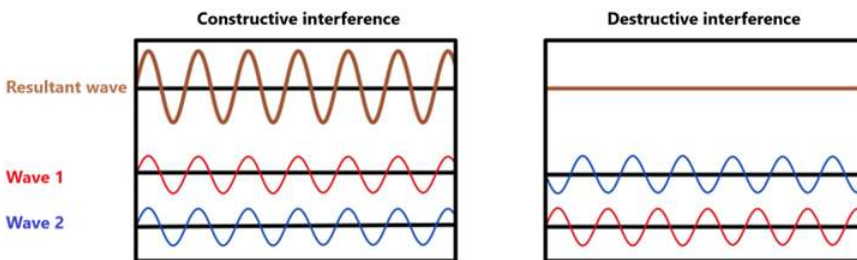


Carbene is a molecule containing a neutral C with two covalent bonds and two non-bonding electrons. Its examples include dichlorocarbene $Cl_2C:$ and methylene $H_2C:$. There are two classes of carbene, singlet and triplet. A singlet carbene is usually sp^2 -hybridized C with trigonal planar geometry, containing two covalent bonds and a lone pair in an sp^2 -orbital and an empty p -orbital perpendicular to the trigonal plane, as illustrated in the figure on the left. A triplet carbene is usually sp^3 -hybridized C with two covalent bonds and two sp^3 -orbitals occupied by an unpaired electron, as illustrated in the figure on the right. Since it has an octet incomplete with six valence electrons and empty or singly occupied valence orbitals, it is a highly reactive intermediate.



Molecular orbital (MO) theory

Atomic orbitals (AO) are regions around the nucleus where electrons are most likely found. AOs are obtained by wave functions treating electrons as waves. Interference of two or more waves (wave superposition) can be constructive interference, enhancing each other, or destructive interference, cancelling each other, as illustrated in the figure on the right (Copyright: Public domain).



Similarly, molecular orbital (MO) theory describes molecular orbitals (MOs) derived mathematically by a linear combination of atomic orbitals of compatible symmetry, creating an equal number of molecular orbitals. For example, an electron wavefunction of one H, ψ_1 may combine with that of second H, ψ_2 , either constructively resulting in a bonding MO ($\Psi = \psi_1 + \psi_2$) or destructively resulting in antibonding MO ($\Psi^* = \psi_1 - \psi_2$).

Types of molecular orbitals

The Ψ is called a **bonding molecular orbital** because it places electrons more between the nuclei in the overlapped region, resulting in an increased attractive force and lowering of potential energy than the AOs. The Ψ^* is an **antibonding molecular orbital** because it cancels the orbital between the nuclei, resulting in higher potential energy than AOs, as illustrated in Figure 1.4.7. If an atomic orbital has no compatible orbital to interact with, it becomes a **nonbonding molecular orbital** of energy equal to the corresponding atomic orbital.

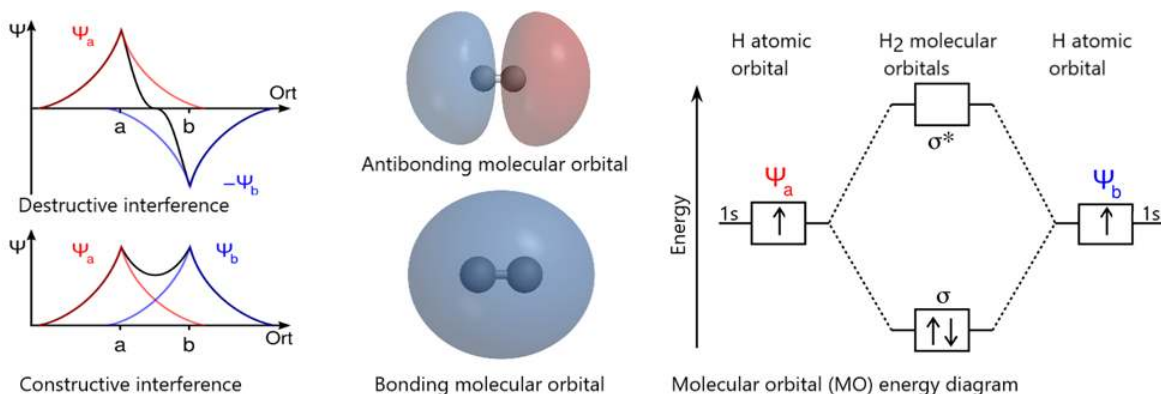


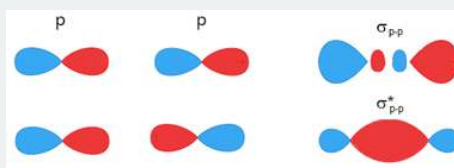
Figure 1.4.7: Illustration of molecular orbital (MO) constructive and destructive interference of H atomic orbitals during H_2 formation (right), resulting in bonding and antibonding molecular orbitals (middle). The MO energy diagram is shown on the right. (Copyright; Public domain)

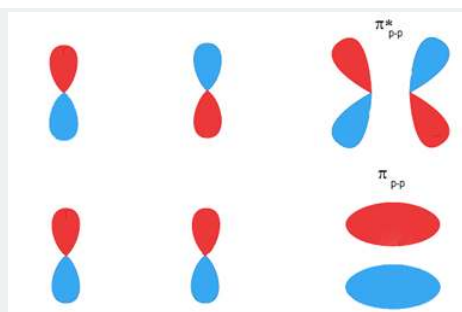
Filling molecular orbitals with electrons

Molecular orbitals are usually shown in an energy diagram to show their relative energies, as illustrated in Figure 1.4.7. In the energy diagram, the AOs are drawn on the sides, and the MOs are in the middle. The MOs are filled with the available valence electrons of the bonded atoms by the same rules as for AOs, i.e., i) the lowest energy orbital is filled first, each orbital can take a maximum of two electrons provided they have opposite spins, and iii) degenerate orbitals are filled singly until all of them is singly occupied, before electron pairing begins.

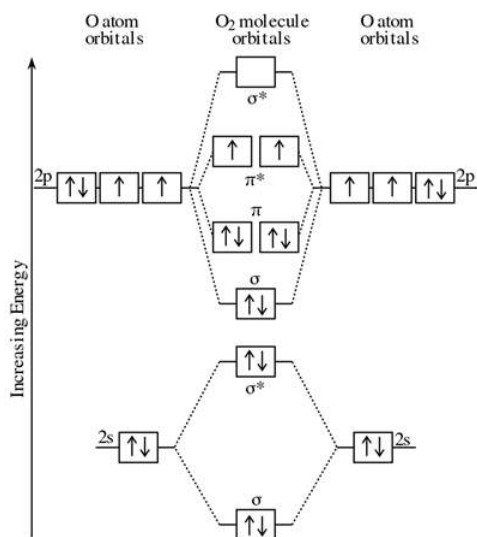
Naming molecular orbitals

The MOs are named σ , π , δ , etc. A σ orbital is formed by the head-on overlap of atomic orbitals, resulting in a cylindrically symmetrical electron density distribution on the bond axis. The bonding and antibonding orbitals formed by a combination of $1s$ AOs of H, shown in Figure 1.4.7, are an example of σ MO. Figure on the right illustrates σ orbitals formed by overlapping p orbitals.



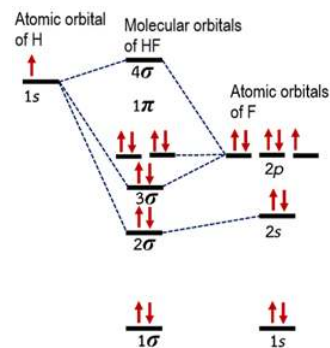


A π MO is formed by a lateral overlap of atomic orbitals, e.g., two parallel p orbitals, placing electron density above and below the bond axis with a nodal plane passing through the bond axis. Figure on the left illustrates π bonds formed by overlapping p orbitals. δ and other MOs are not described here.



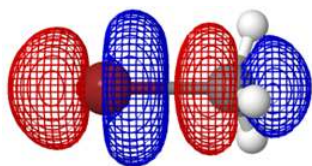
A linear combination of n atomic orbitals produces n molecular orbitals by the following general formula $\sum_{n=1}^n c_n \psi_n = \Psi_n$, where Ψ_n is the n^{th} molecular orbital, ψ are atomic orbitals, and c_n are weighted contribution of the atomic orbitals ranging from 1 to n .

Figure on the right illustrates MO energy diagram of HF molecule, where 1π are nonbonding molecular orbitals derived from $2p_x$ and $2p_y$ atomic orbitals of F without any interference. Figure on the left illustrates the MO energy diagram of O_2 . Note that it shows two unpaired electrons in the degenerate π^* molecular orbitals. The unpaired electrons in O_2 explain its paramagnetic property that valence bond theory could not explain.

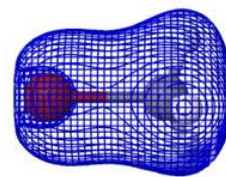


📌 Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO)

Two of the molecular orbitals are important in describing their chemical reactions. One is the highest energy occupied molecular orbital (HOMO), e.g., π^* in the case of O_2 and 1π in the case of HF shown in the energy diagrams on the left and right. The other is the lowest energy unoccupied molecular orbital (LUMO), e.g., σ^* in the case of O_2 and 4π in the case of HF shown in the energy diagrams on the left and right.



Atomic orbitals are associated with atoms. Valence bond theory describes primarily the orbitals localized between two bonded atoms. Molecular orbital theory describes molecular orbitals related to molecules. Some of the molecular orbitals may span the entire molecule. For example, the figure on the right shows one of the bonding molecular orbitals of CH_3Br that spans the whole molecule. The figure on the left



shows the LUMO of CH_3Br , showing phases of the wavefunction in red and blue colors. It will be described in later chapters concerning the reaction of CH_3Br .

Most of the time, the valence bond theory and the molecular orbital theory explain the chemical phenomena equally well. Valence bond theory will be used more often because it is relatively simple. However, molecular orbital theory sometimes offers a better explanation and is needed. Therefore, a hybrid approach combining the two theories will be employed in the later chapters to explain the chemical concepts.

Bond strength

One measure of bond strength is the bond dissociation energy (BDE)

Bond dissociation energy (BDE)

Bond dissociation energy is the amount of energy released as heat when $A-B$ cleaves into fragments $A\cdot$ and $B\cdot$.

The following are some of the factors affecting bond strength.

- A bond between smaller valence orbitals is usually stronger than between larger orbitals because of the larger distance between the shared electrons and the nuclei.
- Other factors being equal, a triple bond is stronger and shorter than a double bond, and a double bond is stronger and shorter than a single bond. This is because the number of shared electrons is six in a triple bond, four in a double bond, and two in a single bond.
- A σ bond formed by head-on overlap is stronger than a π bond formed by lateral overlap due to more overlap in the former case.
- A π bond is strongest when the overlapping orbitals are parallel, becomes weaker with less overlap as the orbitals rotate from parallel orientation, and becomes zero when they are at 90° from each other, due to the overlap of + lobe being equal with the + and the -lobes of the other cancelling each other and vice versa, as illustrated in Figure 1.4.8 a) and b).
- A bond between two orbitals of comparable sizes is stronger than when the overlapping orbitals are of different sizes; the larger the difference in sizes, the weaker the overlap and the weaker the bond. Comparison of Figure 1.4.8 a) and c) illustrates this point.
- A σ bond is strongest when the overlapping orbitals are oriented parallel along the bond-axis and become weaker when they are bent from the parallel orientation. Comparison of Figure 1.4.8 d) and e) illustrates this point.

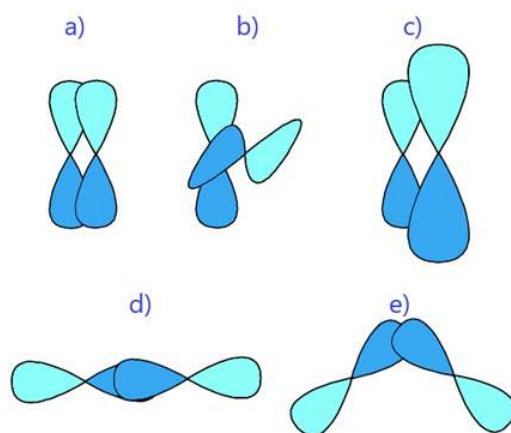


Figure 1.4.8: Illustration of two orbitals making a strong π bond when they are of comparable sizes in parallel orientation (a) becoming weaker and reaching zero bond when they rotate to 90° (b), become weaker with less overlap when they are of different sizes (c). Copy and Paste Caption here. (Copyright; Public domain)

These points will be discussed with examples in later chapters.

This page titled [1.4: Bonding theories and geometries of molecules](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [1.2: What is a chemical bond](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

1.5: Polarity of bonds and molecules

Polar covalent bonds

Formal charge calculations assume the covalent bonds are equally distributed between the bonded atoms. It is true only when the two bonded atoms are the same. Different atoms have different abilities to attract the bonded electrons, which is measured in terms of electronegativity (χ).

Electronegativity

Electronegativity is the ability of an atom to draw bonded electrons to itself.

There are different scales developed to calculate the electronegativity. Figure 1.5.1 shows electronegative values using the most common Pauling electronegativity scale.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.291		

Figure 1.5.1: Periodic table of electronegativity (χ) values by Pauling scale. (Copyright; Cooper.dav.j, CC0, via Wikimedia Commons)

When the bonded atoms are the same, e.g., $\text{Cl}-\text{Cl}$, the electronegativity difference $\Delta\chi$ is zero, and the bond is a pure covalent bond. When the bonded atoms are different, e.g., $\text{H}-\text{Cl}$ the bonded electrons are nearer the more electronegative atom, creating a dipole with a partial negative (δ^-) end on the more electronegative atom and a partial positive (δ^+) end on the more electropositive atom. The bond dipole is shown by δ^+ and δ^- signs on electropositive and electronegative atoms, as in $\overset{\delta^+}{\text{H}}-\overset{\delta^-}{\text{Cl}}$ or by a Polarity vector starting with a plus sign on the tail over the more electropositive atom and the arrow head on the more electronegative atom as in $\overset{+}{\text{H}}\longrightarrow\text{Cl}$. However, for a slight difference of $\Delta\chi$, less than 0.5, is considered a covalent bond. A $\Delta\chi$ between 0.5 and 1.7 is a polar covalent. For a large $\Delta\chi$ more than 1.7, the bonding electrons are considered transferred to the more electronegative atom, resulting in an ionic bond. Figure 1.5.2 illustrates $\text{Cl}-\text{Cl}$ bond having $\Delta\chi = 0$ as covalent, $\text{H}-\text{Cl}$ having $\Delta\chi = 3.16 - 2.2 = 0.94$ as polar covalent, and NaCl having $\Delta\chi = 3.16 - 0.93 = 2.23$ as ionic bond.

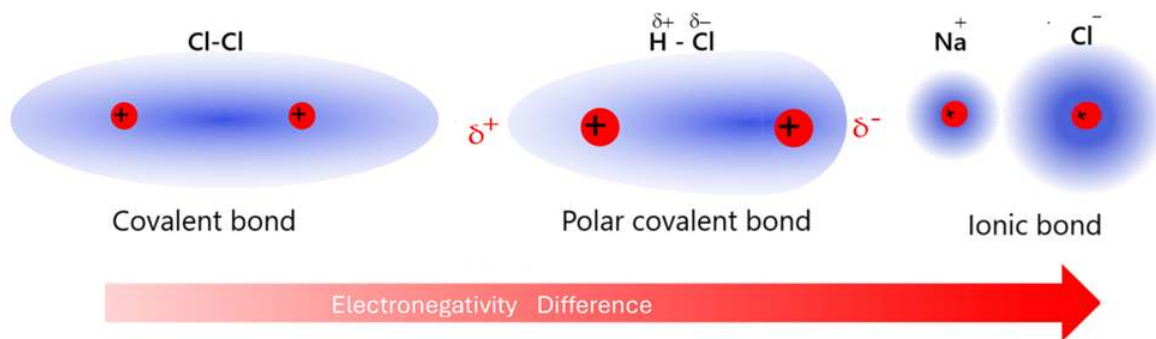


Figure 1.5.2: Illustrates of a covalent Cl–Cl bond having $\Delta\chi = 0$, a polar covalent H–Cl bond having $\Delta\chi = 3.16 - 2.2 = 0.94$, and an ionic NaCl bond having $\Delta\chi = 3.16 - 0.93 = 2.23$. (Copyright; Public domain)

Caution

The $\Delta\chi$ numbers between 0.5 and 1.7 should be considered as a rough guide, not as sharp cutoff points, because there is a diffused boundary between covalent and polar covalent, as well as between polar covalent and ionic bond. For example, $\text{H}_3\text{C}-\text{Li}$ bond is drawing as a polar covalent $\text{H}_3\text{C}^{\delta-}-\text{Li}^{\delta+}$, as well as as ionic $\text{H}_3\text{C}^-\text{Li}^+$, and both ways are acceptable.

Molecular orbital theory explains the polarity of a bond related to the difference in the energy of the valence orbitals of the combining atoms. In the case of the nonpolar covalent bond, the bonding atomic orbitals are of similar energy, and the molecular orbital is equally lower than them in energy, as illustrated in Figure 1.5.3. In the case of a covalent bond, the valence atomic orbital of an electronegative atom is lower in energy due to a stronger attraction to the nuclei than that of the electropositive atom. The bonding molecular orbital has a lower energy than both atomic orbitals, but is closer to that of the electronegative atom. The molecular orbital has more character of the atomic orbital that is closer to it in energy. In other words, the electrons in the bonding orbitals are more on the electronegative atom than on the electropositive, resulting in the bond polarity.

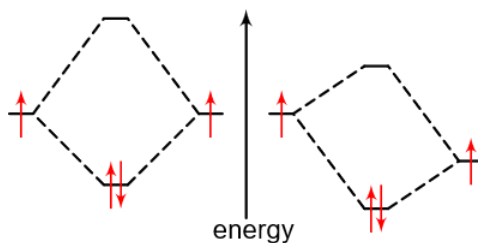


Figure 1.5.3: Depiction of a MO diagram of a covalent bond (left), e.g., as in H–H and a polar covalent bond (right), as in H–Cl. In both cases, a bond is a shared pair of electrons. (Copyright; Krishnavedala, Public domain, via Wikimedia Commons)

Electrostatic potential map

The polarity of the bonds and molecules can be visualized using electrostatic potential (ESP) maps, which display their electrostatic potential through color schemes. Red typically represents an electron-rich region (negative potential), green is neutral, and blue is an electron-deficient region (positive potential). Figure 1.3.4 displays electrostatic potential maps of $\text{H}_3\text{C}-\text{I}$, $\text{H}_3\text{C}-\text{Br}$, $\text{H}_3\text{C}-\text{Cl}$, and $\text{H}_3\text{C}-\text{F}$, respectively. The $\Delta\chi$ increases in the order $\text{H}_3\text{C}-\text{I} < \text{H}_3\text{C}-\text{Br} < \text{H}_3\text{C}-\text{Cl} < \text{H}_3\text{C}-\text{F}$, which is reflected in the ESP maps by increasing δ^- (red region) on halogen and increasing δ^+ (blue region) on carbon end of the electron cloud in the same order.

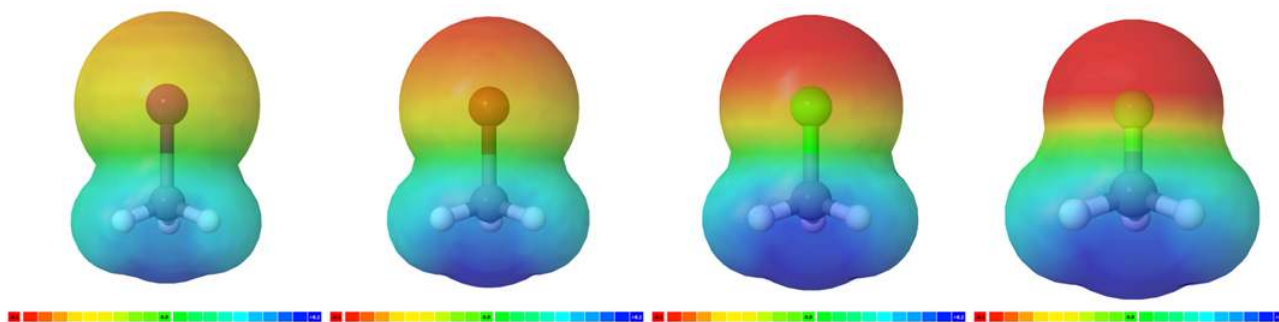


Figure 1.5.4: Electrostatic potential maps showing increasing polarity of C–X bond (from left to right) in the order $\text{H}_3\text{C}-\text{I} < \text{H}_3\text{C}-\text{Br} < \text{H}_3\text{C}-\text{Cl} < \text{H}_3\text{C}-\text{F}$. The color scale is shown in the bar below each figure. (Copyright: Public domain).

Caution

Electrostatic potential maps (ESP) are comparable only if they were prepared by using the same color scale. Do not compare the ESP maps from different books or different pages or figures of the same book as the color schemes may be different.

Bond dipole moment μ

Bond dipole moment (μ) is a measure of the polarity of a chemical bond, calculated by the following formula: $\mu = \delta \times d$, where δ is the charge (either $\delta+$ or $\delta-$ as both have the same magnitude) and d is the distance between the centers of positive and negative charge, i.e., bond length. SI unit of μ is Coulomb-meter (C m), but the commonly used unit is Debye (D), where $1\text{D} = 3.336 \times 10^{-30} \text{ C m}$.

Dipole moment is a vector quantity. For a molecule having more than one polar bond, the vector addition of individual bond dipole moments gives the dipole moment of the molecule. However, for diatomic molecules, the dipole moment of the bond is the dipole moment of the molecule, which varies from 0D to 11D. For example, dipole moment of Nonpolar $\text{Cl}-\text{Cl}$ is 0D and on the other extreme the dipole moment of ionic Na^+Cl^- is 9.001D.

The dipole moment of a molecule can be measured in the laboratory. The experimental measured dipole moment (μ_{observed}) is usually less than theoretical dipole moment ($\mu_{\text{theoretical}}$) calculated by assuming the $\delta-$ is equal to charge of an electron (1e), i.e., $1.6022 \times 10^{-19} \text{ C}$ and d is the bond length, assuming an electron is completely transferred in the ionic bond. It allows for calculating the percentage ionic character of the bond using the following formula.

$$\% \text{ Ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{theoretical}}} \times 100$$

✓ Example 1.5.1

a) Given the bond distance of $\text{H}-\text{Cl}$ is $1.275 \text{ \AA}$ and charge on an electron (1e) is $1.6022 \times 10^{-19} \text{ C}$, what will be its theoretical dipole moment $\mu_{\text{theoretical}}$ if it was 100% ionic? b) Given the observed dipole moment μ_{observed} is 1.03 D, what is the % ionic character and what is the % covalent character of $\text{H}-\text{Cl}$

Solution

a)

Given:	$d = 1.275 \text{ \AA} = \frac{1.275 \text{ \AA} \times 1 \text{ m}}{10^{10} \text{ \AA}} = 1.275 \times 10^{-10} \text{ m}$	$\delta = 1.6022 \times 10^{-19} \text{ C}$
--------	--	---

Calculations: $\mu_{\text{theoretical}} = \delta \times d = 1.275 \times 10^{-10} \text{ m} \times 1.6022 \times 10^{-19} \text{ C} = 2.0428 \times 10^{-29} \text{ C m}$

b)

Given:	$\mu_{\text{observed}} = \frac{1.03 \text{ D} \times 3.336 \times 10^{-30} \text{ C m}}{1 \text{ D}} = 3.436 \times 10^{-30} \text{ C m}$
--------	---

Calculations: $\% \text{ Ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{theoretical}}} \times 100 = \frac{3.436 \times 10^{-30} \text{ C m}}{2.0428 \times 10^{-29} \text{ C m}} \times 100 = 17\%$

$$\% \text{ covalent character} = 100 - \% \text{ Ionic character} = 100 - 17 = 83\%$$

✓ Example 1.5.2

a) Given the bond distance of Na^+Cl^- is $2.361 \text{ \AA}$ and charge on an electron ($1e$) is $1.6022 \times 10^{-19} \text{ C}$, what will be its theoretical dipole moment $\mu_{\text{theoretical}}$ if it was 100% ionic? b) Given the observed dipole moment μ_{observed} is 9.001 D , what is the % ionic character and what is the % covalent character of $\text{H}-\text{Cl}$

Solution

a)

Given:	$d = 2.361 \text{ \AA} = \frac{2.361 \text{ \AA} \times 1 \text{ m}}{10^{10} \text{ \AA}} = 2.361 \times 10^{-10} \text{ m}$	$\delta = 1.6022 \times 10^{-19} \text{ C}$
--------	--	---

Calculations: $\mu_{\text{theoretical}} = \delta \times d = 2.361 \times 10^{-10} \text{ m} \times 1.6022 \times 10^{-19} \text{ C} = 3.783 \times 10^{-29} \text{ C m}$

b)

Given:	$\mu_{\text{observed}} = \frac{9.001 \text{ D} \times 3.336 \times 10^{-30} \text{ C m}}{1 \text{ D}} = 3.003 \times 10^{-29} \text{ C m}$
--------	--

Calculations: $\% \text{ Ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{theoretical}}} \times 100 = \frac{3.003 \times 10^{-29} \text{ C m}}{3.783 \times 10^{-29} \text{ C m}} \times 100 = 79\%$

$\% \text{ covalent character} = 100 - \% \text{ Ionic character} = 100 - 79 = 21\%$

The above two examples clarify that polar covalent bonds have some ionic character and ionic bonds have some covalent character.

For example, covalent $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{Cl}}$ has 17% ionic character, and ionic Na^+Cl^- has 20% covalent character.

Polar molecules

Polarity is a vector quantity. If there is more than one polar bond in a molecule, the polarity of the molecule is a result of the vector addition of the individual bond polarities. Therefore, the polarity of a molecule is determined by the following general rules.

- A molecule having no polar bonds is nonpolar.
- A molecule having one polar bond is polar.
- A non-symmetric molecule having more than one polar bond is usually polar because the individual bond polarities typically do not entirely cancel each other, but,
 - A symmetric molecule having more than one polar bond is non-polar because the individual bond polarities cancel each other.

Examples of nonpolar molecules having no polar bonds are $\text{Cl}-\text{Cl}$, CH_4 , etc. Examples of polar molecules having one polar bond

include $\overset{+}{\text{H}}-\overset{-}{\text{Cl}}$, $\overset{+}{\text{H}_3}\text{C}-\overset{-}{\text{Cl}}$, etc.

Examples of polar non-symmetric molecules having more than one polar bond include CCl_3H with tetrahedral geometry but one $\text{C}-\text{H}$ bond different than the others, NH_3 with trigonal pyramidal geometry and the fourth electron domain is a lone pair, H_2O with bent geometry having two bonding pairs and two lone pairs in a tetrahedral electron group geometry, etc., as illustrated in the Figure 1.5.5.

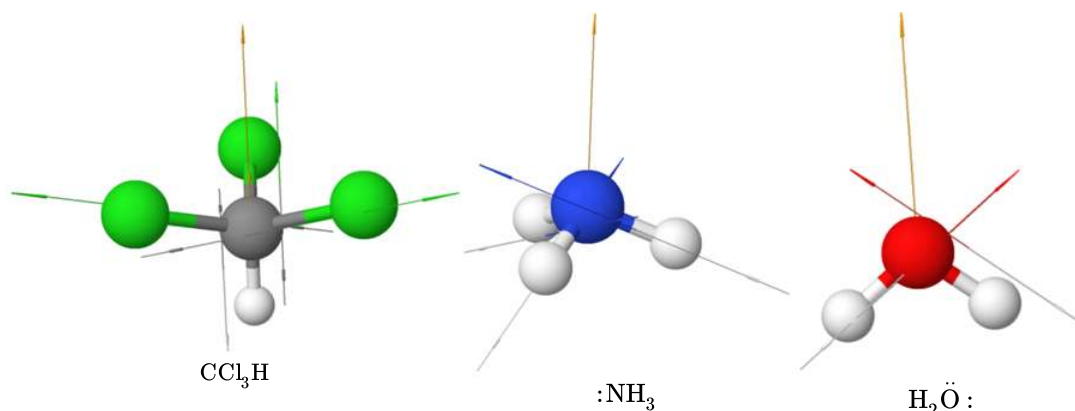


Figure 1.5.5: Examples of polar non-symmetric molecules having more than one polar bond: CCl_3H with one bond different than the other three, $:\text{NH}_3$ with one lone pair and three polar bonds, and $\text{H}_2\ddot{\text{O}}:$ with two lone pairs and two polar bonds. The individual bond polarities are shown by the arrows of the same color as the atoms in the models, and the orange arrow indicates the overall polarity, drawn using the online app <https://molview.org> (Copyright: Public domain).

Examples of symmetric nonpolar molecules having all equal polar bonds include those having two equal bonds in a linear geometry, e.g., $\text{O}=\text{C}=\text{O}$, three equal bonds in a triangular planar geometry, e.g., BF_3 , four equal bonds in a tetrahedral geometry, e.g., CCl_4 , etc., as illustrated in Figure 1.5.6.

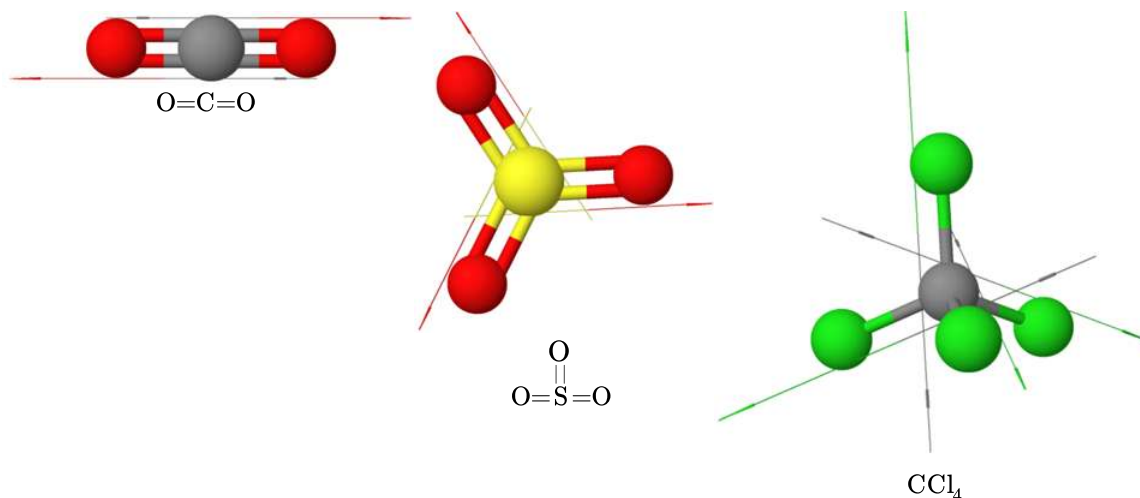


Figure 1.5.6: Examples of symmetric nonpolar molecules having all equal polar bonds. Arrows show individual bond polarity vectors drawn using the online app <https://molview.org> (Copyright: Public domain).

The set of molecular polarities compared in Figure 1.5.7 demonstrates the partial or full cancellation of individual bond polarities within a molecule. CH_3Cl has one polar $\text{C}-\text{Cl}$ bond and dipole moment $\mu = 1.20\text{D}$, while CH_2Cl_2 has two polar $\text{C}-\text{Cl}$ bonds, but the dipole moment is not twice because the two bond polarity vectors partially cancel each other. CHCl_3 has three polar $\text{C}-\text{Cl}$ bonds, but the $\mu = 1.20\text{D}$ equal to one polar $\text{C}-\text{Cl}$ bond, and CCl_4 has four polar $\text{C}-\text{Cl}$ bonds, but is a nonpolar molecule because the individual bond dipole vectors cancel each other in this symmetric molecule.

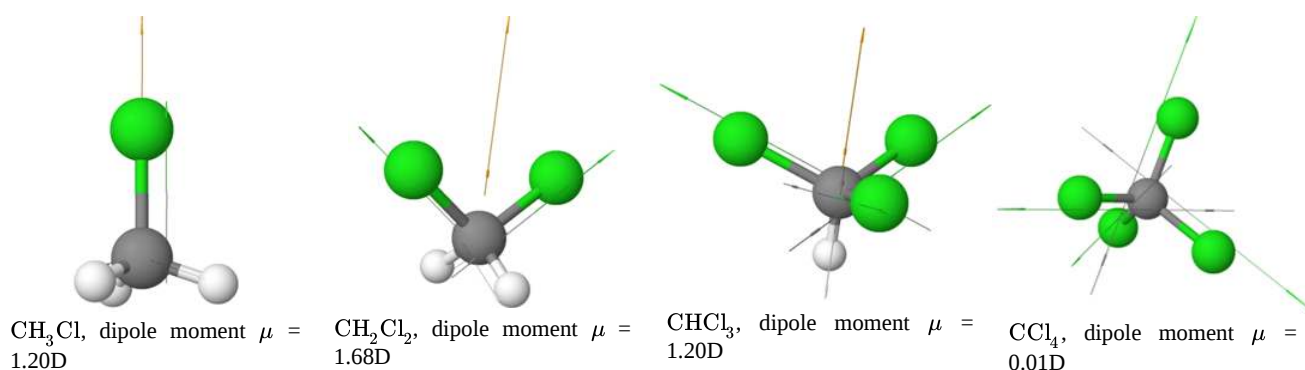


Figure 1.5.7: Illustration of bond polarities indicated by arrows of the same color as the bonded atom and the overall bond polarity by orange arrows, and dipole moments for CHCl_3 , CH_2Cl_2 , CHCl_3 , and CCl_4 . Arrows showing polarity vectors were drawn using the online app <https://molview.org>, and the dipole moments μ were calculated using online app <https://molcalc.org/> (Copyright: Public domain).

Intermolecular forces

Intermolecular forces are the electrostatic interactions between molecules. The intermolecular forces are usually much weaker than the chemical bonds (intramolecular forces), but still, they play an important role in determining the properties of the compounds. The major intermolecular forces include London dispersion forces, dipole-dipole interactions, and hydrogen bonding.

London dispersion forces

The electron cloud around atoms is not always symmetrical around the nuclei. It temporarily sways to one side or the other, generating a **transient dipole**. The transient dipole induces a dipole in the neighboring molecule, resulting in an attractive force between the opposite poles, called the transient dipole-induced dipole interaction, **London dispersion force**, or **van der Waals' force**, as illustrated in Fig. 1.5.8. Although London dispersion forces are transient, they keep reappearing randomly.

London dispersion forces are not unique to nonpolar molecules; they are present in all types of molecules, but these are the only intramolecular forces present in nonpolar molecules.

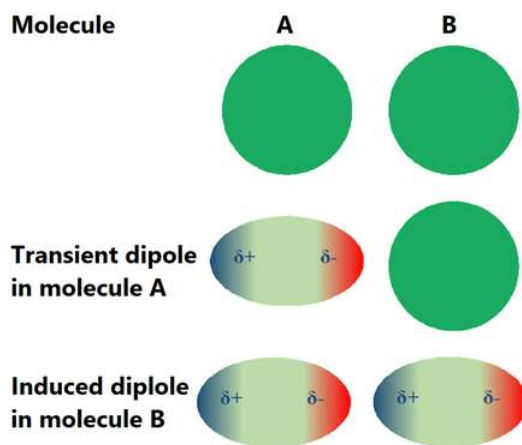


Figure 1.5.8: Illustration of transient dipole-induced dipole, i.e., London dispersion forces (Copyright: Public domain).

Effect of London dispersion forces on melting point (MP) and boiling point (BP)

London dispersion forces are responsible for maintaining the molecules in a solid or liquid state at lower temperatures. At higher temperatures, thermal forces become stronger and separate the molecules to larger distances, with almost no intermolecular interactions in the gas state. Therefore, melting point and boiling point values are indicators of the intermolecular forces in the compounds.

Since molecular weight (MW) is directly proportional to the number of electrons, London dispersion forces and, consequently, the melting point and boiling points are directly proportional to molecular weight, i.e., the higher the molecular weight, the higher the melting and boiling point.

Figure 1.5.9 shows that the molecular weight gradually increases from compounds I to IV, V, and VI; the melting points and the boiling points also increase in the same order.

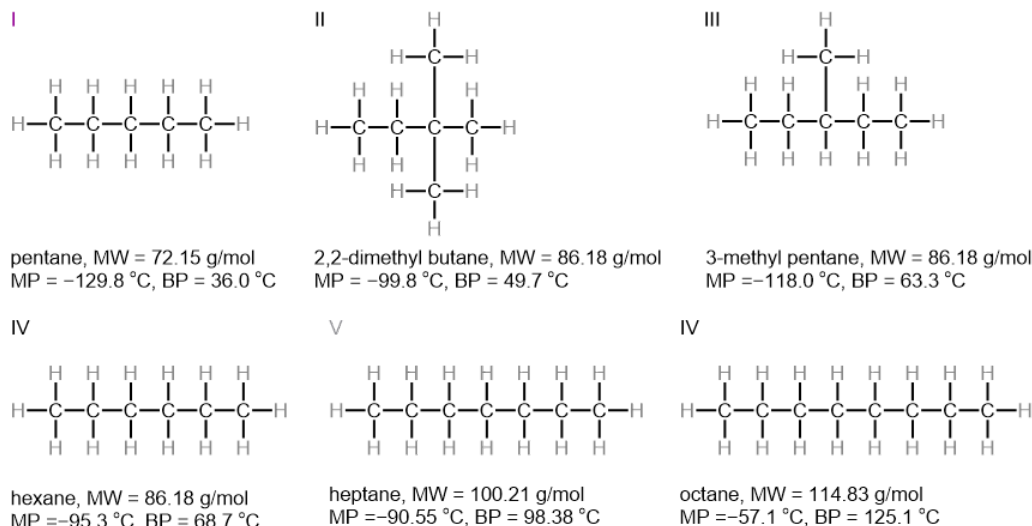


Figure 1.5.9: Illustration of i) increase in melting and boiling points of example organic compounds with increase in their molecular weights (compare compounds I, II, IV, V, and VI) and ii) decrease in melting and boiling points with increase in branching for the same molecular weight (compare compounds II, III, and IV (Copyright; Public domain)).

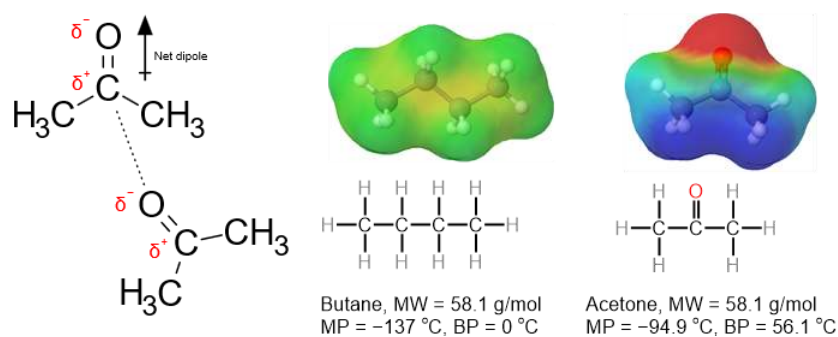
The transient dipole induces a dipole in the neighboring molecule through surface-to-surface contact. Therefore, linear chain organic molecules having a cylindrical shape with a larger surface area have higher melting and boiling points than branched molecules of the same molecular weight having a globular shape that can make less area of contact with the neighboring molecules.

For example, melting and boiling points decrease as the branching increases from IV to III to II in Figure 1.5.9.

Note that the effect of molecular weight is stronger than the effect of branching on the melting and boiling points.

For example, the melting points of compounds II, III, and IV, having the same molecular weights, are higher than that of compound I, which has a lower molecular weight, and lower than that of compound V, which has a higher molecular weight.

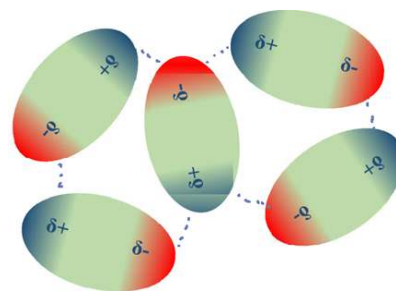
Dipole-dipole interactions



opposite charges and minimize the repulsive forces between the same charges, as illustrated in the figure on the left (Copyright; Public domain).

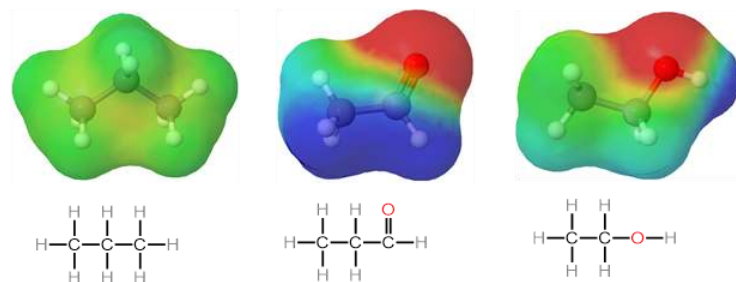
Polar molecules have permanent dipoles; one end of the molecule is partially positive (δ^+) and the other is partially negative (δ^-). The polar molecules have dipole-dipole interaction, i.e., electrostatic attraction between opposite partial charges on the dipoles, in addition to transient dipole-induced dipole interactions, as illustrated by dotted line in the figure on the right. The polar molecules orient in a way to maximize the attractive forces between the

Polar molecules usually have higher melting and boiling points than nonpolar molecules of comparable molar mass. For example, a nonpolar butane has significantly lower melting and boiling points (mp = -137 °C, bp = 0 °C) compared to polar acetone (mp = -94.9 °C, bp = 56.1 °C) of the same molar mass, but having a polar $\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$ group, as illustrated in the figure on the right (Copyright: Public domain). Note, in the electrostatic potential maps shown in the figure on the right, green is neutral, blue is $\delta+$, and red is $\delta-$.



Hydrogen bonds

Hydrogen bonding is a dipole-dipole interaction between $\overset{\delta+}{\text{H}}$ of $\overset{\delta-}{\text{X}}-\overset{\delta+}{\text{H}}$ bond with the $\overset{\delta-}{\text{X}}$ of a neighboring molecule, where X is N, O, or F, as illustrated by dotted lines between H_2O molecules in the figure on the right (Copyright: Magasjukur2 / Public domain, via Wikimedia Commons). Although a hydrogen bond is a dipole-dipole interaction, it is distinguished from the usual dipole-dipole interactions because of the following special features.

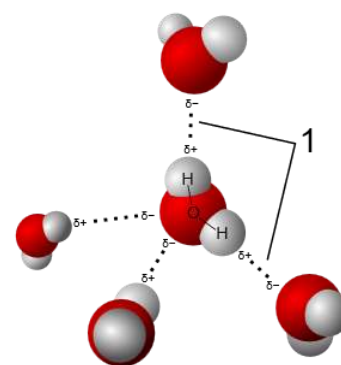


Propane, MW = 44.1 g/mol
MP = -187.7 °C, BP = -42.0 °C

Ethanal, MW = 44.1 g/mol
MP = -123.4 °C, BP = 20.2 °C

Ethanol, MW = 46.1 g/mol
MP = -114.1 °C, BP = 78.2 °C

1. The electronegativity difference between H and N, O, or F is typically greater than that of other polar bonds.
2. The charge density on $\overset{\delta+}{\text{H}}$ is higher due to the smaller size than on other dipoles.
3. Because of its smaller size, $\overset{\delta+}{\text{H}}$ can penetrate less



accessible spaces to interact with the $\overset{\delta-}{\text{N}}$, $\overset{\delta-}{\text{O}}$, or $\overset{\delta-}{\text{F}}$ of the other molecule.

A hydrogen bond is usually stronger than the usual dipole-dipole interactions. For example, it is reflected by higher melting and boiling points of hydrogen-bonded ethanol (mp = -114.1 °C, bp = 78.2 °C) higher than polar ethanal (mp = -123.4 °C, bp = 20.2 °C), and nonpolar propane (mp = -187.7 °C, bp = -42.0 °C) of comparable molar masses. Hydrogen bonding is the most common and essential intermolecular interaction in biomolecules. For example, two strands of DNA molecules are held together through hydrogen bonding, as illustrated in Figure 1.5.10. Proteins also acquire structural features needed for their functions mainly through hydrogen bonding.

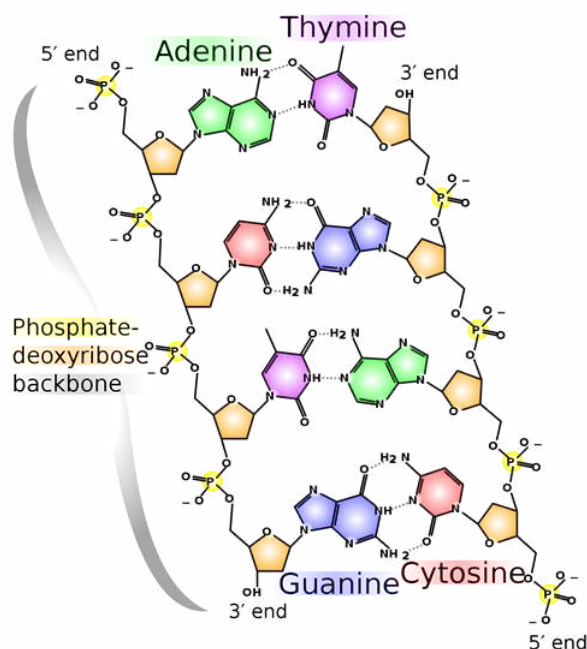


Figure 1.5.10: Chemical structure of DNA, with a colored label identifying the four bases as well as the phosphate and deoxyribose components of the backbone. Dotted lines are the hydrogen bonds holding the two strands of DNA together. Source: Madprime (talk · contribs) / CC0

Effect of multiple factors on intermolecular forces

The effect of multiple factors on intermolecular forces usually adds up. For example, nonpolar hexane has a lower melting point and boiling point than polar pentan-1-ol, which, intrinsically, has a lower melting point than hydrogen-bonded pentan-1-ol of comparable molar masses, as listed in Table 1.5.11. Butanoic acid of similar molar mass has significantly higher melting and boiling point than pentan-1-ol, because it has a polar $\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$, and a hydrogen bonding $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ in one molecule, i.e., in

$\overset{\delta-}{\text{O}}=\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ group. Similarly, butan-1,4-diol having two hydrogen bonding $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ groups in one molecule, has higher melting and boiling points than butanoic acid, as listed in Table 1.5.11

Table 1.5.11: Compares boiling points and solubility of a carboxylic acid, alcohol, and aldehyde of comparable molar mass.

Condensed formula	IUPAC name	Molar mass (g/mol)	Melting point (°C)	Boiling point (°C)	Solubility in water
$\text{HO}(\text{CH}_2)_4\text{OH}$	Butan-1,4-diol	90.1	20.1	235	Miscible
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	Butanoic acid	88.1	-5.1	164	Miscible
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$	Pentan-1-ol	88.2	-78	138	22 g/L
$\text{CH}_3(\text{CH}_2)_3\text{CHO}$	Pentanal	86.1	-60	103	14 g/L
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	Hexane	86.2	-95	69	Immiscible

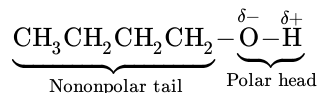
Effect of intermolecular forces on solubility

A general rule of thumb, "like dissolves like," means polar compounds are soluble in polar solvents and nonpolar compounds in nonpolar solvents. For example, nonpolar hexane is soluble in nonpolar toluene but immiscible in polar water. Pentanal having a

polar $\overset{\delta-}{\text{O}}=\overset{\delta+}{\text{C}}-\text{H}$ group and butanol having hydrogen bonding $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ group are partially soluble in polar water, as listed in Table

1.5.11. Butanoic acid having a polar $\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$, and a hydrogen bonding $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ group and butan-1,4-diol having two hydrogen bonding $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ groups are missible in water, as listed in Table 1.5.11. Note that all the compounds listed in Table 1.5.11 have similar molar masses.

Polar organic compounds usually have a polar head that tends to dissolve in polar solvents like water but not in nonpolar solvents like toluene, and a nonpolar tail that tends not to dissolve in polar solvents but dissolves in nonpolar solvents.



The factors contradict, and the overall solubility is determined by which one is stronger. When the nonpolar tail is small, up to three or four carbons, the effect of the polar head is strong, making the compound soluble in water. When the nonpolar tail is medium size, from ~4 to ~7, the compounds are partially soluble in water. When the nonpolar tail is large, the compounds are immiscible in water, as illustrated in Table 1.5.12

Table 1.5.12: Melting points, boiling points, and solubility of alcohols in water (Note: Miscible means make a solution in all proportions, and immiscible have solubility less than 1 g/L)

Formula	Boiling point (°C)	Melting point (°C)	Solubility in water (g/L) at 25 °C
CH ₃ OH	64.8	-97	Miscible
C ₂ H ₅ OH	78.5	-114	Miscible
C ₃ H ₇ OH	97	-126	Miscible
C ₄ H ₉ OH	117	085	73
C ₅ H ₁₁ OH	138	-79	22
C ₆ H ₁₃ OH	157	-48	5.9
C ₇ H ₁₅ OH	175	-35	1.7
C ₈ H ₁₇ OH	195	-16	immiscible
C ₉ H ₁₉ OH	212	-5.1	immiscible
C ₁₀ H ₂₁ OH	232	6.4	immiscible

This page titled [1.5: Polarity of bonds and molecules](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [3.9: Intramolecular forces and intermolecular forces](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).
- [2.5: Functional groups containing mix of sp³- and sp²-, or sp-hybridized heteroatom](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

CHAPTER OVERVIEW

2: Representing organic structures

2.1: Drawing organic structures

2.2: Resonance

2.3: Organic nomenclature -alkanes

2.4: Organic nomenclature -functional group containing compounds

This page titled [2: Representing organic structures](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

2.1: Drawing organic structures

Lewis structure

The molecular formula tells the elemental composition of a compound. For example, $C_5H_{10}O_2$ is a molecular formula. Multiple Lewis structures, representing different compounds, may have the same formula.

The compounds that have the same molecular formula but different structures are isomers of each other.

Lewis structure, also called Kekulé structure or a fully expanded formula, shows bonds between atoms as lines and lone pairs as dots. For example, pentanoic acid, 2-methyl butanoic acid, and 2,2-dimethylpropanoic acid are isomers having the same molecular formula $C_5H_{10}O_2$, as shown in Figure 2.1.1.

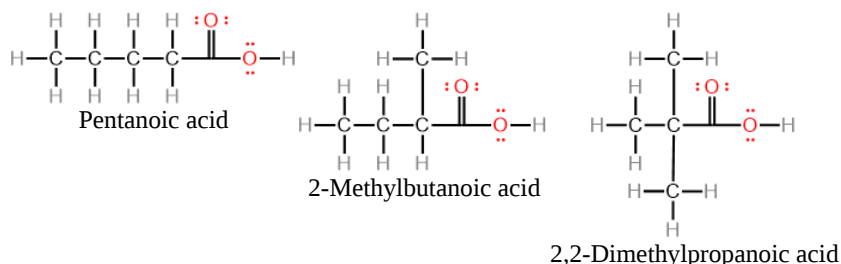


Figure 2.1.1: Lewis structures of three isomers of molecular formula $C_5H_{10}O_2$ (Copyright: Public domain)

Major drawbacks of Lewis structures are (i) they are not practical for large molecules, and (ii) they do not accurately represent the bond angles.

Condensed formula

The condensed formula simplifies the Lewis structure.

How to write a condensed formula?

- A condensed formula is written as a sequence of central atoms in the parent chain: each central atom is followed by its peripheral atoms other than the atoms of the parent chain.
- A branch is shown either connected to the corresponding atom of the chain by a line or
 - grouped in central brackets written next to the corresponding central atom, like peripheral atoms.
- Lone pairs are often omitted, but may be shown when needed. It is understood that with zero formal charge, C has no lone pair, N has one, and O has two.

For example, the condensed formula of pentanoic acid (Figure 2.1.1) is $CH_3CH_2CH_2CH_2COOH$, 2-methylbutanoic acid is

$\begin{array}{c} CH_3 \\ | \\ CH_3CH_2CHCOOH \end{array}$ or $CH_3CH_2CH(CH_3)COOH$, and 2,2-dimethylpropanoic acid is $\begin{array}{c} CH_3 \\ | \\ CH_3CCOOH \\ | \\ CH_3 \end{array}$ or $CH_3C(CH_3)_2COOH$.

Note that the repeat H_3C- groups in the last example are placed in the same center bracket with a subscript indicating the repeat number. The same can be applied to the repeat CH_2 groups. For example, the condensed formula of pentanoic acid may be written as $CH_3(CH_2)_3COOH$.

Small variations in the condensed formulas are acceptable if needed, as long as they represent the same structure. For example, the condensed formula of 2,2-dimethylpropane may be written $CH_3C(CH_3)_2COOH$ or as $(CH_3)_3CCOOH$. Similarly, some sections of the condensed formula may be shown in expanded form for emphasis, if needed. For example, the condensed form of pentanoic

acid may be written as $CH_3(CH_2)_3-\overset{\overset{O}{||}}{C}-OH$ showing more details of carbon-to-oxygen bonds.

Skeletal formula

The skeletal formula is based on the fact that C—C bonds in the parent chain of carbons can be placed on the plane of a page as a zig-zag line, as shown by the models of pentanoic acid, 2-methyl butanoic acid and 2,2-dimethylpropanoic in Figure 2.1.2.

How to draw a skeletal formula?

1. Omit C and H from the model of the molecule, keeping the C—C bonds as zig-zag lines, while maintaining heteroatoms, and hydrogens on the heteroatoms, results in the skeletal structure of the compound.
2. If there is any sp hybridized atom, show bonds around it at 180° , because the zig-zag line accommodates sp^3 and sp^2 hybridized atoms, but sp hybridized atoms have a linear geometry around them.

Examples of the first rule are the skeletal structures of pentanoic acid, 2-methylbutanoic acid, and 2,2-dimethylpropanoic acid shown in Figure 2.1.2. Examples of rule 2 are 2-hexyne, having two sp carbons (a triple bond), along with 2-hexene, having two sp^2 carbons (a double bond), and hexane, having all sp^3 atoms are shown in Figure 2.1.3. Note that four atoms on and around the triple bond are in a linear geometry.

Recall that the tetrahedral geometry of four bonds on a carbon is two Vs, perpendicular to each other and joined at the vertex. If one V is placed in the plane of the page, one bond of the other V is protruding outward to the viewer, and the other is recessing away from the viewer. The third and the fourth bonds on a tetrahedral carbon are shown as solid lines in the skeletal drawing of 2-methylbutanoic acid, and 2,2-dimethylpropanoic acid in Figure 2.1.2. This drawing does not distinguish whether the third or the fourth bond shown is protruding outward or recessing inward. If needed, it is shown as a solid wedge for the bond protruding outward or a hashed wedge for a bond recessing inward. For example, there are two isomers of 2-methylbutanoic acid: one with the 2-methyl bond protruding outward and the other with 2-methyl recessing inward when the molecule is drawn left to right with

$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OH} \end{array}$ on the right. This is distinguished in the skeletal drawing by converting the relevant portion of the drawing into a perspective drawing with the use of solid or hashed wedges, as shown in Figure 2.1.4. The solid or hashed wedges are not used in the skeletal drawing of 2,2-dimethylbutanoic acid because both bonds are the same.

Variations in the structural formula

A single bond is a σ bond symmetrical around the bond axis, allowing rotation of one bonded atom from 0° to 360° relative to the other in most cases. Different structures obtained by rotating around a single bond are not different compounds; they are called conformations of the same compound. Different conformations have different energies and exist in equilibrium with each other, where the most stable conformation is the most predominant in the mixture. The zig-zag line often used in skeletal structures to represent C—C chain, as in Figure 2.1.5a, is usually the most stable conformation. However, it can be drawn in multiple ways that may result from rotation around any single bond. For example, n-hexane shown in Figure 2.1.5a is rotated around the middle C—C bond to acquire new confirmation shown in Figure 2.1.5b and rotated further along the next C—C to acquire another confirmation shown in Figure 2.1.5c. All three structural formulas are shown in Figures 2.1.5a, b, and c are correct skeletal structures representing the same molecule.

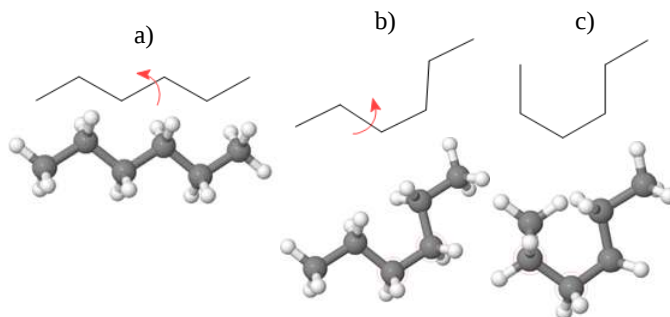


Figure 2.1.5: a) n-Hexane in a linear configuration and its model in the same configuration, b) the n-hexane in a bent configuration rotated $\sim 120^\circ$ around the middle C—C bond indicated by the arrow, i.e., between C's in red circles and the model in the same configuration, and c) the n-hexane in another bent configuration rotated $\sim 120^\circ$ again around the 2nd C—C bond indicated by the arrow, from the left, i.e., between C's in red circles and the model in the same configuration. (Copyright; Public domain).

Lone pairs are usually omitted but may be shown if needed. Similarly, a hybrid of skeletal formula and condensed or fully expanded formula is also used if required. For example, Figure 2.1.5a shows the skeletal formula of pentanoic acid ((

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$, its variations shown in Figure 2.1.5b and Figure 2.1.5c are also acceptable and may be used if needed.

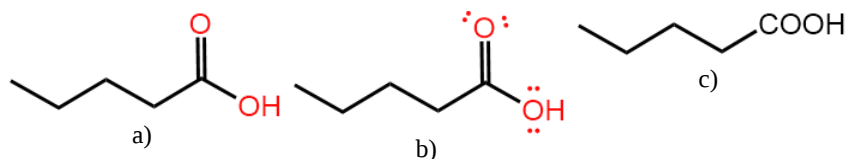


Figure 2.1.1: Skeletal formula of pentanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ drawn in usual way (a) and its two variations (b) and (c) that may be used in needed (Copyright: Public domain).

How to interpret a skeletal formula

1. If an element symbol is not shown at the end or bend of a line in the skeletal structure, it is a C.
2. Since C has four bonds, $\text{H on the C} = 4 - \text{number of lines on the C}$.
3. Heteroatoms and H on them, if present, are shown in the skeletal formula.
4. Lone pairs, if present, can be figured out from the formal charge and the number of bonds on an atom. The following is a summary of number of bonds, formal charges, and number of lone pairs for elements commonly found in organic

molecules: $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$, $\begin{array}{c} + \\ -\text{C}- \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{C}- \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{N}- \\ | \end{array}$, $\begin{array}{c} | \\ -\text{N}^+- \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{N}- \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{O}- \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{O}^+- \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{O}: \\ | \end{array}$, $\begin{array}{c} \cdot\cdot \\ -\text{X}: \\ | \end{array}$ (where X is a halogen F, Cl, Br, or I), $\begin{array}{c} \cdot\cdot \\ -\text{H} \\ | \end{array}$, and $\begin{array}{c} \cdot\cdot \\ \text{H}^- \end{array}$.

For example, the skeletal formula of the antibiotic amoxicillin is shown in Figure 2.1.6 (left) with C locations labeled by green numbers by rule#1, the numbers are the number of H on the carbon calculated by rule#2 as shown in the middle figure, heteroatoms are already showing on the skeletal formula according to rule#3, and lone pairs on them are determined by rule#4, as shown in the fully expanded formula in 2.1.6 (right).

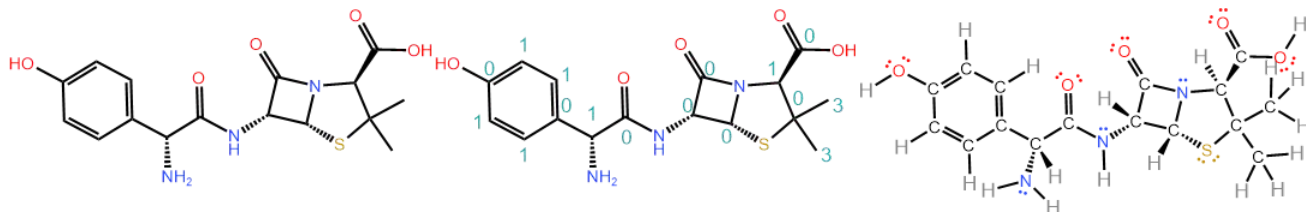


Figure 2.1.6: Skeletal formula of amoxicillin (left), the formula with C labeled with green numbers (rule#1) where the number tells hydrogen on the C (rule#2) (middle), heteroatoms are already showing (rule#3) and lone pairs are determined by rule#4, as shown in the fully expanded formula (right) (Copyright: Public domain).

Note that the skeletal drawing of amoxicillin is showing cyclic structures (a six-member ring on the right, and a four-member ring fused with a five-member ring on the left of the formula) and a 3D drawing (perspective drawing) where needed by hashed or solid wedges. Two more examples are shown in Figure 2.1.7 where skeletal structure of retinol, i.e., vitamin A1 needed for vision and several other functions, and of cholesterol that is essential for several functions but also related with cardiovascular diseases, are shown along with their semi-condensed formulas showing all C, H and lone pair. Note that the perspective drawing is shown where needed by using solid or hashed wedges.

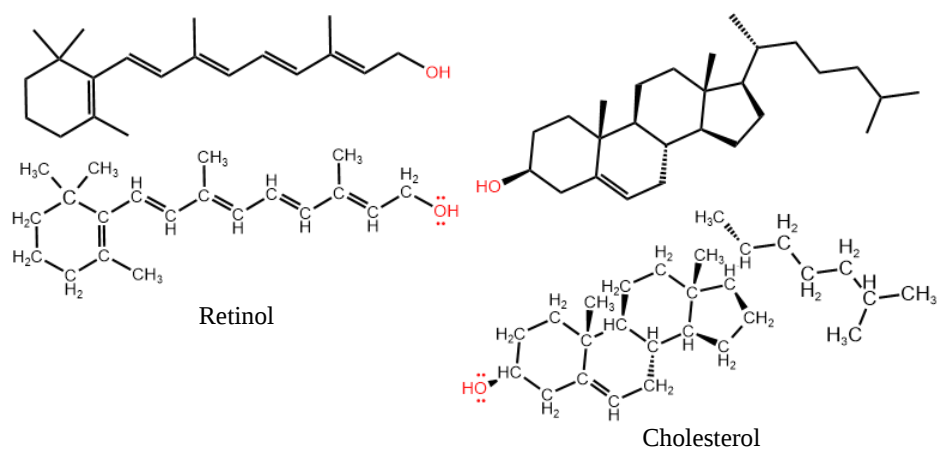


Figure 2.1.7: Retinol (left) and cholesterol (right), where the skeletal formula is shown on the top and semi-condensed formula at the bottom (Copyright: Public domain).

This page titled [2.1: Drawing organic structures](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [1.4: Representing organic compounds](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

2.2: Resonance

Delocalized electrons and resonance

Valence electrons of an atom are associated with one atom. A covalent bond is formed when two valence electrons are shared between two atoms. Bond formation always releases energy because of the increased attraction between the bonding electrons and the two nuclei. The same amount of energy, called the bond dissociation energy (BDE), is needed to separate the bonded atoms back into free atoms. The higher the bond dissociation energy, the stronger the bond.

Localized electrons

Bonding electrons associated with two atoms and nonbonding valence electrons associated with one atom in a molecule are called **localized electrons**.

Lewis structures, or skeletal structures, drawn based on valence bond theory, describe localized electrons as covalent bonds between two atoms and nonbonding electrons as lone pairs (two dots) or unpaired electrons (single dot) on one atom in a molecule. For example, three σ bonding electrons and one lone pair in ammonia $\text{H}-\ddot{\text{N}}-\text{H}$ are localized electrons.



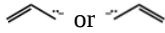
Delocalized electrons

In some molecules, the bonding electrons can spread over more than two atoms, and the nonbonding electrons over more than one atom.

Bonding electrons spread over more than two atoms, and nonbonding valence electrons spread over more than one atom in a molecule are called delocalized electrons.

Delocalization of the valence electrons releases more energy due to the increased attraction between the electrons and the multiple nuclei than the bonding energy of the structures with localized electrons. This additional release of energy resulting from the delocalization of valence electrons is called delocalization energy.

The valence bond theory described so far has a defect in that it represents only the localized valence electrons. It fails to model molecules or ions that involve delocalized electrons. For example, Lewis structure of prop-2-en-1-ide could be $\text{H}-\text{C}=\text{C}-\ddot{\text{C}}-\text{H}$ or

$\text{H}-\ddot{\text{C}}-\text{C}=\text{C}-\text{H}$ which correspond to skeletal structure . These structures are equivalent and imply one double

bond and one single bond between carbons, and one carbon bears a lone pair that causes a -1 charge. Neither structure models the actual molecule. According to the experimental facts, the actual molecule has two equal carbon-carbon bonds, which are between a single and a double bond, and both terminal carbons bear $-\frac{1}{2}$ charge. This is because the π bonding electrons are delocalized over three C atoms, and the lone pair responsible for the -1 charge is also delocalized over the two terminal C atoms.

Resonance and related terms

Visualizing the actual molecule as a hybrid of the two Lewis structures of 1-propenyl anion leads to the following model  where the solid line represents a σ bond and the dotted line represents half π bond, i.e., a π bond spread over three atoms. It models the actual molecule in which both C to $\text{C}=\text{C}$ bonds are equal and the charge is also equal to $-\frac{1}{2}$ on each terminal C. This is the basis of the concept of resonance introduced to valence bond theory to improve the modeling of molecules or ions that involve delocalized electrons.

Resonance is a concept in the valence bond theory to describe delocalized valence electrons by drawing two or more accurate, hypothetical Lewis structures, called **resonance**

contributors, differing in the distribution of delocalized electrons, such that the actual structure, called **the resonance hybrid**, can be visualized as a weighted average of the resonance contributors. The extra energy released due to the delocalization of some valence electrons in the resonance hybrid compared to the most stable resonance contributor is the **resonance energy**, also referred to as **delocalization energy** or **resonance stabilization**

For example, the two hypothetical skeletal structures of 1-propenyl anion, i.e., skeletal structure $\text{CH}_2=\text{CH}-\text{CH}_2^-$ and $^-\text{CH}_2-\text{CH}=\text{CH}_2$ are resonance contributors, and the actual ion $\text{CH}_2=\text{CH}-\text{CH}_2^-$ that is an average or hybrid of them is a resonance hybrid. The resonance energy of 1-propenyl anion is estimated to be about 71 to 75 kJ/mol.

Figure 2.2.1 shows benzene C_6H_6 molecule that has six-membered cyclic chain. The two resonance contributors have alternate single and double bonds between C atoms, and the resonance hybrid has all C to C bonds equal and in the middle of single and double bonds. Note that the resonance contributors are separated by resonance arrow $\longleftrightarrow$ to distinguish it from a reaction arrow $\longrightarrow$ or an equilibrium arrows $\rightleftharpoons$. This distinction is needed because resonance is not a chemical reaction. Resonance contributors are hypothetical, not real. The resonance hybrid is a real entity, and it is separated by an equivalent sign $\equiv$ from the hypothetical contributors.

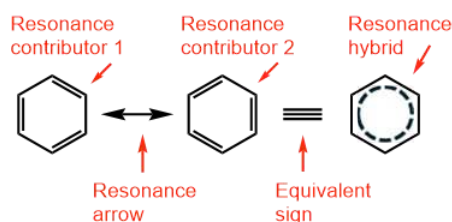


Figure 2.2.1: Two resonance contributors of benzene C_6H_6 separated by a resonance arrow and the corresponding resonance hybrid separated from the contributors by an equivalent $\equiv$ sign. (Copyright; Public domain)

Note that in the example of 1-propenyl anion and benzene, there are two equivalent resonance contributors, and they contribute equally, i.e., 50:50, to the resonance hybrid. This is not always the case. Examples will be described in the later sections where there are more than two resonance contributors, and they may or may not be equal. In those situations, the more stable the contributor, the more it contributes to the hybrid. In other words, when the resonance contributors are unequal, the resonance hybrid resembles the most stable contributor more than the less stable one.

Hybridization of lone pair-bearing atoms involved in resonance

According to the assignment of hybridization described so far, the two double bonded $\text{C}=\text{C}$ atoms of 1-propenyl resonance contributor $\text{H}-\text{C}=\text{C}-\text{C}^--\text{H}$ are sp^2 having a π bond between two p orbitals and the third C bearing a lone pair is sp^3 hybridized

with a lone pair in an sp^3 orbital. However, a C or any other lone pair bearing atom bonded to an sp^2 or sp hybridized atom, is actually sp^2 instead of sp^3 hybridized with lone pair in the p orbital. This allows more effective overlap between the two p orbitals, which is needed for the delocalization. In summary, when a lone pair is involved in resonance, the lone pair-bearing atom is sp^2 instead of sp^3 hybridized with the lone pair in the p orbital.

Delocalization in molecular orbital (MO) theory

According to MO theory, atomic orbitals ψ combine and produce an equal number of molecular orbitals Ψ . For example, 1-propenyl anion $\text{H}-\text{C}=\text{C}-\text{C}^--\text{H}$ has three sp^2 C atoms, two with p orbital occupied with one electron and one with a lone pair (two electrons). The three p atomic orbitals combine to form three molecular orbitals: Ψ_1 , i.e., a bonding MO, Ψ_2 , i.e., a nonbonding MO, and Ψ_3 , i.e., an antibonding MO, as illustrated in Figure 2.2.2. Two electrons occupy Ψ_1 representing π bond spread over three C atoms. The other two occupy the next higher energy Ψ_2 representing $-\frac{1}{2}$ charge on each terminal C atom. This agrees with the experimental results about the 1-propenyl anion.

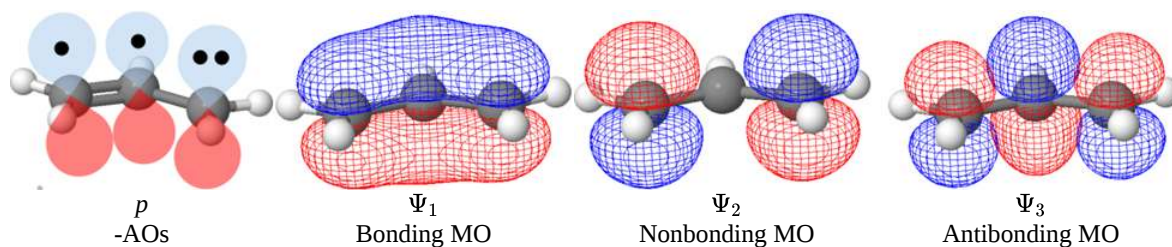


Figure 2.2.2: A cartoon of 1-propenyl anion atomic orbitals (left) that combine to form three molecular orbitals: Ψ_1 i.e., a bonding MO, Ψ_2 i.e., a nonbonding MO, and Ψ_3 i.e., an antibonding MO. The MOs are drawing using an online free app <https://molcalc.org/> (Copyright: Public domain)

Although MO theory better models delocalized electrons, it will be less often used due to its complexity compared to VB theory, which incorporates the resonance concept.

Summary of facts about resonance

1. When more than one correct Lewis structure can be drawn for a compound, these are called **resonance contributing structures**.
2. The actual structure of the compound that is deduced by assuming it is a hybrid of the contributing structures is called the **resonance hybrid**.
3. The extra stability of the resonance hybrid due to the resonance is called **resonance stabilization**.
4. The **contributing structures do not exist**; they are just the correct Lewis structures that help deduce the resonance hybrid. Consequently, the double-headed arrow does not show a chemical reaction; it is used only to separate the contributing structures of a compound.

Drawing resonance contributors

Resonance describes delocalized valence electrons. There are three types of valence electrons in molecules and ions: σ bonding, π bonding, and nonbonding electrons. Focus on π bonding and nonbonding electrons and avoid involving σ bonding electrons. Resonance involving σ bonds is rare and will be described separately when needed in this course. Resonance being described here involves π bonding in sp^2 or sp hybridized atoms, between consecutive p orbitals that are parallel or almost parallel to each other. Therefore, lone pair bearing atoms involved in resonance are sp^2 instead of sp^3 with the lone pair in p orbital.

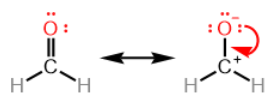
Movement of electrons and curly arrows

Movement of electrons is shown by curly arrows . The tail of the arrow is placed where the electrons to be moved are located, and the head points where the electrons move to (**tail** **head**). The arrow color is red here for emphasis only; it can be any color. When a π bond moves, the tail of the curly arrow is placed in the middle of the bond, and when a lone pair moves, the tail is placed on the atom bearing the lone pair. When the electron movement results in a new π bond, the head of the curly arrow points to the middle of the bond, and when it makes a new lone pair, the head points to the atom that will bear the lone pair. These conventions of using curly arrows to show electron movements are explained below with the examples of drawing resonance contributors.

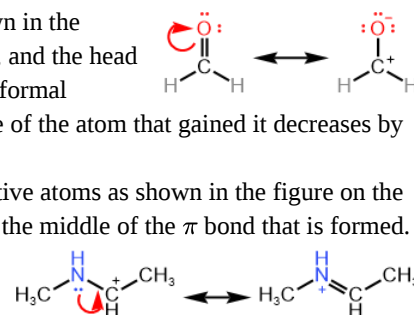
Delocalization of electrons between two consecutive atoms

There are two possibilities for this situation.

1. A π bond between two atoms can become a lone pair on one of the two atoms, as shown in the figure on the right. Note the tail of the arrow is in the middle of the π bond that moves, and the head is pointing to O on which the π electrons end up as a new lone pair. Also note that the formal charge of the atom that lost a shared π electrons increases by +1, and the formal charge of the atom that gained it decreases by -1.
2. The reverse of the above step, i.e., a lone pair becomes a π bond between two consecutive atoms as shown in the figure on the left. Note that the tail of the arrow is on O from which a lone pair moves and points to the middle of the π bond that is formed.



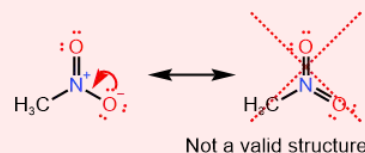
The formal charge of the atom that gains a shared π electron decreases by -1 (i.e., decreases from +1 to 0 on C), and that of the atom that loses the lone pair in



exchange for a shared π bond increases by +1 (i.e., increases from -1 to 0 on O). Another example is shown in the figure on the right.

Do not violate octet rule for second row elements

Do not violate the octet rule for second row elements (duet rule for H, i.e., any second row element can not have more than eight valence electrons in any resonance contributor. For example, the figure on the right is not a resonance because N in the second structure has ten valence electrons (five covalent bonds).



Exceptions to the octet rule included the following.

An incomplete octet is acceptable. For example, CH_3^+ in the resonance contributor shown on the left has six valence electrons (three covalent bonds) and it is an acceptable structure.

- Third row and higher elements may have more than eight valence electrons. For example P in $\text{HO}-\text{P}(\text{OH})_3$ has five covalent



bonds, i.e., ten valence electrons and S in $\text{HO}-\text{S}(\text{OH})_2$ has six covalent bonds, i.e., twelve valence electrons (note: two lone

pairs on each oxygen in these two structures are omitted for simplicity). Although it is usually explained by the involvement of inner $(n-1)d$ orbitals in the bonding, it is controversial. This controversy will be discussed later.

Delocalization of electrons between three consecutive atoms

Allylic position

Allylic position is the atom or a structure feature directly bonded to a double bonded atom, as illustrated with one example in the following: $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$.
 not allylic allylic double bond

A lone pair, a positive charge, or an unpaired electron (radical) moves to the third position on an allylic system, with a simultaneous movement of the π bond between three consecutive sp^2 or sp atoms, as illustrated in Figure 2.2.3.

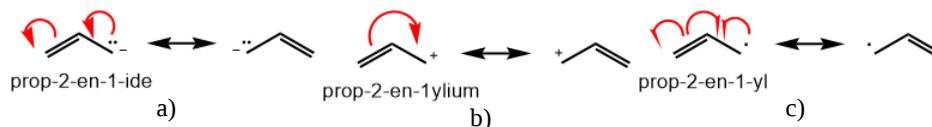


Figure 2.2.3: Illustration of resonance of a) an allylic lone pair, b) positive charge, and c) a radical, between three consecutive sp^2 hybridized atoms (Copyright: public domain).

Note that curly arrows show the following:

- movement of electrons and not the movement of positive charge, e.g., in Figure 2.2.3 a), two arrows are used, one for lone pair and one for π electrons and only one in Figure 2.2.3 b) for π electrons, and
- a regular curly arrows show movement of two electrons, a lone pair or a π -bonding pair, as in Figure 2.2.3 a) and b) and curly half-headed arrows show movement of a single electron, as in Figure 2.2.3 c).

Note that Figure 2.2.3 c) one of the two π bonding electrons moves to the right to pair-up with the unpaired allylic electron to make a new π bond and the second electron moves to the left to become an unpaired nonbonding electron on the right terminal C. The allylic lone pair, positive charge, or radical moves to the third atom with a simultaneous movement of π bond between three consecutive sp^2 or sp atoms.

A second row element with octet complete can not receive electrons by resonance because it will exceed octet, as illustrated in Figure 2.2.4 a) and b). However, it can receive electrons, provided it loses one simultaneously, as illustrated in Figure 2.2.4 c)

and d). Note that when an atom receives electrons and loses an equal number of electrons, its valence electrons are not changed, and its formal charge is also not changed.

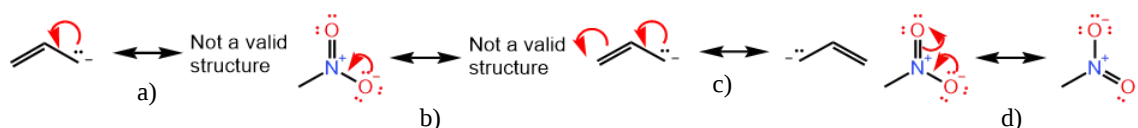


Figure 2.2.4: Illustration of a) and b) as not valid resonance because of the octet of middle C in a) and of N in b) would be violated, and c) and d) are valid resonances because electrons received and lost are equal that avoids octet violation for these 2nd row elements (Copyright: Public domain).

Figure 2.2.5 shows more examples of resonance in allylic systems.

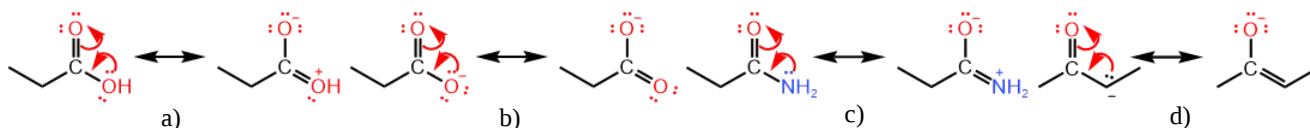


Figure 2.2.5: Examples of lone pair resonance in allylic systems (Copyright: Public domain)

Delocalization of electrons in a conjugated double-bond system

- Three or more consecutive atoms with p orbitals that can overlap with each other are a conjugated system in which electrons can delocalize. For example, ethenol $\text{H}-\text{C}=\text{C}-\ddot{\text{O}}-\text{H}$, is a conjugated system of three atom in which two C and O atoms are sp^2 hybridized with parallel p orbitals that can overlap.

- Alternating double and single bonds are conjugated double bonds. For example, $\text{H}-\text{C}=\text{C}-\text{C}=\text{C}-\text{H}$ is a

conjugated double bond system of four atoms, but $\text{H}-\text{C}=\text{C}-\text{C}-\text{C}=\text{C}-\text{H}$ is not because the middle carbon is sp^3 that breaks the conjugation.

Benzene is a conjugated double-bond system of three double bonds in a cyclic structure, as shown in Figure 2.2.6 a). Moving one π -bond between three consecutive atoms of a conjugated double system is not valid, as it will exceed the octet of the atom receiving the new double bond, as illustrated in 2.2.6 a). However, moving all π -bonds simultaneously avoids this problem and leads to a valid second resonance contributor, as shown in Figure 2.2.6 b). Each C receives a π -bond and loses one at the same time, with no change in its valence electrons and formal charge.

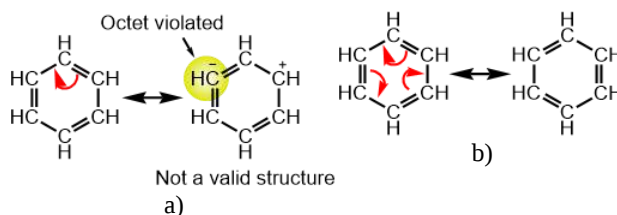


Figure 2.2.6: Delocalization of π -bonds in a cyclic conjugated double bond a) moving one bond does not lead to a valid structure due to octet violation in the C receiving new π -bond, but b) moving all π -bonds in the ring leads to a valid resonance contributor (Copyright: Public domain)

Delocalization in more than three conjugated atoms

A system of three or more conjugated atoms usually has more than two total resonance contributors. The resonance contributors can be drawn from any one starting structure by step-by-step applying the procedure of two or three conjugated atoms described above. For example, Figure 2.2.7 shows five resonance contributors of phenol drawing by consecutive steps of allylic lone pair resonance between three atoms. The resonance hybrid is also shown, illustrating the $\delta+$ and $\delta-$ regions in the molecule.

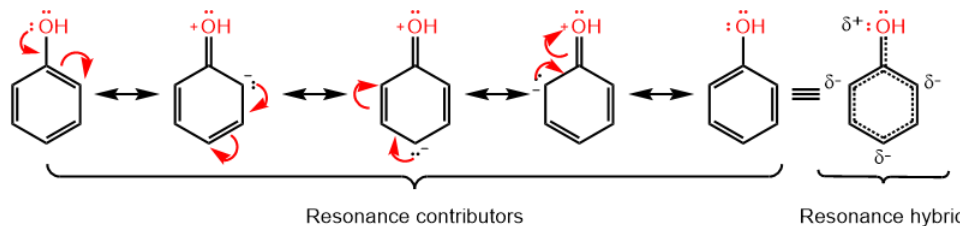


Figure 2.2.7: Five resonance contributors of phenol are drawn by applying the procedure of allylic lone pair resonance, one step at a time, between three conjugated atoms. The resonance hybrid is depicted on the right, with partial charges indicated. (Copyright; Public domain)

Figure 2.2.8 is another example, illustrated by the case of resonance in benzaldehyde.

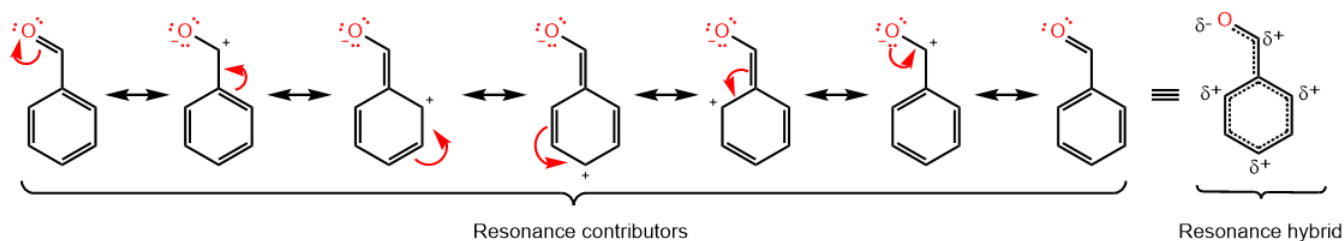


Figure 2.2.8: Seven resonance contributors of benzaldehyde are drawn by applying the procedure of resonance between two conjugated atoms in the first step, followed by allylic cation resonance between three conjugated atoms in the second to sixth steps. The resonance hybrid is depicted on the right, with partial charges indicated. (Copyright; Public domain)

The curly arrows in the examples described so far depict the electron movements in the forward direction. The same steps can be applied in the reverse direction. For example, Figure 2.2.9 shows a drawing of resonance contributors by using red arrows in the forward direction and blue arrows for the reverse direction.

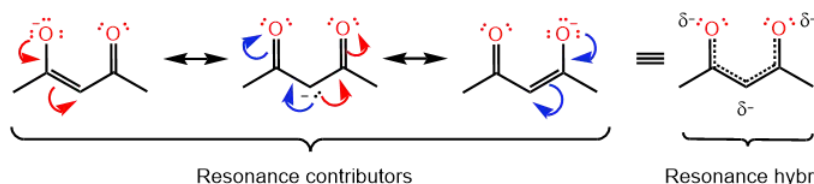
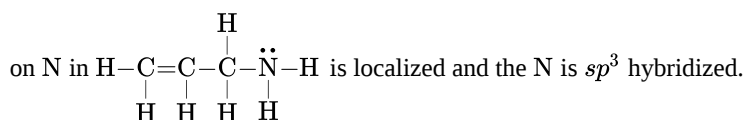
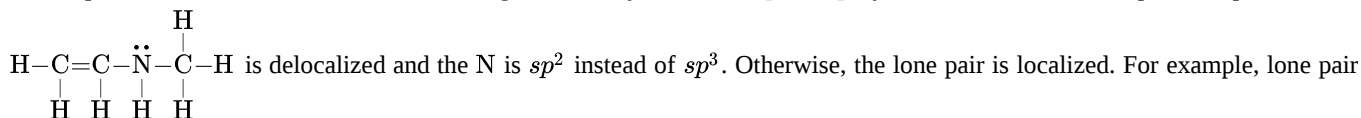


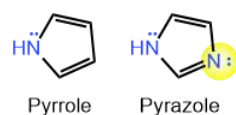
Figure 2.2.9: Three resonance contributors of acetoacetate are drawn by applying twice the procedure of allylic lone pair resonance between three conjugated atoms shown in red curly arrows. Blue arrows show the reverse steps. The resonance hybrid is depicted on the right, with partial charges indicated. (Copyright; Public domain)

Recognizing a localized and a delocalized lone pair

A lone pair is delocalized when the atom bearing it is directly bonded to sp^2 or sp hybridized atom. For example, lone pair on N in

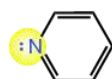


The structure of pyrrole is shown in the figure on the left. The sp^2 orbitals of pyrrole are shown in blue and p orbitals in yellow in the figure on the right (drawing using <https://chemagic.org/molecules/amini.html>, Copyright: Public domain). N of pyrrole is sp^2 hybridized. Its lone pair is in a p -orbital and it is delocalized as shown in Figure 2.2.10



However, when a lone pair is in an orbital that is perpendicular to the p -orbitals of neighboring atoms, it is localized. Orbitals perpendicular to each other can not overlap to make a π -bond.

For example, pyrazole has a structure similar to pyrrole with one more N in the ring, as shown in the figure on the left. One N of pyrazole has a delocalized lone pair in p orbital. The second N (highlighted in yellow) has a p orbital occupied by one electron that is involved in π -bonding, while the lone pair occupies a sp^2 orbital, as shown in Figure 2.2.10. This sp^2 orbital is perpendicular to p orbitals, and the lone pair in it is localized.



Pyridine

Pyridine is another compound with a similar structure, as shown in the figure on the right. Lone pair on N of pyridine is also in sp^2 -orbital and localized, as illustrated in Figure 2.2.10.

Similarly one lone pair on O of ethenol $\text{H}-\text{C}=\text{C}-\ddot{\text{O}}-\text{H}$ is in a p -orbital and delocalized, while the second is in an sp^2 -orbital and localized.



orbital and delocalized, while the second is in an sp^2 -orbital and localized.

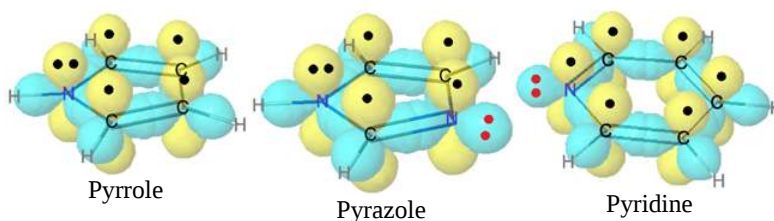
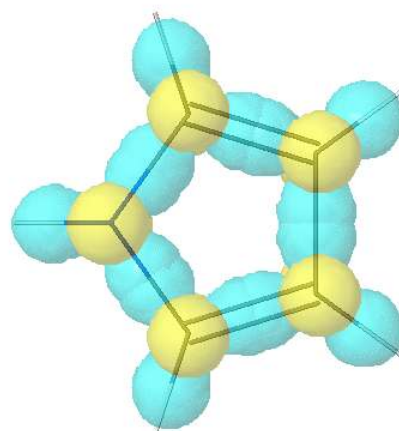


Figure 2.2.10: Cartoon of sp^2 -orbitals in blue and p -orbitals in yellow of pyrrole, pyrazole, and pyridine. Lone pair of pyrrole and one lone pair of pyrazole in black are p -orbitals and are delocalized, while the lone pair of pyridine and the second lone pair of pyrazole in red are in sp^2 orbitals and localized. (Figures prepared using <https://chemagic.org/molecules/amini.html>, Copyright: Public domain).

Estimating the relative importance of the resonance contributors

If the resonance contributors are equal, they contribute equally to the resonance hybrid. For example, the acetate ion has two equal resonance contributors and the carbonate ion has three. Their resonance hybrids are the average of the resonance contributors, as shown in Figure 2.2.11.

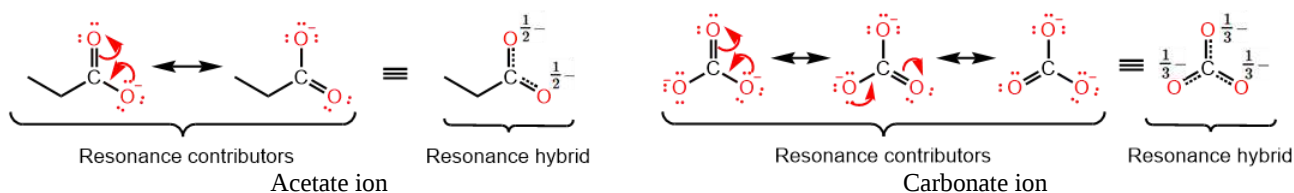


Figure 2.2.11: Examples of equal resonance contributors, acetate has two equal resonance contributors, and carbonate ion has three (Copyright: Public domain).

Often, the resonance contributors are not equal. In these cases, the more stable resonance contributors contribute more to the hybrid, i.e., the structure of the hybrid resembles the more stable contributors than the less stable ones. The more the difference in the energy of the contributors, the weaker the resonance and the less the resonance stabilization.

Rules for estimating the relative importance of resonance contributors

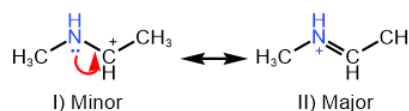
The following rules, in the decreasing order of importance, are used to estimate the relative importance of resonance contributors.

1. More atoms with an octet are more stable and are a more important contributor.
 - A structure with an octet is complete and also has more covalent bonds, making it more stable than a structure with an incomplete octet.

- Structures with fewer formal charges are more stable and more important contributors than those with more formal charges.
 - The more the unlike charges (+ and -) are separated, the less stable the structure.
- A negative charge on a more electronegative atom is more stable than a negative charge on a less electronegative atom.
 - A positive charge on a more electropositive atom is more stable than a positive charge on a less electropositive atom.

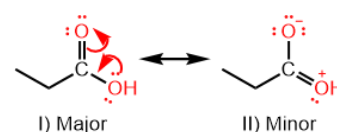
The application of these rules is explained with the help of the following examples.

Structure I of $\text{CH}_3\text{NH}^+\text{CH}_3$ in the figure on the right, has octet incomplete on C and should be minor according to rule#1, but II has positive charge on a more electronegative N and should be minor according to rule#3. Rule#1 is more important and overrides rule#3, making II a major and I a minor contributor.



The structure II of $\text{H}_2\text{C}=\text{O}$ in the figure on the left is a major contributor with octet completeness on all atoms and no charge separation, I is minor because of the octet of C incomplete (rule#1) and charge separation (rule#2), and III is negligible because of octet of O incomplete (rule#1), charge separation (rule#2), and positive charge on electronegative O (rule#3). Usually, there is no need to draw negligible contributors.

In the structures of propanoic acid $\text{CH}_3\text{CH}_2\text{COOH}$ shown in the figure on the right, II is minor because of more formal charges (rule#2), i.e., positive on one and negative on the other O and I with no formal charges is major.



In the structures of an anion of a ketone shown in the figure on the left, II is major due to the negative charge on the more electronegative O than on C in I (rule#3). In the example of the figure on the right, I is major with octet complete (rule1) and no charge separation (rule#2), II is minor with octet complete but two formal charges (rule#2), and III is negligible with two formal charges (rule#2) and incomplete octet on C (rule#1).



Comparing resonance stabilization of similar compounds

In addition to estimating the relative importance of resonance contributors of the same compounds, the above three rules described in the previous section can also be applied to assess the relative importance of resonance or resonance stabilization in similar

compounds. For example, comparing the resonance donation of lone pair on N in acetamide $\text{CH}_3-\text{C}(=\text{O})-\text{NH}_2$ and on O in acetic

acid $\text{CH}_3-\text{C}(=\text{O})-\text{OH}$, the former is a stronger resonance due to less electronegative N being more able to donate its lone pair than O. In addition to octet completeness, formal charges, and electronegativity factors, the relative size of orbitals overlapping is also a critical factor in determining the extent of resonance when comparing different compounds.

The orbitals of comparable sizes overlap more effectively, resulting in stronger resonance than orbitals of different sizes -the larger the difference in the sizes, the weaker the resonance.

For example, resonance donation of lone pair on Cl in acetyl chloride $\text{CH}_3-\text{C}(=\text{O})-\text{Cl}$ is negligible due to 3p-orbital of Cl being significantly larger than 2p-orbitals of C, O, and N, as shown in Figure 2.2.12

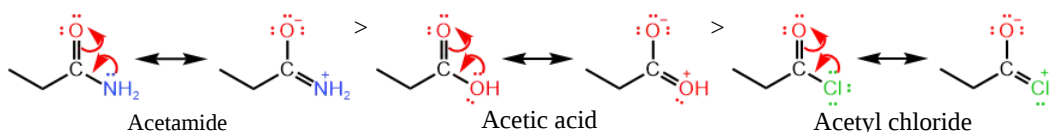
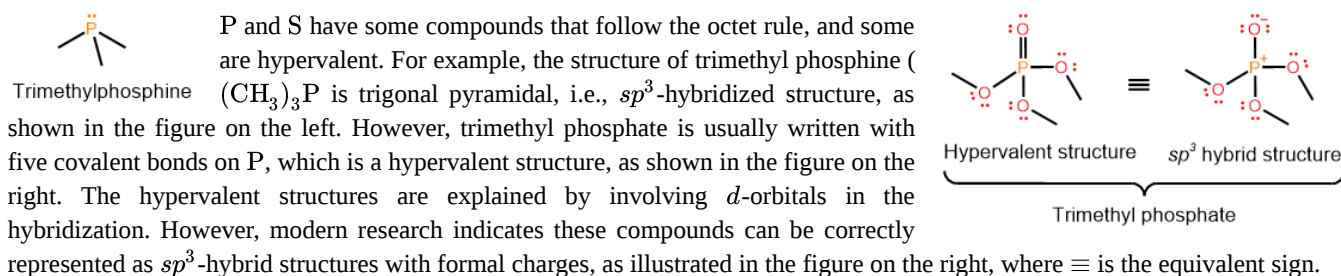


Figure 2.2.12: Relative Strength of allylic lone pair on N in 2p-orbital, with that of more electronegative O in 2p-orbital and of Cl in 3p-orbital with 2p-orbitals of $\text{C}=\text{O}$ group (Copyright: Public domain)

A controversy over hypervalent or octet-valent states of P and S compounds

A structure with a central atom of a third-row or higher main group element having more than eight valence electrons is called **hypervalent** or **expanded octet state**.



Phosphorus pentafluoride PF_5 is another example of a hypervalent structure. This structure is considered as dsp^3 -hybrid phosphorus, which according to VSEPR theory has a trigonal bipyramidal structure, as shown in Figure 2.2.13a). Three bonds that form a triangular planar portion of PF_5 are called equatorial bonds, and two bonds perpendicular to the triangular plane are called axial. The PF_5 can be represented with eight valence electrons on P as a hybrid of five resonance structures, each with four covalent bonds and one ionic bond, as illustrated in 2.2.13b).

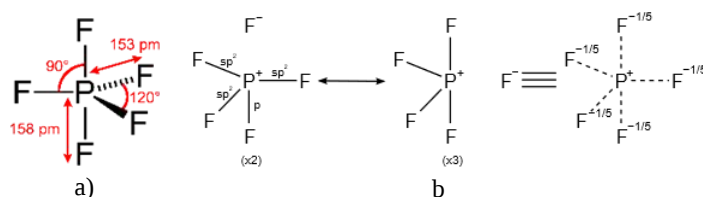
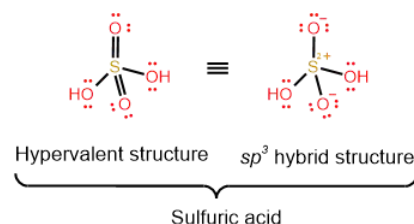


Figure 2.2.13: a) Hypervalent structure of phosphorus pentafluoride PF_5 and b) equivalent resonance structures with eight valence electrons on P, involving resonance between covalent and ionic bonds. There are two possible structures with an axial ionic bond that are major contributors, plus three possible structures with an equatorial ionic bond, which are minor contributors (Copyright: Public domain)

Several compounds of S are depicted as hypervalent structures. For example, S in sulfuric acid H_2SO_4 is usually represented as a hypervalent structure with six covalent bonds (twelve valence electrons) on S as shown in the figure on the right. However, its sp^3 -hybrid structure, shown in the figure on the right, with 2+ formal charge on S and -1 formal charge on two O, is being increasingly accepted as its proper structure.



It should be mentioned here that, despite the controversy over hypervalent versus sp^3 -hybrid structure described above, IUPAC recommends drawing expanded octet structures for these S and P compounds. Therefore, these structures will usually be drawn as hypervalent structures in this book, except when needed otherwise.

This page titled 2.2: Resonance is shared under a Public Domain license and was authored, remixed, and/or curated by Muhammad Arif Malik.

- 1.6: Resonance by Muhammad Arif Malik is licensed Public Domain.

2.3: Organic nomenclature -alkanes

Drawing Lewis structures, or line-bond structures, and describing delocalized electrons by resonance and resonance hybrid is a graphical way of representing organic molecules. Names are given to things to represent them in words. The same applies to organic molecules; they are assigned names to represent them in words. For example, ethanol is a molecule that has the following

Lewis structure: $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\ddot{\text{O}}-\text{H} \\ | \\ \text{H} \end{array}$, or the following line bond structure: . Before systematic nomenclature was developed,

organic compounds were known by common names. The International Union of Pure and Applied Chemistry (IUPAC) has developed a systematic nomenclature, called the **IUPAC nomenclature** or **systematic nomenclature** of organic compounds. Systematic names are assigned so that each organic molecule has a unique name, such that one may be able to draw the structure from the name and deduce the name from the structure.

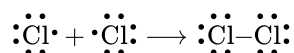
Systematic nomenclature is based on the name of the C chain and the name of the reactive part of the molecule, called a functional group. Chemical reactions involve the making and breaking of chemical bonds that usually take place in the functional groups. Therefore, the making and breaking of chemical bonds, followed by functional groups, are described next before describing IUPAC nomenclature.

Basic chemical reaction types

Chemical reactions, i.e., making and breaking of chemical bonds, are divided into two major classes, homolytic and heterolytic bond making and breaking, as described next.

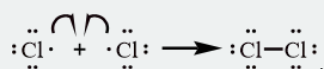
Homolytic bond making and breaking

A covalent bond is formed by sharing valence electrons, one from each atom, e.g., as in the formation of Cl_2 molecule by the following reaction:

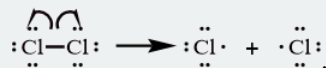


Movement of valence electrons in chemical reactions is shown by curly arrows . The tail of the arrow is placed where the electrons to be moved are located, and the head points where the electrons move to (tail  head). Regular curly arrows  show movement of two electrons, a lone pair or a π -bonding pair, and curly half-headed arrows  show movement of a single electron.

Bond formation, in which both atoms contribute one electron to form a covalent bond, is known as **homolytic bond formation**. e.g.,



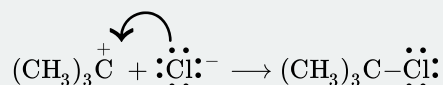
The reverse of it, i.e., bond breaking, in which both fragments receive one electron, is called **homolytic bond breaking**, e.g.,



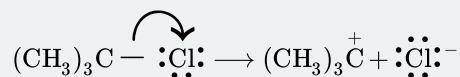
Energy released during homolytic bond making is the same amount of energy needed for homolytic bond breaking, which is called the bond dissociation energy (BDE).

Heterolytic bond making and breaking

Bond formation in which both the bonding electrons are donated by one atom is known as **heterolytic bond formation**, e.g.,



Reverse of it, i.e., bond breaking, in which both the bonding electrons are received by one of the fragments, is called **heterolytic bond breaking**, e.g.,



Energy needed for heterolytic bond breaking is not the same as in homolytic bond breaking, because the products of the two are different. Heterolytic bond breaking typically occurs in polar bonds, where the bonding electrons are transferred to the more electronegative atom, whereas homolytic bond breaking usually takes place in nonpolar bonds. This is because the atomic orbital of the more electronegative atom is closer in energy to the molecular orbital. In contrast, in a nonpolar bond, the atomic orbitals of both atoms are about the same distance away from the molecular orbital in terms of energy, as shown in Figure 2.3.1. Furthermore, most chemical reactions in biological systems, as well as in the laboratory, occur in solution, where polar solvents stabilize charges, making heterolytic processes more favorable. Therefore, the reactive sites in organic molecules, called functional groups, are usually associated with polar bonds between C and heteroatoms like O, N, halogens, etc.

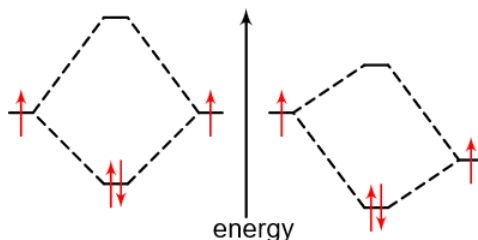


Figure 2.3.1: Depiction of a MO diagram of a nonpolar covalent bond (left) and a polar covalent bond (right). In both cases, a bond is a shared pair of electrons. (Copyright; Krishnavedala, Public domain, via Wikimedia Commons)

Functional groups

A **functional group** is a group of atoms in an organic molecule that is associated with a characteristic set of chemical properties.

A functional group usually contains polar bonds, e.g., alkyl halide $(\text{R})_3\text{C}^{\delta+}-\text{Cl}^{\delta-}$, alcohol $(\text{R})_3\text{C}^{\delta+}-\text{O}^{\delta-}-\text{H}^{\delta+}$, carbonyl $(\text{R})_2\text{C}^{\delta+}=\text{O}^{\delta-}$, etc.,

or a combination of these, e.g., carboxylic acid $\text{R}-\overset{\text{O}^{\delta-}}{\underset{\text{O}^{\delta+}}{\parallel}}-\text{O}^{\delta-}-\text{H}^{\delta+}$, which is a combination of a carbonyl and an alcohol groups, and

acid halide $\overset{\text{O}^{\delta-}}{\underset{\text{O}^{\delta+}}{\parallel}}-\text{C}^{\delta+}-\text{Cl}^{\delta-}$, which is a combination of a carbonyl and an alkyl halide groups, etc., where R represents the rest of the organic molecule. Functional groups usually react through heterolytic chemical processes, known as the polar reaction mechanism.

Organic compounds containing only C and H atoms are called hydrocarbons. Hydrocarbons that have only single bonds are called alkanes, those having at least one double $\text{C}=\text{C}$ bond are called alkenes, and those having at least one triple $\text{C}\equiv\text{C}$ bond are called alkynes. The π -bonds in $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ are also called unsaturation. Since π -bond is weaker than a σ -bond and its electrons are relatively less tightly held by the nuclei, they are easily donated in chemical reactions. Therefore, $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ are functional groups. Alkanes are the least reactive class of organic compounds as they do not have functional groups. Alkanes typically react through a homolytic chemical process, known as the free radical mechanism.

The structure and names of the most common functional groups in organic compounds are described in the next section about organic nomenclature. Further details are provided in the next chapters.

Introduction to IUPAC nomenclature

This introduction to the IUPAC nomenclature is extracted from: IUPAC, Pure Appl. Chem. 2020, <https://doi.org/10.1515/pac-2019-0104>. The IUPAC names are generated using [ACD/ChemSketch \(freeware\)](#). The structures are drawn using [KingDraw for PC](#).

The structure of the IUPAC nomenclature of an organic compound, with the parts labeled, is shown in Figure 2.3.2 and described next.

- It is the parent chain, which is usually the longest carbon chain on which a characteristic functional group is present.
 - It is a suffix representing unsaturation, i.e., it tells whether C atoms have only single bonds or also have double or triple bonds.
 - Represents the suffix of the senior functional group.
 - It is an alphabetical list of prefixes representing branches on the parent chain or non-senior functional groups, collectively called substituents.
 - The locant that tells the position on the parent chain of a substituent is listed next to it; the numbers are listed in increasing order, separated by commas, and are distinguished from alphabets by hyphens.
 - It is a multiplier telling how many times the substituted attached to it is repeated; the multiplier is not counted in alphabetization of the substituents, and
 - is a stereodescriptor preceded by the locant number of the stereogenic center if present in a molecule and enclosed in brackets.
- When parts of a name belong together, they are enclosed in brackets in the nesting order $\{[()]\}$.

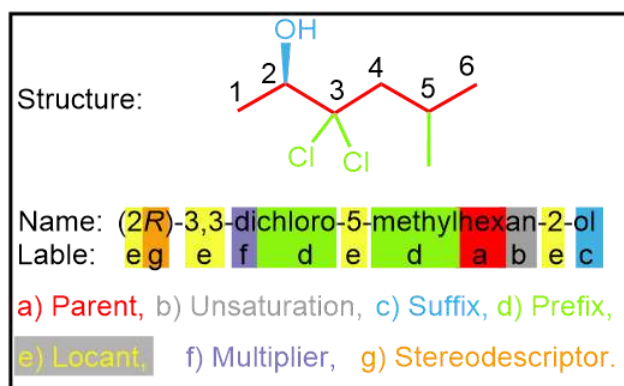


Figure 2.3.2: Structure of the IUPAC nomenclature is illustrated with components labeled: a) is the parent chain, b) is suffix indicating unsaturation, c) is the suffix representing senior group, d) are prefixes representing substituents listed in alphabetic order, e) are locant numbers separated from each other by comma and from the alphabets by hyphens, f) is the multiplier, g) is the stereodescriptor enclosed in brackets. (Copyright; Public domain).

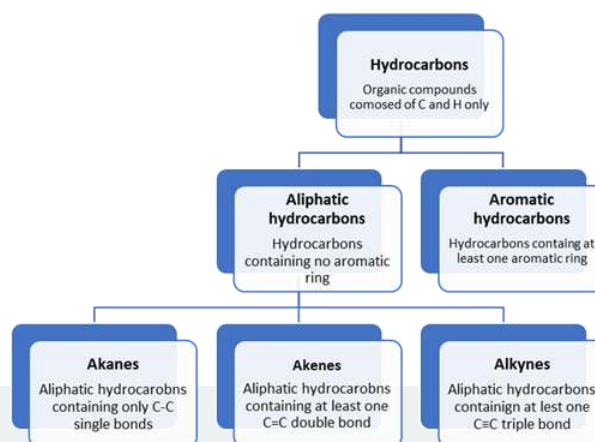
Naming simple organic compounds needed in this course is described in the next section, starting with hydrocarbons, followed by compounds containing non-characteristic functional groups, and finally, compounds containing characteristic functional groups. Note: stereodescriptors are ignored in this chapter and will be described and added to the nomenclature in the next chapter.

Nomenclature of hydrocarbons

Hydrocarbons are organic compounds containing only C and H atoms. They are divided into two major classes: i) aliphatic, which do not have any aromatic ring, and ii) aromatic, which contain at least one aromatic ring, most often a benzene ring, C_6H_6 a six-C chain containing alternate single and double bonds. The aliphatic hydrocarbons are divided into three sub-classes: i) alkane containing only single C—C bonds, ii) alkene containing at least one double C=C, and alkyne containing at least one triple C≡ bond, as illustrated in the figure on the right.

Straight-chain alkane

IUPAC name of a straight chain has two parts: stem name, listed in Table 2.3.3 that tells how many C atoms are in the chain and suffix -ane where -e tells it is a hydrocarbon and -an- tells it is an alkane.



For example, $CH_3CH_2CH_2CH_2CH_3$ is pentane, where pent- is the stem name for five-C chain and -ane is the suffix for an alkane. Similarly, CH_4 is methane, CH_3CH_3 is ethane, $CH_3CH_2CH_3$ is propane, and so on.

Table 2.3.3: List of stem names for up to twenty C atoms in a chain.

Number of carbons	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Stem name	Meth	Eth	Prop	But	Pent	Hex	Hep	Oct	Non	Dec	Undec	Dodec	Tridec	Tetradec	Pentadec	Hexadec	Hepadec	Octadec	Nonadec	Icos

Skeletal structure of a straight chain may be zigzag or wobble-wobble

A straight chain alkane is usually drawn as a zigzag line, but rotation is allowed around each single bond, which may change it into a wobble-wobble line bond structure, as shown in Figure 2.3.4.

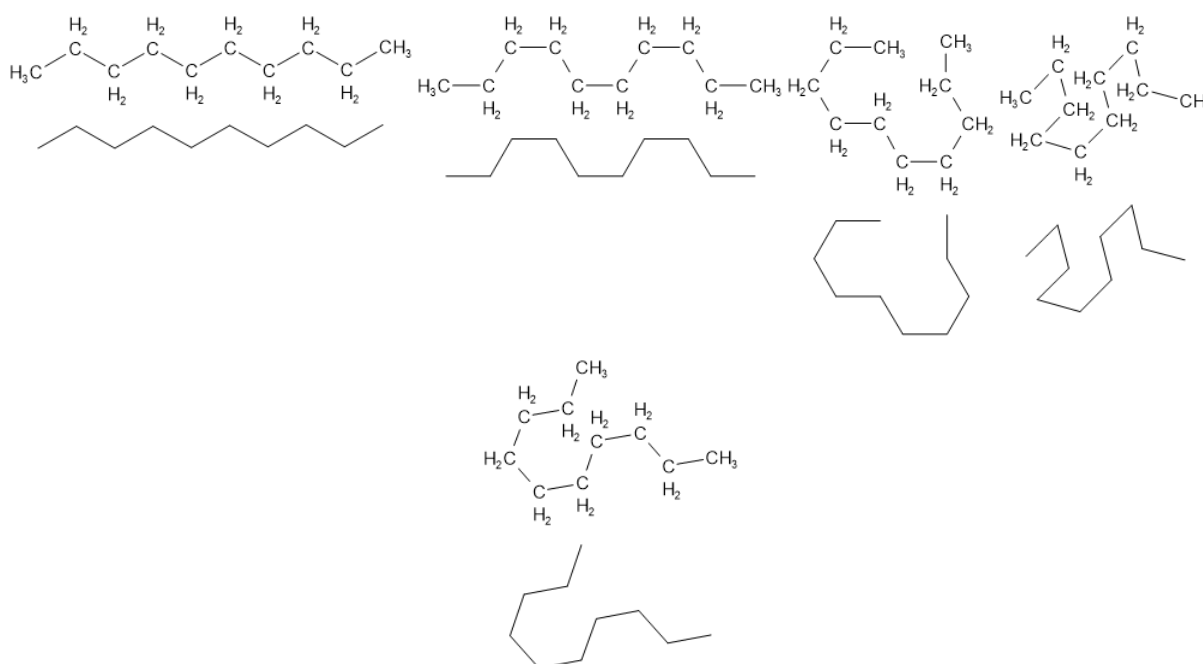


Figure 2.3.4: Skeletal structures of decane (C₁₀H₂₂) drawn as regular zigzag (left) and in four other shapes resulted by rotation around C—C single bonds: semi-condensed formulas (top) and the corresponding skeletal formulas (bottom) are shown. (Copyright; Public domain)

Branched alkane

- Find the longest continuous C-chain and name it as a straight chain alkane; it is the parent chain in the IUPAC name of the compound.
 - If there is a tie, preference goes to the chain with more branches.
- Name all of the branches as straight chain alkanes, but with the suffix -ane replaced with -yl for the branch name; list the branches, referred to as **substituents**, alphabetically before the parent name with no spaces between the names.
 - If the same branch appears more than once, list it once with a multiplier prefix. The multiplier prefixes are listed in Table 2.3.5.
- Number the C atoms of the parent chain from #1 for one end, continuously increasing till the other end, beginning from the end that assigns a lower number to the point of attachment of the first branch.
 - If there is a tie, preference goes to the branch that is first in alphabetical order.

- If there is still a tie, the preference goes to the third branch.
- 4. Insert the locant number, which is the point of attachment of the branch on the parent chain, before the branch name, separated by hyphens from the alphabet.
 - If a branch is repeated, list the locant number of each in increasing numeric order, separated by commas before the multiplier prefix.
 - If a repeat branch is on the same locant, repeat the locant number.
- 5. If a branch is further branched, name it by the above four rules with the following changes.
 1. Numbering of the parent chain in the branch begins from the end that assigns a lower number to the C attached to the parent chain of the compound.
 2. Suffix -ane is replaced with -yl with a locant number before it, which is the number of the C in the branch that is attached to the parent chain of the compound.
 3. The entire name of the branch is enclosed in brackets and listed in alphabetical order, along with other branches, preceded by its locant number.

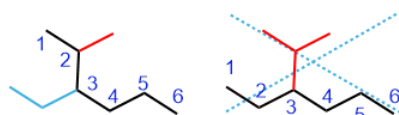
Table 2.3.5: Multiplier prefixes for simple/complex entities*

No	Simple	Complex	No	Simple	Complex	No	Simple	Complex	No	Simple	Complex
2	di	bis	5	penta	pentakis	8	octa	octakis	11	undeca	undecakis
3	tri	tris	6	hexa	hexakis	9	nona	nonakis	12	dodeca	dodecakis
4	tetra	tetrakis	7	hepta	heptakis	10	deca	decakis	20	icosa	icosakis

*Example simple: dipropyl, example complex: bis(2-methylpropyl).

The rules #1 to 5 above are explained through application to the following examples.

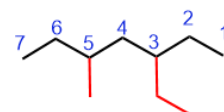
The structure shown in the figure on the right is 4-ethyldecane —numbers in blue show the numbering of the parent chain in this and the following structures. Here is the breakdown of the nomenclature: the parent chain is "decane" (not nonane, rule#1); the branch name is "ethyl" note ethane and listed before the parent "ethyldecane" with no space between the words by rule#2; numbering begins from the end that assigns #4 to the branch (not from the other end that will assign it #7) rule#3, and its final name after applying rule#4 is "4-ethyldecane".



The structure in the figure on the left is 3-ethyl-2-methylhexane. Here is the breakdown of the nomenclature: the parent chain is the one with two branches, not the one with one branch (rule#1, if there is a tie, preference goes to the chain with more branches); the branches are listed in alphabetic order (not by the locant number) rule#2, and the locant

number of each branch is inserted before the branch name (rule#4).

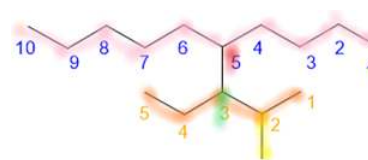
The structure in the figure on the right is 3-ethyl-5-methylheptane. Numbering from either side gives #3 to the first substituent. The tie is broken by giving preference to ethyl, which alphabetically comes before methyl (Rule#3).



The structure on the left is 3,3,4-trimethylhexane. The numbering from either side is the same for the first substituent, so preference is given to the third substituent (rule#3). Methyl substituent repeats three times, so it is listed once with a multiplier of three (Rule#2). Methyl substituent repeats on #3, so the locant number is also repeated (rule#4).

The structure on the right is 5-(2-methylpentan-3-yl)decane. Numbers in blue represent the numbering of the parent, and numbers in orange represent the numbering in the branch chain. Here is its breakup. The longest chain is ten-C atoms, so the parent name is decane. Numbering of the parent begins from left to assign a lower number to the branch. The branch is complex, so it is named according to rule#5: Numbering from either side assigns #3 to the point of attachment to the parent, so numbering begins from left

to give preference to the methyl branch. The prefix -ane is replaced with -yl with locant, i.e., the point of attachment from the branch to the parent is inserted before the prefix (3-yl). The branch name is enclosed in brackets and listed before the parent name, preceded by its locant number on the parent (5-).



5-(2-methylpentan-3-yl)decane

Cycloalkane

Open-chain aliphatic hydrocarbons are called **acyclic**, and those containing a cyclic structure are **cyclic** hydrocarbons. The rules of the acyclic alkanes, but with the following change, name a cycloalkane.

1. A cycloalkane with no substituent on it has the same name as a straight-chain alkane containing the same number of C atoms, but with the prefix cyclo- attached.
2. A cycloalkane with one branch is named by listing the branch name before the parent cycloalkane name, without locant number or space.
 - According to the current IUPAC rules, cyclic structure is the parent name, even if the branch has more C atoms, except when there is a characteristic group or other factor that can change the preference. (Note: in earlier versions, between cyclic and acyclic, the one with more C atoms was the parent.)
3. A cycloalkane with two branches is named by listing the branch names in alphabetical order before the parent name, preceded by their locant numbers.
 - The branch alphabetically first receives locant #1, and the numbering proceeds clockwise or counterclockwise, whichever assigns a lower number to the second branch.
4. A cycloalkane with more than two branches is named by listing the branch names in alphabetical order before the parent name, preceded by their locant numbers, where the locant number #1 and the direction to proceed clockwise or counterclockwise is chosen such that the total of the set of locant numbers is the lowest possible.

The application of the above rules is explained with examples in Figure 2.3.6. The structure on the left in Figure 2.3.6 is three-C cycle named cyclopropane by rule#1. The next one has one methyl branch and is named methylcyclohexane by rule#2. The location number for one branch is not needed, as it is always #1. The next structure is named 1-ethyl-3-methylcyclopentane by rule#3; it has two branches, numbering begins from ethyl, which is alphabetically before methyl, and numbering continues counterclockwise to assign a lower number to the methyl branch. The next structure is named 2-ethyl-1,4-dimethylcyclohexane by rule#4: locant of methyl near ethyl is chosen #1 and continued counterclockwise to achieve the lowest total of the set of locant numbers ($1 + 2 + 4 = 7$). All other options will have a higher total set of locant numbers, e.g., 1-ethyl-2,5-dimethylcyclohexane ($1 + 2 + 5 = 8$) and 3-ethyl-1,4-dimethylcyclohexane ($3 + 1 + 4 = 8$). The structure on the right in Figure 2.3.6 is named (4-methylhexyl)cyclobutane by rule#4: cyclobutane is the parent instead of hexane because the cyclic structure has preference over acyclic if other factors are the same. The branch is complex, so it is named by rule#5 of branched alkane rules.

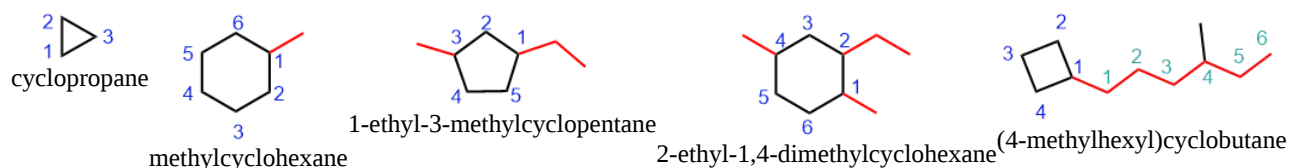


Figure 2.3.6: Examples of cycloalkane nomenclature. Numbers in blue show the parent chain numbering, and numbers in green show numbering in the branch. Explanation is in the text above. (Copyright; Public domain)

Bicycloalkane

Compounds containing more than one cyclic structure are called polycyclic. Nomenclature of bicycloalkanes, i.e., alkanes containing two cyclic structures, is described here. There are four major classes of bicycloalkanes, as shown in Figure 2.3.7. Isolated rings have no atoms in common. They are named by the rules of alkanes and cycloalkanes, by selecting a larger ring as the parent and the smaller a substituent. For example, the structure on the left in Figure 2.3.7 is cyclobutylcyclopentane.

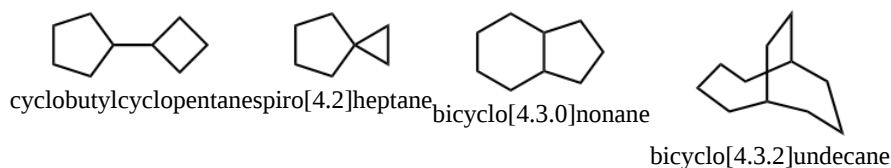
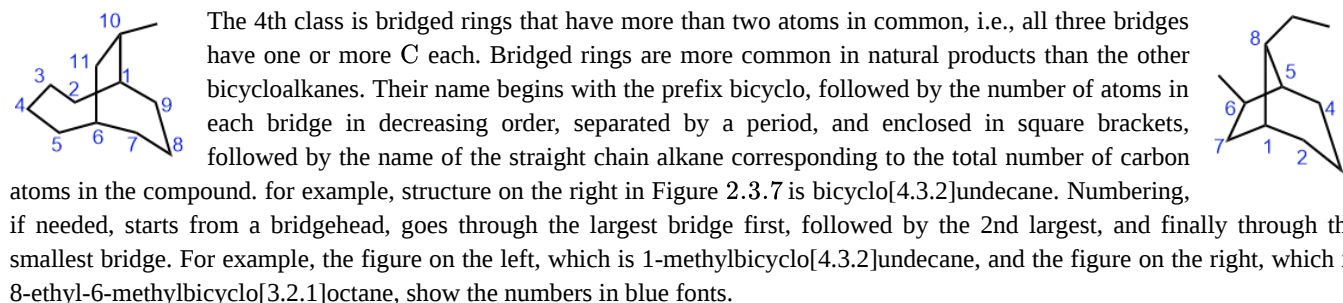


Figure 2.3.7: Paste Caption Here

The second class consists of spiro-rings that share one atom in common. The spiro-rings have two bridges comprising carbons that are not common between the rings. They are named by using the prefix spiro, followed by the number of atoms in each bridge in decreasing numeric order, separated by a period, and enclosed in square brackets, followed by the name of the straight chain alkane corresponding to the total number of carbon atoms in the compound. For example, the structure in Figure 2.3.7, 2nd from left, is spiro[2,4]heptane: 2,4 represents two carbons in the smaller and four in the larger bridge, and heptane because it has a total of seven C atoms. Note that the shared C is not counted in any bridge.

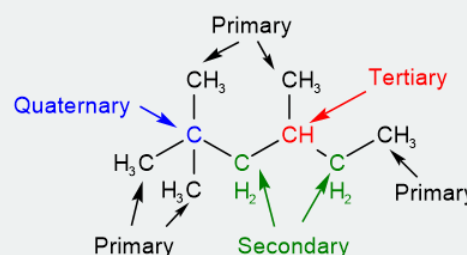
The 3rd major class is fused rings that have two atoms and one covalent bond in common. The common atoms connect the three bridges and are called bridgehead carbons. Their name begins with the prefix bicyclo, followed by the number of atoms in each bridge in decreasing order, separated by a period, and enclosed in square brackets, followed by the name of the straight chain alkane corresponding to the total number of carbon atoms in the compound. For example, the 3rd structure from left in Figure 2.3.7 is bicyclo[4.3.0]nonane. It has four carbons in the largest bridge, three in the second largest, and the middle bridge without any carbon is the smallest, which makes [4.3.0] part of the name, and there are a total of nine carbons, which is represented by nonane in the last part of the name. Note that the bridgehead carbons do not count in any bridge.



Primary, secondary, tertiary, and quaternary C and H

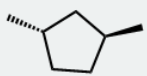
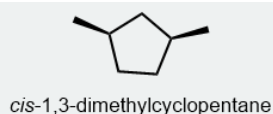
The designations primary, secondary, tertiary, and quaternary for carbons and for hydrogens on them are illustrated in the figure on the right, and described below.

- The terminal C, i.e., the C with only one single bond with another C is a **primary carbon**.
- The C with two single bonds to other C atoms is a **secondary carbon**.
- The C with three single bonds to other C atoms is a **tertiary carbon**.
- The C with four single bonds to other C atoms is a **quaternary carbon**.
- A H on a primary C is a primary hydrogen, a H on a secondary C is a secondary hydrogen, and a H on a tertiary C is a tertiary hydrogen. A quaternary C does not have any H on it.



Cis/trans isomerism in cycloalkane and alkene

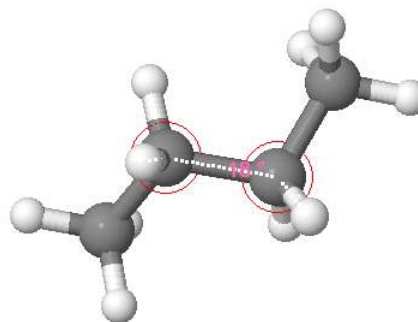
There is almost free rotation possible around a single bond, as shown for C^3-C^4 bond of butane in the figure on the right (prepared using <https://chemagic.org/molecules/amini.html>, Copyright: Public domain). However, the rotation around C—C bonds of a cycloalkane is restricted due to the carbon-bridge connecting the bonds. Rotation around a double bond ($\text{C}=\text{C}$) is also restricted because a π -bond weakens when the p -orbitals are not aligned and breaks completely when they are at a 90° angle from each other. Therefore, two groups on any two C atoms of a cycloalkane ring or on the two C atoms of a $\text{C}=\text{C}$ pointing in the same direction are called in a *cis*-relationship, and those pointing in the opposite direction are called in a *trans*-relationship. For example, *cis*-1,2-cyclopentane and *trans*-1,2-cyclopentane, shown in the figure on the right, are different



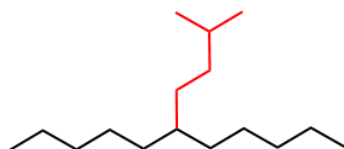
trans-1,3-dimethylcyclopentane Stereoisomers need stereodescriptors in their IUPAC nomenclature. The cis/trans were stereodescriptors before, but they have been replaced with new stereodescriptors in the current IUPAC nomenclature. Still, cis/trans terms are used to describe the orientation of two groups relative to each other. The stereodescriptors and the IUPAC nomenclature with the stereodescriptors will be described in the next chapter.

compounds having the same molecular formula, i.e., they are isomers. Such isomers, which have the same atom-connectivity but different orientations, are called stereoisomers.

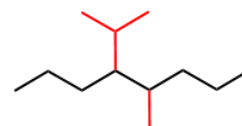
Click a bond to select it. After selection, Click-Drag on one of the circled atoms to rotate its branch.



Common branch names accepted in IUPAC nomenclature

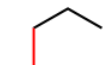


Some common names that are often used in literature are accepted in IUPAC nomenclature. They will be mentioned when used in this course. Some alkyl branch names accepted in IUPAC nomenclature are shown in Table 2.3.7. These branch names should be better committed to memory.



For example, 6-(3-methylbutyl)undecane and isopentylundecane are both IUPAC names of the same structure shown on the left, and 4-methyl-5-(propan-2-yl)octane and 4-isopropyl-5-methyloctane are both IUPAC names of the same structure shown on the right.

Table 2.3.7: Common names of some alkyl branches accepted in IUPAC names along with the corresponding systematic branch names.*

Structure:									
Common name:	Parent	Parent	Parent	Parent	Parent	Parent	Parent	Parent	Parent
Common name:		isopropyl		sec-butyl	isobutyl	tert-butyl		isopentyl	neopentyl
Systematic name:	propyl	(propan-2-yl)	butyl	(butan-2-yl)	(2-methylpropyl)	(1,1-dimethylethyl)	pentyl	(3-methylbutyl)	(2,2-dimethylpropyl)

* Iso- and neo- are merged with the name and counted in alphabetization, but sec- and ter- are italicized and not counted in alphabetization of the branch name. Either one can be used in an IUPAC name. (Copyright; Public domain)

This page titled 2.3: Organic nomenclature -alkanes is shared under a Public Domain license and was authored, remixed, and/or curated by Muhammad Arif Malik.

- 2.1: Hydrocarbons is licensed Public Domain.

2.4: Organic nomenclature -functional group containing compounds

Alkene

An alkene is named using the rules for the corresponding alkane, with the following modifications.

- Suffix -ane is replaced with -ene, preceded by the locant number of the C=C group.
 - If there are multiple C=C groups, use multiplier, diene, triene, etc., and insert the locant number of each double bond.
- Numbering of the parent chain begins from the end that assigns a lower number to the first C of the C=C group that becomes its locant, in preference over alkyl substituents.
 - If C=C group receives the same locant from either end, the preference goes to the first branch following the relevant rules for branched alkane.
- In a cycloalkene, the carbons in the C=C group are always #1 and #2, continuing clockwise or counterclockwise, whichever assigns a lower set of locant numbers to other C=C if there is any, and after it to the other substituents according to the rules for branched alkane and cycloalkane.
 - Locant number is not needed if there is one C=C in a cycloalkene, as it is always #.
- According to the new IUPAC rule, the parent chain is the longest chain, whether it contains C=C group in it or not.
 - If the C=C group is in a branch, the branch is named according to the rules for alkane branches, but with the -yl suffix of the branch replaced with -enyl suffix preceded by the locant number of the C=C group in the branch.

Table 2.4.1: Alkene IUPAC nomenclature rules explained with applied examples (Note: numbers in blue fonts are IUPAC numbering of the parent, not part of the structure)

Structure:						
IUPAC name:	but-1-ene	buta-1,3-diene	5,5-dimethylcyclohexa-1,3-diene	(4E)-3-methyloct-4-ene	cyclopentene	5-(prop-2-en-1-yl)nonane
Alkene rule#:	Rule#1 & #2	Rule#1, part 2**	Rule#2, part 2, and Rule#3**	Rule#2, part 2*	Rule#3, part 2	Rule#4

* (4E) is stereodescriptor for a *trans*- alkyl groups around C=C, at C4. The stereodescriptors are explained in the next chapter.

** last letter -a in the Greek multipliers buta, penta, hexa, etc. is elided when the next alphabet is a vowel, but in these examples it is retained as the next alphabet is not a vowel.

Alkyne

An alkyne, i.e., a hydrocarbon containing at least one C≡C, is named by the same rules as an alkene, but with the following changes.

- The suffix -ene is replaced with -yne.
 - When both C=C and C≡C groups are present, the suffix becomes en-yne, preceded by their corresponding locant.
- Both C=C and C≡C groups have equal priority in numbering the parent chain, except when there is a tie, preference goes to C=C.

Table 2.4.2: Alkyne IUPAC nomenclature rules explained with applied examples (Note: numbers in blue fonts are IUPAC numbering of the parent, not part of the structure)

Structure:	
------------	--

Structure:				
IUPAC name	5-methylhept-3-yne	3-methylhept-1-ene-4-yne	3,5-dimethylhex-4-ene-1-yne	pent-1-en-4-yne
Alkyne Rule#:	Rule#1	Rule#1, part 2	Rule#2	Rule#2

Aromatic hydrocarbons

Aromaticity is described in a separate chapter. Nomenclature of benzene and its derivatives -the most common class of aromatic compounds is described here.

1. A six-C cycle with alternate single and double bonds takes the parent name benzene.
2. A substituted benzene is named following the rules for a substituted cycloalkane with the parent name benzene.
3. Alternatives to using locant numbers: a 1,2-relationship can be replaced with "*ortho*" or "o", a 1,3-relationship with "*meta*" or "m-", and a 1,4-relationship with "*para*" or "p-".
4. Some groups, when they are the most senior among substituents on a benzene, take a combination of benzene and the functional group parent name; the benzene C bearing the group is #1 in numbering in this case.
5. Benzene ring as a substituent is named phenyl.

Table 2.4.3: Aromatic nomenclature rule#1 to #3 explained with applied examples. (Note: numbers in blue fonts are IUPAC numbering of the parent, not part of the structure)

Structure:					
IUPAC name	benzene	ethylbenzene	1,2-diethylbenzene or o-diethylbenzene	1,3-diethylbenzene or m-diethylbenzene	1,4-diethylbenzene or p-diethylbenzene
Aromatic rule#:	Rule#1	Rule#2	Rule#2 and Rule#3	Rule#2 and Rule#3	Rule#2 and Rule#3

Table 2.4.4: Aromatic nomenclature rule#4 and #5 explained with applied examples. (Note: numbers in blue fonts are IUPAC numbering of the parent, not part of the structure)*

Structure:						
IUPAC name	toluene	anisole	styrene	aniline	phenol	benzaldehyde
Structure:						

IUPAC name	benzoic acid	1,2-dimethylbenzene or o-xylene *	1,3-dimethylbenzene or m-xylene	1,4-dimethylbenzene or p-xylene	2-ethylphenol	2-phenylethan-1-amine **
------------	--------------	-----------------------------------	---------------------------------	---------------------------------	---------------	--------------------------

* Dimethylbenzene is also named xylene. ** This example is added for explaining rule#5, i.e., benzene ring as substituent is named phenyl, otherwise the nomenclature involving characteristic functional groups is described in the next section

Non-characteristic functional groups

In the structure of organic compounds, $-R$ is used to refer to the rest of the organic structure, or a H atom, or an alkyl branch. $-R$ is not a functional group, but it is a group in IUPAC nomenclature. A double bond $C=C$ and a triple bond $C \equiv C$ are functional groups that have preference over an alkyl group in parent chain numbering but no preference over any characteristic group. Benzene ring of an aromatic ring is represented as ϕ - or as $-C_6H_5$. An alkyl group as a parent chain, $C=C$, and $C \equiv C$ always take a primary suffix -an-, -en-, or -yn-, as shown in the Table. These suffixes end with the letter -e, i.e., -ane, -ene, or -yne, if there is no characteristic functional group in the compound. The benzene ring, as a branch, is designated by the prefix phenyl, and as the parent chain, it is named benzene. There are some other non-characteristic functional groups, e.g., alkyl halides $R-X$, nitro $-N^+ \equiv N-O^-$, also written in condensed form as $-NO_2$, azido $-N=N=N^+$, also written in condensed form as $-N_3$, etc., that take only

a prefix and are treated like alkyl branches without any preference, except for the alphabetical order among the substituents. Main non-characteristic groups are listed in Table 2.4.5 along with their suffix or prefix, and their use in nomenclature is explained with examples in 2.4.6.

Table 2.4.5: Some Non-characteristic groups in IUPAC nomenclature

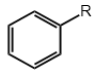
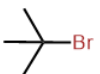
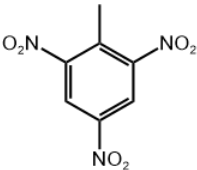
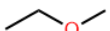
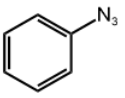
Structure:	$-R$	$>C=C<$	$-C \equiv C-$		$-F$	$-Cl$	$-Br$	$-I$	$-NO_2$	$-O-R$	$-N_3$
Suffix:	-an-	-en-	-yn-	-benzene	-	-	-	-	-	-	-
Prefix:	-	-	-	phenyl-	fluoro-	chloro-	bromo-	iodo-	nitro-	alkoxy-	azido-

Table 2.4.6: Nomenclature of some non-characteristic groups explained with applied examples

Structure:					
IUPAC Name	2-bromo-2-methylpropane	iodomethane	2,4,6-trinitrotoluene or 2-methyl-1,3,5-trinitrobenzene	methoxyethane	azidobenzene

Alkyl halide

Compounds containing an alkyl group bonded to a halogen, i.e., $R-X$, where X is F, Cl, Br, or I, are a class of organic compounds called alkyl halides. In substitutive IUPAC nomenclature, described above, the alkyl group is the parent and halide, i.e., fluoro, chloro, bromo, or iodo as a substituent, equal in priority to alkyl branches. The substitutive name is preferred, the IUPAC name, but they can also be named by functional class nomenclature, where alkyl groups are listed in alphabetical order, followed by the class name, separated by spaces. For example, CH_3-Br is named bromomethane in substitutive nomenclature and named methyl bromide in functional class nomenclature. Similarly, $(CH_3)_3-Br$ is 2-bromo-2-methylpropane in substitutive nomenclature, and it is tertiary butyl bromide in functional class nomenclature.

Ether

Compounds containing two alkyl groups bonded to oxygen, i.e., $R-O-R'$, are a class of organic compounds called ethers. In substitutive nomenclature, the longer alkyl group is the parent, and the shorter alkyl group plus oxygen is the alkoxy substituent. In

functional class nomenclature, the alkyl groups are listed in alphabetical order, followed by the class name ether, separated by spaces. For example, $\text{CH}_3\text{CH}_2\text{--O--CH}_3$ is named "methoxyethane" in substitutive nomenclature and named "ethyl methyl ether" in functional class nomenclature. Similarly, a common organic solvent $\text{CH}_3\text{CH}_2\text{--O--CH}_2\text{CH}_3$ is named ethoxyethane or diethyl ether.



Cyclic ethers have a C in the cyclic structure replaced with an O. Their nomenclature is not described here, but their name will be provided wherever needed. The structure shown on the left is tetrahydrofuran, a five-membered cyclic ether, which is a common organic solvent. The structure on the right is oxirane, also known as epoxyethane, a three-membered cyclic ether that is a reactive compound used as a reagent in organic synthesis.



Characteristic functional groups

Characteristic functional groups have a seniority order, as listed in Table 2.4.7 for the most common groups.

Table 2.4.7: Seniority order (highest at the top), of the most common characteristic functional groups: functional class names, Lewis structures, condensed formula, prefixes, and suffixes

Functional class	Lewis structure	Condensed formula*	Suffix	Prefix
Carboxylate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--C--O}^- \\ \text{O} \\ \parallel \\ \text{--(C)--O}^- \end{array}$	$\begin{array}{l} \text{--COO}^- \\ \text{--(C)OO}^- \end{array}$	carboxylate oate	carboxylato
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--C--OH} \\ \text{O} \\ \parallel \\ \text{--(C)--OH} \end{array}$	$\begin{array}{l} \text{--COOH} \\ \text{--(C)OOH} \end{array}$	carboxylic acid oic acid	carboxy
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--C--O--R} \\ \text{O} \\ \parallel \\ \text{--(C)--O--R} \end{array}$	$\begin{array}{l} \text{--COOR} \\ \text{--(C)OOR} \end{array}$	Alkyl carboxylate** Alkyl oate**	alkoxycarbonyl
Acid halide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--C--X} \\ \text{O} \\ \parallel \\ \text{--(C)--X} \end{array}$	$\begin{array}{l} \text{--COX} \\ \text{--(C)OX} \end{array}$	carbonyl halide oyl halide	halocarbonyl
Amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--C--NRR}' \\ \text{O} \\ \parallel \\ \text{--(C)--NRR}' \end{array}$	$\begin{array}{l} \text{--CONRR}' \\ \text{--(C)ONRR}' \end{array}$	carboxamide amide	carbamoyl or amino-oxo
Nitrile	$\begin{array}{l} \text{--C} \equiv \text{N} \\ \text{--(C)} \equiv \text{N} \end{array}$	$\begin{array}{l} \text{--CN} \\ \text{--(C)N} \end{array}$	carbonitrile nitrile	cyano
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--C--H} \\ \text{O} \\ \parallel \\ \text{--(C)--H} \end{array}$	$\begin{array}{l} \text{--CHO} \\ \text{--(C)HO} \end{array}$	Carbaldehyde al	formyl oxo
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R--C--R}' \end{array}$	>C=O	one	oxo
Alcohol	--OH	-	ol	hydroxy

Thiol	—SH	-	thiol	sulfanyl***
Amine	—NRR'	-	amine	amino
Imine	$\begin{array}{c} \text{NR} \\ \\ \text{R}' - \text{C} - \text{R}'' \end{array}$		imine	imino

* (C) means the carbon is counted in the parent chain, and C means it is part of the functional group, but not counted in the parent chain.

** R is an alkyl group expressed as a separate prefix, but in the cases of amides, amines, and imines, it may be alkyl that is expressed as prefix N-alkyl or it may be H which is not expressed separate.

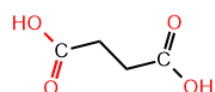
*** The suffix "mercepto" was used in early nomenclature, which is replaced with sulfanyl in the current version of IUPAC nomenclature.

📌 Naming a compound containing a characteristic functional group

A compound containing one or more characteristic functional groups is named by the IUPAC rules described before for hydrocarbons, but with the following changes.

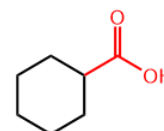
1. The parent chain is the longest chain containing the most senior functional group, even if it is not the longest chain without it.
2. The parent chain is numbered from a direction that assigns the lowest possible number to the most senior group, in preference to other substituents.
3. The last letter 'e' of the primary suffixes ane, ene, or yne is replaced with the suffix of the most senior group, preceded by its locant, and other groups are listed as prefixes in alphabetic order, preceded by their locant number.
 - When there is an alkyl group on N in addition to the parent chain, its locant is N, i.e., it is listed as N-alkyl.

For example, the structure on the right is named N-methyl-3-propylhept-6-en-2-amine, where amine is the parent functional group. The parent is the longest chain containing an amine; it is heptane, not octane (Rule #1). The parent chain is numbered from left to right to assign a lower number to the amine in preference to the other side that would have assigned #1 to the C=C group (Rule#2). The last letter "e" is replaced with "amine", preceded by its locant number (Rule #3). Methyl group on N is listed as N-methyl (Rule#3).



Depending on the arrangement of a C-containing functional group on the parent chain, the C of the functional group may be numbered as a part of the parent chain, or it may be a separate attachment. For example, the structure on the left is butanedioic acid in which C of the functional group

is part of the parent chain. In contrast, the structure on the right is cyclohexanecarboxylic acid, in which the (C) of the functional group is not a part of the parent chain. Note that in both cases, the locant number is not written in the name as it is understood. Also note that the last "e" of -ane is not dropped when the following letter is not a vowel, as in cyclohexanecarboxylic acid. Further examples are in the following sections.

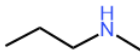
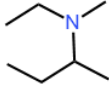
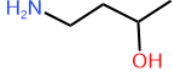


Amine

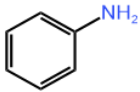
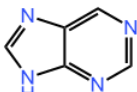
A N single bonded to one or more hydrocarbons is a class of organic compound called an amine. A N single bonded to one alkyl group $\text{R}-\text{NH}_2$ is a primary amine, single bonded to two alkyl groups $\text{R}-\underset{\text{H}}{\text{N}}-\text{R}'$ is a secondary amine and single bonded to three alkyl groups is $\text{R}'-\underset{\text{R}}{\text{N}}-\text{R}''$ is a tertiary amine. The following rules name amines.

1. A primary amine is named as alkanamine.
2. A secondary amine is named as N-alkylalkanamine, where the longer chain alkyl is the parent and the smaller in the N-alkyl substituent.
3. A tertiary amine is named as N-alkyl-N-alkylamine, where the longest chain alkyl is the parent and the smaller ones are listed as N-alkyl substituents in alphabetical order.
4. When a senior group is present, the amine group takes the suffix "-amino".

The following examples illustrate the above rules with practical applications.

Structure:					
Preferred IUPAC name:	propan-2-amine	N-methylpropan-1-amine	N-ethyl-N-methylbutan-2-amine	N,N-dimethylmethanamine	4-amino-butan-2-ol
Amine rule:	Rule#1	Rule#2	Rule#3	Rule#3	Rule#4

Among the important aromatic amines: an amine group on a benzene takes the parent name aniline, a benzene ring with one C replaced with N is pyridine, illustrated below along with purine and pyrimidine structures that are found in nucleic acid.

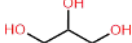
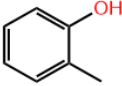
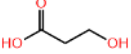
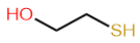
			
aniline	pyridine	purine	pyrimidine

Alcohol and thiol

—OH is an alcohol group. The class of organic compounds that contains an alcohol group is called alcohol. An alcohol is designated primary, secondary, or tertiary depending on whether it is on a primary, secondary, or tertiary C.

1. An alcohol —OH is a characteristic group in IUPAC nomenclature, taking the suffix -ol if it is a senior or the prefix hydroxy if there is another more senior group present.
2. An alcohol group on a benzene ring together takes the parent name phenol, provided there is no other more senior group present.
3. —SH is the sulphur analogue of alcohol, called thiol, that takes the suffix -thiol in IUPAC nomenclature or, when there is a more senior group present, it takes the prefix sulfanyl-.

An alcohol is designated primary, secondary, or tertiary depending on whether it is on a primary, secondary, or tertiary C. Alcohol also has functional class names, which are usually alkyl alcohol. The following examples explain the IUPAC naming of alcohols and thiols with applied examples.

Structure:								
IUPAC name:	ethanol	propan-2-ol	2-methyl-2-propanol	propan-1,2,3-triol	2-methylphenol	3-hydroxypropanoic acid	ethanthiol	2-sulfanylethanol-1-ol
Functional class name;	ethyl alcohol	isopropyl alcohol	tert-butyl alcohol	Common name: Glycerol	-	-	-	-
Comment	a primary alcohol	a secondary alcohol	a tertiary alcohol	use of a multiplier	aromatic alcohol	alcohol as not a senior group	-	—SH as not a senior group

Aldehyde, ketone, and imine

A $>\text{C}=\text{O}$ is a carbonyl group. It has several subgroups, which differ in the two groups attached to the carbonyl C. For example,

when one of the group attached to the carbonyl C is H it is an aldehyde $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—H}$, which is usually written in abbreviated form as

—CHO . When both groups attached to the carbonyl C are alkyl groups, it is a $\text{R—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—R'}$. When O of an aldehyde or a ketone is

replaced with N it is an imine $\text{R'—}\overset{\text{NR}}{\underset{\text{||}}{\text{C}}}\text{—R''}$, where R could be an alkyl or a H. The class of organic compound containing aldehyde, ketone, or imine groups are called aldehydes, ketones, and imines, respectively.

- When carbonyl C of an aldehyde is counted in the parent, numbering begins from the carbonyl C and it takes the suffix -al when it is senior or the prefix oxo- when it is not a senior group.
 - When carbonyl C of an aldehyde is not counted in the parent, numbering begins from the carbonyl C and it takes the suffix -carbaldehyde when it is senior or prefix formyl- when it is not a senior group. Single aldehyde does not need locant as it is always #1.
 - An aldehyde and benzene ring together take the parent name benzaldehyde, with the numbering of the benzene ring beginning from the point of attachment of the aldehyde group.
 - When an aldehyde on a benzene ring is not the senior group, it takes the prefix -carbaldehyde.
- A ketone takes the suffix -one (pronounced as own) when it is senior, and the numbering begins from the end that assigns it a lower locant. Alternatively, it takes the prefix oxo- when it is not a senior group.
 - Although not preferred, ketones can be named by functional class nomenclature, listing alkyl groups in alphabetical order, followed by the word 'ketone', separated by spaces.
- An imine takes the suffix -imine when it is senior or the prefix imino- when it is not a senior group and follows the parent chain numbering convention of the corresponding aldehyde or ketone.

The following examples illustrate the above rules with practical applications.

Structure:					
IUPAC name:	methanal or formaldehyde	ethanal or acetaldehyde	cyclohexanecarbaldehyde	3-formylcyclohexanecarboxylic acid	3-oxopropanoic acid
Comment:	2nd Name is also accepted.	2nd Name is also accepted	Carbonyl C is not counted in the parent chain.	Aldehyde is not senior, and the carbonyl C is not counted in the parent chain.	Aldehyde is not senior, and the carbonyl C is counted in the parent chain.
Structure:					
IUPAC name:	propan-2-one or acetone	pent-4-en-2-one	3-oxobutanal	3-chlorobenzaldehyde	N-methylpentan-3-imine
Comment:	2nd name is also accepted	Ketone is a senior group	Aldehyde is a senior group	Aldehyde is a senior group on the benzene ring	imine nomenclature

Carboxylic acids and their derivatives

A **carboxylic acid** group has a carbonyl $\text{C}=\text{O}$ and an alcohol $-\text{OH}$ groups together, i.e., $-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$. There are several related groups, called carboxylic acid derivatives, which differ in the $-\text{OH}$ part of the $-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$. For example,

1. **carboxylate anion** $-\overset{\text{O}}{\parallel}\text{C}-\text{O}^-$ has H of the $-\text{OH}$ is removed as a proton leaving the bonding electrons on O,
- 2.
3. **ester** $-\overset{\text{O}}{\parallel}\text{C}-\text{OR}$ has H of the $-\text{OH}$ group replaced with an alkyl R group,
4. **amide** $-\overset{\text{O}}{\parallel}\text{C}-\text{NRR}'$ has H of the $-\text{OH}$ group replaced with an amine $-\text{NRR}'$ group,
5. **acid halide** $-\overset{\text{O}}{\parallel}\text{C}-\text{X}$ has the $-\text{OH}$ replaced with a halide (fluoride $-\text{F}$, chloride $-\text{Cl}$, bromide $-\text{Br}$, or iodide $-\text{I}$) group.
6. **Nitrile** $-\text{C}\equiv\text{N}$ has both O atoms of a carboxylic acid group $-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ replaced with N

Carboxylic acids and their derivatives are named by following the rules described so far, but with the following changes.

1. When the carbonyl-C is counted in the parent chain and the group is the senior, numbering begins from the carbonyl-C and: carboxylic acid $-\text{COOH}$ takes suffix -oic acid; carboxylate anion $-\text{COO}^-$ takes suffix -oate; ester $-\text{COOR}$ takes prefix + suffix alkyl-....oate; acid halide $-\text{COX}$ takes suffix -oyl halide; amide $-\text{CONRR}'$ takes prefix + suffix N-alkyl-N-alkyl....amide; and nitrile $-\text{CN}$ takes suffix -nitrile.
 - When these groups are not the most senior, carboxylic acid $-\text{COOH}$ takes prefix carboxy-; carboxylate anion $-\text{COO}^-$ takes prefix carboxylato; ester $-\text{COOR}$ takes alkoxycarbonyl-; acid halide $-\text{COX}$ takes halocarbonyl-; amide $-\text{CONRR}'$ takes carbamoyl or amino-oxo-; and nitrile $-\text{CN}$ takes prefix cyano-.
2. When the carbonyl-C is not counted in the parent chain and the group is the senior, numbering is done to assign lowest number to them and carboxylic acid $-\text{COOH}$ takes suffix -carboxylic acid; carboxylate anion $-\text{COO}^-$ takes suffix --carboxylate; ester $-\text{COOR}$ takes prefix + suffix alkyl-....carboxylate; acid halide $-\text{COX}$ takes suffix -carbonyl halide; amide $-\text{CONRR}'$ takes prefix + suffix N-alkyl-N-alkyl....carboxamide; and nitrile $-\text{CN}$ takes suffix -carbonitrile.
 - When these groups are not the most senior, their prefixes are the same as those in Rule #1, Part 2.

The following examples illustrate the above rules with practical applications.

Examples of the use of Rule#1 carboxylic acids and derivatives, suffixes

Structure:						
IUPAC name:	propanoic acid	sodium propanoate	methyl propanoate	propanoyl chloride	N-methylpropanamide	propanenitrile
Comment:	a carboxylic acid	a carboxylate anion	an ester	an acid halide	an amide	a nitrile

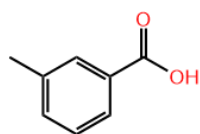
Examples of use of rule#1, part 2 of carboxylic acids and derivatives, prefixes

--	--	--	--	--	--	--

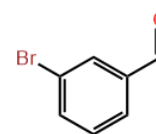
Structure:					
IUPAC name:	2-amino-3-carboxypropanoate	4-methoxy-4-oxobutanoic acid	4-chloro-4-oxobutanoic acid	4-amino-4-oxobutanoic acid	3-cyanopropanoic acid
Comment:	prefix carboxy- for -COOH	prefix alkoxycarbonyl for -COOR	prefix halocarbonyl for -COX	prefix amino-oxo for -CONRR'	prefix cyano- for -CN

Examples of use of rule#2 of carboxylic acids and derivatives, suffixes

Structure:						
IUPAC name:	cyclohexanecarboxylic acid	potassium cyclohexanecarboxylate	methyl cyclohexanecarboxylate	cyclohexanecarbonyl chloride	N-methylcyclohexanecarboxamide	cyclohexanecarbonitrile
Comment:	a carboxylic acid	a carboxylate anion	an ester	an acid halide	an amide	a nitrile



A carboxylic acid on a benzene ring is collectively referred to as benzoic acid, e.g., the structure on the left is 3-methylbenzoic acid. An aldehyde on a benzene ring is collectively referred to as benzaldehyde; for example, the structure on the right is 3-bromobenzaldehyde.



Methanoic acid $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ and ethanoic acid $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ have trivial names formic acid and acetic acid, respectively, which are accepted as alternate IUPAC names for these compounds.

2.4: Organic nomenclature -functional group containing compounds is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3: Stereochemistry

- 3.1: Introduction to stereochemistry
- 3.2: Conformational analyses
- 3.3: Conformational analysis of cyclohexanes
- 3.4: Configurational stereoisomerism
- 3.5: Assigning R/S stereodescriptors to chirally center
- 3.6: Optical activity
- 3.7: Types of chiral molecules
- 3.8: Chirality related topics

3: Stereochemistry is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

3.1: Introduction to stereochemistry

Introduction to stereochemistry

Stereochemistry is the study of the three-dimensional arrangement of atoms in molecules and their effects on the physical and chemical properties.

A major area of stereochemistry is the study of isomers.

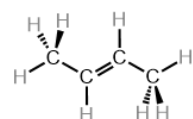
Isomers

Isomers are species that have the same molecular formula, but the atoms in them are arranged differently in space.

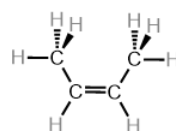
Two major classes of isomers are **constitutional isomers**, in which the atoms are connected differently, and **stereoisomers**, in

which the connectivity of the atoms is the same, but they are oriented differently in space. For example, ethanol $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$

and diethyl ether $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\ddot{\text{O}}-\text{C}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ are constitutional isomers because they have the same formula $\text{C}_2\text{H}_6\text{O}$ but their atoms are



connected differently. On the other hand, the structures shown on the left and right margins are stereoisomers because they have the same molecular formula (C_4H_8), the same atom connectivity, but the atoms are oriented differently in space.



Both constitutional isomers and stereoisomers have subclasses that are illustrated in Figure 3.1.1 and described in the following sections.

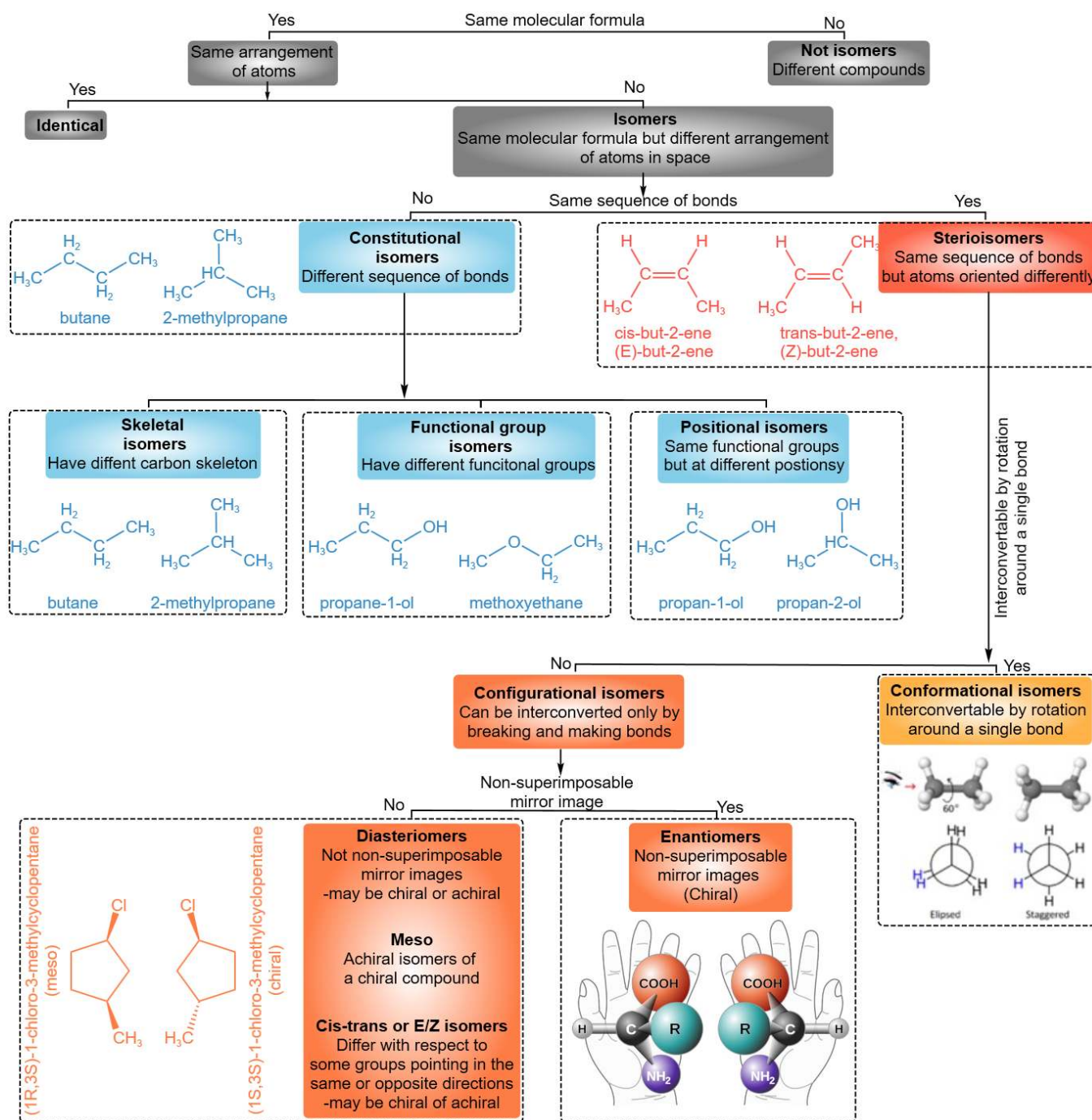


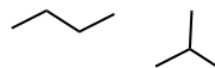
Figure 3.1.1: Classification of isomers. (Copyright; Public domain)

Constitutional isomers

Constitutional isomers, i.e., the isomers in which atoms are connected differently, have three major subclasses: skeletal isomers, functional group isomers, and positional isomers. These are described below.

Skeletal isomers

Skeletal isomers, also called chain isomers, are constitutional isomers that differ primarily in the carbon backbone or the skeleton. Up to three C atoms can be connected to give one alkane, methane, ethane, and propane, respectively, but four C's can be arranged in two different ways with single bonds to yield butane or 2-methylpropane, as shown in the structures on the right margin. The number of possible ways of arranging C's in the backbone of



alkanes increases exponentially as the number of C atoms increases, as shown in Table 3.1.1. For example, six C's can be arranged in five ways to yield five alkane isomers, as shown in Figure 3.1.2.

Table 3.1.1: Number of skeletal isomers of some alkanes

Alkane:	Propane	Butane	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Pentadecane	Eicosane	pentacosane
Molecular formula:	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{15}H_{32}$	$C_{20}H_{42}$	$C_{25}H_{52}$
Number of constitutional isomers:	1	2	3	5	9	18	35	75	4,347	366,319	36,797,588

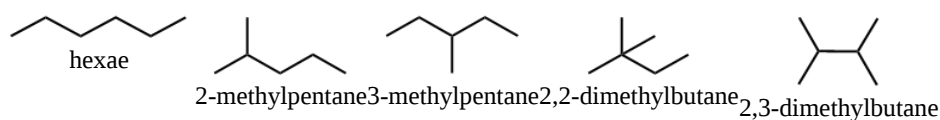


Figure 3.1.2: Constitutional isomers of alkanes of formula C_6H_{14} . (Copyright; Public domain)

Functional group isomers

Functional group isomers are constitutional isomers that differ in their functional groups. For example, propanal $H-C(H)-C(H)-C(=O)H$ having an aldehyde $R-C(=O)H$ functional group is a functional group isomer of propanone $H-C(H)-C(=O)-C(H)-H$ that has a ketone $R-C(=O)-R'$ functional group. Another example is ethanol $H-C(H)-C(H)-O-H$ that has an alcohol $-OH$ functional group is a

functional group isomer of diethyl ether $H-C(H)-O-C(H)-H$ that has an ether $R-O-R'$ functional group.

functional group isomer of diethyl ether $H-C(H)-O-C(H)-H$ that has an ether $R-O-R'$ functional group.

Positional isomers

Positional isomers are constitutional isomers that differ in the position of a functional group or a substituent within the skeleton of the compound. For example, Figure 3.1.3 shows four positional isomers of compounds having formula $C_5H_{12}O$ that differ in the position of the alcohol $-OH$ group on the skeleton of the compound.

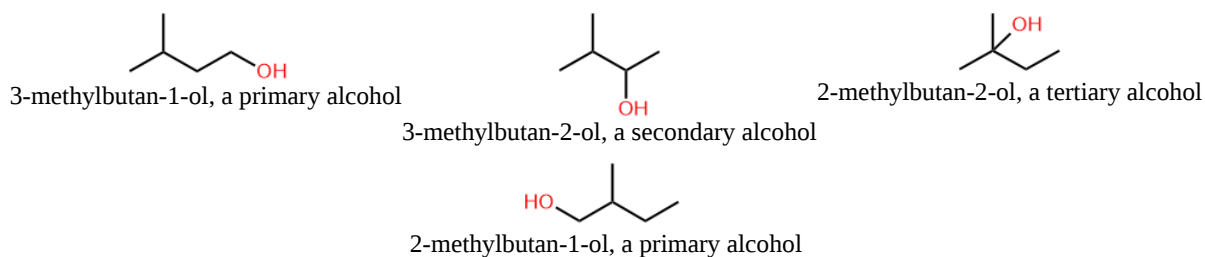


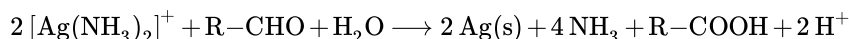
Figure 3.1.3: Four positional isomers of compounds having formula $C_5H_{12}O$, differing the position of alcohol group on the skeleton of the compounds. (Copyright: Public domain)

Comparing the properties of constitutional isomers

Constitutional isomers are different compounds with different physical and chemical properties.

For example, melting point (mp) and boiling point (bp) of propanal ($\text{CH}_3\text{--CH}_2\text{--}\overset{\text{O}}{\parallel}\text{C--H}$, mp $-81\text{ }^\circ\text{C}$, bp $48\text{ }^\circ\text{C}$) are significantly different from its functional group isomer propanone ($\text{CH}_3\text{--}\overset{\text{O}}{\parallel}\text{C--CH}_3$, mp $-95\text{ }^\circ\text{C}$, bp $56\text{ }^\circ\text{C}$).

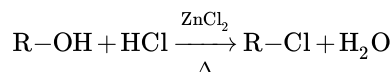
Both aldehydes and ketones have a set of common chemical reactions due to common carbonyl $\text{--}\overset{\text{O}}{\parallel}\text{C--}$ group in them, but H on the carbonyl C of an aldehyde $\text{R--}\overset{\text{O}}{\parallel}\text{C--H}$ makes it a different functional group with a different set of chemical reactions than ketones $\text{R--}\overset{\text{O}}{\parallel}\text{C--R'}$. For example, aldehydes R--COH are oxidized into carboxylic acids R--COOH by several oxidizing agent, while ketones $\text{R--}\overset{\text{O}}{\parallel}\text{C--R'}$ usually do not. This property is used in the silver mirror test to distinguish between aldehydes and ketones. In the silver mirror test, Tollens' reagent $\text{Ag}(\text{NH}_3)_2\text{OH}$ is added to an aldehyde or a ketone in a test tube. The reagent oxidizes aldehydes at the cost of reducing silver ion Ag^+ into solid silver Ag that deposits on the inner walls of the test tube as a silver mirror, by the following general reaction.



The silver mirror test will be positive for propanal because it is an aldehyde, as illustrated in the test tube on the left side in the figure on the right margin (Copyright; FK1954, Public domain, via Wikimedia Commons). However, it will be negative for its functional group isomer, propanone, because the latter is a ketone, as illustrated in the test tube on the right side in the figure on the right margin.



The difference in physical and chemical properties is not limited to functional group isomers; it applies to all constitutive isomers. Functional groups have a characteristic set of chemical properties, but they are typically affected, usually in a predictable manner, by the environment surrounding the group. For example, alcohol group --OH can be substituted by chloride --Cl , but under different conditions for primary, secondary, and tertiary alcohols. This reaction can be monitored without any instrument for small alcohols R--OH that are soluble in water, because the product alkyl halide R--Cl is water insoluble, making the solution turbid. Lucas test uses the reagent ZnCl_2 in concentrated HCl , to distinguish between primary, secondary, and tertiary alcohols, based on the following reaction.



The solution in the Lucas test becomes turbid almost immediately for tertiary alcohols, becomes turbid after about five minutes for secondary alcohols, and stays clear for primary alcohols, except when heated. The figure on the left margin illustrates a Lucas test negative in the test tube on the left and positive, making the solution turbid in the test tube on the right (Copyright: Talos & Andel, CC BY-SA 3.0, via Wikimedia Commons). Table 3.1.4 compares some physical and chemical properties of alcohol positional isomers having formula $\text{C}_5\text{H}_{12}\text{O}$.

Table 3.1.4: Comparison of some physical and chemical properties of positional isomer alcohols having formula $\text{C}_5\text{H}_{12}\text{O}$

Structure:				
IUPAC name:	3-methylbutan-1-ol	3-methylbutan-2-ol	2-methylbutan-2-ol	2-methylbutan-1-ol

Classification (primary, secondary, or tertiary)	primary	secondary	tertiary	primary
Physical properties (mp, bp):	mp 117 °C, bp 131.1 °C	mp 117 °C, bp 131.1 °C	mp 117 °C, bp 131.1 °C	mp 117 °C, bp 131.1 °C
Chemical property (Lucas test):	Will not respond without heating	Positive test in about five minutes	Positive test almost immediately	Will not respond without heating

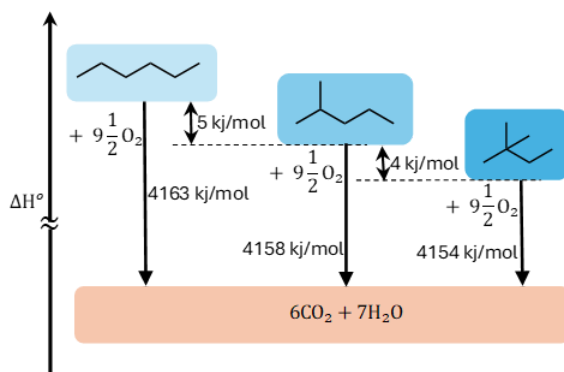
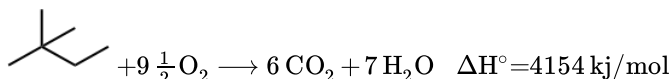
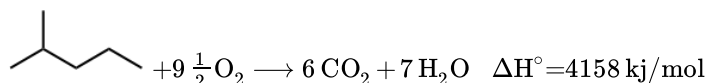
The difference in chemical properties is not limited to isomers of functional group-containing compounds, but it applies to almost all constitutional isomers. For example, skeletal isomers of alkanes that lack functional groups, but still exhibit distinct physical and chemical properties. Alkanes are relatively inert in chemical reactions due to the absence of functional groups; however, they do undergo some chemical reactions. They are found in petroleum and their primary use is as fuels, i.e., combustion.

Octane rating is a measure of the performance of gasoline in an internal combustion engine -the higher the number, the better the fuel burns. The structure shown on the left margin is 2,2,4-Trimethylpentane (mp -107.4 °C, bp 99.3 °C) that has an octane number of 100, while its skeletal isomer, octane (mp -57.4 °C, bp 125.6 °C, shown on the right margin), has an octane number of -15. This data shows a significant difference in both physical and chemical properties of these skeletal isomers of alkanes.

The combustion reaction of hexane is shown below, where ΔH° is the change in enthalpy (heat released) when 1 mol of hexane is completely burned in oxygen.



When the same reaction is repeated with its branched isomer 2-methylpentane, the ΔH° is 5 kJ/mol less, and with more branched isomer 2,2-dimethylbutane, the ΔH° is 9 kJ/mol less, as shown in the reaction equations below.

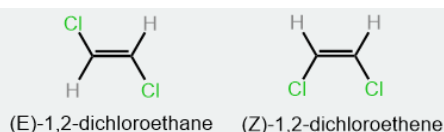


Since the products in the three cases are exact same, the differences in ΔH° allows estimating relative stability of the isomers, i.e., 2-methylpentane is five kJ/mol more stable than hexane and 2,2-dimethylbutane is nine kJ/mol more stable than hexane. In general, the more branched isomers of alkane are more stable, as illustrated in the figure on the right margin (Copyright; public domain).

The purpose of the above discussion is to highlight the importance of understanding the structural features of organic compounds being described in these early chapters. It will help in understanding the characteristic reactions of functional groups and how they are affected predictably by their environment and by the stability of the species involved.

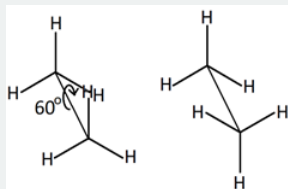
Stereoisomers

Stereoisomers are the isomers that have the same sequence of bonds, but the atoms or groups of atoms are oriented differently in space.

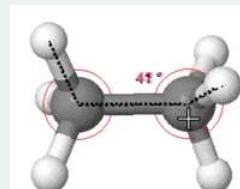


For example, the two structures of 1,2-dichloroethene shown on the right margin are stereoisomers differing in the orientation of -H and -Cl substituents around the C=C bond. The (E) and (Z) in the names are stereodescriptors that will be explained in a later section. There are two major classes of stereoisomers: conformational isomers and configurational isomers, which are briefly described next and further detailed later.

Conformational isomers



Conformations are different structures of the same molecule that result from rotation around single bonds.

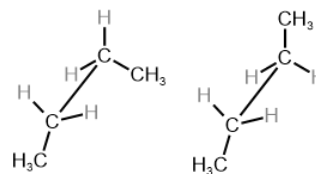


For example, the two structures shown on the left margin (copyright: public domain) are conformations of ethane $\text{CH}_3\text{—CH}_3$ in which three H atoms on one C are oriented differently relative to three H atoms on the other C. It is a result of 60° rotation around C—C bond. Figure on the right margin (prepared by using [Chemagic](#), copyright: public domain) demonstrates rotation around C—C bond of ethane.

All conformers of the same compound are not equal in energy, and there are energy barriers for interconversion; however, the energy barriers are usually low, allowing the conformations to interconvert rapidly at room temperature.

Different conformations that exist at distinct potential energy minima are called **conformational isomers** or **conformers**.

For example, the two conformations of butane shown on the right margin are conformational isomers because they exist at distinct potential energy minima. The two structures of ethane shown before are not conformational isomers, because ethane has only one potential energy minimum; the other structure exists at the energy maximum. The study of the energetics of bond rotations, resulting in the formation of conformers, is referred to as **conformational analysis**. Conformational analysis helps to understand the mechanisms, outcomes, and rates of certain reactions, as well as to assess the medical effects of drugs.



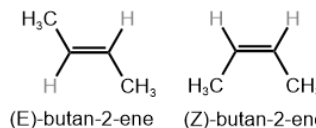
Note

The term "conformational isomer" is introduced here, without a full explanation, to complete the listing of isomer types. However, it will be explained in a later section during the description of the conformational analysis of ethane, butane, and cycloalkanes.

Configurational isomers

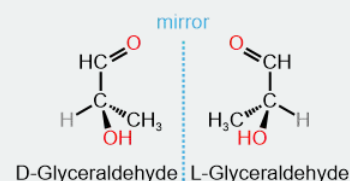
Configurational isomers are stereoisomers that can be interconnected only by breaking and making some bonds.

For example, (E)-butan-2-ene and (Z)-butane-2-ene, shown on the right margin, are configurational isomers of butan-2-ene in which —H and —CH_3 substituents are oriented differently. The (E) and (Z) are stereodescriptors that are described later. Unlike conformational isomers, which are different structures of the same molecule that exist in equilibrium with each other, configurational isomers are different compounds that can be separated. The specific arrangement of atoms in each configurational isomer is called its **configuration**. The configuration is defined by stereodescriptors in UPAC nomenclature, which is described later.



There are two major classes of configurational isomers: enantiomers and diastereomers.

Enantiomers are stereoisomers that are related as nonsuperimposable mirror images of each other.



For example, D-glyceraldehyde and L-glyceraldehyde, shown on the right margin, are enantiomers because they are stereoisomers that are nonsuperimposable mirror images of each other. D and L in the names of glyceraldehyde are stereodescriptors that are described later.

Diastereomers are stereoisomers that are not enantiomers.

For example, (E)-butan-2-ene and (Z)-butan-2-ene, shown above, are not enantiomers; i.e., they are not nonsuperimposable mirror images of each other. In other words, stereoisomers are either enantiomers when they are related as nonsuperimposable mirror images of each other, or they are diastereomers when they are not nonsuperimposable images of each other. Every molecule has its mirror image, but when the molecule and its mirror image are superimposable on each other, they are called identical, i.e., they are the same compound, just rotated by 180° . The following section provides a detailed explanation of configurational isomers.

This page titled [3.1: Introduction to stereochemistry](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [3.1: Introduction to stereochemistry](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

3.2: Conformational analyses

Sawhorse projection and Newman projection

Multiple ways have been developed to represent organic molecules, as illustrated in Figure 3.2.1. Each of these helps visualize the molecule and explain certain aspects of its properties. Lewis structures, zig-zag projections or perspective drawings, and skeletal structures were described in the previous chapters. Sawhorse projection and Newman projection are described here. These, particularly the Newman projection, are helpful in the study of conformational analysis.

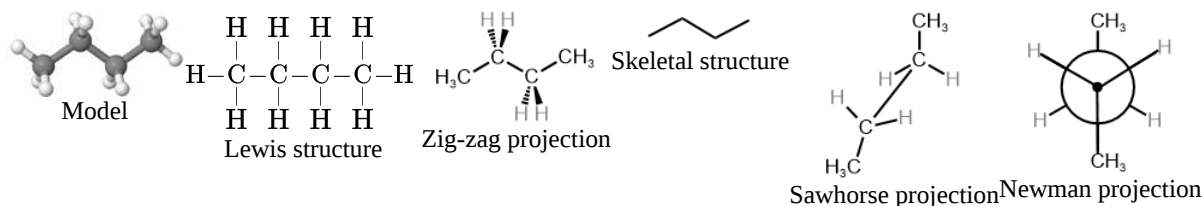


Figure 3.2.1: Representation of butane molecule in multiple ways, from left: model, zig-zag projection, skeletal structure, sawhorse projection along C2 to C3, and Newman projection through C2 to C3. (Copyright; Public domain).

📌 Sawhorse projection

Sawhorse projection is a drawing of a molecule along a C—C bond drawn as a diagonal line, where the left-hand bottom end is the carbon near the viewer and the right-hand top end is the carbon that is further away, as illustrated in Figure 3.2.1.

📌 Newman projection

The Newman projection is drawn as a view through a C—C bond perpendicular to the paper, with the bonds from it to other groups as projections in the plane of the paper. The C near the observer is shown as a dot and three groups projecting from it like in a trigonal planar geometry, while the rear C is represented as a circle with bonds from it to other groups drawn as if projecting from behind the circle, as illustrated in Figure 3.2.1.

✏️ Dihedral angle or torsion angle

Dihedral angle or **torsion angle** α is the clockwise angle between half-planes through two sets of three atoms, e.g., the half-planes defined by R—C—C and R'—C—C in Figure 3.2.2, having two atoms (C—C in this case) in common.

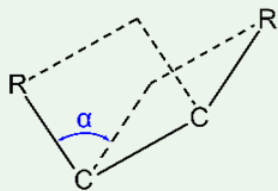
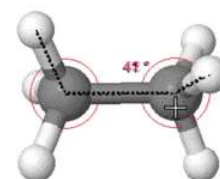


Figure 3.2.2: Dihedral angle α between the half-planes defined by R—C—C and R'—C—C in a hydrocarbon RCH_2CH_2R' molecule (Copyright; Д.Ильин: vectorization, Public domain via Wikimedia commons)

For example, the dihedral angle between $-CH_3$ on the front C and $-CH_3$ on the rear C is 180° ; and $-CH_3$ on the front C and any of the $-H$ on the rear C 60° . Rotation around a single bond results in different conformations, as illustrated for ethane CH_3-CH_3 on the right margin. These conformations are easier to view using Newman projections. Particularly, converting one conformation to another is easier to draw by keeping the front C fixed and rotating the rear C in a Newman projection, i.e., by rotating the wheel.



Conformational analysis of ethane

Rotation occurs around C—C bond in ethane, resulting in various conformations, as shown by simulation in the right margin above. However, the rotation is not entirely free; three energy barriers limit its movement. Therefore, as the dihedral angle

gradually changes from 0° to 360° , the relative potential energy of the molecule goes through local minima to local maxima, often at intervals of 60° .

The conformation of ethane in which a H on the front C in a Newman projection is at a dihedral angle of 0° from the nearest H on the rear C is called eclipsed. The one in which they are at 60° is called a staggered, as illustrated in the figure on the right margin.

The eclipsed conformation of ethane corresponds to the energy maximum. As the dihedral angle gradually increases from 0° , the energy gradually decreases, reaching a minimum at 60° , followed by a gradual increase reaching a maximum again at 120° . This cycle repeats, resulting in a sinusoidal curve of potential energy versus dihedral angle, as shown in Figure 3.2.3.

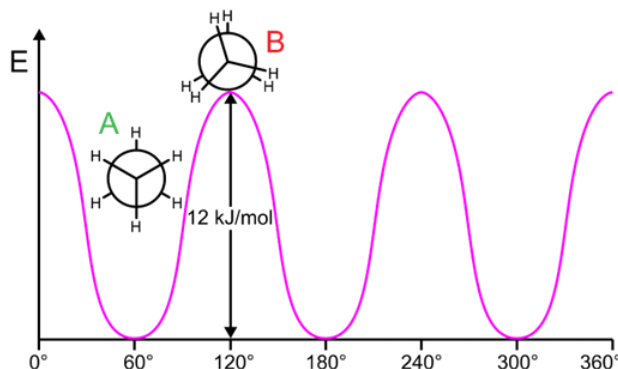
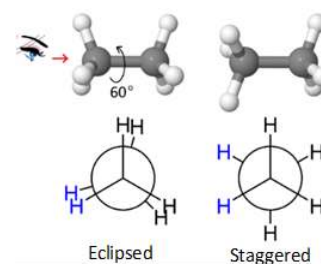


Figure 3.2.3: Newman projections of ethane conformations for rotation around C-C bond & their relative energy differences (not total energies) vs. torsional/dihedral angle curve, where the conformation A is staggered, and B is eclipsed. (Copyright; Keministi, Public domain via Wikimedia COMMONS)

The energy difference between the staggered conformation of ethane at the energy minima and the eclipsed conformation at the energy maxima is 12 kJ/mol. Since there are three H to H eclipsing interactions, each H to H eclipsing costs 4 kJ/mol.

Factors in stabilizing or destabilizing conformations

The following factors contribute to the stabilization or destabilization of the conformation.

1. Destabilization due to electrostatic repulsion between the identical charge dipoles nearby in eclipsed conformation,
2. destabilization due to steric repulsion, i.e., physical repulsion due to electron cloud on one group penetrating the electron cloud space of the other when they are nearby in eclipsed conformation, and
3. stabilization due to hyperconjugation, i.e., an overlap of a σ -bond on one atom with an antibonding orbital on the neighboring atom in staggered conformation.

These factors are illustrated in Figure 3.2.4 for the case of ethane.

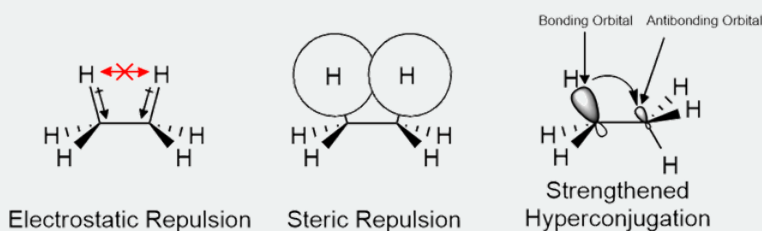
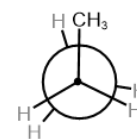


Figure 3.2.4: Illustrates the contributions of steric and electrostatic interactions as well as hyperconjugation to the energy barrier of rotation in ethane (Copyright; UMMedChemStudent, CC BY-SA 3.0, via Wikimedia Commons)

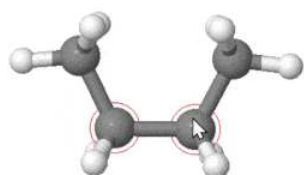
Note that the hyperconjugation is a resonance involving σ -bond. In the case of eclipsed ethane, the staggered conformation is stabilized by hyperconjugation, i.e., an overlap between a σ -bond and an antibonding orbital. The hyperconjugation is lost as the orbitals move out of alignment in the eclipsed conformation. Hyperconjugation and static repulsion could be the reason for

destabilising the eclipsed conformation, also referred to as an **eclipsing strain**. Steric repulsion is not responsible for it because the size of $-H$ substituent is small.

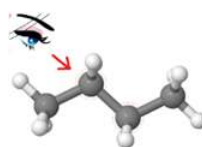
The potential energy versus dihedral angle curve of propane is similar to that of ethane, except that the difference between the staggered and eclipsed conformation is 14 kJ/mol in propane. There are two H to H eclipsing interactions and one CH_3 to H eclipsing in the staggered conformation of propane, as shown in the figure on the right margin. Two H to H eclipsing interactions are 4 kJ/mol each, the same in ethane and propane, which means CH_3 to H eclipsing in propane is 6 kJ/mole resulting in a total of 14 kJ/mole in propane. Since $-CH_3$ is bulkier than $-H$, steric repulsion, also called steric strain, contributes to the eclipsing strain of propane.



Conformational analysis of butane



The conformational analysis of butane $CH_3CH_2CH_2CH_3$ is discussed concerning rotation around $C2\backslash, -C3\backslash$ bond, as shown in the simulation on the left margin. The most stable conformation is illustrated on the right margin. This is a staggered conformation of lowest energy with the bulky $-CH_3$ groups farthest apart at 180° , which is labeled A in the relative energy vs. torsion angle curve shown in Figure 3.2.5. It is referred to as anti-conformation.



Butane: side view



View along C1-C2



Newman projection

A 60° rotation converts it to an eclipsed conformation labeled C in the figure. It has one H to H eclipsing interaction of 4 kJ/mole and two H to CH_3 eclipsing interactions of 6 kJ/mol each, which totals to 16 kJ/mol higher energy relative to the anti-conformation.

A further 60° rotation converts the eclipsed conformation to another staggered conformation called gauche-conformation, labeled B. It is at a local energy minimum but 3.8 kJ/mol higher than the anti-conformation. The gauche conformation has the bulky $-CH_3$ groups at a 60° torsion angle where they are close enough to cause some steric repulsion between each other. Another 60° rotation converts the gauche-conformation to an eclipsed conformation called cis, labeled D, in which the bulky $-CH_3$ groups are eclipsing each other. The cis-conformation is 19 kJ/mole higher than the anti-conformation. There are two H to H eclipsing interactions of 4 kJ/mol each, and the remaining 11 kJ/mol is due to CH_3 to CH_3 eclipsing interaction. This cis-conformation, labeled C, is 3 kJ/mol higher in energy than the other eclipsed conformation, labeled B, and it is the highest energy conformation of butane. These conformations repeat at an interval of 60° torsion angles, as illustrated in Figure 3.2.5.

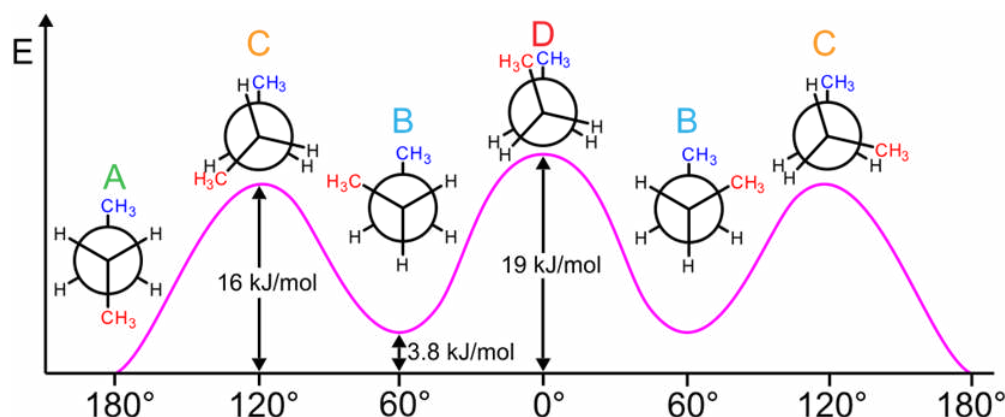


Figure 3.2.5: Newman projections of butane conformations for rotation around $C2-C3$ bond and their relative energy differences (not total energies) vs. torsional/dihedral angle curve. A: antiperiplanar, anti or trans, B: gauche, C: eclipsed, D: synperiplanar or cis. (Copyright; aKeministi, Public domain via Wikimedia commons).

Figure 3.2.6 shows the models of the conformations, labeled A, B, C, and D in Figure 3.2.5, with the van der Waals electron cloud spaces shown. It also provides a summary of the nomenclature associated with the conformations.

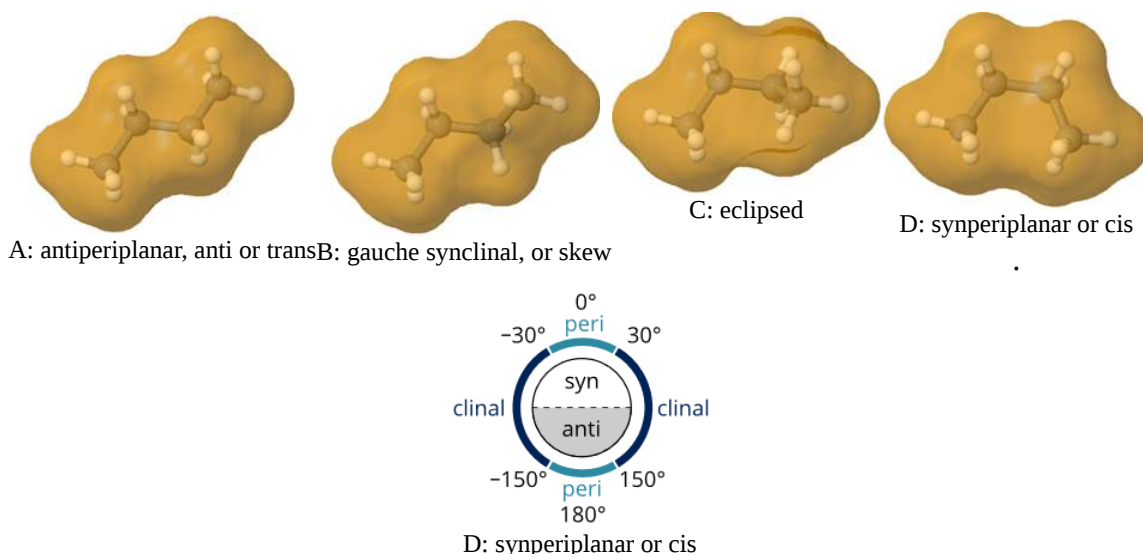


Figure 3.2.6: The electron clouds of anti, gauche, eclipsed, and cis conformations, labeled A, B, C, and D, respectively in Figure 3.2.5 (Copyright; public domain) and summary of nomenclature of the conformations illustrated in the figure on the right (Copyright Dreamtheater at English Wikipedia, CC BY-SA 3.0, via Wikimedia Commons).

✎ Conformational isomers

- Conformations corresponding to local minima on the potential energy curve, e.g., anti- and gauche-conformations in the case of butane, are called **conformational isomers** or **conformers**.
- The conformations corresponding to the local maxima on the energy curve, such as the eclipsed conformations in the case of butane, are **transition states** between conformational isomers that have a fleeting existence.

📌 Energy cost of eclipsing and gauche interaction of -H and -CH_3 groups

It can be calculated from Figure 3.2.4 and Figure 3.2.6 that each

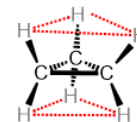
- ✎ H to H eclipsing costs 4 kJ/mol,
- ✎ H to CH_3 eclipsing costs 6 kJ/mol,
- ✎ CH_3 to CH_3 eclipsing costs 11 kJ/mol, and
- ✎ CH_3 to CH_3 gauche interaction costs 4 kJ/mol,

Conformations of cycloalkanes

If a cycloalkane is a planar ring, there will be two kinds of strain:

- angle strain**, i.e., the strain caused by bending the bond angles from the ideal tetrahedral bond angles of 109.5° , and
- eclipsing strains** between a pair of H on each C with pairs of H's on the two neighboring carbons.

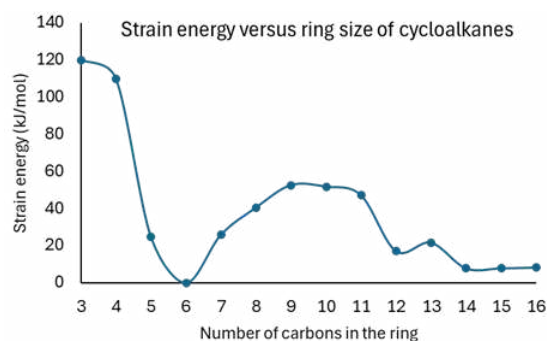
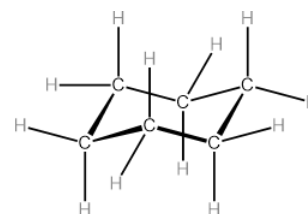
Cyclopropane is a planar ring with bond angles reduced to 60° and three H to H eclipsing interaction on the top face and three on the bottom face, as shown by red dotted lines in the figure on the right margin. The planar conformation of cyclopropane with the eclipsing interactions between H's can be seen in the interactive model in Figure 3.2.7. The overall strain on a cyclopropane is ~ 120 kJ/mol, of which 24 kJ/mol ($6 \times 4 = 24$ kJ/mol) is accounted for by the H eclipsing strain and the remaining 96 kJ/mol is due to angle strain. Cyclopropane is the most strained cycloalkane.



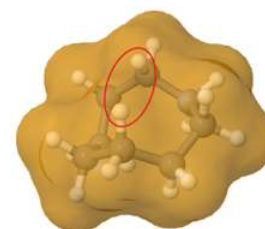
A planar cyclobutane would be square with 90° bond angles and 8 H to H eclipsing. The actual conformation of cyclobutane is puckered confirmation as shown in the interactive model in Figure 3.2.7. The puckered conformation increases angle strain by reducing angles to 88° but significantly reduces the H to H eclipsing strain, resulting in an overall ring strain of ~ 110 kJ/mol.

A planar cyclopentane would be a pentagon with bond angles of 108° , i.e., close to the regular value of 109.5° , but ten H to H eclipsing interaction that would be 40 kJ/mole ($10 \times 4 = 40$ kJ/mol) overall strain. The actual conformation of cyclopentane is puckered, shown in the interactive model in Figure 3.2.7. The puckered conformation slightly increases angle strain but significantly reduces eclipsing strain, resulting in an overall strain of ~ 25 kJ/mol. Four of the C's of cyclopentane are almost in one plane, and the fifth is raised, giving it an envelope shape, also known as an envelope conformation. The raised C position keeps shifting between the five ring C's, and the resulting five envelop shape isomers exist in an equilibrium mixture. Cyclopentane is one of the most common ring structures found in nature due to its low angle strain. For example, ribose, a sugar that is a component of DNA monomers, and fructose, or fruit sugar, are five-membered rings.

A planar cyclohexane would be a hexagon with all C—C—C bond angles expanded to 120° and 12 H to H eclipsing interactions. The actual conformations of cyclohexane are bent, with the most stable conformation resembling a chair, known as the chair conformation, as shown in the figure on the right margin and the interactive model in Figure 3.2.8. In the chair conformation of cyclohexane, all bond angles are close to the tetrahedral value of 109.5° and all H's are staggered with no ring strain. Cyclohexane is the most common ring structure found in nature due to its zero ring strain. For example, glucose -the most common monosaccharide (sugar) is six-membered rings. Starch, a carbohydrate component of food, and cellulose, a major component of wood, are made of glucose units.



Medium-size rings (7-13 C's) can pucker or bend to minimize angle strain, as shown in Figure 3.2.8 Still, some **transannular strain**, i.e., steric repulsion between groups attached to non-adjacent ring atoms, appears between groups on some C's with other groups at a distance across the ring. For example, the figure on the right margin highlights the transannular strain between two H's with a red oval shape in the lowest energy conformation of cyclooctane (Copyright; public domain). In larger rings (14 or more C's), there is little or no ring strain because they are more flexible and can



acquire conformations with minimal angle strain, eclipsing strain, and transannular strain. The figure on the left margin summarizes the strain energy concerning the ring size trend (Copyright; Public domain).

This page titled [3.2: Conformational analyses](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [3.2: Confirmations](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

3.3: Conformational analysis of cyclohexanes

Chair conformations of cyclohexane

The chair conformation is the most stable conformation of cyclohexane, as illustrated in the 3D interactive model in Figure 3.3.1 and depicted in the figure on the right margin. Cyclohexane is six-C cyclic structure. Every ring C has two bonds in addition to the two C—C bonds in the ring. One is pointing perpendicular to the ring along the axis of the ring, called axial, and labeled 'a', and the other is almost along the equator of the ring, labeled 'e' in the figure on the right margin.

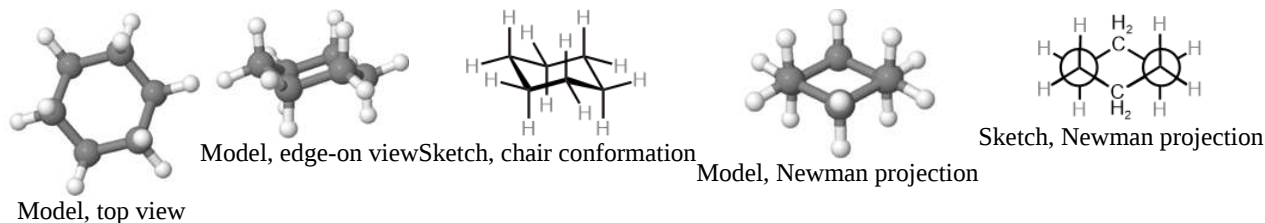
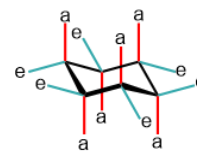


Figure 3.3.1: Models and sketches of a chair conformation of cyclohexane (Copyright; Public domain)

All C—C—C bond angles in cyclohexane are 111° , i.e., very close to tetrahedral value 109.5° , and all six pairs of H's are staggered as shown in Figure 3.3.9. Three alternate axial bonds are on the top face, pointing up, and the other three axial bonds are on the bottom face, pointing down. The C on which an axial bond is pointing up, the equatorial is pointing down, and vice versa.

✚ Drawing chair conformations of cyclohexane

1. Draw two parallel lines slanting up, separated by about half their length, and the top line starting from about the middle of the first as shown in Figure 3.3.2 (a).
2. Start a line from the top end of the top line, making a wide V shape, and extend it to about parallel to the bottom end of the bottom line. Draw a line parallel to it, starting from the bottom end of the bottom line and extending to about the top end of the top line. Figure 3.3.2 shows these two lines in blue.
3. Connect the open ends of the lines of step#2 with the nearest end of the other line of step#1. These are shown in red in Figure 3.3.2. The chair skeleton of the cyclohexane ring is now complete.
4. Draw lines starting from the corners of the ring, going straight upwards from the corners pointing up, and going straight downwards from the corners pointing down. These are **axial bonds**, shown in green in Figure 3.3.2.
5. Draw lines starting from the corners, making a big V-shape to the axial bond and approximately parallel to one bond away in the ring. These are **equatorial bonds**, shown in black, blue, and red, corresponding to the color of the bonds one bond away to which they are drawn parallel in Figure 3.3.2.

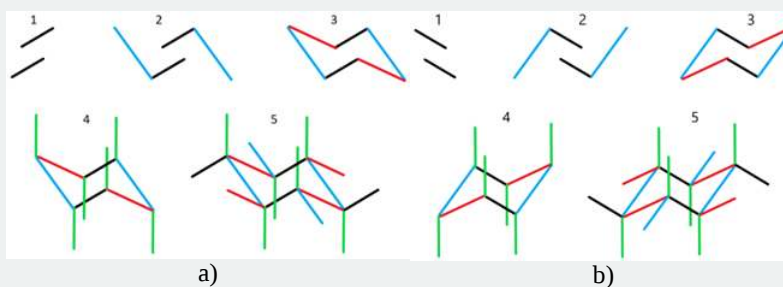


Figure 3.3.2: Illustration of steps to draw chair conformation of cyclohexane (right) and its flipped form (left). (Copyrights; Public domain)

The flipped form of the chair conformation in Figure 3.3.2 (a) is shown on the Figure 3.3.2 (b). To draw the flipped form, follow the same five steps but start with two parallel lines slanting downwards and replace up with down and vice versa in the instructions, as illustrated in Figure 3.3.2 (b).

Ring flipping in cyclohexane

There is limited rotation around C—C bond in a cyclohexane chain that allows flipping of the cyclohexane chair conformation, converting all the axial bonds into equatorial and all the equatorial bonds to axial as illustrated by animation and drawing in Figure 3.3.3.

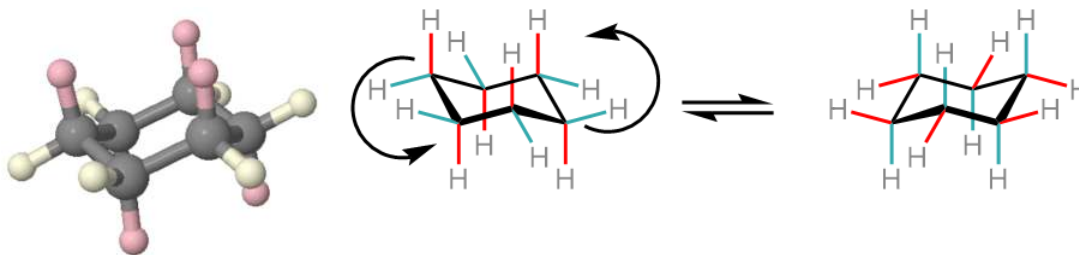


Figure 3.3.3: Animation of cyclohexane ring flipping (left) and sketch showing all axial bonds become equatorial and vice versa upon flipping the ring. (The animation is derived from the [CheMagic](#) app, Copyright; Public Domain)

The energy versus reaction time curve for ring flipping reaction of cyclohexane is illustrated in Figure 3.3.4. The ring flipping, starting from one bending one corner of a chair conformation labeled A1, proceeds to a transition state labeled D1 and then to a twist-boat conformation labeled B1. The twist boat B1 transforms into another twist boat conformation, B2, via a boat transition state labeled C. The twist boat B2 converts into a flipped chair conformation A2 via transition state D2. Proceeds through twist boat conformation and half-chair and boat transition states, with higher energy conformations, as shown in Figure 3.3.4.

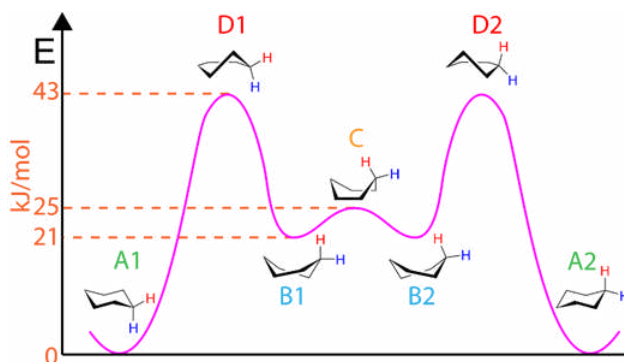


Figure 3.3.4: Cyclohexane chair flip (ring inversion) reaction plotted against their energy differences. Inversion happens quickly & constantly at room temperature. A1 & A2: chair; B1 & B2: twist-boat; C: boat; and D1 & D2: half-chair. (Copyright; Keministi, Public domain via Wikimedia commons)

The two chair conformations are of equal energy in the case of cyclohexane and predominant in the mixture due to their low energy. For every 10,000 molecules in chair conformations, there is no more than one molecule in the twist boat conformation. All other conformations are higher energy than the two chair conformations due to angle strain, eclipsing strain, trans-annular strain, or a combination of these. For example, the boat conformation, labeled C in the figure, has four H to H eclipsing interactions and a trans-annular interaction between two H pointing up from the top corners, like flagpoles. The latter is a trans-annular steric strain, referred to as a flagpole interaction in a boat conformation, as illustrated by red lines in Figure 3.3.4.

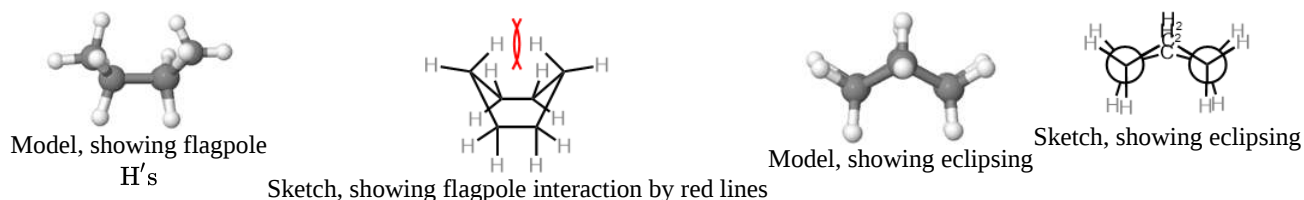


Figure 3.3.5: Boat conformation of cyclohexane shown in different views to highlight flagpole strains (two figures on the left) and eclipsing strains (two figures on the right) (Copyright; Public Domain).

Conformations of monosubstituted cyclohexanes

When one —H of cyclohexane is replaced with another group, e.g., —CH₃, it becomes a monosubstituted cyclohexane. Two chair conformations of cyclohexane are of equal energy, but in a monosubstituted cyclohexane, the bulky group like —CH₃ is less stable

at axial position by 7.1 kJ/mol than at equatorial position, as illustrated in Figure 3.3.6. The bulky group at the axial position has steric repulsion with the other two axial H's on the same face of the ring, called 1,3-diaxial interaction. The bulky group at the equatorial position is in free space with no steric interaction.

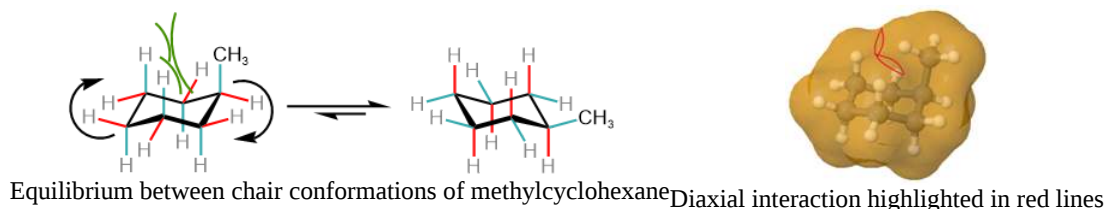


Figure 3.3.6: Equilibrium between axial and equatorial conformations of methylcyclohexane with 1,3-Diaxial interaction illustrated by green lines (left) and electron cloud model of axial methylcyclohexane with 1,3-diaxial interaction illustrated by red lines (right). (Copyright; Public domain)

Each of the two 1,3-diaxial interactions in methylcyclohexane is similar to a gauche interaction in butane, as illustrated in Figure 3.3.7.

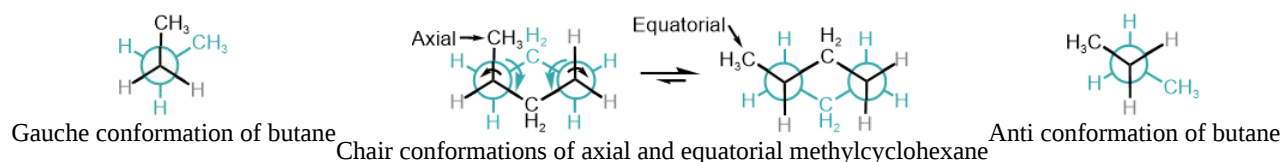


Figure 3.3.7: Comparing Newman projections of the gauche conformation of butane with the axial conformation of methylcyclohexane and the anti conformation of butane with the equatorial conformation of methylcyclohexane (Copyright; Public domain).

Equilibrium constant K of any chemical reaction is related with the free energy change ΔG , by the following relation:

$$\Delta G = -RT \ln K$$

, where R is gas constant equal to $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$, and T is absolute temperature equal to 298 K at room temperature. It rearranges to:

$$\ln K = -\frac{\Delta G}{RT}$$

Plugging in $\Delta G = -7100 \text{ J/mol}$ for axial to equatorial methylcyclohexane conversion, gives the value of K :

$$\ln K = -\frac{-7100 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{K.mol}} \times 298 \text{ K}} = 2.9$$

$$K = \frac{18.2 \text{ equatorial}}{1 \text{ axial}}$$

It means the percentage of equatorial methylcyclohexane at equilibrium = $\frac{18.2}{18.2+1} \times 100 = 95\%$

The 1,3 diaxial strain varies with the size of the substituent -the larger the substituent, the higher the strain, as shown in Table 3.3.8.

Table 3.3.8: 1,3-diaxial strain, also called A-values, of some substituents on a cyclohexane ring. (taken from https://en.Wikipedia.org/wiki/A_value, 07/10/2025)

Group:	-F	-Cl	-Br	-I	-C $\equiv$ N	-CH ₃	-CH ₂ CH ₃	-CH(CH ₃) ₂	-C(CH ₃) ₃
Strain ($\frac{\text{kJ}}{\text{mol}}$)	0.63	1.8	1.6	1.9	0.71	7.1	7.3	9.9	23
Group:	-Ph	-COOH	-COOCH ₃	-OH	-OCH ₃	-NH ₂	-NO ₂	-COCH ₃	-SH
Strain ($\frac{\text{kJ}}{\text{mol}}$)	12.6	5.6	5.3	3.6	2.5	6.7	4.6	4.9	3.8

The bulky substituents nearly lock the substituted cyclohexanes in one chair conformation in which the bulky substituent is in the equatorial position. For example, the above calculations for $-\text{CH}_3$ substituent show that only five in a sample of a hundred molecules are expected to have a methyl substituent in the axial position. When the same calculation is repeated for bulky $-\text{C}(\text{CH}_3)_3$ substituent, the results show that only one in a sample of ten thousand molecules is expected to have the substituent in the axial position.

Disubstituted cyclohexane

Stereoisomers have the same atom connectivity, but the atoms are oriented differently. There are two major classes of stereoisomers: i) conformational isomers in which the different orientation of atoms is a result of rotation around single bonds, and ii) configurational isomers in which the different orientation of atoms is not interconvertible by simple rotation around bonds, it requires making and reforming some bonds. Gauche and anti-conformations of cyclobutane are examples of conformational isomers. Axial and equatorial conformations of monosubstituted cyclohexanes, described in the previous section, are also examples of conformational isomers. One type of configurational isomers, called cis-trans isomerism, is described in the next section. Other types of configurational isomerism are described in a later section.

Cis-trans isomerism

Two substituents on two $\text{C}'\text{s}$ of a double bond or on two $\text{C}'\text{s}$ of a cycloalkane exhibit a subclass of configurational isomers called cis-trans isomerism. Cis- means the two substituents are pointing on the same side, and trans- means they are pointing on the opposite side. For example, two $-\text{CH}_3$ substituents on different $\text{C}'\text{s}$ of a $\text{C}=\text{C}$ are pointing on the same side in cis-but-2-ene and pointing on the opposite side in trans-but-2-ene, as shown in Figure 3.3.9

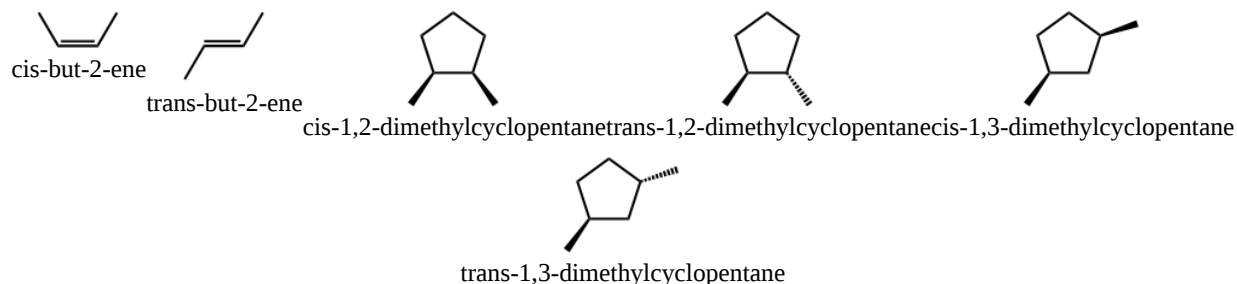


Figure 3.3.9: Examples of cis-trans isomers of alkenes and cycloalkanes (Copyright: Public domain).

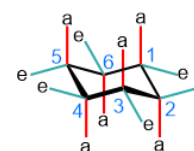
When an acycloalkane is shown in a planar configuration, the two substituents pointing in the same direction can either point up towards the viewer, as indicated by a solid wedge, or point down away from the viewer, as shown by a hashed wedge. For example, cis-1,2-dimethylcyclopentane has both methyl substituents on a solid wedge, and trans-1,2-dimethylcyclopentane has one on a solid wedge and the other on a hashed wedge, as shown in Figure 3.3.9. The two substituents need not be on adjacent $\text{C}'\text{s}$ for cis-trans isomerism, they can be on any two different $\text{C}'\text{s}$ of cycloalkane structure. For example, the last two structures in Figure 3.3.9 show cis- and trans- isomers of 1,3-dimethylcyclopentane.

Usually, the cis-isomer of an alkene or cycloalkane is less stable due to the steric strain of the bulky substituents on the same side as the trans-isomer. For example, cis-but-2-ene is 5.0 kJ/mol higher in energy than trans-but-2-ene, and cis-1,2-dimethylcyclopentane is 7.1 kJ/mol higher in energy than trans-1,2-dimethylcyclopentane.

Cis-trans isomerism in cyclohexane

Cis-trans isomerism in cyclohexane can be shown by drawing the ring in a planar configuration as a hexagon and the substituents on solid wedge or hashed wedge. For example, the structure on the left margin is cis-1,2-dimethylcyclohexane, and the one on the right margin is trans-1,2-dimethylcyclohexane. However, drawing it on a chi plane is more realistic and can also show the ring flipping, resulting in conformational isomers.

In the chair conformation of cyclohexane, every C has two bonds outside the ring, an axial and an equatorial, one pointing up and the other pointing down, as illustrated in the figure on the right margin. Suppose axial is pointing up in a $\text{C}\#1$, the axial on the neighboring $\text{C}\#2$ and $\text{C}\#6$ are pointing down, the axial on one C away that is $\text{C}\#3$ and $\text{C}\#5$ are pointing up, and axial on the C across, i.e., $\text{C}\#4$ is pointing down, and vice versa. The



same is true for equatorial bonds. This information allows the drawing of cis-trans isomers of disubstituted cyclohexanes.

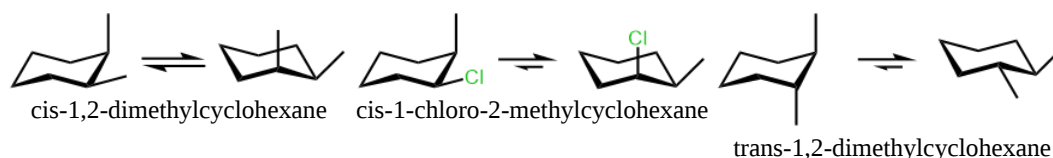
Two groups on two different rings C, s pointing in the same direction, both up or both down, is cis, irrespective of whether they are both on axial or equatorial or one on axial and the other on equatorial. The opposite, i.e., one pointing up and the other down, is a trans isomer. For example, two substituents,

1. one on C#1 and the other on #2 or on #6, are cis- if one is on axial and the other on equatorial, and
 - trans- if both are axial or both are equatorial.
 - The same is true for two substituents, one on C#1 and the other on #4.
2. The opposite is true for two substituents, one on C#1 and the other on #3 or on #5, i.e., they trans- if one is on axial and the other on equatorial, and
 - cis- if both are axial or both are equatorial.

These rules are explained with examples in the following sections.

1,2-Disubstituted cyclohexanes

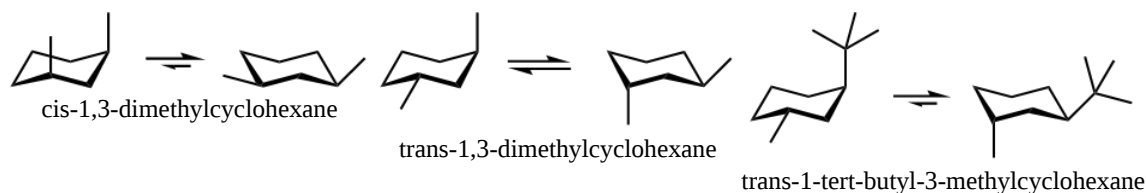
Cis 1,2 substituents are one axial and the other equatorial, or the other way around. For example, cis-1,2-dimethylcyclohexane has one -CH_3 axial and the other equatorial, as shown in the figure below. The ring flip reaction converts every axial bond into equatorial and vice versa. Both chair conformations of cis-1,2-dimethylcyclohexane are of equal energy. When the two substituents are not the same, the bulky substituent in the equatorial position is a more stable configuration. For example, the methyl group in the equatorial position of cis-1-chloro-2-methylcyclohexane (1.8 kJ/mol for axial -Cl) is more stable than the chloride in the equatorial position (7.1 kJ/mole for axial -CH_3), as shown in the figure below.



A trans-1,2-dimethylcyclohexane has both methyl substituents in axial positions in the less stable conformation or both methyl groups in equatorial positions in the more stable conformation, as shown in the figure above. The less stable conformation has two 1,3-diaxial interactions, whereas the more stable conformation features only one gauche interaction between methyl groups. The ΔG for diaxial to diequatorial conversion reaction is 10.4 kJ/mol (two diaxial interactions (7.1 kJ/mol + 7.1 kJ/mol = 14.2 kJ/mol) - one gauche interaction (3.8 kJ/mol) = 10.4 kJ/mol).

1,3-Disubstituted cyclohexanes

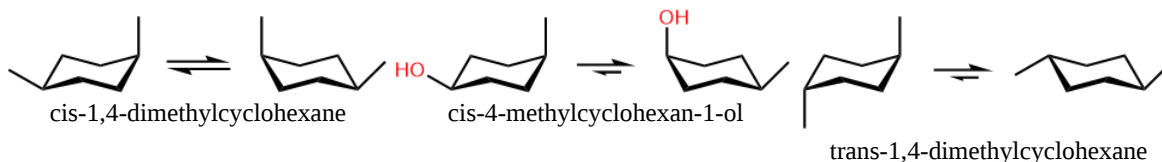
Cis-1,3 substituents are either both axial or both equatorial. For example, cis-1,3-dimethylcyclohexane has both -CH_3 axial in less stable or both equatorial in more stable conformation as shown in the figure below. Both chair conformations of cis-1,3-dimethylcyclohexane are of equal energy. The ΔG for diaxial to diequatorial conversion reaction is 14.2 kJ/mol (two diaxial interactions (7.1 kJ/mol + 7.1 kJ/mol = 14.2 kJ/mol) - 0 strain in diequatorial = 14.2 kJ/mol).



Trans-1,3 substituents are one axial and the other equatorial, or the other way around. For example, trans-1,3-dimethylcyclohexane has one -CH_3 axial and the other equatorial, as shown in the figure above. Both chair conformations of trans-1,3-dimethylcyclohexane are of equal energy. When the two substituents are not the same, the bulky substituent in the equatorial position is a more stable configuration. For example, tert-butyl group in the equatorial position of trans-1-tert-butyl-3-methylcyclohexane ((27.1 kJ/mol for -CH_3 axial) is more stable than the methyl in the equatorial position ((23 kJ/mol for $\text{-C(CH}_3)_3$ axial), as shown in the figure above.

1,4-Disubstituted cyclohexanes

Cis 1,4 substituents are one axial and the other equatorial, or the other way around. For example, cis-1,4-dimethylcyclohexane has one $-\text{CH}_3$ axial and the other equatorial, as shown in the figure below. Both chair conformations of cis-1,4-dimethylcyclohexane are of equal energy. When the two substituents are not the same, the bulky substituent in the equatorial position is a more stable configuration. For example, the methyl group in the equatorial position of cis-4-methylcyclohexan-1-ol is more stable (3.6 kJ/mol for axial $-\text{OH}$) than the hydroxyl group in the equatorial position (7.1 kJ/mol for axial $-\text{CH}_3$), as shown in the figure below.



A trans-1,4-dimethylcyclohexane has both methyl substituents in axial positions in the less stable conformation or both methyl groups in equatorial positions in the more stable conformation, as shown in the figure above. The less stable conformation has two 1,3-diaxial interactions, whereas the more stable conformation has no such destabilizing interaction. The ΔG for diaxial to diequatorial conversion reaction is 14.2 kJ/mol (two diaxial interactions (7.1 kJ/mol + 7.1 kJ/mol = 14.2 kJ/mol) - 0 strain in diequatorial isomer = 14.2 kJ/mol).

Polysubstituted cyclohexanes

Polysubstituted cyclohexanes also have two chair conformations, in which one is usually more stable. If the given structure is in a planar configuration, the direction of the substituents, up or down, is indicated by the use of solid or hashed wedges. The following rules convert the planar to a chair conformation.

1. Number the cyclohexane chain. The numbers could be IUPAC numbering of the parent chain, or they can be arbitrary numbers beginning from any one of the substituents.
2. Draw a cyclohexane chair and place the first substituent, axial or equatorial, at its designated number.
3. Place the second and the third substituents at their designated numbers, but the direction, axial or equatorial, is determined by the cis- or trans-relationship to the first substituent.
4. Draw a flipped cyclohexane chain and place the substituents at their designated numbers such that all axial substituents become equatorial and vice versa in the flipped conformation.
5. Calculate the strain, i.e., 1,3-diaxial interaction energies and gauche interactions for each conformation.
 - The confirmation that has less strain is more stable.
6. Subtract the larger strain value from the smaller to calculate the ΔG for conversion from more stable to less stable conformation.

Note: If the value of gauche interaction is not known, it can be ignored because, usually, it is common in the two flipped conformations and cancels out when the overall strain energy of one is subtracted from the other to calculate the ΔG for conversion from more stable to less stable conformation.

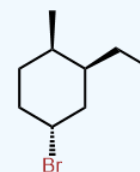
Application of these rules is demonstrated below with the applied examples.

✓ Example 3.3.1

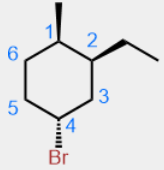
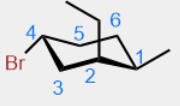
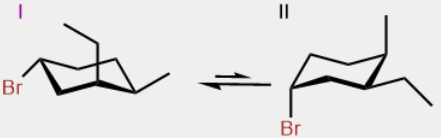
Convert the following structure of cyclohexane into two chair conformations and calculate which one is more stable.

Solution

The given structure is 4-bromo-2-ethyl-1-methylcyclohexane. The steps to convert it into chair conformations are shown below.



Step 1	Step 2	Step 3	Step 4

			
IUPAC numbering	Methyl drawn equatorial at #1	Ethyl at #2 is cis and bromo at #4 is trans to methyl	All axial substituents become equators and vice versa in the flipped conformation

Step 5:

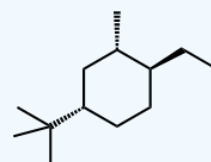
- Strain in conformation I = (7.3 kJ/mol for $-\text{CH}_2\text{CH}_3$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$)
- Strain in conformation II = (7.1 kJ/mol for $-\text{CH}_3$ axial + 1.6 kJ/mole for $-\text{Br}$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$).
- Confirmation I with one axial substitute is more stable because the diaxial strain is less in it, and the gauche interaction is the same in the two.

Step 6: ΔG released for II to I conversion = (7.1 kJ/mol for $-\text{CH}_3$ axial + 1.6 kJ/mole for $-\text{Br}$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$) - (7.3 kJ/mol for $-\text{CH}_2\text{CH}_3$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$) = 1.4 kJ/mole

Note that in the above example, confirmation I with fewer axial substituents is more stable, but this is not always the case. This is because the 1,3-Diaxial strain is a steric strain dependent on the bulk of the substituent -the more bulky the substituent, the larger the strain. The following example proves the above point.

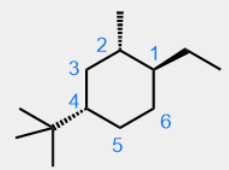
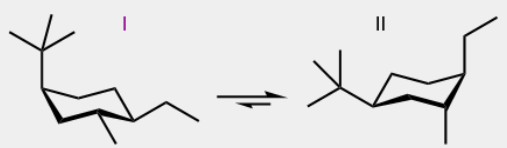
✓ **Example 3.3.2**

Convert the following structure of cyclohexane into two chair conformations and calculate which one is more stable.



Solution

The given structure is 4-*tert*-butyl-1-ethyl-2-methylcyclohexane. The steps to convert it into chair conformations are shown below.

			
IUPAC numbering	Ethyl drawn equatorial at #1	Methyl at #2 is trans and <i>tert</i> -butyl at #4 is cis to ethyl	All axial substituents become equators and vice versa in the flipped conformation

Step 5:

- Strain in conformation I = (23 kJ/mol for $-\text{C}(\text{CH}_3)_3$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$)
- Strain in conformation II = (7.1 kJ/mol for $-\text{CH}_3$ axial + 7.3 kJ/mole for $-\text{CH}_2\text{CH}_3$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$).
- Confirmation II with $-\text{C}(\text{CH}_3)_3$ is more stable because the diaxial strain is less in it, and the gauche interaction is the same in the two.

Step 6: ΔG released for I to II conversion = (23 kJ/mol for $-\text{C}(\text{CH}_3)_3$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$) - (7.1 kJ/mol for $-\text{CH}_3$ axial + 7.3 kJ/mole for $-\text{CH}_2\text{CH}_3$ axial + gauche for $-\text{CH}_3$ to $-\text{CH}_2\text{CH}_3$) = 8.6 kJ/mole

Caution

The descriptor *cis* or *trans* used to identify stereoisomers, e.g., *cis*-1,2-dimethylcyclohexane, *trans*-1,3-dimethylcyclohexane, etc., in the previous section is not an IUPAC name of these compounds. IUPAC uses stereodescriptors, like R, S, E, Z, etc., that are described in a later section.

Preference for equatorial over axial substitutions in nature

Six-membered rings are the most common cyclic structures found in nature. Those with all or most of the bulky groups in equatorial positions are significantly more common because of the stability of the equatorial relative to the axial bulky groups. For example, the majority of monosaccharides (sugars) exist as six-membered cyclic structures having more equatorial than axial substituents. Glucose -the most common monosaccharide exists primarily as a six-membered ring structure with all the bulky groups at the equatorial positions, as shown in Figure 3.3.10. Glucose is synthesized during photosynthesis, and either consumed as an energy source or for the synthesis of other biochemicals. For example, glucose units combined through an equatorial group form a polymer called cellulose, the major component of wood. Starch is also a polymer of glucose, but with one connecting bond axial. This change of the connecting bond from equatorial to axial changes it from cellulose, a hard structural material, to starch. This carbohydrate is an energy storage compound in animals and plants.

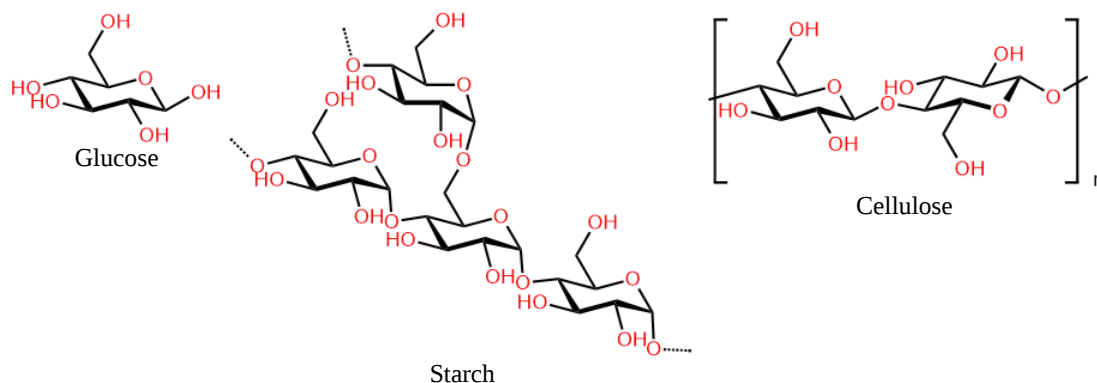


Figure 3.3.10: Structure of glucose, starch, and cellulose. (Copyright; Public domain)

Fused ring systems also exist in nature; most have six- and five-membered rings. They also show a preference for bulky substituents on equatorial positions. Some of these fused ring systems are described in the next section.

Cyclohexanes in polycyclic systems

Cyclohexane is commonly found as a part of polycyclic systems in biochemicals. One example is decalin (bicyclo[4,4,0]decane), which has two cyclohexane rings in chair conformations fused by sharing one bond. It has two isomeric forms: *cis*-decalin, which is less stable, and *trans*-decalin, which is more stable and more common. The *trans*-decalin model from the top view appears to resemble the planar conformation. Still, its actual 3D structure with two cyclohexane rings in chair conformation reveals, when viewed from edge-on, as shown in Figure 3.3.11.

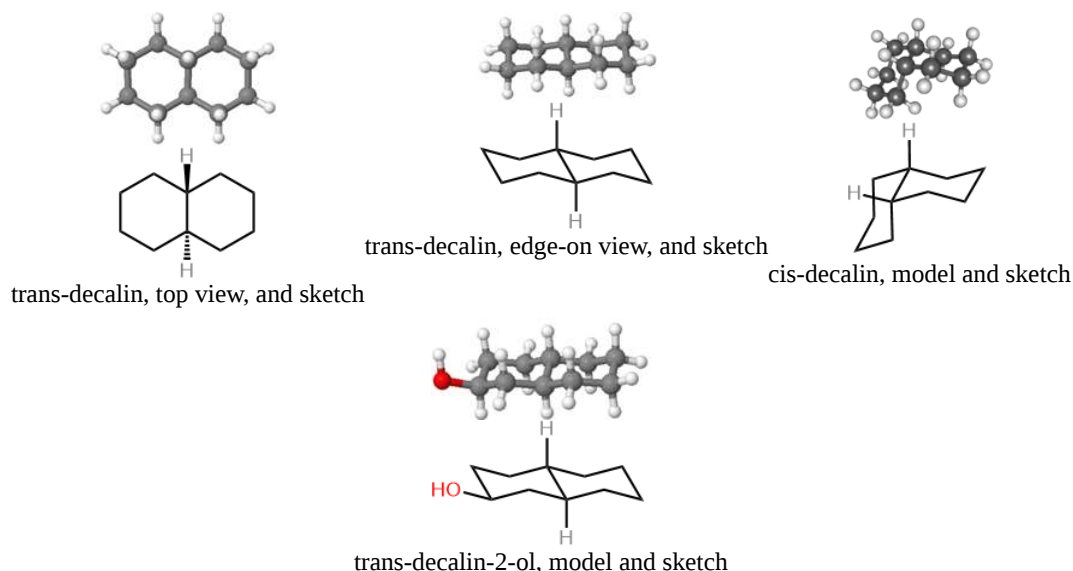


Figure 3.3.11: Decalin (bicyclo[4,4,0]decane) systems, models of cis and trans isomers, and an example trans-decalin-2-ol used in fragrance compositions (Copyright; Public domain).

The trans relationship of trans-decalin can be easily observed by viewing the orientation of two H atoms at ring junctions, which are 1,2-axial. The bulky groups, i.e., the alkyl parts of the second ring, are 1,2-diequatorial, the more stable trans-conformation. Cis-decaline has one alkyl substituent on each cyclohexane ring in an unstable axial position. An example is trans-decalin-2-ol used in fragrance compositions. It has a trans-decalin backbone, as shown in Figure 3.3.11.

Another common fused cyclohexane system is norbornane (bicyclo[2,2,1]heptane), as shown in Figure 3.3.12. It is a cyclohexane locked in boat conformation by the one C bridge. Although the boat conformation of cyclohexane is an unstable transition state due to flagpole interaction, the flagpole H's are replaced by $>\text{CH}_2$ bridge in norbornane, which removes the strain and keeps the cyclohexane locked in boat conformation.

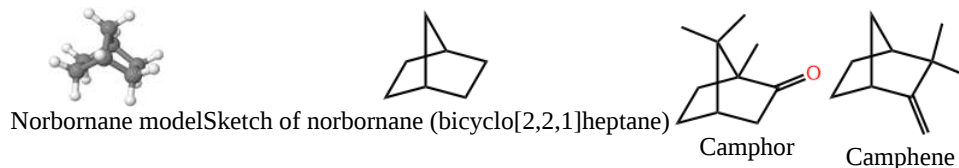


Figure 3.3.12: Norbornane (bicyclo[2,2,1]heptane) model, sketch, and examples: camphor, a strongly scented natural product, and camphene, a constituent of many natural oils (Copyright; Public domain).

Examples of natural products having a norbornane backbone are camphor, a strongly scented compound isolated from evergreen trees, and camphene, which is a component in several natural oils, such as pine oil and ginger oil.

Steroids are a class of biologically active compounds that are derivatives of the gonane structure, also called sterane, which is composed of three cyclohexane rings in chair conformation and one cyclopentane ring in envelope conformation, fused in a specific way, as shown in Figure 3.3.13. All four rings are trans-fused, except for a few examples where only the first cyclohexane ring is cis-fused.

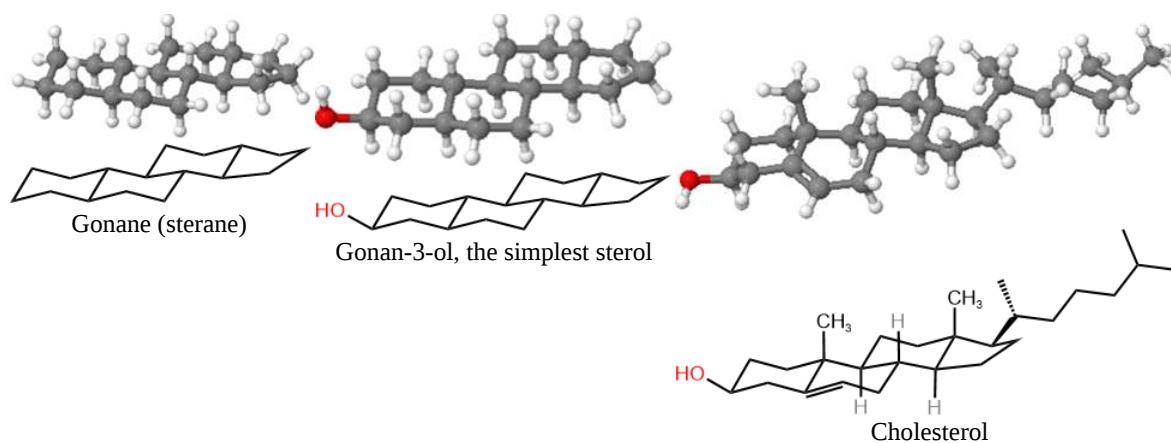
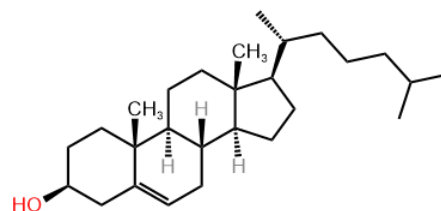


Figure 3.3.13: Models and sketches of steroids based on fused ring system of three cyclohexane and one cyclopentane in a specific way as in gonane, gonan-3-ol, the simplest sterol, cholesterol, a well know sterol, and cholestanol, a derivative of sterol (Copyright; Public domain).

Sterols, a subclass of steroids, have an —OH group at equatorial position of C#3 of gonane, as in gonan-3-ol shown in Figure 3.3.13 Cholesterol, shown in a planar configuration in the figure on the right margin and in cyclic chair conformations of six membered rings and envelop conformation of cyclopentane in Figure 3.3.13 is a well-known sterol present in blood, brain, spinal cord, fats, oils, and cell membranes of all higher animals.

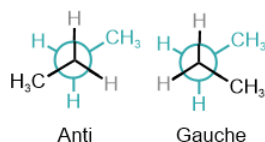


3.3: Conformational analysis of cyclohexanes is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

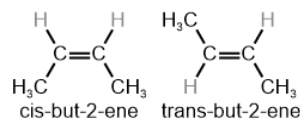
- **3.2: Confirmations** by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

3.4: Configurational stereoisomerism

What is a configurational isomer?



Isomers are molecules or species that have the same molecular formula but different arrangements of atoms in their structure. If the different arrangement of atoms is due to a different sequence of atoms, these are **constitutional isomers**. If the sequence of atoms is the same, but their orientation in space is different, they are **stereoisomers**. If the different orientation of atoms in

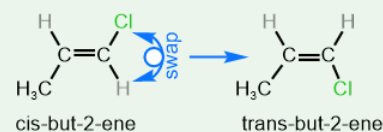


stereoisomers is a result of free rotation around single bonds, they are **conformational isomers**. For example, anti and gauche-forms of butane, shown on the left margin, are conformational isomers that interconvert by rotating parts of the molecule around single bonds relative to other parts. On the other hand, if different orientation of stereoisomers is a permanent geometry that requires making and re-making some bonds for their interconversion, they are **configurational isomers**. For example, cis- and trans-but-2-ene, shown on the right margin, are configurational isomers.

A molecule's permanent geometry, which results from the spatial arrangement of its bonds, is called its **configuration**.

Stereogenic center

An atom within a molecule bearing groups such that interchanging any two of them leads to a stereoisomer of the original molecule is referred to as a **stereogenic center**.



For example, both double-bonded carbons $C=C$ in but-2-ene, shown in the figure on the right margin, are stereogenic centers, interchanging $-H$ with $-CH_3$ on any one of them converts cis- to trans isomer and vice versa.

Types of configurational isomers

Every object, including molecular structure, has its reflection when it is placed against a mirror, called its mirror image. Suppose the object and its mirror image are real. In that case, they are either **identical**, i.e., they superpose on each other thoroughly after rotating the entire object or molecule around some axes, or they are non-superposable mirror images. Stereoisomers are either non-superimposable mirror images of each other, known as **enantiomers**, or they are not mirror images of each other, referred to as **diastereomers**. This difference between identical structures, enantiomers, and diastereomers is illustrated in Figure 3.4.1.

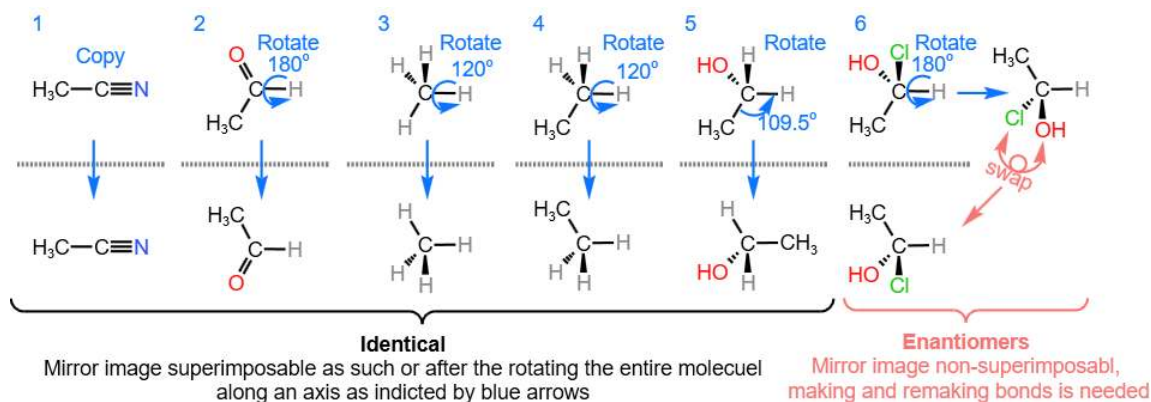


Figure 3.4.1: Molecular structures in the first row and their mirror images in the bottom row. Straight arrows show translational movement, curly arrows represent rotations of the molecule, and curly double-headed arrows represent the swap of two substituents, i.e., breaking their previous bonds and making new bonds. Structures 1, 2, 3, 4, and 5 are identical to their mirror images. Structure 6 and its mirror image are stereoisomers, as they are not superposable mirror images. Stereoisomers 7 are diastereomers, as they are stereoisomers but not mirror images of each other (Copyright; Public domain).

If the stereoisomers are non-superposable mirror images of each other, they are **enantiomers**; otherwise, they are **diastereomers**.

Chirality

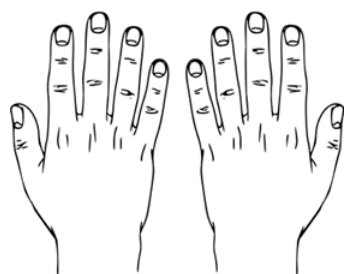
Chirality is a property related to a superposable relationship between an object and another object that would be like its mirror image. Mirrors reflect light and produce an inverted, or imaginary, picture of the object seen behind the mirror. For example, the water surface of Mirror Lake reflects the beautiful scenery of Mount Hood, as shown in the figure below (Copyright: Oregon's Mt. Hood Territory, Public domain, via Wikimedia Commons)



Chirality, chiral and achiral

The geometric property of a rigid object, including molecules, that prevents it from being superposable on its mirror image is referred to as **chirality**. An object, including a molecule, that is not superposable on its mirror image is referred to as **chiral**. An object or a molecule that is superposable on its mirror image is referred to as **achiral**.

Figure 3.4.2 shows some examples of chiral objects. Chirality is usually associated with life. For example, human eyes, ears, hands, and feet are chiral objects. Chiral molecules are also usually biochemicals. For example, amino acids that constitute proteins, DNA molecules, carbohydrates, etc., are generally chiral molecules.



Left and right hands,



clockwise and counterclockwise springs, left- and right-handed shells of sea snails, and



left and right shoes.

Figure 3.4.2: Some examples of chiral objects (Copyright: Public domain).

Chiral objects do not have a plane of symmetry and do not have a point of symmetry. Achiral objects have a plane of symmetry and/or a point of symmetry.



A **plane of symmetry** is a flat surface that divides the object into two halves, such that one half is a mirror image of the other.



For example, a cup of coffee, shown on the right margin, is an achiral object with a plane of symmetry, shown as a red line frame overlaid on the picture.

A **point of symmetry** is a point in the middle of an object such that if any feature of the object is reflected, an identical feature will be found on the opposite side of the point at the same distance.

For example, the point in the center of the plate, as shown in the left margin, through which red lines are crossing, is its point of symmetry. A sphere has a point of symmetry at its center and also has unlimited symmetry planes. Figure 3.4.3 shows some examples of achiral objects.



A baseball,



a pencil,



a shovel, a fork, a plate, a knife, a spoon, and



a sphere.

Figure 3.4.3: Some examples of achiral objects (Copyright; Public domain).

Chirality at the molecular level

Like objects, molecules are either achiral when their mirror image superposes on them or chiral when their mirror image does not superpose on them. For example, molecules #1, #2, #3, #4, and #5 in Figure 3.4.1 are achiral, having superposable mirror images, while molecule #6 is chiral as its mirror image is non-superposable on it.

Often, achiral molecules have one or more planes of symmetry that divide them into equal halves, as illustrated in Figure 3.4.4. The figure on the right margin illustrates formaldehyde $\text{H}_2\text{C}=\text{O}$ that is a planer molecule having two-fold axis of symmetry C_2 and σ_v and σ_v' are two planes of symmetry: one is in the plane of the molecule, cutting every atom in two halves and the other of dotted liens is perpendicular to the plane of the molecule, cutting it in two halves along $\text{C}=\text{O}$ bond (Copyright: Public domain).

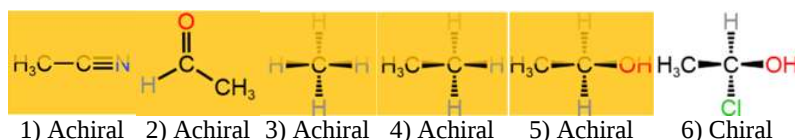
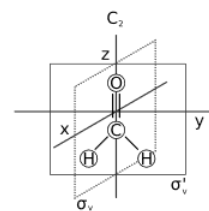
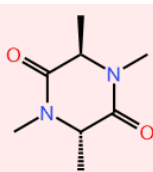
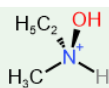


Figure 3.4.4: Examples of plane of symmetry in **achiral** molecules. The plane is perpendicular to the page/screen in examples #1, 3, 4, and 5, and in the plane of the page/screen in example#2. Example #6 is a **chiral** with neither a plane of symmetry nor a point of symmetry (Copyright: Public domain).



The presence of a plane of symmetry is sufficient to define a molecule as achiral; its absence usually means the molecule is chiral, but not necessarily always. There are a few exceptions where a molecule has no plane of symmetry, but it is still achiral due to the presence of a point of symmetry. For example, the molecule shown in the left margin, ((3R,6S)-1,3,4,6-tetramethylpiperazine-2,5-dione), does not have a plane of symmetry; however, it is achiral because it possesses a point of symmetry.

Chirality center



An atom holding a set of ligands (groups) in a spatial arrangement that is not superposable on its mirror image is referred to as a **chirality center**. A carbon that is a chirality center is also called an **asymmetric carbon atom**.



For example, N^+ in the figure on the left margin and C in the figure on the right margin are chirality centers. The C in the figure on the right margin is also an asymmetric carbon atom.

Identifying chirality centers

Often, the presence of an asymmetric C is the cause of chirality of the molecule. C chirality centers in a molecule can be identified by the following rules.

1. An $sp\text{C}$ or $sp^2\text{C}$ is not a chirality center. For example, central C in example#1 and #2 in Figure 3.4.4 are not chirality centers.
2. An $sp^3\text{C}$ with two or more same substituents is not a chirality center. For example, central C in example#3, #4, and #5 in Figure 3.4.4 having two or more H 's are not chirality centers.
3. An $sp^3\text{C}$ with four different substituents is a chirality center. For example, central C in example#6 in in Figure 3.4.4 is a chirality center.

When substituents contain more than one atom, first compare the atoms directly bonded to the atom under consideration, then the atoms two bonds away, then the atoms three bonds away, until the first point of difference is reached. For example, the first structure in Figure 3.4.5 has H , O , C , and C at one bond away from the C highlighted yellow. The last two substituents have C , H , and H , i.e., the same two bonds away. First difference is at three bonds away C , H , H versus C , C , H , as highlighted red. So the four substitutions are different, making the C highlighted yellow a chirality center. If all atoms are compared this way and no difference is found, the two substituents are the same, and the atom under consideration is not a chirality center.

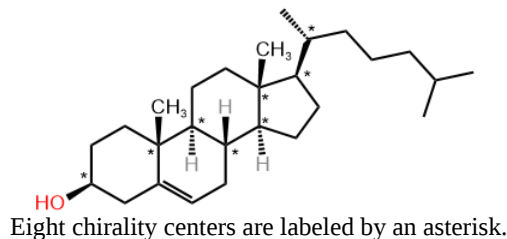
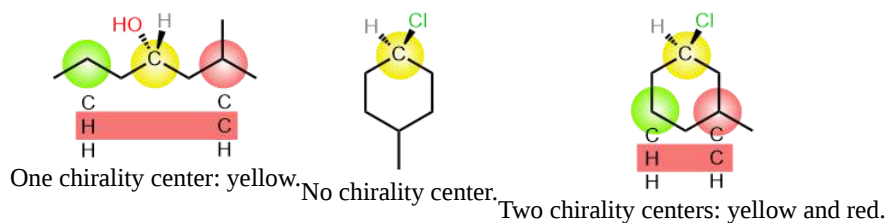


Figure 3.4.5: Examples of finding chirality centers in molecules (Copyright; Public domain).

If the atom under consideration is part of a cyclic chain, two substituents are the parts of the chain on the two sides of the atom. As usual, compare the atoms directly bonded to the atom under consideration, then two bonds away, then three bonds away, and so on, until the first point of difference is found, or the group of atoms common to both sides is reached, meaning the two sides of the cyclic structure are the same substituent. For example, C highlighted yellow in the second structure in Figure 3.4.5 as —Cl , —H and two $\text{C}'\text{'s}$ of the cyclic structure at one bond away. The atoms two bonds away are C, H, H, the same one on both sides, and the atoms three bonds away are common to both sides. Therefore, the C highlighted yellow in this structure is not a chirality center. The C highlighted yellow in the third structure in Figure 3.4.5 is chiral, having four different substituents. The first difference in the two sides of the cyclic structure is at two bonds away, i.e., C, H, H versus C, C, H, as shown in the figure. The C highlighted red in this structure is the second chirality center, for which the first difference in the two sides of the cyclic structure is at three bonds away, i.e., C, H, H versus Cl, C, H.

Biochemicals often have more than one chirality center. They are usually labeled with an asterisk if needed. For example, cholesterol, the fourth structure in Figure 3.4.5, has eight chirality centers labeled with an asterisk. Note that two of the H's on C's are shown in this skeletal structure as they were needed to show the correct configuration of the C's. The rest of the H's on C's are implicit, as usual.

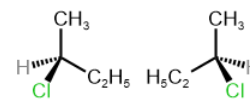
Representing the configuration of a chirality center

A sp^3 -hybridized atom is tetrahedral, i.e., four σ -bonds as two V's of 109.5° internal angle joined perpendicular to each other at

vortexes, e.g., methane CH_4 modeled as . Tetrahedral geometry is a 3D geometry typically represented by perspective drawings or Fisher projections, which are described in the following sections.

Perspective drawing

Since the tetrahedral geometry is two V's perpendicular to each other, one V is placed in the plane of the screen (or page) and represented by solid lines. The other V is represented by a solid wedge, indicating the bond emerging from the screen towards the viewer, and a hashed wedge, representing the bond extending beyond the screen away from the viewer. When the central atom is a chirality center, two configurations of enantiomers are possible, as illustrated in the figure on the right margin for two enantiomers of 2-chlorobutane. The view angle is from the direction of the top-left corner. The V in the plane of the screen appears larger, and the other appears smaller. Typically, the solid wedge is positioned closer to the viewer than the hashed wedge.



If the configuration of two or more connected C's needs to be shown, the V's in the plane of the screen are usually drawn pointing downwards or upwards, making a zig-zag line. For example, four stereoisomers of 3-chlorobutan-2-ol, which have two chirality centers, are shown in Figure 3.4.6. Semi-condensed formulas show all atoms, but skeletal formulas do not show C's and H's, except when it is necessary to show the configuration of the chirality center, as illustrated in the case of skeletal formulas, C's and H's are not shown. However, the configuration is still readable correctly from the bonds shown, as illustrated in Figure 3.4.6.

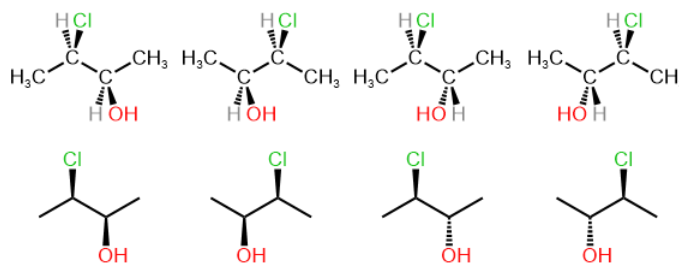


Figure 3.4.6: Perspective drawing of semi-condensed formula (top row) and the corresponding skeletal formula of four stereoisomers of 3-chlorobutan-2-ol. (Copyright; Public domain)

Fisher projections

Fisher projections represent the configuration as a 2D projection of the molecule, with four bonds arranged in the shape of a cross. The following steps and Figure 3.4.7 (left) illustrate how to draw a Fisher projection from a perspective drawing.

1. Look at the chirality center such that the bonds extending towards the viewer are placed horizontally and the bonds extending away from the viewer are drawn vertically.
2. Replace solid and hashed wedges with straight lines, assuming the horizontal lines are bonds forward and the vertical lines are bonds backward.

The steps are applied to an example of alanine enantiomers shown in Figure 3.4.7 (right)

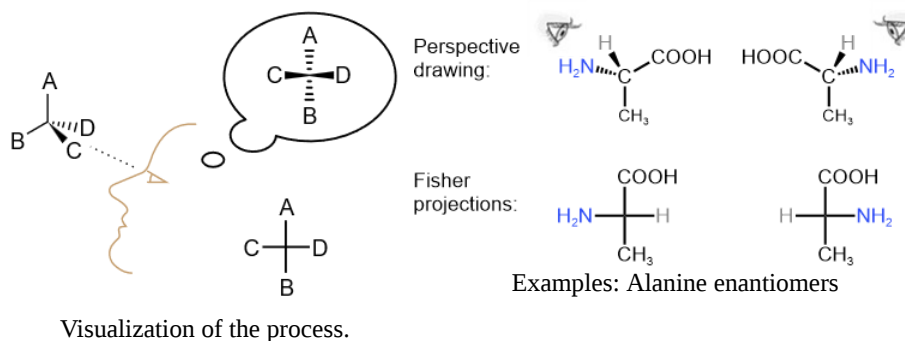


Figure 3.4.7: Illustration of how to visualize a Fisher projection of a chirality center (left, copyright; Slashme, CC BY-SA 3.0, via Wikimedia Commons) and examples: enantiomers of alanine (right) shown in perspective drawing with view point indicated by eye symbol (Copyright; Public domain).

When there is more than one chirality center, the following steps convert the skeletal drawing into the Fischer projection.

1. The C-backbone is oriented from horizontal to vertical by a 90° rotation of the entire molecule. The most oxidized carbon is usually placed at or near the top.
2. Part of the molecule is rotated 180° around C—C single bond between two chirality centers, resulting in a semi-cyclic conformation.
 - If there are more than two chirality centers, this step is repeated for the third chirality center, then for the fourth, and so on.
3. The chirality centers are viewed from the edge-on so that the bonds of the C-backbone are pointing away from the viewer and the bonds to the two substituents are horizontal, pointing towards the viewer. This step is repeated for each chirality center, as illustrated in Figure 3.4.8.

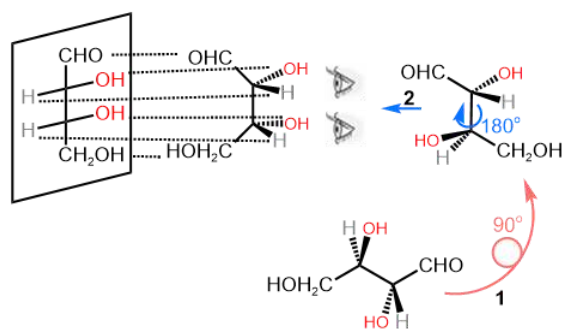


Figure 3.4.8: Illustration of how to modify the perspective drawing of more than one chiral center into a semi-circle conformation (step#1 and #2) and then visualize its Fisher projection by viewing each chirality center separately, such that bonds in the backbone are away and substations are pointing towards the viewer, as if a light beam is shining from the point of view and the projection of the structure is seen on the screen. (Copyright: Public domain).

This page titled [3.4: Configurational stereoisomerism](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

- [3.3: Configurations](#) by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

3.5: Assigning R/S stereodescriptors to chirality center

Necessity for assigning R/S stereodescriptors to chirality centers

A compound containing a C-chirality center, i.e., an asymmetric carbon, is chiral. A chiral molecule has an enantiomer, which is its nonsuperposable mirror image. For example, the central C of 1-chloroethanol is a chirality center. It exists in two configurations that are enantiomers, as shown in Figure 3.5.1 a). If the enantiomer on the left is moved to superpose on the other, only —Cl superpose, the other three —OH , —CH_3 , and —H mismatch. Rotate the enantiomer on the left along C—Cl bond axis by 120° clockwise and superpose. This time —Cl and —OH superpose while —CH_3 , and —H mismatch, as shown in Figure 3.5.1(b). No matter how an enantiomer with one chirality center is moved to superpose on the other, at most two substituents can match, leaving two mismatched.

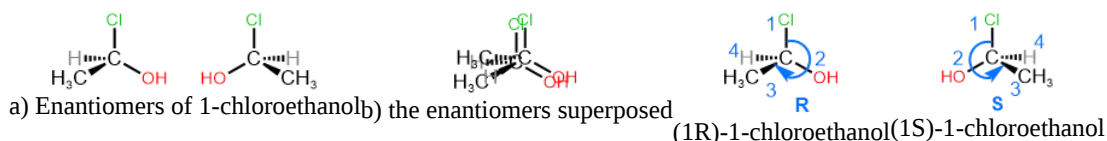


Figure 3.5.1: Paste Caption Here

No matter how an enantiomer with one chirality center is moved to superpose on the other, at most two substituents can match, leaving two mismatched.

As an exercise, interactive models of enantiomers of alanine -an amino acid with one chirality center are provided in Figure 3.5.2. Try to rotate one enantiomer and see how it superposes on the other to verify the above statement. The skeletal drawings and the common names of the two enantiomers (L-alanine and D-alanine) are shown in the last two structures in Figure 3.5.2.

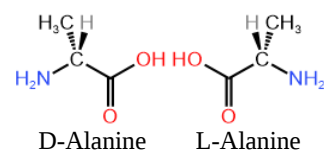


Figure 3.5.2: Interactive models of enantiomers of alanine: (2R)-2-aminopropanoic acid, which is D-alanine (left), and (2S)-2-aminopropanoic acid, which is L-alanine (right). The model can be enlarged by two-finger gestures on the touchpad or by right-clicking and dragging, and rotated by swiping one finger in the image area or by left-clicking the mouse and dragging. As an exercise, rotate one enantiomer and observe that any two substituents can superpose at a time, but the other two mismatch.

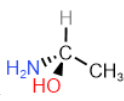
The IUPAC name of a compound containing a chirality center is incomplete without specifying which of the two configurations it refers to. IUPAC nomenclature uses R/S stereodescriptors, preceded by the locant number of the chiral center if needed, enclosed in brackets, and separated from the rest of the name by a hyphen. It requires assigning priority to the four substituents on a chirality center, followed by assigning R/S stereodescriptors based on the relative orientations of the substituents with respect to their priorities.

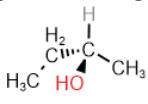
CIP priority sequence rules

The following rules assign priorities 1, 2, 3, and 4, where 1 is the highest priority and 4 the lowest.

1. Compare the atomic number of the atoms directly bonded to the chirality center (one bond away): the higher the atomic number, the higher the priority.
 - When isotopes are compared, the higher the atomic weight, the higher the priority.
 - When one of the substituents is a lone pair, it is the lowest priority, #4.
2. If there is a tie, compare the atoms two bonds away: arrange the atoms in a substituted two bonds away from the chirality center according to atomic number and compare them with those of the other substituent. Stop at the first point of difference. The constituent of a higher atomic number at the first point of difference has higher priority over the other.
 - If there is a tie, compare atoms three bonds away, then four bonds away, and so on, until the first point of difference is reached.
3. If there is a tie, compare isomeric structures: (Z) is preferred over (E) and (R) is preferred over (S).

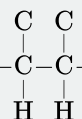
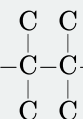
The application of rule#1 and rule#2 is explained in the following with examples. Special case of how to compare atoms in a double or a triple bond is explained next. The application of rule#3 is explained later after learning how to assign stereodescriptors R/S to a chirality center, or E/Z to diastereomers containing a double bond.

1. Rule#1, the priority of the four groups in  is: $\text{—OH} > \text{—NH}_2 > \text{—CH}_3 > \text{—H}$.

2. Rule#2, applied to , there is a tie between —CH_3 and $\text{—CH}_2\text{—CH}_3$; comparison of atoms two bonds away:
 —CH_3 : H, H, H
 $\text{—CH}_2\text{—CH}_3$: C, H, H assigns higher priority to $\text{—CH}_2\text{—CH}_3$ over —CH_3 , i.e., the priority order is:
 $\text{—OH} > \text{—CH}_2\text{—CH}_3 > \text{—CH}_3 > \text{—H}$.

CIP rule for atoms with double or triple bond

The atoms of a double bond are treated as connected twice, and the atoms of a triple bond are treated as connected three times,

i.e., —CH=CH_2 is treated as  and $\text{—C}\equiv\text{CH}$ is treated as .

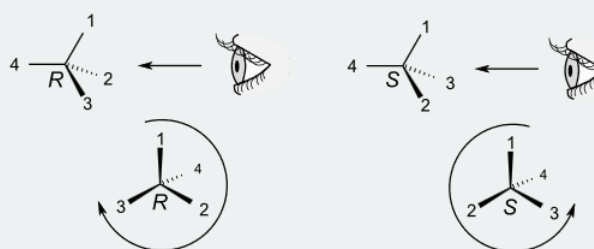
1. Suppose —CH=CH_2 and $\text{—C}\equiv\text{CH}$ attached to a chirality center are compared: the atoms one bond away are C versus C, i.e., a tie; the atoms two bonds away are C, C, H versus C, C, C, assigning higher priority to $\text{—C}\equiv\text{CH}$.
2. Suppose —CH=CH_2 and —CH=CH—CH_3 attached to a chirality center are compared: there is a tie at one bond and two bonds away, but at three bonds away C, H, H versus C, C, H, assigning higher priority to —CH=CH—CH_3 .
3. Suppose $\text{—C}\equiv\text{CH}$ and —equivC—C_3 attached to a chirality center are compared: there is a tie at one bond and two bonds away, but at three bonds away C, C, H versus C, C, C, assigning higher priority to —equivC—C_3 .

Caution

The rule is to stop at the first point of difference, even if the order may change later. For example, comparing $\begin{array}{c} \text{F} \\ | \\ -\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$ and $\begin{array}{c} \text{F} \\ | \\ -\text{C}-\text{NH}_2 \\ | \\ \text{CH}_3 \end{array}$ attached to a chirality center, there is a tie at one bond away, but at two bonds away $\text{F}, \overline{\text{O}}, \text{H}$ versus $\text{F}, \overline{\text{N}}, \text{C}$, assigning higher priority to $\begin{array}{c} \text{F} \\ | \\ -\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$, even though the priority at the next atom compared is reversed.

Assigning R/S stereodescriptors

1. Assign a priority sequence of $1 > 2 > 3 > 4$ to the four substituents on the chirality center according to CIP priority rules.
2. Reorient the molecule to place the lowest priority #4 on a bond going away from the viewer, i.e., on a hashed wedge in a perspective drawing or on a vertical line in Fisher projection. (Ignore this step if the lowest priority #4 is already on the hashed wedge.)
3. Draw a circular arrow going from #1 to #2 to #3: i) if the arrow is clockwise, assign *rectus* (R), which means right in Latin, and ii) if the arrow is counterclockwise, assign *sinister* (S), which means left in Latin, as illustrated in the figure on the right margin (Copyright; Roland.chem, CC0, via Wikimedia Commons).
 - The R/S stereodescriptor is usually italicized, preceded by locant, placed in parentheses, and separated by a hyphen before the name.
 - If there is more than one chirality center, the R/S stereodescriptors are separated by a comma.



IUPAC names (1R)-1-chloroethanol and (1S)-1-chloroethanol are examples of it, as shown in the last two structures in Figure 3.5.1 where the priority numbers and the circular arrows are in blue.

Easier ways for assigning R/S stereodescriptors

After assigning CIP priority sequence, if the lowest priority substituent #4 is at the hashed wedge in perspective drawing or on a vertical line in Fisher projection, the assignment of R/S stereodescriptor is straightforward: if the circular arrow from #1 to #2 to #3 is clockwise, the configuration is R, otherwise it is S. If this is not the case, then the molecule has to be re-oriented to place the lowest priority substituent at a bond going away from the viewer before drawing the circular arrow from #1 to #2 to #3. It requires visualizing the rotation of a 3D structure and redrawing, which is a complex and error-prone process. The following strategies are recommended in textbooks to address this issue.

It can be observed from the exercises suggested in Figure 3.5.2 that overlapping enantiomers can match two substituents of the chirality center, but the other two mismatch. Swapping the two mismatched substituents in one enantiomer inverts its configuration, resulting in identical structures that superpose on each other, as illustrated in Figure 3.5.3.

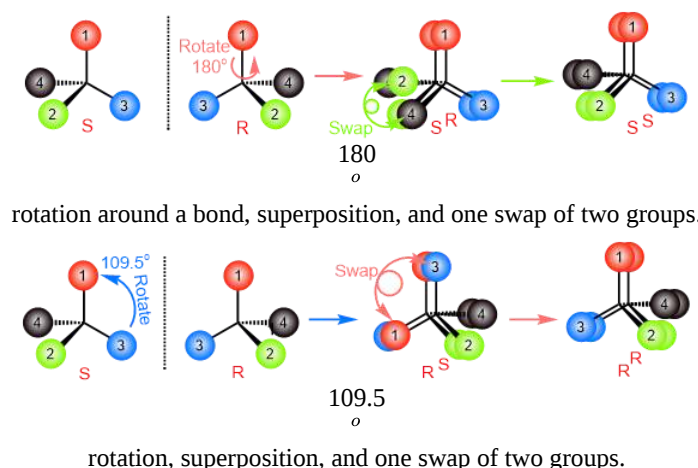
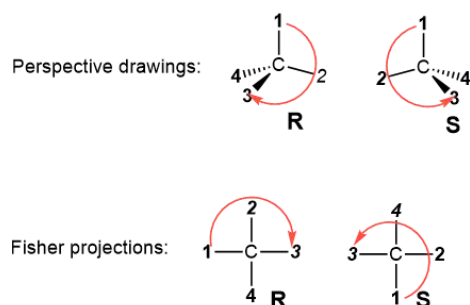


Figure 3.5.3: Illustration that enantiomers do not superpose by rotation and translation motions, but one swap (exchange) of two substituents inverts the configuration, making it superposable on the other (Copyright; Public domain).

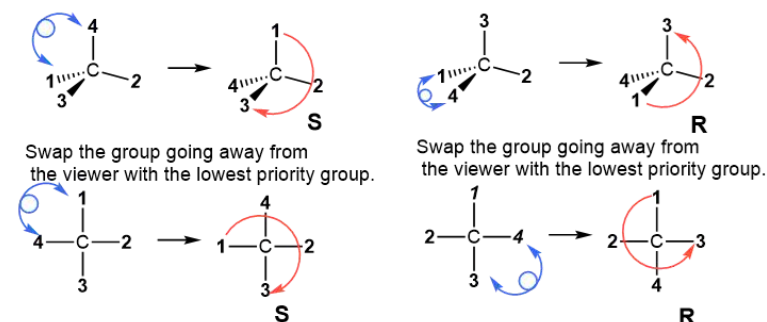
A general rule is that an odd number of swaps (exchanges) of substituents invert the configuration, and an even number of swaps (exchanges) retain the configuration. Based on this general rule, if the lowest priority group #4 is not on hashed wedge in a perspective drawing or not on a vertical line in a Fisher projection, swap it with the substituent on the hashed wedge/vertical line and reverse the assignment, i.e., if the circular arrow from #1 to #2 to #3 is clockwise, the configuration is S, otherwise it is R, as illustrated in Figure 3.5.4. This strategy makes R/S assignment relatively easier, but still requires redrawing, which is a complex and error-prone process, particularly for more complex organic structures.

Case 1: Lowest priority group is going away from the viewer



Clockwise is R and counterclockwise is S

Case 2: Lowest priority group is not going away from the viewer



Reverse the assignment, i.e., clockwise is S and counterclockwise is R

Figure 3.5.4: Illustration of assigning R or S configuration to a chiral center based on priority# 1, 2, 3, and 4, where 1 is the highest priority, and 4 is the lowest. (Copyright; Public domain)

Another approach suggested in some textbooks is that if the lowest priority group is at a solid wedge in a perspective drawing or on a horizontal line in a Fisher projection, draw a circular arrow from #1 to #2 to #3 without re-drawing the structure, but reverse the assignment, i.e., if the circular arrow from #1 to #2 to #3 is clockwise, the configuration is S, otherwise it is R.

Caution

The above approach does not work when the lowest-priority substituent (#4) is in the plane of the page, i.e., on a solid line in a perspective drawing.

The easiest and most universal approach is the hand rule for assigning R/S stereodescriptors, which is described below.

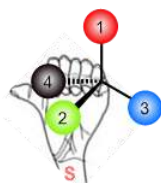
Hand rule for assigning R/S stereodescriptors to a chirality center

This rule requires reading the 3D orientation of the four substituents of the chirality center from the drawing. The rule is:

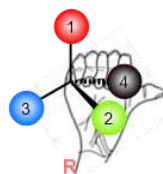
- visualize the 3D orientation of substituents 1, 2, 3, and 4 and curl the figures of the right-hand in the direction of priority #1 to #2, or #2 to #3, or #3 to #1; if the thumb is pointing in the direction of the lowest priority (#4), the structure is right-handed; assign *rectus* (R);

- if not, repeat with the left hand and the thumb points towards #4, the structure is left-handed, assign *sinister* (S)

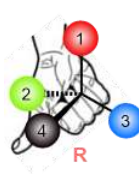
Figure 3.5.5 shows the practical application of the hand rule in different situations using perspective drawing models. Figure 3.5.6 shows its application in perspective drawing and the Fisher projections of enantiomers of alanine in which -NH_2 is #1, -COOH is #2, -CH_3 is #3, and -H is #4.



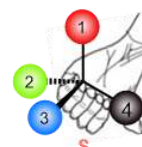
Left-handed finger curving 1 to 2



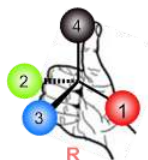
Right-hand finger curving 1 to 2



Right-hand finger curving 3 to 1

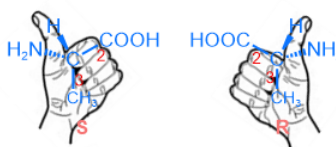


Left-hand finger curving 1 to 2

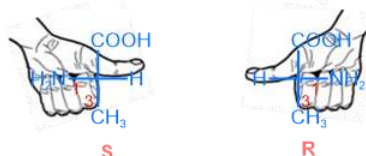


Right-hand finger curving 2 to 3

Figure 3.5.5: Examples of the use of hand-rule under different orientations of substituents in perspective drawing models (Copyright; Public domain).



Perspective drawing with the left hand (left) and the right hand (right)



Fisher projections with the left hand (left) and the right hand (right)

Figure 3.5.6: Examples of the use of hand-rule on enantiomers of alanine in perspective drawings and Fisher projections. The numbers in red show the curving of fingers from #2 to #3 in the perspective drawing and from #3 to #1 in Fisher projections. (Copyright; Public domain).

An example of applying the hand rule to interactive models is given below. It is suggested to practice the hand rule on enantiomers of alanine in Figure 3.5.2, where perspective drawings and interactive models of both enantiomers are shown, and their configurations, (R) or (S), are mentioned in the figure caption.

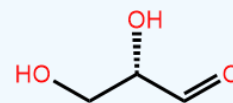
✓ Example 3.5.1



Camphor

GLmol

Camphor



Glyceraldehyde

GLmol

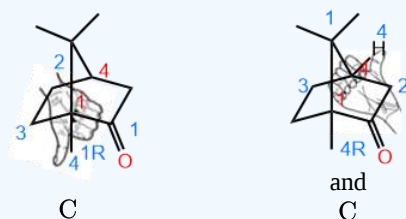
Glyceraldehyde

Use the hand rule to assign the configuration of the two chiral centers of camphor isomer, labeled 1 and 4, and one chiral center in glyceraldehyde isomer shown in the figure. The interactive models of the two isomers are also provided to help in this exercise. The model can be enlarged by two-finger gestures on the touchpad or by right-clicking and dragging, and rotated by

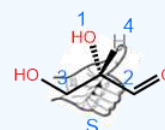
swiping one finger in the image area or by left-clicking the mouse and dragging (Copyright; Public domain).

Solution

The given enantiomer of camphor has both chiral centers in R-configuration, and the given enantiomer of glyceraldehyde has S-configuration. It is illustrated in the figure below where the priority order around the corresponding chirality is shown in blue numbers along with the right hand for R and left hand for S configurations. Note that the implicit $-H$ on the chirality center C4 of camphor is going away from the viewer, and on the chirality center of glyceraldehyde is pointing towards the viewer on a solid wedge, which is shown in the answers below.



1 of the given enantiomer of camphor is R 4 is also R.



Chirality center of the given enantiomer of glyceraldehyde is S.

E/Z Stereodescriptors for double bond systems

R/S stereodescriptors define the configuration of chiral centers. In the case of polysubstituted cycloalkanes, *cis/trans* stereodescriptors are used to indicate the relative orientation of two substituents on the same side (*cis*) or the opposite sides (*trans*); but have been replaced with R/S stereodescriptors in IUPAC nomenclature. However, *cis/trans* isomers of alkene and related double bond systems do not have chirality centers. The two stereogenic centers of alkenes usually have one $-H$ and another substituent. *Cis/trans* usually refers to the relationship of substituents other than $-H$. It becomes confusing when both substituents are other than $-H$. For example, if the structure shown on the right margin is named *cis*-2-chlorobut-2-ene, it is not clear $-Cl$ on one and $-CH_3$ on the other stereogenic carbons are *cis* or $-CH_3$ on one and $-CH_3$ on the other are *cis*. To avoid this confusion, IUPAC has replaced *cis/trans* with *E/Z* stereodescriptors for double-bond systems, such as alkenes.

The following steps assign E or Z to the diastereomers of the double bond system.

1. Assign priorities 1 and 2 to the two substituents of one stereogenic center using CIP priority, where 1 is higher priority and 2 is lower.
2. Do the same to the second stereogenic center.
3. If the two high-priority (#1) substituents on the two stereogenic centers are on the same side, assign *zusammen* (Z), which means together (*cis*) in German; otherwise, assign *entgegen* (E), which in German means opposite (*trans*). The *E/Z* capital, italicized, preceded by its locant, placed in brackets before the name, and separated by a hyphen from the name.
 - If there is more than one double bond systems, the corresponding E and/or Z are preceded by the locant number and separated by a comma.

Figure 3.5.9 provides examples of the applications of the above rules.

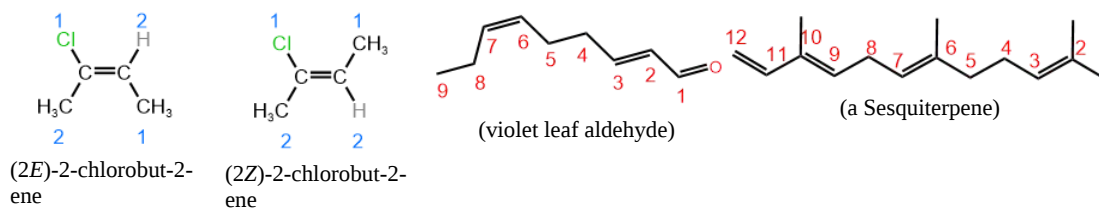


Figure 3.5.9: Examples of E/Z assignments. The numbers in blue in the first two examples are the priority order 1 and 2 of the substituents, and the numbers in red in the last two examples are the numbers of the parent chain in the IUPAC nomenclature (Copyright; Public domain).

Breaking the tie in CIP sequencing based on isomeric structures

Rule #3 of CIP sequencing, described earlier, is as follows.

IF there is a tie, compare isomeric structures: $\backslash(Z\backslash)$ is preferred over $\backslash(E\backslash)$ and $\backslash(R\backslash)$ is preferred over $\backslash(S\backslash)$.

Examples in Figure 3.5.10 are a practical explanation of this rule. In example 'a)', there is tie between two alkenyl substituents at one, two, and three bonds away, but the tie is broken at four bonds away, where $\overline{C}$, H, H versus $\overline{H}$, H, H makes *E* branch preferred over *Z* by Rule#2, resulting in *R* configuration of the chiral center. Note that all stereodescriptors are placed together in parentheses, separated by commas. However, in example 'b)', the tie does not break by rule #1 and rule #2. The tie is broken by Rule #3, making *Z* the preferred branch over *E* and assigning an *S* configuration to the chirality center.

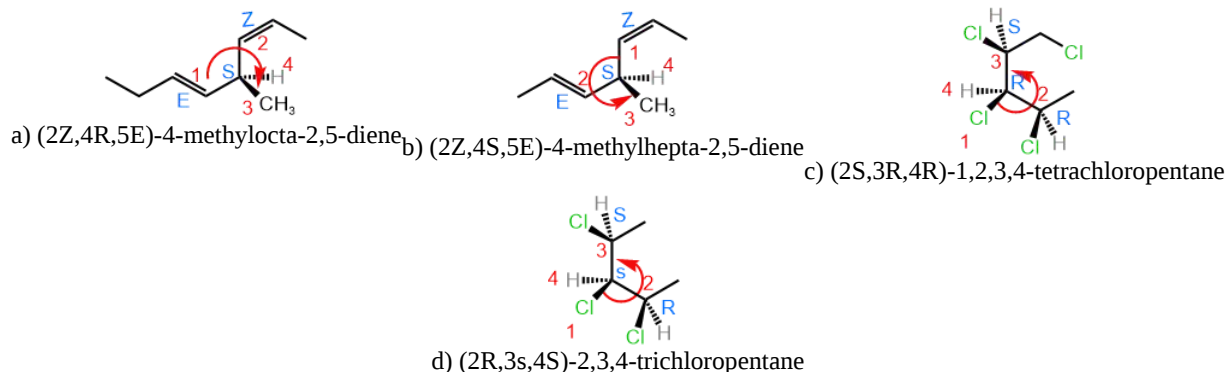


Figure 3.5.10: Examples of CIP priorities assigned based on isomeric structures, when a tie can not be broken by comparing atomic weights (Copyright: Public domain).

In example 'c)', there is tie between two alkyl substituents at one, and two bonds away but the tie is broken at three bonds away, where $\overline{Cl}$, H, H versus $\overline{H}$, H, H makes *S* configuration side preferred over *R* by Rule#2, resulting in *R* configuration of the chiral center at locant#3. However, in example 'd)', the tie does not break by rule #1 and rule #2. The tie is broken by Rule #3, making *R* preferred over *S* and assigning an *s* configuration to the chirality center at locant#3.

📌 Lowercase italic *r/s* stereodescriptors

A **pseudochirality** center has four different substituents, but two of them are identical except for the configuration of the chirality centers that are non-superposable mirror images of each other. A compound with a pseudochiral center is meso, having a symmetry plane that passes through the pseudochiral center. A pseudochiral center is assigned a lowercase italic *r/s* stereodescriptor, to distinguish it from a regular chiral center. For example, the structure in Figure 3.5.10d) has a pseudochiral center at locant#3 that is assigned *s* configuration.

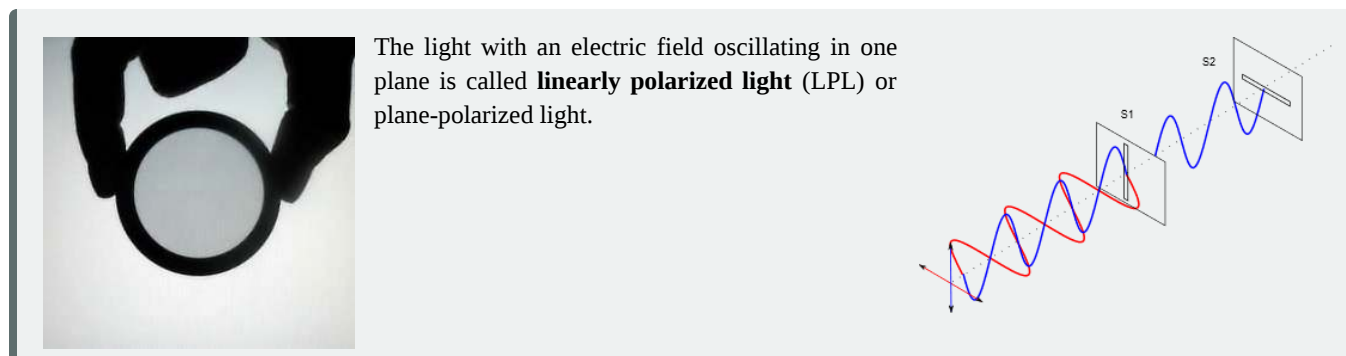
3.5: Assigning R/S stereodescriptors to chirally center is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

- 3.3: Configurations by Muhammad Arif Malik is licensed [Public Domain](#).

3.6: Optical activity

Chirality of light

Light, like all electromagnetic radiations, is an oscillating electric field and magnetic field, perpendicular to each other and perpendicular to the axis of propagation of the wave, as simulated in Figure 3.6.1 b). Electric and magnetic fields oscillate in all directions perpendicular to the direction of their propagation. Such light is called **unpolarized light**. When unpolarized light is passed through a filter, called a polarizer, it emerges with electric field oscillation in one plane, say the yx -plane, and the magnetic field perpendicular to it, say in the zx -plane, as simulated in Figure 3.6.1 b).



The polarizer can be viewed as a slit that allows the electric field to pass through it if it is parallel to its orientation. For example, the electric field represented by the blue wave in the illustration on the right margin is parallel to the slit and passes through it, whereas the red one is blocked because it is not parallel to the slit (Copyright: Jcwf, CC0, via Wikimedia Commons). If a second polarizer is placed next, it will allow the radiation to pass through with full brightness if its slit is aligned with the plane of the plane-polarized light, otherwise it will dim the light when it is out of alignment and completely block it when it is perpendicular, as demonstrated in the simulation on the left margin (Copyright; Rogilbert, Public domain, via Wikimedia Commons).

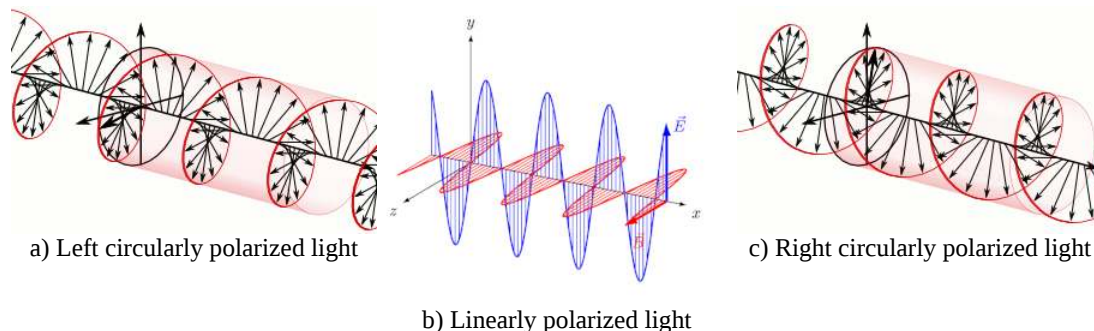


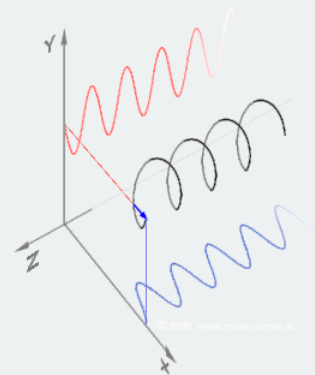
Figure 3.6.1: Polarization of light (electromagnetic radiations): a) Left circularly polarized (LCP) light, electric field vector represented by spiraling arrows b) linearly polarized light (LPL), also known as plane polarized light, blue on y -axis is electric field, red on z -axis is magnetic field, and the wave is propagating along x -axis, and c) right circularly polarized (RCP) light (Copyright; a) & c) Circular polarized, electric field component is represented by spiraling arrows: Dave3457, Public domain, via Wikimedia Commons, b) linear polarized: And1mu, CC BY-SA 4.0, via Wikimedia Commons)

Another form of polarized light is circularly polarized light.

Circularly polarized light has an electric field of constant magnitude that rotates, either clockwise or counterclockwise, as the wave propagates. If the electric field is rotating counterclockwise, it is **left circularly polarized light**, and if rotating clockwise, it is **right circularly polarized light**.

Simulations in Figure 3.6.1 a) and c) illustrate the electric field component of left and right circularly polarized lights. The left and right circularly polarized lights are nonsuperposable mirror images of each other, similar to left- and right-handed springs, as shown in Figure 3.4.2.

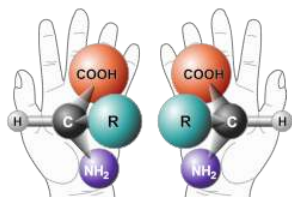
Circularly polarized light is chiral, like chiral objects, which have nonsuperposable mirror images.



Circularly polarized light can be resolved into two linearly polarized components, as shown by the black helical curve in the simulation on the right margin, which is resolved into two linear sign waves shown by red and blue curves (Copyright; de:Benutzer:Averse, CC BY-SA 2.0, via Wikimedia Commons). Similarly, adding the left and right circularly polarized lights, as shown in Figure 3.6.1 a) and c), results in linearly polarized light as shown in Figure 3.6.1 c). In other words, linearly polarized light can be viewed as composed of two equal left and right circularly polarized components, which are nonsuperposable mirror images of each other.

Linearly polarized light is chiral, composed of equal left and right circularly polarized components, which are nonsuperposable mirror images of each other.

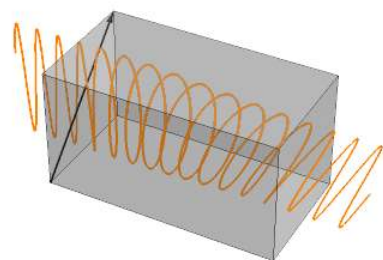
Interaction of plane polarized light with matter



A chiral object and its nonsuperposable mirror object are called enantiomorphs. A chiral molecule and its nonsuperposable mirror molecule are enantiomers. Enantiomers and enantiomorphs exhibit the same physical and chemical properties, except when they interact with another chiral thing. For example, a tennis ball, which is achiral, fits equally well on chiral left and right hands, but a chiral left glove fits on the left hand and a right glove on the right hand, not the other way around. Similarly, a model of the chiral amino acid L-alanine fits in the left hand, but its enantiomer D-alanine fits the same way in right hand, as illustrated in the figure on the left margin (Copyright;

Original: Unknown Vector: -- $\pi\epsilon\rho\eta\lambda\iota\omicron$, Public domain, via Wikimedia Commons).

Plane polarized light is chiral. When light passes from a vacuum to another medium, its speed slows down. When the medium is chiral, the left- and right-circularly polarized components of the plane-polarized light slow down unequally. Therefore, the plane of plane-polarized light rotates either clockwise or counterclockwise as it traverses a chiral medium, as shown in the simulation on the right margin (Copyright Jacopo Bertolotti, CC0, via Wikimedia Commons). If the left circularly polarized component is slower, the plane of the emerging light rotates clockwise, and if the right component is slower, it rotates counterclockwise.



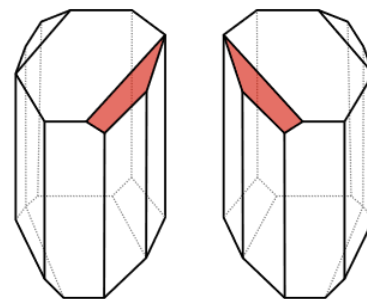
A chiral medium that rotates the plane of the plane polarized light clockwise is called **dextrorotatory** (*d*) or (+), and the one that rotates it counterclockwise is called **levorotatory** (*l*) or (-). The ability of chiral compounds to rotate the plane of plane-polarized light is called **optical activity**. Chiral compounds are **optically active**, and achiral compounds are **optically inactive**.

History of optica activity

Rotation of linearly polarized light as it passes through a quartz crystal was first observed in 1811. It is called optical activity. It was discovered in 1820 that quartz has two types of crystals, which are nonsuperposable mirror images of each other. One rotates the plane-polarized light clockwise, and the other rotates it by the same degree but counterclockwise. In 1815, Jean Baptiste Biot

observed that some organic liquids or their vapors also rotate the plane of the plane polarized light. In 1822, Fresnel found that the rotation of light is related to the two components of light being affected differently in an optically active medium.

It was observed that tartaric acid salts derived from living sources were optically active, whereas a synthetic one with the same composition was optically inactive. In 1849, Louis Pasteur recrystallized ammonium potassium tartrate and separated two types of crystals by hand-picking, which were enantiomorphs, as shown in the figure on the right margin (Copyright; Tom Murphy VII (Brighterorange), Public domain, via Wikimedia Commons). The original mixture was optically inactive, but upon dissolving the crystals in water, one type exhibited dextrorotatory properties, and its enantiomorph showed levorotatory properties. Their 1:1 mixture was optically inactive. Pasteur concluded that the molecules that constitute the enantiomorphous crystals were asymmetric forms that resembled each other, much like the left and right hands. Pasteur's discovery is considered the beginning of chirality in organic chemistry.



van 't Hoff and Le Bel proposed in 1849 that four single bonds of C are oriented as if they are directed towards the corner of a tetrahedron. If the four substituents are different, they can be arranged in two different ways, which will be mirror images of each other. It proved the Pasteur's conclusion about asymmetric forms of molecules responsible for the optical activity.

Measuring optical activity

The instrument used to measure optical activity is called a polarimeter, as illustrated in Figure 3.6.2.

A polarimeter typically features a source of light, usually a sodium lamp that emits unpolarized light of a wavelength of 589 nm, known as the D line of sodium. A polarizer converts it into linearly polarized light, which is then passed through a sample tube containing a solution of the test sample. An analyzer measures the rotation of the plane of the light by rotating it clockwise or counterclockwise until it transmits the brightest light. The angle or rotation (α) is measured in degrees ($^\circ$) and assigned dextrorotatory (+) for a clockwise rotation, or levorotatory (-) for a counterclockwise rotation.

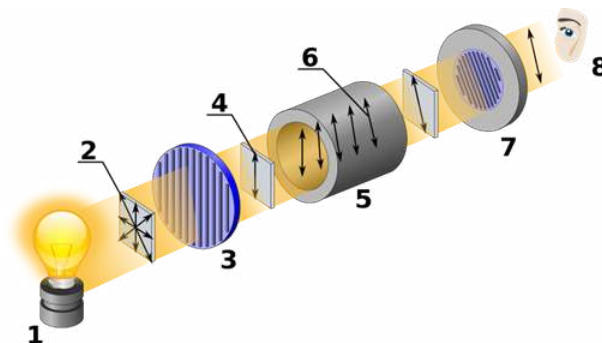


Figure 3.6.2: Illustration of the operating principle of a polarimeter: 1. light source, 2. unpolarized light, 3. Polarizer, 4. Plane polarized light, 5. the tube containing sample solution, 6. rotation of the plane of the polarized light, 7. Rotatable analyzer, 8. Detector. (Copyright; Kaidor, CC BY-SA 3.0, via Wikimedia Commons)

he angle or rotation (α) is called **observed rotation**. The observed rotation depends on the concentration of the sample (c), the path length of the light through the sample (l), the wavelength (λ) of the light used, and the temperature (T).

Specific rotation $[\alpha]$

When the concentration is fixed to 1 g/mL (or density of the pure sample in g/mL) and path length to 1 dm, the observed rotation is called **specific rotation** $[\alpha]$.

Usually, the wavelength (λ) is the sodium D line 589 nm and the temperature (T) is room temperature, which are shown as subscript and superscript: $[\alpha]_{\lambda}^T$. The following formula relates these parameters.

$$[\alpha]_{\lambda}^T = \frac{\alpha(\text{in degree})}{l(\text{in dm})} \times c(\text{in } \frac{\text{g}}{\text{mL}})$$

The specific rotation is a characteristic physical property of chiral compounds. If one enantiomer is dextrorotatory, the other is levorotatory to the same degree, as shown in the examples in Figure 3.6.3.

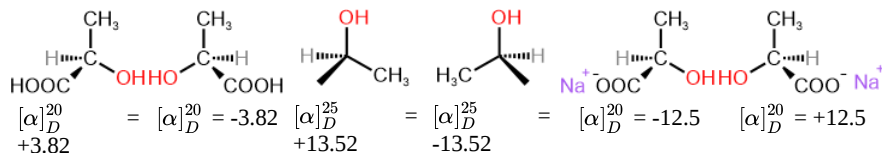


Figure 3.6.3: Examples of IUPAC names with R/S stereodescriptors, +/- descriptors for optical activity and specific rotations of some enantiomers (Copyright; Public domain).

S and R define the absolute configuration of the chirality center, and dextrorotatory (+) or levorotatory (-) is an experimental property of the compound. A compound with S configuration may be dextrorotatory (+) or levorotatory (-), the same for R configuration. For example, (S)-lactic acid is dextrorotatory (+), and its salt (S)-sodium lactate is levorotatory (-), as shown in Figure 3.6.3. Similarly, it is essential to note that the specific rotation varies with temperature. For example, (S)-aspartic acid is levorotatory at 20 °C, but it is dextrorotatory at 100 °C.

✓ Example 3.6.1

A solution of 3.00 g of table sugar (sucrose) dissolved in 100 mL of water, when placed in a 10.0 cm sample tube, shows $\alpha = +1.99^\circ$ when the sodium D line is used at 20°. What is the specific rotation of sucrose?

Solution

Given: Concentration = $\frac{3.00 \text{ g}}{100 \text{ mL}} = 0.03 \frac{\text{g}}{\text{mL}}$, $\alpha = +1.99^\circ$, path length $l = 10 \text{ dm}$, $[\alpha]_\lambda^T = ?$

Calculations:

$$[\alpha]_\lambda^T = \frac{\alpha(^{\circ})}{l(\text{dm})} \times c\left(\frac{\text{g}}{\text{mL}}\right) = \frac{1.99^\circ}{10 \text{ dm}} \times 0.03 \frac{\text{g}}{\text{mL}} = +66.3$$

Enantiomeric excess

Enantiomers have equal specific rotation ($[\alpha]_\lambda^T$) but with opposite sign. Suppose *d*-isomer is 100%, its specific rotation is $[\alpha]_\lambda^T$. If *x* *l*-isomer is in a mixture, it will cancel the activity of an equal amount of *d*-isomer, leaving $(100 - 2x)\%$ **enantiomeric excess** (%*ee*) of *d*-isomer, which will show the specific rotation of the mixture. The **enantiomeric excess** (%*ee*) can be calculated by the following formula, provided *x* of *l*-isomer is less than 50%.

$$\%ee = (100 - 2x)\% = \frac{[\alpha]_\lambda^T (\text{mixture})}{[\alpha]_\lambda^T (\text{pure})} \times 100\%$$

,where *x*% is the enantiomer less than 50% and $[\alpha]_\lambda^T (\text{pure})$ is for the enantiomer more than 50% in the mixture. If the specific rotation of the mixture and the pure enantiomer are known, the above formula allows calculating the percentage composition of the mixture.

✎ Racemic mixture

Mixing enantiomers diminishes the optical activity until it reaches a 50:50 mixture of enantiomers, which is optically inactive and referred to as a **racemic mixture**.

✓ Example 3.6.1

(+)-butan-2-ol has $[\alpha]_D^{25} +13.52^\circ$. Suppose a mixture of + and - enantiomers of butan-2-ol shows specific rotation of $+10.0^\circ$, what is the enantiomeric excess of (+)-butan-2-ol, and what is the percentage composition of the mixture with respect to (+) and (-)butan-2-ol?

Solution

Given: $[\alpha]_{\lambda}^T ((+)\text{-butan-2-ol}) = +13.52^\circ$, $[\alpha]_{\lambda}^T (\text{mixture}) = +10.0^\circ$, enantiomeric excess of enantiomeric excess of (+)-butan-2-ol (%ee = ?, %(-)-butan-2-ol = ? %(+)-butan-2-ol = ?

Calculations:

$$\%ee = (100 - 2((-)\text{-butan-2-ol})\%) = \frac{[\alpha]_{\lambda}^T (\text{mixture})}{[\alpha]_{\lambda}^T (\text{pure } (+)\text{-butan-2-ol})} \times 100\% = \frac{10.0^\circ}{13.52^\circ} \times 100\% = 74.0\%$$

$$(100 - 2((-)\text{-butan-2-ol})\% = 74.0\% \implies (-)\text{-butan-2-ol})\% = \frac{74.0 - 100}{-2} = 13\%$$

$$(+)\text{-butan-2-ol})\% = (100\% - (-)\text{-butan-2-ol})\% = 100\% - 13\% = 87\%$$

3.6: Optical activity is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

- **3.3: Configurations** by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

3.7: Types of chiral molecules

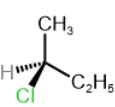
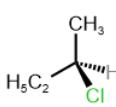
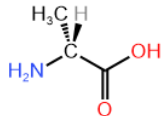
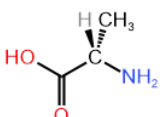
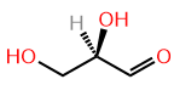
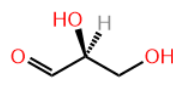
Often, an asymmetric carbon is the cause of molecular chirality. There are exceptions: i) some molecules have asymmetric carbons, yet they are achiral, ii) some molecules do not have any chirality center, yet they are chiral, iii) some chiral molecules have chirality centers that are atoms other than carbon. The molecules that are chiral due to the presence of an asymmetric carbon are described in the following. The exceptions are described in between where they are relevant or at the end of this section.

Chiral molecules containing one asymmetric carbon

Compounds containing one chiral center are chiral. They have a stereoisomer called an enantiomer, which is their non-superposable mirror image.

Enantiomers have the same physical and chemical properties, except when they react with or interact with other chiral things. Pure enantiomers have a characteristic specific rotation $[\alpha]_{\lambda}^T$ that has a + sign for dextrorotatory and an equal amount but a - sign for levorotatory enantiomer.

For example, hands and gloves are chiral objects. The right-hand glove fits on the right hand, and the left-hand glove fits on the left. Similarly, enantiomer molecules react equally, and when they are produced in a chemical reaction, they are made in equal amounts, except when one of the reagents is chiral. For example, enzymes are chiral reagents and usually react with one of the two enantiomers preferentially or exclusively or produce one of the two enantiomers preferentially or exclusively. Enantiomers of some chiral molecules containing one asymmetric carbon are shown below, along with their IUPAC names and physical properties, which are common for the enantiomer pair. Their differences when they interact with chiral entities are described later.

 (2S)-2-chlorobutane $[\alpha]_D^{20} = -12.9$	 (2R)-2-chlorobutane $[\alpha]_D^{20} = +12.9$	 (2R)-2-aminopropanoic acid (D-alanine) $[\alpha]_D^{20}$ (in water) = -2.8	 (2S)-2-aminopropanoic acid (L-alanine) $[\alpha]_D^{20}$ in water = +2.8	 (2R)-2,3-dihydroxypropanal (D-glyceraldehyde) $[\alpha]_D^{25} = +8.7$	 (2S)-2,3-dihydroxypropanal (L-glyceraldehyde) $[\alpha]_D^{25} = -8.7$
Density $0.873 \frac{g}{cm^3}$, mp -140 °C, bp 70 °C		Density $1.424 \frac{g}{cm^3}$, mp 258 °C, bp 415 °C sublime		Density $1.455 \frac{g}{cm^3}$, mp 145 °C, bp 228 °C	

Chiral molecules containing more than one asymmetric carbon

A chirality center has two configurations. Therefore, a molecule having one chirality center has two stereoisomers which are enantiomers of each other. If there are more than one chirality centers, each one can have two possible configurations, resulting in 2^n possible stereoisomers, where n is the number of chiral centers. For example, glyceraldehyde has one chiral center and ($2^1 = 2$) two stereoisomers: D-glyceraldehyde and L-glyceraldehyde, as shown in the previous table. Glyceraldehyde is a monosaccharide, i.e., a type of sugar. Erythrose is another monosaccharide that has two chirality centers and ($2^2 = 4$) four stereoisomers, as shown in Figure 3.7.1.

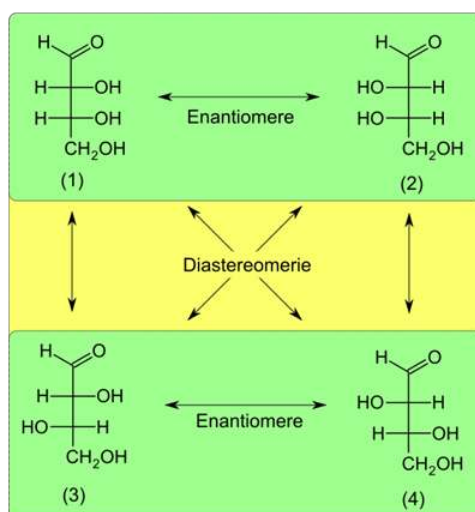


Figure 3.7.1: Illustration of enantiomer and diastereomer relationship among stereoisomers: **(1)** D-erythrose, **(2)** L-erythrose, **(3)** L-threose, and **(4)** D-threose. (Copyright; Roland.chem, CC0, via Wikimedia Commons)

Each chiral compound can have one enantiomer. D-erythrose and L-erythrose are enantiomers, and the other two, i.e., D-threose and L-threose are diastereomers to them. Similarly, D-threose and L-threose are enantiomers of each other and D-erythrose and L-erythrose are their diastereomers, as illustrated in Figure 3.7.1.

Diastereomers

Stereoisomers that are not enantiomers are **diastereomers** of each other.

D-Ribose is another monosaccharide found in DNA, that has four chirality center and ($2^3 = 8$) possible stereoisomers, shown in Figure 3.7.2. Each has one enantiomer and six diastereomers. For example, L-ribose is an enantiomer of D-ribose and the other six are their diastereomers.

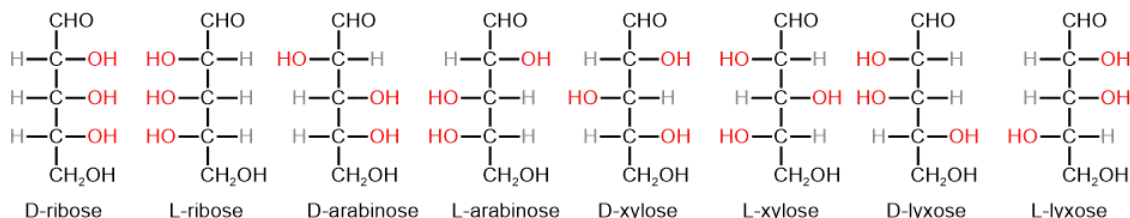


Figure 3.7.2: An example of three chirality center and ($2^3 = 8$) stereoisomers, each has one enantiomer and six diastereomers (Copyright; Public domain).

D/L stereodescriptors

D/L Stereodescriptors pre-date R/S stereodescriptors in IUPAC nomenclature, but they are still commonly used in biochemistry for naming monosaccharides, which are monomers of carbohydrates, and α -amino acids, which are monomers of proteins. D/L are designated by relating to the Fischer projection of glyceraldehyde drawing by placing aldehyde —CHO on the top of the vertical line. If the —OH of the penultimate C, i.e., second from the bottom end, is pointing towards right, it is designated dexter (D), which in Latin means left; and if it is pointing towards left, it is designate laevus (L) meaning left, as shown in Figure 3.7.3. For other monosaccharides having more than one chirality centers, D/L defines the configuration of penultimate C. The configuration of the rest of the chirality centers is implicit in the name, e.g., D-ribose and its isomers shown in Figure 3.7.2. All naturally occurring monosaccharides have D-configuration.

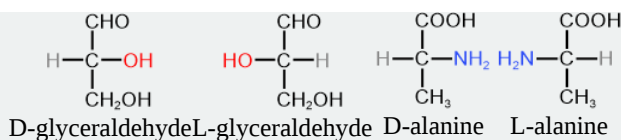


Figure 3.7.3: Examples of D/L stereodescriptors assignments by relating to the configuration of D-glyceraldehyde (Copyright; public).

In α -amino acids, α carbon bears $-\text{COOH}$ and $-\text{NH}_2$ groups. In a Fischer projection, $-\text{COOH}$ is placed on the top of vertical line and if $-\text{NH}_2$ is pointing towards right, it is designated D and if pointing towards left, it is designated L, as shown in Figure 3.7.3. All amino acids present in proteins have L-configuration.

The formula 2^n tells the maximum possible number of stereoisomers of compounds having n chiral centers. The actual number may be less than the maximum. For example, tartaric acid has two chiral centers and only three stereoisomers: (+) tartaric acid and (-) tartaric acid, which are enantiomers, and meso-tartaric acid, which is achiral, as illustrated in Figure 3.7.4. The third isomer is achiral because it has a symmetry plane that divides it into two equal halves, which are mirror images of each other. Figure 3.7.5 and Figure 3.7.6 are interactive modules of tartaric acid provided as exercises to verify that the enantiomers are nonsuperposable and the meso isomer has a superposable mirror image.

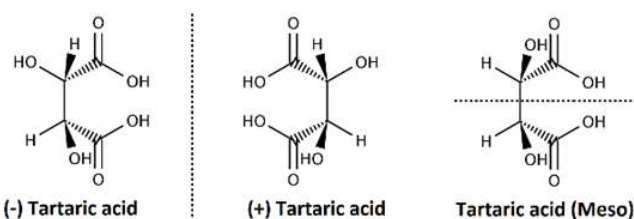


Figure 3.7.4: Illustration of enantiomers of tartaric acid: (2S,3S)-2,3-dihydroxybutandioic acid is (-)-tartaric acid; (2R,3R)-2,3-dihydroxybutandioic acid ((+) tartaric acid; and their achiral (meso) stereoisomer (2R,3S)-2,3-dihydroxybutandioic acid. The dotted line represents a mirror plane between enantiomers and the mirror plane, i.e., the symmetry plane in the meso isomer. (Copyright; Public domain)

(2S,3S)-2,3-dihydroxybutandioic acid

(2R,3R)-2,3-dihydroxybutandioic acid

Figure 3.7.5: Interactive models of enantiomers of tartaric acid for exercise: rotate them in different ways to verify they are nonsuppressible mirror images of each other (Copyright; Public domain).

(2R,3S)-2,3-dihydroxybutandioic acid

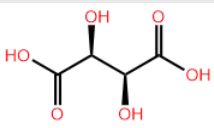
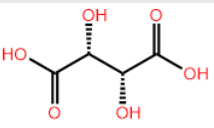
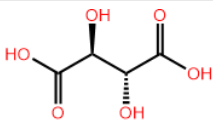
(2R,3S)-2,3-dihydroxybutandioic acid

Figure 3.7.6: Interactive models of meso isomer of tartaric acid for exercise: They are identical (superposable), but rotate one of them horizontally 180° to verify it becomes mirror image of the other (Copyright; Public domain).

Meso compound

A meso compound is i) an achiral compound with two or more chiral centers, ii) optically inactive, and iii) has a plane of symmetry that divides it into two mirror-image halves.

Enantiomers have the same physical and chemical properties, except when interacting with chiral objects, chiral reagents, or chiral plane polarized light, where they exhibit different properties. Diastereomers have different physical and chemical properties, as shown in the table below for stereoisomers of tartaric acid: enantiomers (2S,3S)-2,3-dihydroxybutandioic acid and (2R,3R)-2,3-dihydroxybutandioic acid and their diastereomer (2R,3S)-2,3-dihydroxybutandioic acid.

Stereoisomer			
$[\alpha]_D^{25}$	-12.0	+12.0	0
IUPAC Name	(2S,3S)-2,3-dihydroxybutandioic acid	(2R,3R)-2,3-dihydroxybutandioic acid	(2R,3S)-2,3-dihydroxybutandioic acid
Density ($\frac{g}{cm^3}$)	1.73	1.73	1.886
Melting point ($^{\circ}C$)	169-172	169-172	165-166
Solubility in water ($\frac{g}{ml}$) at 25 $^{\circ}C$	1.33	1.33	1.25
pK_{a1} (it represent acidity)	2.89	2.89	3.22
pK_{a2} (it represent acidity)	4.40	4.40	4.45

Disubstituted cycloalkanes usually have two chiral centers and can have four ($2^2 = 4$) stereoisomers, i.e., two pairs of enantiomers. If two substituents are different, usually all stereoisomers are observed. For example, 1-chloro-2-methylcyclohexane has four stereoisomers shown in Figure 3.7.7, where the first two are *trans* enantiomers and the second two are *cis* enantiomers, which are diastereomers of the first two.

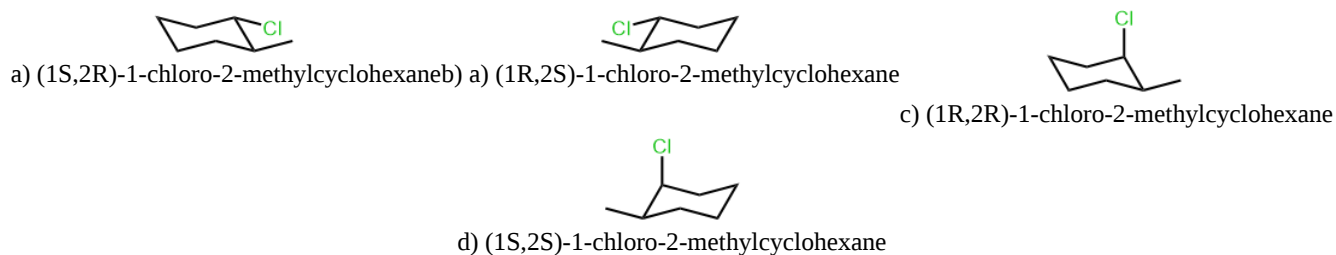


Figure 3.7.7: Four stereoisomers of 1-chloro-2-methylcyclohexane: a) and b) are *trans* enantiomer pair and c) and d) are *cis* enantiomer pair, which are diastereomers of a) and b) (Copyright; Public domain).

If two substituents in disubstituted cycloalkanes are identical, they usually have three stereoisomers: a pair of enantiomers and a meso form, as illustrated in Figure 3.7.8 with the example of 1,2-dimethylcyclohexane.

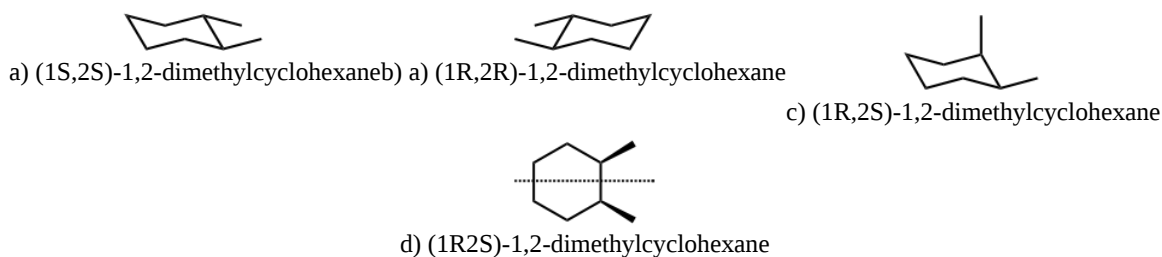


Figure 3.7.8: Three stereoisomers of 1,2-dimethylcyclohexane: a) and b) are *trans* enantiomer pairs, and c) is *meso* form, which is a *cis* isomer and diastereomer of a) and b), and d) is the most symmetric planer conformation of the *meso* isomer showing the plane of symmetry as dotted line (Copyright; Public domain).

 Caution

The enantiomers of *trans* and *cis* conformations, Figure 3.7.7 and *trans* conformation in Figure 3.7.8, may appear identical by flipping the molecule horizontally. It is not so because flipping converts the bonds pointing away from the viewer behind the page to pointing towards the viewer above the page. It is suggested to use the Interactive 3D model of enantiomers of *trans*-1,2-dimethylcyclohexane presented below to verify that they are nonsuperposable.

GLmol

(1S,2S)-1,2-dimethylcyclohexane

GLmol

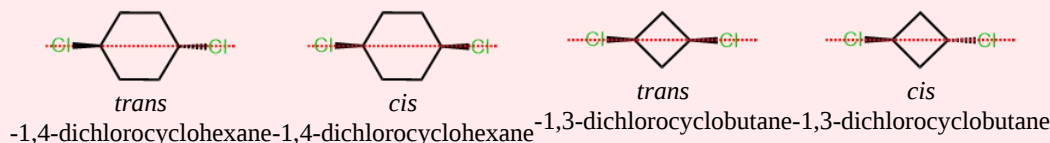
(1R,2R)-1,2-dimethylcyclohexane

📌 Finding symmetry plane in meso isomers

The symmetry plane is not evident in every conformation. It becomes obvious when the most symmetric conformation is drawn. For example, eclipsed conformation of meso tartaric acid in which every group on one stereogenic C is eclipsing the same group on the second stereogenic C is the most symmetric conformation, showing symmetry plane as in Figure 3.7.4. The most symmetric conformation of cycloalkanes is their planar conformation. For example, Figure 3.7.8 d) is the most symmetric conformation of the meso form of 1,2-dimethylcyclohexane, showing the symmetric plane as a dotted line in it.

🚫 Caution

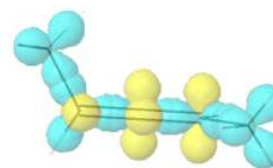
1,2-Disubstituted cyclohexanes that have an even number of atoms in the ring and identical substituents across the ring are achiral and do not have any chirality center. The plan of symmetry passes through the substituents, as observed in the examples shown below, which are presented in their most symmetric planar conformations. The *cis* and *trans* isomers, which are diastereomers, still exist.



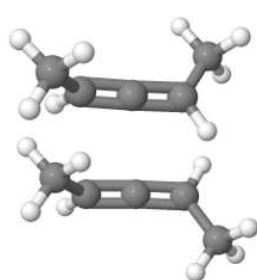
Chiral compounds without achirality center

Chiral allenes

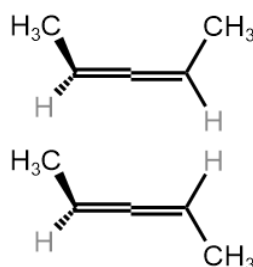
Allenes are conjugated alkenes that have an sp -C in the middle making a π -bond to an sp^2 -C on one side and a second π -bond to an sp^2 -C on the other side. Since the two p -orbitals of sp -C are perpendicular to each other, the two π -bonds are perpendicular to each other. Similarly, the two substituents on one sp^2 -C are in a V shape, perpendicular to the two substituents in a V shape on the other sp^2 -C, as illustrated Figure 3.7.9. If two substituents on each sp^2 -C are different, e.g., a and b on one and a' and b' (a & a' can be the same, and b and b' can be the same), the molecule is chiral. For example, penta-2,3-diene, shown in Figure 3.7.9, is a chiral molecule without any chirality center.



Hybrid atomic orbitals



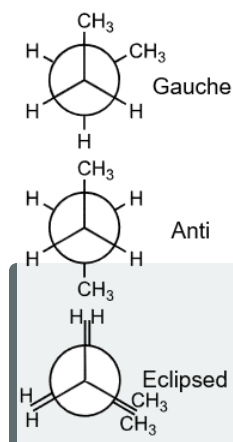
Models of enantiomers



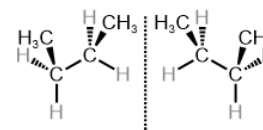
Perspective drawings of enantiomers

Figure 3.7.9: Penta-2,3-diene: interactive model (left); model showing p orbitals (yellow), sp^2 & sp^3 (blue); models of enantiomers, and perspective drawings of enantiomers (Copyright; Public domain).

Chiral conformations



Achiral molecules may have chiral conformers. For example, butane has gauche, anti, and eclipsed conformers, as shown on the right margin. The anti and eclipsed are achiral because they possess a plane of symmetry. Still, the gauche is chiral, lacking any plane or point of symmetry. Enantiomers of gauche conformers of butane are illustrated in the figure on the right margin. The gauche enantiomers are practically not separable due to rapid inversion through free rotation around single bonds.



The separation of enantiomers from their mixture is called the **resolution** of enantiomers. Molecules that have chiral conformations or structures, but their enantiomers can not be resolved, are considered achiral.

For example, butane is achiral, having two gauche conformers, which are enantiomers, but they cannot be resolved.

Atropisomers

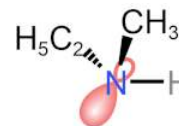
In some molecules, the chiral conformers are locked due to severely restricted rotation around the single bond. The rotation is usually restricted because the geometry and size of the substituents (steric factors) prevent rotation.

The molecules in which chiral conformations are locked due to restricted rotation around single bonds, and as a result, the enantiomers can be resolved, are chiral, and the enantiomers are known as **atropisomers**.

For example, ([1,1'-Binaphthalene]-2,2'-diyl)bis(diphenylphosphane), commonly known as BINAP, exhibits atropisomerism due to restricted rotation around the single bond between naphthyl groups as shown in the figure on the right margin (copyright: Public domain). It is an example of a chiral compound without a chirality center in it. Its atropisomers, (*R*)-BINAP and (*S*)-BINAP, are resolved and used as ligands to synthesize chiral catalysts, which, in turn, are employed for some enantioselective organic syntheses. 2,2'-Dibromo-6,6'-diiodo-1,1'-biphenyl, shown in the left margin (copyright: public domain), is another example that exhibits atropisomerism.

N, P, and S Chirality centers

Tetrahedral N, P, and S are common in organic compounds and can be chiral centers. N in amines is tetrahedral with a lone pair and three other substituents. According to CIP sequence rules, a lone pair is a substituent of the lowest priority. If the other three substituents on the amine nitrogen are different, it is a chirality center. For example, N in ethyl methyl amine is a chirality center, but its (*R*) and (*S*) configurations rapidly interconvert at room temperature, as shown in the simulation on the right margin (Copyright: Public domain).



- This process of lone pair of N in an sp^3 orbital changing to a sp^2 transition state with lone pair in a p orbital and then to sp^3 orbital in an inverted configuration is called **nitrogen inversion** or **pyramidal inversion**.
- Since the enantiomers of amines with a N chirality center are not resolvable, they are considered achiral molecules.

Quaternary ammonium compounds having four different substituents are chiral. For example, the enantiomers of the quaternary ammonium salt, shown in Figure 3.7.10, have been synthesized and resolved. Since there is no lone pair on N of quaternary ammonium compounds, there is no inversion of configuration.

Phosphines are similar to amines with P in the place of N. If three substituents of phosphine are different, it is a chiral center. It undergoes inversion like amines, but it is slower, taking a few hours. Therefore, phosphines with three different substituents are chiral molecules. For example, the enantiomers of chiral methylpropylphenylphosphine, shown in Figure 3.7.10, have been resolved.

The sulfur atom in sulfoxides, sulfones, and sulfates is tetrahedral and chiral if the substituents on the S are all different. The configuration S chirality center is relatively stable up to several days, and the enantiomers can be resolved, making these compounds chiral. A well-known example is coenzyme S-adenosyl methionine, a methylating agent involved in numerous metabolic pathways. S in S-adenosyl methionine has (*S*) configuration, as shown in Figure 3.7.10.

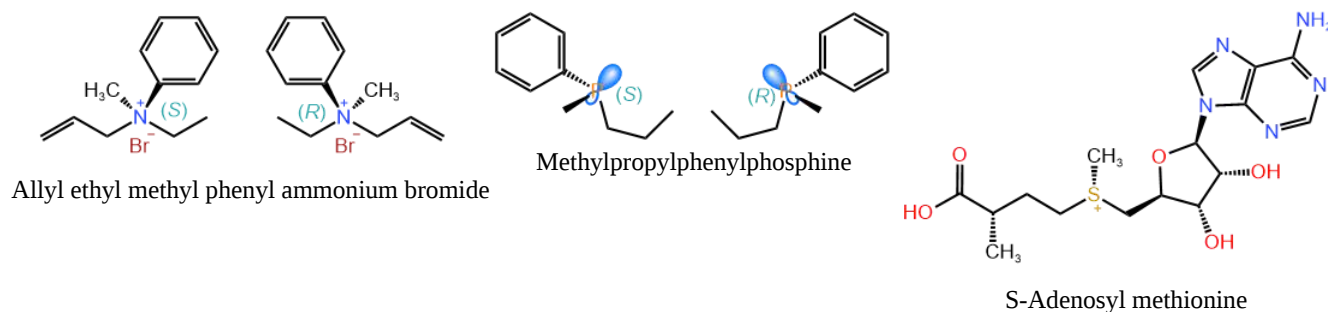


Figure 3.7.10: Examples of chiral compounds containing N, P, and S Chirality centers (Copyright; Public domain).

E/Z Stereodescriptors for double bond systems

R/S stereodescriptors define the configuration of chiral centers. In the case of polysubstituted cycloalkanes, *cis/trans* stereodescriptors are used to indicate the relative orientation of two substituents on the same side (*cis*) or the opposite sides (*trans*); but have been replaced with R/S stereodescriptors in IUPAC nomenclature. However, *cis/trans* isomers of alkene and related double bond systems do not have chirality centers. The two stereogenic centers of alkenes usually have one $-H$ and another substituent. *Cis/trans* usually refers to the relationship of substituents other than $-H$. It becomes confusing when both substituents are other than $-H$. For example, if the structure shown on the right margin is named *cis*-2-chlorobut-2-ene, it is not clear $-Cl$ on one and $-CH_3$ on the other stereogenic carbons are *cis* or $-CH_3$ on one and $-CH_3$ on the other are *cis*. To avoid this confusion, IUPAC has replaced *cis/trans* with *E/Z* stereodescriptors for double-bond systems, such as alkenes.

The following steps assign E or Z to the diastereomers of the double bond system.

1. Assign priorities 1 and 2 to the two substituents of one stereogenic center using CIP priority, where 1 is higher priority and 2 is lower.
2. Do the same to the second stereogenic center.
3. If the two high-priority (#1) substituents on the two stereogenic centers are on the same side, assign *zusammen* (Z), which means together (*cis*) in German; otherwise, assign *entgegen* (E), which in German means opposite (*trans*). The *E/Z* capital, italicized, preceded by its locant, placed in brackets before the name, and separated by a hyphen from the name.
 - o If there is more than one double bond systems, the corresponding E and/or Z are preceded by the locant number and separated by a comma.

Figure 3.7.9 provides examples of the applications of the above rules.

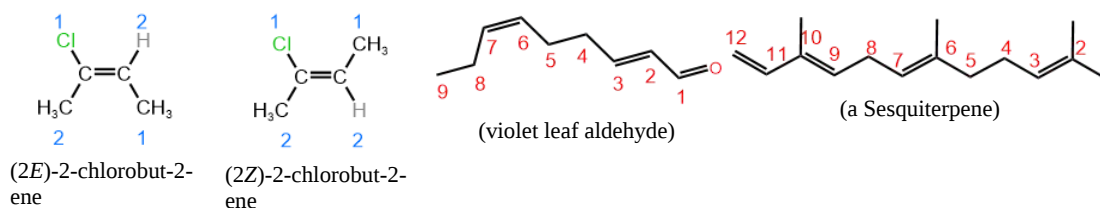


Figure 3.7.9: Examples of E/Z assignments. The numbers in blue in the first two examples are the priority order 1 and 2 of the substituents, and the numbers in red in the last two examples are the numbers of the parent chain in the IUPAC nomenclature (Copyright; Public domain).

3.7: Types of chiral molecules is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

- **3.3: Configurations** by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

3.8: Chirality related topics

Chirality in nature

A large number of compounds in living things are chiral. For example, amino acids, which are the building blocks of proteins and carbohydrates, are chiral. Macromolecules, such as proteins and nucleic acids, are also chiral. Chirality is also observed on a macro-scale, e.g., our hands, feet, and ears are chiral. Similarly, horns and spots in deer, as shown in Figure 3.8.1.



Stereospecific reactions in living things

Chiral objects have the same physical properties except when they interact with another chiral object, where the interaction is enantiomorph-selective. For example, an achiral tennis ball fits equally in the right-hand and left-hand gloves, but a chiral left-hand glove fits only on the left hand, and a right-hand glove fits only on the right hand. Similarly, chemical reactions of enantiomers are the same with achiral reagents, but stereospecific with chiral reagents.

Most chemical reactions in living organisms are **stereospecific**, meaning that one stereoisomer selectively reacts and one is selectively produced.

For example, the human digestion enzyme chymotrypsin has 268 chiral centers and 2^{268} possible stereoisomers, but only one isomer is produced in the human body. The enzyme-catalyzed reactions are often stereospecific because their binding sites are chiral, and only one enantiomer fits in them nicely for the reaction, as illustrated in Figure 3.8.1.



L-alanine matches with the enzyme, fits on it, and reacts, but R-alanine does not match, and is repelled without reacting.

Figure 3.8.1: Illustration of three point interaction model: a) L-alanine having an anion COO^- on one substituent, cation NH_3^+ on second, and hydrophobic CH_3 on the third substituent, matching the geometric, size, and charge/hydrophobicity, of the corresponding sites on a hypothetical enzyme model, allowing selective binding and reaction; b) R-alanine have the identical three substituents but oriented different resulting in repulsive, instead of attractive interaction, not allowing it to retain and react. (Copyright; Public domain)

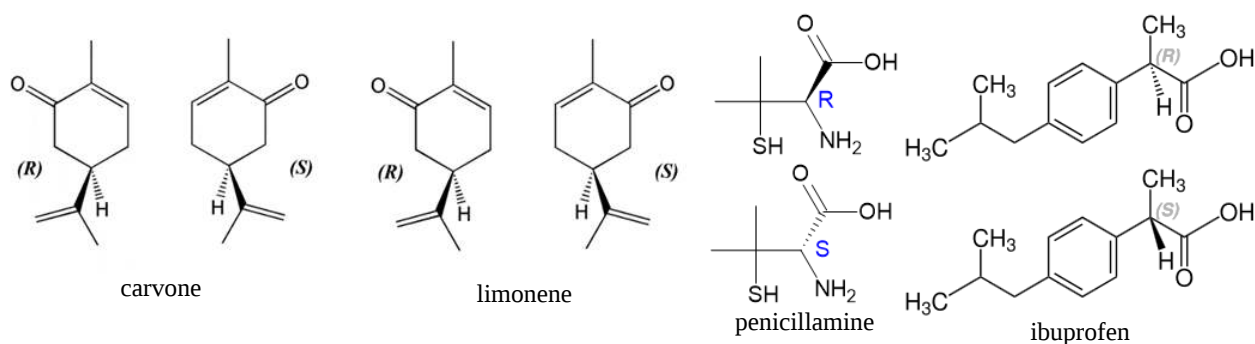
📌 Three-point Interaction model

According to the three-point interaction model, three substituents on a chiral center typically have the proper geometry, size, and polarity to match the corresponding three spaces in the reactive site of the enzyme. This matching allows one enantiomer to bind selectively on the enzyme surface and undergo a stereoselective reaction, as illustrated in Figure 3.8.1. The three-point interaction model usually explains enantiomer selectivity of biochemical reactions mediated by chiral enzyme catalysts.

Chirality manifests not only in enantioselective reactions but also in various other biological activities, such as taste, flavor, odor, and drug action, as their receptors possess chiral binding sites. Examples, illustrated in the figure below, include:

- L-aspartame tastes sweet and is used as an artificial sweetener, but D-aspartame is tasteless,
- R(-)-carvone smells like spearmint, and S(+)-carvone smells like caraway,

- R-(+)-limonene smells like orange and lemon, and S-(-)-limonene smells like a spruce tree,
- (S)-penicillamine has antiarthritic activity, and (R)-penicillamine is toxic, and
- S-ibuprofen has anti-inflammatory action, and R-ibuprofen is inactive.



Prochirality

When an achiral object interacts with a chiral object, there is usually no differentiation between the enantiomorphs. For example, a chiral plane tennis ball fits in the left hand and the right hand the same. However, some objects, like a cup of coffee, do differentiate between the enantiomorphs. For example, the coffee cup shown in Figure 3.8.2 a) is positioned to fit in the right hand. If a person holds it with the right hand, takes a sip, and leaves a lip mark on it, it becomes a chiral object shown in Figure 3.8.2 c). The coffee cup shown in Figure 3.8.2 b) is positioned to fit in the left hand. If the same person holds it with the left hand, takes a sip, and leaves a lip mark on it, it becomes a chiral object shown in Figure 3.8.2 d), which is an enantiomorph of c).

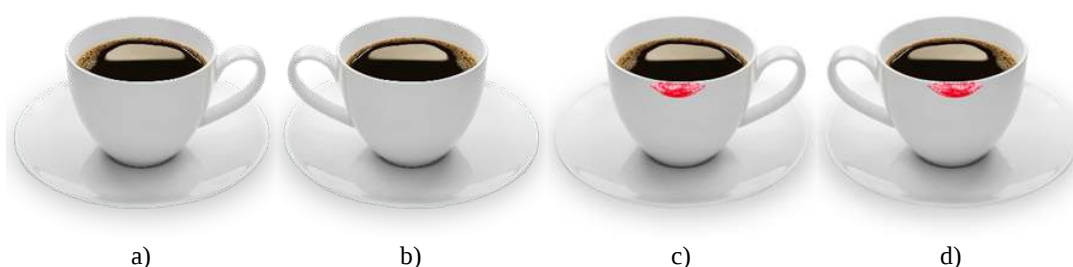


Figure 3.8.2: Illustration of difference in the interaction of an achiral object (a cup of coffee) with enantiomers of a chiral object (hands); holding a cup of coffee with left or right hand, taking a sip, and leaving a lip make on it, converts it into enantiomorphs (Copyright: Public domain).

Symmetry of achiral objects that interact differently with enantiomers, like a cup of coffee with left and right hands, is broken with one change that converts them into chiral objects, as illustrated in Figure 3.8.2.

The same is true for molecules. For example, an sp^2 -C with three different substituents becomes chiral with one addition, as shown in Figure 3.8.3 a) and an sp^3 -C with two same and two different substituents becomes chiral with substitution of one of the two same substituents, as shown in Figure 3.8.3 b).

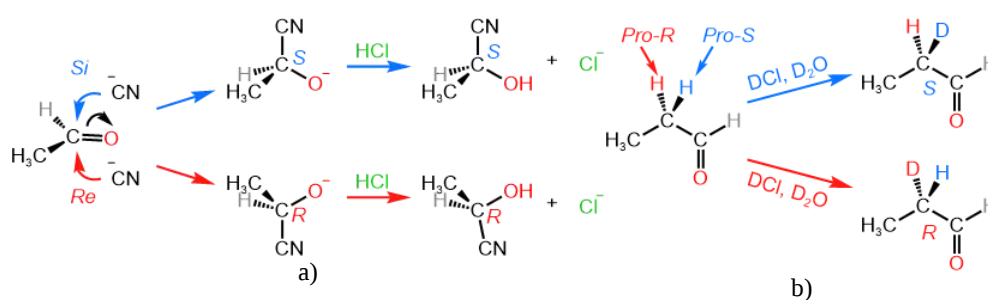


Figure 3.8.3: Examples of prochiral molecules: a) a prochiral molecule having an sp^2 -C with three different substituents and *Re/Si* phases, b) a prochiral molecule having an sp^3 -C and *pro-R/pro-S* substituents (Copyright: Public domain).

Prochirality and prochiral

Prochirality is the geometric property of an achiral object or molecule that is capable of becoming chiral in a single desymmetrization step. A **prochiral** molecule is an achiral molecule that becomes chiral after a single-step reaction, e.g., by addition or by substitution of a single group on it.

For example, the property of a plane cup of coffee to become chiral by making a mark on it, as shown in Figure 3.8.2, is prochirality. Figure 3.8.3 shows examples of prochiral molecules that become chiral by an addition or a substitution step.

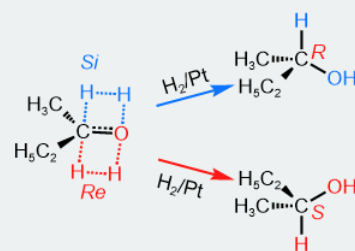
Re/Si phases

A prochiral molecule that has an sp^2 -atom with three different substituents is trigonal planar with two phases: a *Re* and a *Si* phase. The following steps assign $\blacktriangledown$ *Re/Si*-stereodescriptor to a prochiral phase.

1. Assign priority 1, 2, and 3 (1 is the highest and 3 is the lowest priority) to the three substituents by CIP sequence rules, then
2. draw a circular arrow from 1 to 2 to 3.
 - If the arrow is clockwise, the face you are looking at is *Re*-face.
 - If the arrow is counterclockwise, the face you are looking at is *Si*-face.

A simple method is the right-hand rule: curl the fingers of the right hand from 1 to 2, or from 2 to 3, or from 3 to 1; the thumb of the right hand points to *Re*-face, and the opposite to it is *Si*-face. For example, in CH_3COH shown in Figure 3.8.3 a), the priority#1 is $=\text{O}$, #2 is $-\text{CH}_3$, and #3 is $-\text{H}$. *Re*-face is the bottom, and *Si*-face is at the top.

Addition of a substituent from *Re*-face produces a chiral molecule, and addition of the same substituent from *Si*-face produces its enantiomer, as shown in Figure 3.8.3 a). An addition to a *Re*-face doesn't necessarily create a chirality center with *R*-configuration; it can be *R* or *S*, depending on the priority order after the new substituent is added. For example, addition of ^-CN to the *Re*-face of the aldehyde in Figure 3.8.3 a) produces *R*-enantiomer, but addition of H to the *Re*-face of the ketone in the figure on the right margin produces *S*-enantiomer.



Pro-R/Pro-S substituents

A prochiral molecule that has an sp^3 -atom has two same and two different substituents. $\blacktriangledown$ The two identical substituents are prochiral: one is designated Pro-*R* and the other Pro-*S*. The following steps assign Pro-*R*/Pro-*S* stereodescriptors to the prochiral substituents.

1. Raise the priority of one of the identical substituents over the other, keeping their priority order the same relative to the two different substituents. For example, if the two identical substituents are $\text{H}'\text{s}$, replace one with a higher priority deuterium D isotope.
2. Assign *R/S*-stereodescriptor to the new chirality center created by the previous step.
 - If the configuration of the new chirality center is *R*, the substituent that got the priority raised over the other is pro-*R*, and the other is pro-*S*.
 - If the configuration of the new chirality center is *S*, the substituent that has had its priority raised is pro-*S*, and the other is pro-*R*.

Figure 3.8.3 b) is an applied example of the above rules, where two $\text{H}'\text{s}$ are the same substituents. Replacing $\blacktriangledown$ Pro-*R* $-\text{H}$ with D makes a *R*-enantiomer and Replacing $\blacktriangledown$ Pro-*S* $-\text{H}$ with D makes a *S*-enantiomer.

Recognition of prochirality by chiral reagents

Chiral reagents, like chiral enzymes, recognize prochirality and interact with the prochiral parts, i.e., *Re/Si* phases and Pro-*R*/Pro-*S* substituents, differently. Consequently, the reactions of prochiral molecules catalyzed by chiral enzymes are stereoselective, i.e., one stereoisomer is produced either exclusively or in preference over the other. This can be explained by the three-point interaction model described in the previous section. Suppose ethanal CH_3CHO shown in Figure 3.8.3 (left) arrives with *Re*-phase facing a

hypothetical chiral enzyme that has a reactive site of size, shape, and intermolecular interactions suitable to hold the Re-phase. The aldehyde will be held in the active site and react from the *Si*-phase. Since the product is a different shape, it is released, refreshing the active site for the next cycle of reaction. If the aldehyde arrives with *Si*-phase facing the catalyst, it will not fit in the active site and will bounce off without reacting, as illustrated in Figure 3.8.4 (right).



Figure 3.8.4: Simulation of prochiral phase recognition of ethanal by a hypothetical active site of an enzyme, substrate adsorbs from the *Re*-phase, reacts, and releases the product (left), but *Si*-phase does not fit on the active site, is not retained, bouncing off without reacting (right) (Copyright; Public domain).

Similarly, if the prochiral substrate has sp^3 -atom having two same and two different substituents, the two different substituents and either the pro-*R* or the pro-*S* substituent will fit on the active site, allowing selective production of one enantiomer.

Resolution of enantiomers

Chiral compounds synthesized in living things are usually pure enantiomers, but those synthesized in the laboratory are usually a 50:50 mixture of the two enantiomers.

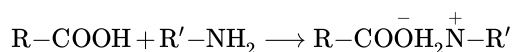
A 50:50 mixture of two enantiomers is an optically inactive racemic mixture. The experimental process of separating the enantiomers from a mixture is called the **resolution of the enantiomers**.

The discovery of molecular chirality is associated with the recrystallization of racemic potassium ammonium tartarate salt. Louis Pasteur carried out the recrystallization and noticed that there were two types of crystals, which were mirror images of each other. He separated the crystals by hand-picking using tweezers, dissolved them separately in water, and found that one was dextrorotatory and the other was levorotatory. He concluded from this observation that the molecules constituting the two types of crystals were also asymmetric, i.e., enantiomers.

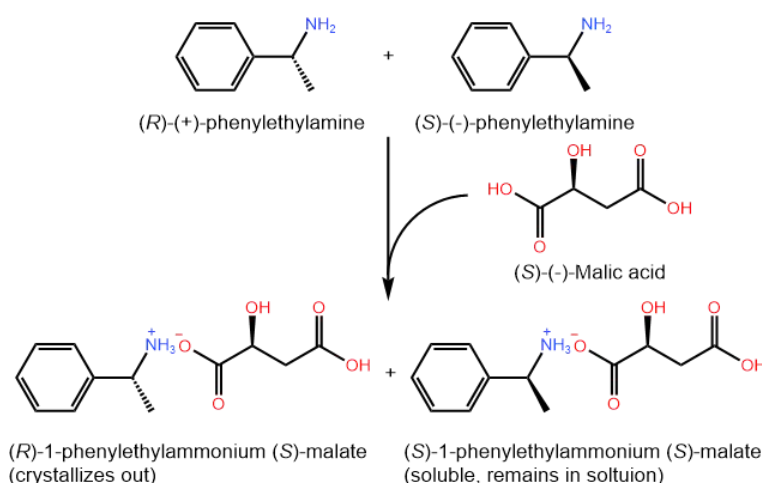
Recrystallization is one of the methods for resolving enantiomers, but it works only in a few cases. Since the enantiomers have the same physical and chemical properties, except when interacting with another chiral reagent, the resolution process usually involves a chiral reagent, called a resolving agent.

Resolution by forming diastereomer salts

Most of the organic compounds are either acidic, e.g., those with carboxylic acid $-\text{COOH}$ groups, or basic, e.g., those with amine $-\text{NH}_2$ groups. Acids neutralize bases by forming salts, e.g., a carboxylic acid neutralizes an amine, forming ammonium carboxylate salt, as shown in the following general reaction.

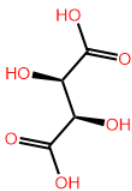
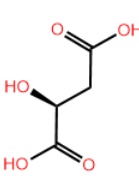
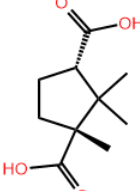
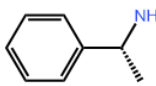
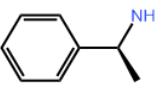


If there is a racemic mixture of a carboxylic acid, it will make a diastereomer salt by neutralization with a pure enantiomer of an amine resolving agent. Similarly, if there is a racemic mixture of an amine, it will make a diastereomer salt by neutralization with a pure enantiomer of an acid resolving agent. The diastereomeric salts have different physical properties



that allow their separation. For example, suppose there is a racemic mixture of 1-phenylethylamine. It can react with (S)-(-)-malic acid forming diastereomer salt: (R)-1-phenylethylammonium (S)-malate, which is less soluble and crystalize out, and (S)-1-phenylethylammonium (S)-malate, which is more soluble and stays in the solution, as illustrated in the figure on the right margin. Filtration can separate the diastereomer salts, then the enantiomers of 1-phenylethylamine can be regenerated by adding HCl solution. (S)-(-)-malic acid is a resolving agent in this example.

Common resolving agents include (+)-tartaric acid, (-)-malic acid, (+)-camphoric acid, (+)-phenylethylamine, (-)-phenylethylamine, etc., as shown blow.

				
(2R,3R)-(+)-tartaric acid	(S)-(-)-malic acid	(1R,3S)-(+)-camphoric acid	(R)-(+)-phenylethylamine	(S)-(-)-phenylethylamine

Enzymes are also used as resolving agents. For example, a racemic mixture of ethyl esters of naproxen forms crystals that are insoluble in water. The racemic mixture is treated with esterase enzyme in an alkaline solution. The enzyme hydrolysis of the S-ester and the product S-naproxen dissolves in water. R-ester remains insoluble, which is separated by filtration.

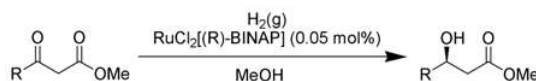
Resolution by chiral-chromatography

Chromatography is a separation technique in which a mixture is passed through a porous or beaded stationary phase by flowing a solvent through the medium. The compounds in the mixture that have a greater tendency to dissolve in the solvent and a lesser tendency to adsorb on the stationary phase travel with the solvent faster than the others. It results in the separation of the mixture, as illustrated in the figure on the right margin (Copyright: Modified from Beige, Public domain, via Wikimedia Commons).

In chiral chromatography, the solid phase is chiral or its surface is made chiral by chemical modification. The chiral-stationary phase interacts with the enantiomers in the mixture differently, resulting in their separation.

Enantioselective synthesis

No matter how efficient the resolution of an enantiomer is, it results in the waste of the unwanted enantiomer. Therefore, there is a growing trend of using enantioselective synthesis, i.e., synthesis involving chiral reagents or chiral catalysts that produce the desired enantiomer or the desired diastereomer either exclusively or in preference over the other stereoisomers. For example, β -ketones can be reduced by H_2 in the presence of a chiral catalyst, into chiral alcohols by enantioselective synthesis. The chiral catalyst is a complex of a pure enantiomer of chiral ligands, e.g., $RuCl_2[(R)-BINAP]$, where the chiral ligand is ([1,1'-Binaphthalene]-2,2'-diyl)bis(diphenylphosphane), commonly known as BINAP. The general reaction is the following.



3.8: Chirality related topics is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

- 3.3: Configurations by Muhammad Arif Malik is licensed [Public Domain](#).

CHAPTER OVERVIEW

4: Acids and bases

- 4.1: Importane of acids, bases and their reactions
- 4.2: Arrhenius Acids and Bases
- 4.3: Brønsted-Lowry Acids and Bases
- 4.4: Predicting the direction of acid-base reactions
- 4.5: Thermochemistry of acid-base reactions
- 4.6: Factors affecting the strength of an acid
- 4.7: Lewis acids and bases

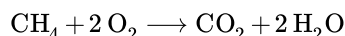
This page titled [4: Acids and bases](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).

4.1: Importance of acids, bases and their reactions

What is a chemical reaction?

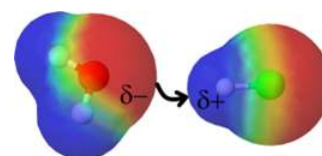
A chemical reaction is a process of rearrangement of atoms in a substance.

For example, the combustion of methane is a chemical reaction.



It involves making and/or breaking chemical bonds. There are a vast number of chemical reactions that are classified in several ways. Organic reactions are usually classified in three major categories based on the way the covalent bonds in them are made and broken. These include free radical reactions, polar reactions, and pericyclic reactions. In a free radical reaction, bonds are made and broken through homolytic bond making and breaking. Polar reactions involve heterolytic bond making and breaking. Pericyclic reactions are a class of organic reactions in which the reactants come together, making a cyclic transition state in which bonds are being formed in one part and broken in another, in a concerted fashion.

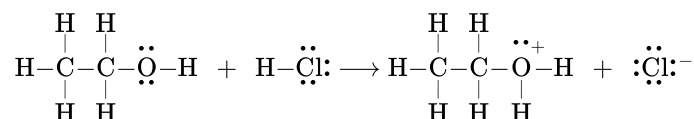
Free radical reactions are relatively less common because homolytic bond breaking requires energy, which is usually supplied in the form of thermal energy, as in the combustion process, or by absorption of a photon of electromagnetic radiation. Once formed, the free radicals are usually very reactive and often challenging to control due to their high reactivity. Pericyclic reactions are also less common due to geometry requirements, particularly the orbital symmetry needed for the overlapping orbitals, making new bonds. Polar reactions involve polar bonds, which are usually more prone to break because the bonding electrons are already unequally shared in them. The process is facilitated by electrostatic attraction between reactants, i.e., the $\delta+$ end of a polar bond, called an electrophile, needing electrons, attracts the $\delta-$ end of the other reactant, called a nucleophile that can donate electrons to make a new bond. For example, $\text{H}^{\delta+}$ of HCl is attracted to $\text{O}^{\delta-}$ of H_2O , as illustrated in the figure on the right margin. Therefore, polar bonds are part of functional groups, i.e., the reactive sites in organic molecules. Polar reactions are the most common and the most versatile class of organic chemical reactions.



Acid-base reactions

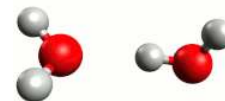
A proton exchange reaction is an **acid-base reaction**.

For example, the following reaction in which a proton is exchanged between HCl and the $-\text{OH}$ group of ethanol is an acid-base reaction.



Acid-base reactions are a subclass of polar reactions involving hydrogen polar bonds $\text{A}-\text{H}^{\delta+}$. Being electron deficient, $-\text{H}^{\delta+}$ tends to gain electrons from atoms of other molecules that may have electron-rich regions or lone pairs. Since H can make one bond, when it gains electrons, making a new bond, it breaks its previous bond, leaving electrons with the more electronegative atom. This proton exchange reaction is important in biochemistry because H is a primary constituent of organic compounds that make up living things and a primary constituent of H_2O , which is usually the reaction medium in living things.

Two aspects of a chemical reaction are important: i) kinetics, i.e., how fast the reaction happens, and ii) thermodynamics, i.e., how much energy is released or absorbed during the reaction per unit amount reacted. The rate of reaction is related to the energy barrier, called activation energy: the lower the activation energy, the faster the reaction. Kinetics is generally not considered for acid-base reactions because they are inherently fast. This is because H is the smallest atom that can penetrate tight spaces to reach the reactive site with little resistance compared to other atoms that face space restrictions, called steric strain. It is facilitated by high charge density due to high charge to volume ratio on H . For example, proton exchange between water molecules in an aqueous medium takes place as



illustrated in the simulation on the right margin (Copyright: Manuel Almagro Rivas, CC BY-SA 4.0, via Wikimedia Commons) at a rate of $1.3 \times 10^{11} M^{-1} s^{-1}$, which is among the fastest reactions known. Kinetics of acids and bases are usually not discussed as it is fast, but their thermodynamics is usually the focus of discussion. Thermodynamics is related to the relative potential energies of reactants and products, which determines the extent of proton donation, i.e., the ratio of products to reactants at equilibrium, and the free energy change

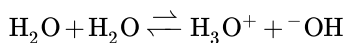
The importance of acid-base reactions lies in the fact that the reactivity of the sites donating and receiving a proton is significantly changed. For example, in the dissociation of water ($H_2O + H_2O \rightleftharpoons H_3O^+ + ^-OH$), products (H_3O^+ and ^-OH) are millions of times more reactive than the reactant H_2O . It is evident from the fact that, at equilibrium about two in a billion molecules exist in ionized form (H_3O^+ and ^-OH), still their rate of reaction (reverse reaction) is equal to forward reaction of neutral H_2O . The ability of the acid-base reactions to significantly change the reactivity of the reactive sites, along with their fast rates of reaction, makes them ideal for catalysis. This explains why most of the enzyme-catalyzed reactions are based on acid-base reactions. It also highlights the importance of acids, bases, and their reactions described in this chapter.

4.1: Importane of acids, bases and their reactions is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

4.2: Arrhenius Acids and Bases

Dissociation of water

Water H_2O is a covalent molecule, but ultra pure water has some electrical conductivity $\sim 0.055 \mu\text{S}/\text{cm}$. It is explained by a proton H^+ transfer between two water molecules by the following reaction.



Ionization of water by proton transfer between water molecules is called **self-ionization**, **autoionization**, or **dissociation** of water.

This is an equilibrium reaction in which concentrations of pure water H_2O is about 55.5 M and that of H_3O^+ and ^-OH are $\sim 10^{-7}$ M at $\sim 25^\circ\text{C}$, where M is molar concentration in $\frac{\text{mol}}{\text{L}}$. Equilibrium constant K_{eq} for the above reaction is the following.

$$K_{\text{eq}} = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{^-\text{OH}}}{a_{\text{H}_2\text{O}} \cdot a_{\text{H}_2\text{O}}}$$

, where a is the chemical activity of the species. The equilibrium constant for dissociation of water has a symbol K_w ; the chemical activities of pure solid and liquids is 1, i.e., $a_{\text{H}_2\text{O}} = 1$; and chemical activities of dilute species are equal to their molar concentrations written in square brackets, i.e., $a_{\text{H}_3\text{O}^+} \cdot a_{^-\text{OH}} = [\text{H}_3\text{O}^+][^-\text{OH}]$. Making these substitutions in the above equation results in the following equation for the dissociation of water.

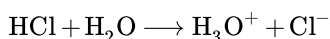
$$K_w = [\text{H}_3\text{O}^+][^-\text{OH}] = 10^{-14}$$

Arrhenius' definition of acids and bases

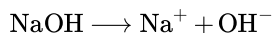
An **acid** is a substance that ionizes in water to form a proton H^+ . Since H^+ does not exist alone, it protonates water forming H_3O^+ and other hydrated cations. Therefore, an **acid** is a substance that increases H_3O^+ in aqueous solution.

A **base** is a substance that dissociates in water to form hydroxide ion ^-OH in water, i.e., a **base** increases the concentration of ^-OH in water.

In neutral water $[\text{H}_3\text{O}^+] = [^-\text{OH}] = 10^{-7}$ and their product is a constant, addition of an acid to water increases $[\text{H}_3\text{O}^+]$, causing a decrease in $[^-\text{OH}]$. For example, addition of 0.1 M HCl in water increases $[\text{H}_3\text{O}^+]$ to 0.1 M by the following reaction.



It causes a decrease in $[^-\text{OH}]$ to 10^{-13} M, keeping $[\text{H}_3\text{O}^+][^-\text{OH}] = 10^{-14}$. Addition of a base increases $[^-\text{OH}]$ causing a proportional decrease in $[\text{H}_3\text{O}^+]$. For example, addition of 1.0 M NaOH in water increases $[^-\text{OH}]$ to 1.0 M by the following reaction.



It causes a decrease in $[\text{H}_3\text{O}^+]$ to 10^{-14} M, keeping $[\text{H}_3\text{O}^+][^-\text{OH}] = 10^{-14}$.

The $[\text{H}_3\text{O}^+]$ is a measure of the acidity of water, and ^-OH is a measure of the basicity of the solution, and the following equation relates the two.

$$K_w = [\text{H}_3\text{O}^+][^-\text{OH}] = 10^{-14}$$

Since the values are powers of ten in negative numbers, take Log and change sign on both sides of the equation.

$$-\text{Log} K_w = -\text{Log} [\text{H}_3\text{O}^+] + -\text{Log} [^-\text{OH}] = -\text{Log} 10^{-14}$$

, where $-\text{Log} K_w = \text{p}K_w$; $-\text{Log} [\text{H}_3\text{O}^+] = \text{pH}$; $-\text{Log} [^-\text{OH}] = \text{pOH}$; and $-\text{Log} 10^{-14} = 14$ Making these substitutions in the above equation results in the following equation.

$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

- The pH, given by $\text{pH} = -\text{Log}_{10}[\text{H}_3\text{O}^+]$ is a measure of the acidity of the solution.
- pH Varies in the range of 0 to 14, where pH 7 is neutral, <7 is acidic, and >7 is basic.
- The lower the pH, the higher the $[\text{H}_3\text{O}^+]$, and the more acidic the solution.

Lower pH corresponds to higher $[\text{H}_3\text{O}^+]$ because $\text{Log}_{10}[\text{H}_3\text{O}^+]$ is multiplied by -1 in: $\text{pH} = -\text{Log}_{10}[\text{H}_3\text{O}^+]$, converting negative numbers into positive. For example, -14 is smaller than -7. Still, after multiplying both by -1, the trend is opposite.

Limitations of Arrhenius' definition of acids and bases

Arrhenius' definition covers acid-base reactions in aqueous medium, which is the primary reaction medium in living things and the environment, but acid-base reactions also occur in the gas phase and solvents other than water. Further, some substances behave as bases but do not have ^-OH in their formula, e.g., NH_3 . A broader definition of acids and bases is described next.

4.2: Arrhenius Acids and Bases is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

4.3: Brønsted-Lowry Acids and Bases

Brønsted-Lowry acid-base related terminology

Brønsted-Lowry defines acid-base reactions as proton-exchange reactions.

- A molecule or ion that donates a proton H^+ is an **acid**, and the one that accepts a proton is a **base**.
- The molecule or ion formed after donating a proton is a **conjugate base**, and the one formed after accepting a proton is a **conjugate acid**.
- Two molecules or ions related by the presence or absence of a proton are a **conjugate acid/base pair**.

For example, HCl in the following reaction is an acid, H_2O is a base, Cl^- is a conjugate base, and H_3O^+ is a conjugate acid.



HCl/Cl^- are a conjugate acid-base pair, and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ are the second conjugate acid-base pair in the above reaction. The reverse reaction is also an acid-base reaction between a conjugate acid and a conjugate base.

The Brønsted-Lowry definition includes the bases that accept a proton but do not have ^-OH ion in their formula. For example, H_2O acid and ammonia NH_3 base in the following reaction that does not have ^-OH ion in its formula.



$\text{H}_2\text{O}/^-\text{OH}$ are a conjugate acid-base pair, and $\text{NH}_4^+/\text{NH}_3$ are the second conjugate acid-base pair in the above reaction.

Note that H_2O acts as an acid when it reacts with NH_3 , but as a base when it reacts with HCl .

Amphoteric

Species that act both as acids and bases are called **amphoteric**. For example, H_2O , NH_3 , HCO_3^- , etc. are amphoteric. Their conjugate acid/base pair when acting as acids are: $\text{H}_2\text{O}/^-\text{OH}$, $\text{NH}_3/^-\text{NH}_2$, $\text{HCO}_3^-/\text{CO}_3^{2-}$, etc, and when acting as bases are: $\text{H}_2\text{O}/\text{H}_3\text{O}^+$, $\text{NH}_3/\text{NH}_4^+$, $\text{HCO}_3^-/\text{H}_2\text{CO}_3$, etc.

The Brønsted-Lowry definition eliminates the need for water as a solvent; the acid-base reaction can take place in any solvent or without a solvent. For example, the following acid-base reaction takes place in the gas phase between HCl acid and ammonia NH_3 base.



HCl/Cl^- are a conjugate acid-base pair, and $\text{NH}_4^+/\text{NH}_3$ are the second conjugate acid-base pair in the above reaction.

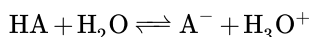
Strength of an acid and a base

- The **strength of an acid** is the ability to donate a proton to a base.
- The **strength of a base** is its ability to accept a proton.

Since the acid/base strength is relative to the counterpart, a reference is needed. Often H_2O is chosen as a reference because it is amphoteric, i.e., it can act as a base when reacting with a stronger acid and as an acid when reacting with a stronger base, and it is often the reaction medium, i.e., solvent. A solvent need not be written in the equilibrium expression because $\text{cea}_{\text{solvent}} = 1$.

Strength of an acid

The strength of an acid of general formula HA is usually measured as its ability to donate a proton to a reference base H_2O by the following general reaction.



The equilibrium expression for the above reaction is the following.

$$K_{eq} = \frac{a_{A^-} \cdot a_{H_3O^+}}{a_{H_2O} \cdot a_{HA}}$$

, where a is the chemical activity of the species. The chemical activities of pure solid and liquids is 1, i.e., $a_{H_2O}=1$; and chemical activities of dilute species are equal to their molar concentrations written in square brackets, and K_{eq} of the above reaction is called acid dissociation constant K_a . Making these substitutions, the above expression becomes the following.

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

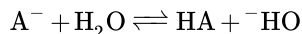
, where K_a is a constant called the acid dissociation constant that expresses the strength of the acid; the higher the value of K_a , the stronger the acid. Since K_a is often a large negative number, it is expressed on a log scale with its sign reversed, as shown in the following formula.

$$pK_a = -\text{Log}_{10}(K_a)$$

The pK_a is a quantitative measure of the acid strength, i.e., the smaller the pK_a means the larger the K_a and the stronger the acid.

Strength of a base

The strength of a base of a general formula A^- is its ability to accept a proton from an acid. Often, the solvent and the reference acid are H_2O , as in the following general reaction.



The equilibrium expression for the above reaction is the following.

$$K_{eq} = \frac{a_{HA} \cdot a_{OH^-}}{a_{H_2O} \cdot a_{A^-}}$$

, where a is the chemical activity of the species. The chemical activities of pure solid and liquids is 1, i.e., $a_{H_2O} = 1$; and chemical activities of dilute species are equal to their molar concentrations written in square brackets, and K_{eq} of the above reaction is called base dissociation constant K_b . Making these substitutions, the above expression becomes the following.

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

, where K_b is a constant called the base dissociation constant that expresses the strength of the base; the higher the value of K_b , the stronger the base. Since K_b is often a large negative number, it is expressed on a log scale with its sign reversed, as shown in the following formula.

$$pK_b = -\text{Log}_{10}(K_b)$$

The pK_b is a quantitative measure of the base strength, i.e., the smaller the pK_b means the larger the K_b and the stronger the base.

Assessing base strength from the strength of its conjugate acid

The K_a of an acid HA and K_b of its conjugate base A^- are inversely proportional to each other as proven below.

$$K_a \times K_b = \frac{[A^-][H_3O^+]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [OH^-][H_3O^+] = K_w = 10^{-14}$$

That rearranges to,

$$K_b = \frac{K_w}{K_a}$$

Since K_b of a base A^- and K_a of its conjugate acid are inversely proportional, it means the following relationships exist between them.

- If an acid is strong, its conjugate base is a weak base.
- If an acid is weak, its conjugate base is a strong base.
- If an acid is of moderate strength, its conjugate base is also of moderate strength.

Taking the log and changing the sign on both sides leads to a relationship between pK_a and pK_b of the conjugate acid-base pair, as shown below.

$$-\log_{10} K_b = -\log_{10} \left(\frac{K_w}{K_a} \right)$$

Substituting $\log_{10} K_b = -\log_{10} K_b$, $\log_{10} K_a = -\log_{10} K_a$, $\log_{10} K_w = -\log_{10} K_w$, the above expression become the following.

$$pK_b = K_w - pK_a$$

Since $K_w = 10^{-14}$ at 25°C at 1 kPa, the above formula become.

$$pK_b = 14 - pK_a$$

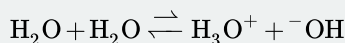
pK_a Values are tabulated in the reference books, and pK_b of their conjugate bases, if needed, are calculated from the pK_a values of their conjugate acids using the above formula.

Controversy over pK_a of H_2O and H_3O^+

In older books pK_a of H_2O , at 25°C and 1 kPa, is listed as 15.7. It is derived from the formula:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

by applying it to the autoionization of water:



by substituting $[A^-][H_3O^+] = [^-\text{OH}][H_3O^+] = K_w = 10^{-14}$ and $[HA] = [\text{H}_2\text{O}] = 55.5$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$$

and then substituting the K_a of water in the following formula:

$$pK_a = -\log_{10}(K_a) = -\log_{10}(1.8 \times 10^{-16}) = 15.7$$

If one H_2O acts as an acid and has $pK_a = 15.7$, the other molecule acts as a base in the same reaction and its pK_b must be 15.7. The formula relating pK_a and pK_b of a conjugate acid-base pair is the following.

$$pK_b = 14 - pK_a$$

Plugging in pK_b for $\text{H}_2\text{O} = 15.7$, results in the pK_a for $\text{H}_3\text{O}^+ = -1.7$, which is the value found in old books. The argument against it is that the concentration of solvent water is removed in the derivation of the formula: $K_a = \frac{[A^-][H_3O^+]}{[HA]}$, assuming $a_{\text{H}_2\text{O}} = 1$. In autoionization of water $[HA] = [\text{H}_2\text{O}] = 1$, which changes the formula to the following.

$$K_a = [^-\text{OH}][H_3O^+] = K_w = 10^{-14}$$

Plug in the K_a for H_2O the pK_a formula:

$$pK_a = -\log_{10}(K_a) = -\log_{10}(10^{-14}) = 14$$

In this reaction, if one H_2O acts as an acid and has $pK_a = 14$, the other molecule acts as a base and must have pK_b must be 14. Plug in $pK_b = 14$ for H_2O and calculate pK_a of its conjugate acid H_3O^+ , using the following.

$$pK_b = 14 - pK_a$$

$$14 = 14 - pK_a$$

$$pK_a = 0$$

It should be mentioned here that IUPAC has not yet defined pK_a of H_2O and H_3O^+ , but pK_a of $H_2O = 14$ and pK_a of $H_3O^+ = 0$, are widely accepted in modern literature. The above description on the controversy of (pK_a) of water and its conjugated acid is based on the following reference: What is the pK_a of water? (2025, April 9). <https://chem.libretexts.org/@go/page/35871>

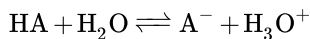
4.3: Brønsted-Lowry Acids and Bases is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

- 4.3: Acid-base reactions by [Muhammad Arif Malik](#) is licensed [Public Domain](#).

4.4: Predicting the direction of acid-base reactions

Qualitative predictions

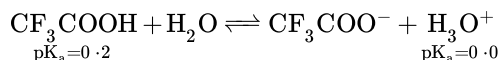
The strength of an acid HA is its ability to donate a proton to a base. K_a and $pK_a = -\log(K_a)$ are quantitative estimates of the strength of an acid in reference to water as a base for the following general reaction.



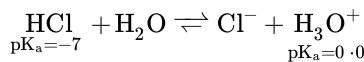
The smaller the pK_a , the larger the K_a , the stronger the acid.

1. When pK_a is ~ 0 , K_a is ~ 1 , and the ratio of reactant to product is about equal at equilibrium.
2. When pK_a is < 0 , K_a is > 1 , products are more than reactants at equilibrium, and the reaction is favored in the forward direction.
3. When pK_a is > 0 , K_a is < 1 , reactants are more than products at equilibrium, and the reaction is favored in the reverse direction.

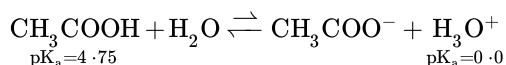
An example of the case#1 is trifluoroacetic acid CF_3COOH that has pK_a 0.2, $K_a = 10^{-0.2} = 0.63$, the products are $\sim 44\%$ in ~ 1.8 M aqueous solution at equilibrium. The equilibrium reaction of such cases is shown with equal forward and reverse arrows, as shown below.



An example of case#2 is HCl that has pK_a -7, $K_a = 10^7$, i.e., HCl is a strong acid that will exist almost completely dissociated into Cl^- and H_3O^+ when dissolved in water. Such a reaction is either written with only a forward arrow or an equilibrium arrow in which the forward arrow is longer than the reverse arrow, as shown below.



An example of case#3 is acetic acid CH_3COOH that has pK_a 4.75, $K_a = 1.8 \times 10^{-5}$, i.e., CH_3COOH is a weak acid, that exists primarily in undissociated form as CH_3COOH , with a very small fraction of molecules dissociated into ions. For example, in a 1 M solution of CH_3COOH , only 4 to 5 molecules in one thousand are dissociated into CH_3COO^- and H_3O^+ . Such a reaction is written with an equilibrium arrow in which the reverse arrow is longer than the forward arrow, as shown below.

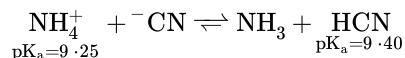


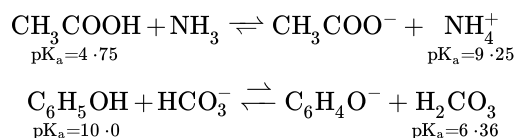
What if the base is other than H_2O ? The answer is to compare $pK_a(\text{reactant})$ of the acid in the reactants with the $pK_a(\text{product})$ of the acid in the product.

A stronger acid has more ability to donate a proton.

1. When the strength of acid in the reactant and product is about the same, i.e., $pK_a(\text{reactant})$ and $pK_a(\text{product})$ are about the same, the reaction is forward and the reverse reaction is about the same.
2. When the acid in the reactant is stronger than the acid in the product, i.e., $pK_a(\text{reactant}) < pK_a(\text{product})$, the reaction is forward directed.
3. When the acid in the reactant is weaker than the acid in the product, i.e., $pK_a(\text{reactant}) > pK_a(\text{product})$, the reaction is reverse directed.

The $pK_a(\text{reactant})$ and $pK_a(\text{product})$ are shown in the above three reactions, which are in agreement with the three cases described above. The following are examples of bases other than H_2O . In first reaction below, representing case#1, the base is cyanide ion CN^- , in the second reaction, representing case#2, the base is ammonia NH_3 , and in the third reaction, representing case#3, the base is bicarbonate HCO_3^- (Note: $\text{C}_6\text{H}_5\text{OH}$ is phenol, and H_2CO_3 is carbonic acid).

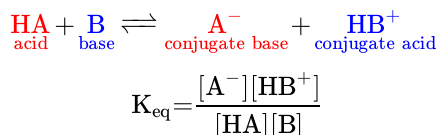




- It is obvious from the above discussion that, in an acid-base reaction, conversion of a stronger acid to a weaker acid is always favored.
- The same is true for a base, i.e., conversion of a stronger base to a weaker base is always favored.
- In summary, conversion of a stronger acid and a stronger base to a weaker acid and a weaker base is always formed in an acid-base reaction.

Calculating the equilibrium constant of an acid-base reaction

Consider a general acid-base reaction and its equilibrium constant K_{eq} expression, shown below.



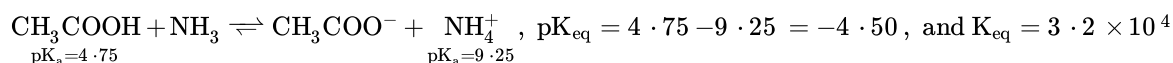
Multiply it with $[\text{H}_3\text{O}^+]/[\text{H}_3\text{O}^+]$ and rearrange:

$$K_{eq} = \frac{[\text{A}^-][\text{HB}^+]}{[\text{HA}][\text{B}]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \times \frac{[\text{HB}^+]}{[\text{B}][\text{H}_3\text{O}^+]} = \frac{K_{a(\text{HA})}}{K_{a(\text{HB}^+)}}$$

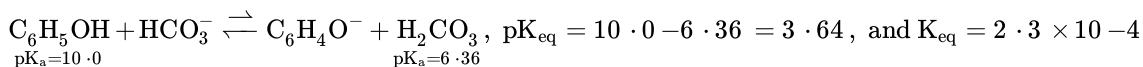
Taking the negative logarithm of both sides changes the above expression to the following.

$$\text{pK}_{eq} = \text{pK}_{a(\text{HA})} - \text{pK}_{a(\text{HB}^+)}$$

It can be observed from the two expression shown above that if the acid in the reactant is stronger, i.e., $\text{pK}_{a(\text{HA})} < \text{pK}_{a(\text{HB}^+)}$; pK_{eq} is negative; K_{eq} is more than one, and the reaction is forward directed, as in the example below.



On the other hand, if the acid in the reactant is weaker, i.e., $\text{pK}_{a(\text{HA})} > \text{pK}_{a(\text{HB}^+)}$; pK_{eq} is positive; K_{eq} is less than one, and the reaction is reverse directed, as in the example below.



4.4: Predicting the direction of acid-base reactions is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

4.5: Thermochemistry of acid-base reactions

Thermochemistry is the study of energy changes during chemical reactions or chemical processes. It is also related to the kinetics, i.e., how fast the reaction occurs, and thermodynamics, i.e., the equilibrium constant defining the proportions of reactants and products after an equilibrium is established. It is usually described using a reaction coordinate diagram in which the potential energy of the species is plotted on the y-axis and the reaction progress on the x-axis.

Reaction coordinate diagram

Chemical species have potential energy stored in chemical bonds and energies due to translational, vibrational, and related motions. Chemical reactions involve breaking and/or making bonds. Breaking bonds always absorbs energy, and bond making always releases energy. Further, the solvation of reactants and products also involves energy due to intermolecular interactions. Overall energy change is the sum of all the energy changes during the chemical transformation.

A reaction coordinate diagram depicts energy changes by plotting the potential energy of the species involved in the reaction on the y-axis and reaction progress on the x-axis. For example, the Figure 4.5.1 shows a general energy diagram of one-step acid-base reactions: a) a product-favored reaction and b) a reactant-favored reaction.

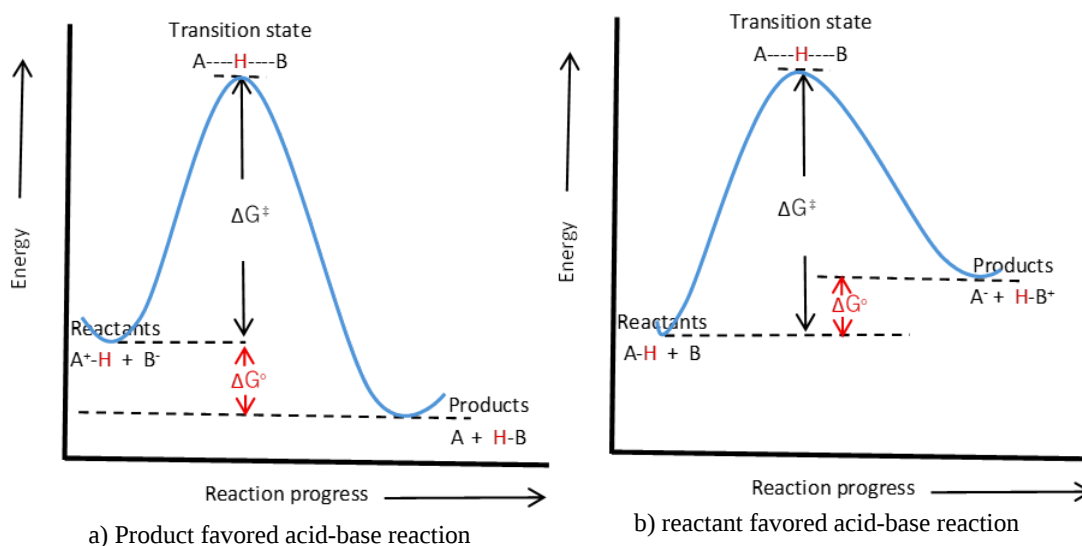


Figure 4.5.1: Reaction coordinate diagram of a) exergonic reaction that is product favored and b) endergonic reaction that is reactant favored. $\Delta G^\ddagger$ is energy of activation and ΔG° free energy change of the reaction (Copyright; Public domain).

Acid-base reactions are usually bimolecular, in which an acid molecule needs to collide with the base molecule to begin the process. Upon collision, the process of bond breaking and making begins, and the reactants begin transitioning to the products. The energy of reacting species increases as the transition states involve the breaking of some bonds and the formation of others. The energy reaches a maximum point, called a transition state, where the bond breaking and making are about midway and shown as dotted lines. The transition state can not be isolated; it has a transient existence. The energy difference from reactants to the transition state is the energy of activation $\Delta G^\ddagger$. The lower the $\Delta G^\ddagger$, the faster the reaction. Acid-base reactions are usually fast because: i) the opposite polarity of the reactive sites facilitates achieving proper orientation at the time of collision, ii) the smaller size of H faces less steric resistance, and iii) the polar bond requires less energy to break heterolytically than hemolytic bond breaking.

If the colliding molecules do not have sufficient energy to reach the transition state, the transitional structure rolls back and the reactants bounce off without reacting. Otherwise, the transition states relax to the product, releasing energy. The difference in energy between reactants and products is called Gibbs free energy ΔG° .

If the products are at a lower energy than the reactants, as in Figure 4.5.1 a), energy is released, ΔG° is negative, and the reaction is **exergonic**.

The reverse reaction follows the same path in reverse. In exergonic reactions, the energy of activation of the reverse reaction is higher than the forward reaction, allowing more products to accumulate than reactants at equilibrium. The exergonic reactions are spontaneous and product-favored.

If the products are at a higher energy than the reactants, as in Figure 4.5.1 b), energy is absorbed, ΔG° is positive, and the reaction is **endergonic**.

In the case of an endergonic reaction, the energy of activation of the reverse reaction is lower than that of the forward reaction, resulting in fewer products than reactants at equilibrium. The endergonic reactions are non-spontaneous and reactant-favored.

Relationship of ΔG° with Enthalpy ΔH and entropy ΔS

Enthalpy H is the sum of internal energy and pressure-volume work. Change in enthalpy ΔH is the heat evolved or absorbed during a reaction.

Standard enthalpy of reaction $\Delta H^\circ_{\text{reaction}}$ is the molar enthalpy change (heat evolved or absorbed) for a reaction under standard conditions of 1 bar and specified temperature, i.e., usually 297 K.

$\Delta H^\circ_{\text{reaction}}$ is approximately equal to the sum of bond energies of bonds broken minus the bond energies of the bonds formed. The sum of the heat of solvation of reactants and products also adds to the total enthalpy change.

Entropy S is a measure of disorder -the more disorder, the higher the entropy. The disorder in a chemical reaction, resulting in a change in entropy ΔS , could be caused by the formation of more molecules than consumed, an increase in vibrational and rotational movements, etc.

Change in Gibbs free energy ΔG° is related with the change in enthalpy ΔH° , entropy ΔS° and absolute temperature T , by the following relationship.

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

Four situations arise related to the feasibility of reaction in relation to ΔH° and ΔS° .

1. When ΔH° is negative and ΔS° is positive, ΔG° is always negative, i.e., the reaction is spontaneous in the forward direction (product-favored).
2. When ΔH° is positive and ΔS° is negative, ΔG° is always positive, i.e., the reaction is non-spontaneous in the forward direction (reactant-favored).
3. When ΔH° is negative and ΔS° is also negative, ΔG° is negative at lower temperatures, i.e., higher temperature disfavors but lower temperature can make the reaction spontaneous in the forward direction (product-favored).
4. When ΔH° is positive and ΔS° is also positive, ΔG° may be positive at lower temperature, but higher temperature can make it negative making the reaction spontaneous in the forward direction (product-favored).

Relationship between acid strength and ΔG°

ΔG° determines whether the reaction favors product or reactants at equilibrium and to what extent. It is expressed quantitatively by the following relationship.

$$\Delta G^\circ = -RT \ln(K_{\text{eq}}) = -2.303 RT \log_{10}(K_{\text{eq}}),$$

where R is the gas constant ($8.31 \text{ J/K} \cdot \text{mol}$) and T is the temperature in kelvins. Exergonic reactions have negative ΔG° corresponding to K_{eq} more than one, i.e., product-favored reaction. In the case of acid-base reactions, $K_{\text{eq}} = K_a$, where K_a is a measure of the strength of an acid, the larger the K_a , the stronger the acid. In the case of an acid-base reaction, any factor that destabilizes the acid, i.e., increases the potential energy of the reactant, or stabilizes its conjugate base, i.e., decreases the potential energy of the product, makes the acid a stronger acid by increasing its K_a . The factors that affect the acid strength of an acid are described in the next section.

4.5: Thermochemistry of acid-base reactions is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

4.6: Factors affecting the strength of an acid

Prelude to the factors affecting the strength of an acid

The strength of an acid is its ability to donate a proton. K_a or its negative logarithm pK_a are quantitative measure of acid strength, i.e., larger the K_a (the smaller the pK_a), the stronger the acid. The $pK_a = pK_{eq}$ in acid-base reactions and it is related to the Gibbs free energy change ΔG° by the following relation.

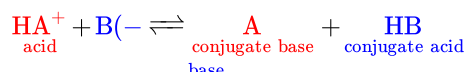
$$\Delta G^\circ = -RT \ln(K_{eq})$$

Any factor that decreases ΔG° , increases K_a and increases the strength of an acid.

It can be observed from Figure 4.5.1 that any factor that destabilizes acid (reactant) or stabilizes its conjugate base (product) results in decreasing ΔG° and increasing K_a . Overall, electric charge is a destabilizing factor. The destabilization by charge is moderated by factors like electronegativity, size of the atom, and resonance, which affect the acidity, as described next.

Effect of charge on acidity

A positive charge on the atom bearing an acidic proton is neutralized upon donating the proton to a base, as shown in the following general acid-base reaction.



- A proton on a positively charged atom is more acidic than a proton on an equivalent neutral atom.
- The opposite is true for a base, i.e., a base bearing a negative charge is a stronger base than a base with an equivalent neutral atom.

For example, H_3O^+ $pK_a = 0$ is stronger acid than H_2O $pK_a = 14$. Similarly, NH_4^+ $pK_a = 9.25$ is stronger acid than NH_3 $pK_a = 36$. The opposite is true for a base. For example, OH^- $pK_b = 0$ is stronger base than H_2O $pK_b = 14$. Similarly, H_2N^- $pK_a = -22$ is stronger base than NH_3 $pK_b = 4.75$.

Effect of electronegativity on acidity

The conjugate base of a neutral acid is an anion, as shown in the following general reaction.



A negative charge is better stabilized on a more electronegative atom than on a less electronegative atom.

Therefore, a proton on a more electronegative atom is more acidic than a proton on a less electronegative atom of comparable size, as shown below.

Electronegativity	C 2.55	N 3.04	O 3.44	F 4.0
Acidity	CH_4 pK_a 50	NH_3 pK_a 36	H_2O pK_a 14	HF pK_a 3.17

This effect is applicable for comparing atoms within the same row, but not when comparing atoms within the same group in a periodic table. This is because the atoms in the same row have comparable sizes, but atoms in the same group have significantly different sizes.

Effect of the size of an atom on acidity

The acidic strength of a proton attached to the atoms of the same group is expected to decrease down the group because electronegativity decreases down the group. The experimental data show the opposite trend.

The proton attached to atoms of the same group becomes more acidic down the group in the periodic table.

This is because the atomic size increases down the group, and the negative charge on the conjugate base is more stable when spread over a larger volume. The effect of the size of the atom is stronger and dominates over the opposing effect of the electronegativity when comparing atoms within the same group, as shown below with examples of hydrohalic acids.

Electronegativity	F 3.98	Cl 3.16	Br 2.96	I 2.66
Covalent radius (pm)	F 57	Cl 102	Br 120	I 139
Acidity (pK_a)	H-F 3.2	H-Cl -7	H-Br -9	H-I -10

Inductive effect on acidity

An electronegative atom draws away some of the negative charge of a conjugate base not just from one bond away but also two or more bonds away -an effect called the **inductive effect**.

- The more electronegative the atom, the stronger the inductive effect, as shown by the acidity trend in the first row of Table 4.6.1.
- Nearer the electronegative atom to the acidic proton, the stronger the effect, as shown in the second row of Table 4.6.1.
- The inductive effect of multiple electronegative atoms adds up, as shown by the third row of Table 4.6.1

Table 4.6.1: Inductive effect on acidity of atoms of different electronegativity, electronegative atom at different distances, and additive effect of more than one electronegative atom

Effect of electronegativity	$\text{F} \quad \text{O}$ $\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 2.7}$	$\text{Cl} \quad \text{O}$ $\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 2.8}$	$\text{Br} \quad \text{O}$ $\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 2.9}$	$\text{I} \quad \text{O}$ $\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 3.2}$
Effect of distance	$\text{CH}_3-\text{CH}_2-\text{Cl} \quad \text{O}$ $\text{H}-\text{C}-\text{OH}$ $pK_a \text{ 2.86}$	$\text{CH}_3-\text{CH}-\text{Cl} \quad \text{O}$ $\text{H}-\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 4.05}$	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl} \quad \text{O}$ $\text{H}-\text{C}-\text{OH}$ $pK_a \text{ 4.52}$	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl} \quad \text{O}$ $\text{H}-\text{C}-\text{OH}$ $pK_a \text{ 4.82}$
Effect of the number	O $\text{CH}_3-\text{C}-\text{OH}$ $pK_a \text{ 4.75}$	$\text{Cl} \quad \text{O}$ $\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 2.8}$	$\text{Cl} \quad \text{O}$ $\text{Cl}-\text{CH}_2-\text{C}-\text{OH}$ $pK_a \text{ 1.3}$	$\text{Cl} \quad \text{O}$ $\text{Cl}-\text{C}-\text{C}-\text{OH}$ Cl $pK_a \text{ 0.6}$

Effect of hybridization on acidity

When an acid donates a proton to a base, the bonding electron pair is left behind as a lone pair on the atom of the conjugate base that was bearing the acidic proton, as shown in a general acid-base reaction below.



A lone pair is more tightly held in an sp orbital than in an sp^2 and least tightly held in an sp^3 . This is because an s orbital is spherical in shape and closer to the nucleus than a p orbital. Therefore, as the proportion of s orbital increases in the hybrid orbital, in the order $sp^3 < sp^2 < sp$, the ability of the atom to attract electrons in the orbital to itself, i.e., its electronegativity, increases in the same order.

As a consequence of increase in electronegativity, the acidity of a proton increases with the change in hybridization of the atom bearing the acidic proton in the order $sp^3 < sp^2 < sp$, as reflected by a decrease in pK_a as shown in Table 4.6.2.

Table 4.6.2: Effect of hybridization of the atom bearing acidic proton on the strength of the acid. The hybrid orbital bearing the lone pair in the conjugated base is shown in red.

Acid	Conjugate base	Hybridization	s-Character	pK _a
		sp ³	25%	50
		sp ²	33%	44
		sp	50%	25

Effect of resonance on acidity

A proton of a group is more acidic if the negative charge of the conjugate base is spread over more than one atom by resonance than an equivalent group with no resonance.

Several examples proving it are shown in Table 4.6.2. This is due to the spread of the negative charge of the conjugate base being stabilized by resonance. This is similar to the effect of the size of the atom; acidity increases down the group because the negative charge of the conjugated base is more stabilized when spread over a larger volume.

Table 4.6.2: Examples comparing acidity pK_a of groups with and without resonance stabilization of the conjugate base. Acidic proton is shown in red.

	Resonance		No resonance	
Example group	Acid	Conjugate base	Acid	Conjugated base
-OH			CH ₃ -CH ₂ -OH pK _a 15.9	CH ₃ -CH ₂ -O ⁻
-NH ₂			CH ₃ -CH ₂ -NH ₂ pK _a ~40	CH ₃ -CH ₂ -NH ⁻
-CH ₃			CH ₃ -CH ₂ -CH ₃ pK _a ~50	CH ₃ -CH ₂ -CH ₂ ⁻
-CH ₃			CH ₃ -CH ₂ -CH ₃ pK _a ~50	CH ₃ -CH ₂ -CH ₂ ⁻

In addition to the effect of resonance on acidity, comparing acidity pK_a) of first three rows of Table 4.6.2 show that the acidity of protons, under identical conditions, increases in the order -CH₃ < -NH₂ < -OH. This trend is explained by the effect of the electronegativity of the atom bearing the acid proton increasing in the same order. Comparison of the last two rows of Table 4.6.2 shows that the more electronegative O of C=O is more able to stabilize the negative charge by resonance than less electronegative N of -C≡N group.

Bases donate a lone pair to the proton they receive from the acid in an acid-base reaction.

The basic groups in which the lone pair of a basic atom is resonance stabilized are less able to donate the lone pair and, consequently, they are less basic (higher pK_b) than the same group with no resonance stabilization.

Recall that stronger acids have weaker conjugate bases and vice versa. All the examples in Table 4.6.2 prove it. Note that all the examples, the conjugate acids are stronger when the bases are resonance stabilized than the same basic groups with no resonance stabilization. Table 4.6.3 is an example of it showing that $-\text{NH}_2$ is a weaker base ($\text{pK}_b = 14$) when lone pair of N is resonance stabilized than the same group without resonance ($\text{pK}_b = 3.3$)

Table 4.6.3: Example comparing basicity pK_b of groups with and without resonance stabilization of the basic lone-pair. Acidic proton is shown in red.

	Resonance		No resonance	
Example group	Base	Conjugate acid	Base	Conjugated acid
$-\text{NH}_2$	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \longleftrightarrow \text{CH}_3-\overset{\text{O}^-}{\parallel}{\text{C}}=\overset{+}{\text{N}}\text{H}_2$ $\text{pK}_b \text{ 14}$	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\overset{+}{\text{N}}\text{H}_2$	$\text{CH}_3-\text{CH}_2-\text{NH}_2$	$\text{CH}_3-\text{CH}_2-\overset{+}{\text{N}}\text{H}_2$

Effect of the oxidation state of the central atom in oxyacids on acidity

In oxyacids, the pK_a decreases and acidity increases with an increase in the oxidation state of the central atom.

Comparison of pK_a values in Table 4.6.3 proves it with the help of an example of oxyacids of chlorine.

Table 4.6.3: Effect of resonance of acidity. Acidic proton is shown in red

Name	Oxidation state of Cl	Acid	Conjugate base	pK_a
Hypochlorous acid	1	$\text{Cl}-\text{O}-\text{H}$	$\text{Cl}-\text{O}^-$	7.53
Chlorous acid	3	$\text{O}=\text{Cl}-\text{O}-\text{H}$	$\text{O}=\text{Cl}-\text{O}^- \longleftrightarrow \text{O}=\overset{+}{\text{Cl}}=\text{O}$	2.0
Chloric acid	5	$\text{O}=\text{O}=\text{Cl}-\text{O}-\text{H}$	$\text{O}=\text{O}=\text{Cl}-\text{O}^- \longleftrightarrow \text{O}=\text{O}=\overset{+}{\text{Cl}}=\text{O} \longleftrightarrow \text{O}=\overset{+}{\text{Cl}}=\text{O}=\text{O}$	-1
Perchloric acid	7	$\text{O}=\text{O}=\text{O}=\text{Cl}-\text{O}-\text{H}$	$\text{O}=\text{O}=\text{O}=\text{Cl}-\text{O}^- \longleftrightarrow \text{O}=\text{O}=\text{O}=\overset{+}{\text{Cl}}=\text{O} \longleftrightarrow \text{O}=\text{O}=\overset{+}{\text{Cl}}=\text{O}=\text{O} \longleftrightarrow \text{O}=\overset{+}{\text{Cl}}=\text{O}=\text{O}=\text{O}$	-8

The effect of the oxidation state of the central atom on the acidity of oxyacids is an additive effect of two factors, induction and resonance stabilization of the conjugate base. Oxidation state of the central atom is increased by 2 when $=\text{O}$ group is added. O is an electronegative atom that increases the acidity of the neighboring $-\text{OH}$ group due to the inductive effect. It also increases the acidity by the resonance effect; one resonance contributor is added to the conjugate base with the $=\text{O}$ group sharing the negative charge.

4.6: Factors affecting the strength of an acid is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.7: Lewis acids and bases

Prelude to Lewis acid-base concept

Chemical reactions are making and/or breaking bonds. A covalent bond is a shared pair of electrons, which is nonpolar if the bonding electrons are equally shared or polar if the bonding electrons are not equally shared. A covalent bond is formed in two ways: i) each two atoms contribute one electron each to make the covalent bond, or ii) one atom contributes both the electrons and the other uses an empty orbital to make a new bond called a dative covalent bond, as illustrated in Figure 4.7.1.

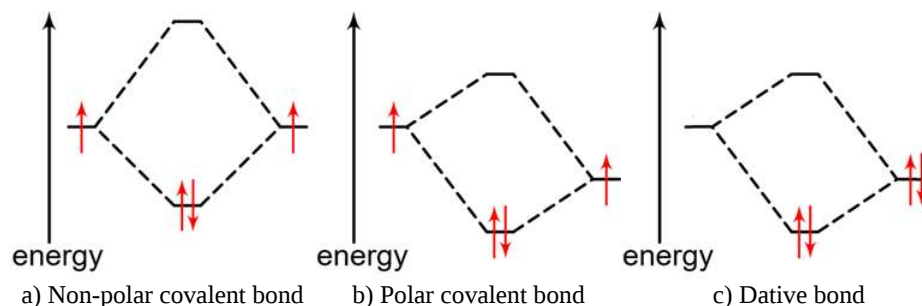


Figure 4.7.1: Molecular orbital diagram of a) non-polar covalent, b) polar covalent, and c) dative bond (Copyright; Public domain)

Brønsted-Lowry acid-base reactions are proton-exchange reactions. Looking at them from the movement of electrons, bases donate a lone pair of electrons to make a dative bond with a proton, making a conjugate acid. Since H can not have more than one covalent bond, it breaks its previous bond, leaving the bonding electrons as a lone pair on the conjugate base. Lewis' concept of acids and bases is based on the electron donation by bases and electron acceptance by acids.

Electron movements in chemical reactions are usually shown by curly arrows. Arrows are also used in multiple other ways in chemical reaction equations. A quick overview of the use of arrows and conventions followed in using curly arrows in chemistry is presented next, before defining Lewis acids and bases.

Uses of arrows in chemistry

Arrows are used in different ways in chemistry. The most common uses of arrows are listed below.

1. A reaction arrow $\longrightarrow$ separates reactants on the left side from products on the right side.
2. An equilibrium arrow $\rightleftharpoons$ or $\rightleftharpoons$ separates reactants and products that are at equilibrium with each other.
 - An equilibrium with a larger arrow pointing to products $\rightleftharpoons$ is used for product-favored equilibrium, i.e., products are more abundant than reactants at equilibrium.
 - An equilibrium with a larger arrow pointing to reactants $\rightleftharpoons$ products is used for a product-favored equilibrium, i.e., products are more abundant than reactants at equilibrium.
3. A resonance arrow $\leftrightarrow$ separates resonance contributors.
4. A curly arrow $\curvearrowright$ shows imaginary movement of a valence electron-pair in resonance or actual movement of a valence electron-pair in a chemical reaction.
5. A curly harpoon $\frown$ (half-headed arrow or fish-hook arrow) shows imaginary movement of a single valence electron in resonance or actual movement of a single valence electron in a chemical reaction.

Conventions followed for using curly arrows

Movement of a valence electron-pair in a chemical reaction is shown by a curly arrow $\curvearrowright$. The tail of the arrow is placed where the electrons to be moved are located, and the head points where the electrons move to (tail $\curvearrowright$ head). The conventions for placing the tail and the head of the curly arrow are the following.

1. When a bonding electron pair moves, the tail of the curly arrow is placed in the middle of the bond. For example, in this

hypothetical reaction the bonding electron in A–B bond moves: $\text{A}-\text{B} + \text{X}^+ \longrightarrow \text{A}^+ + \text{B}-\text{X}$

- When a lone pair moves, the tail is placed on the atom bearing the lone pair. For example in this hypothetical reaction lone pair on B moves: $A^+ + \cdot B^- \longrightarrow A-B$
- When the electron movement results in a new bond, the head of the curly arrow points to the middle of the new bond. For example, in this hypothetical reaction new bond B-X is formed: $A-B + X^+ \longrightarrow A^+ + B-X$
- When electron movements result in a new lone pair, the head points to the atom that will bear the lone pair. For example, in this hypothetical reaction X-Y bonding electron-pair moves and B bears the new lone pair: $X-Y \longrightarrow X^+ + :Y^-$
- The movement of a single electron is shown by a curly harpoon $\curvearrowright$ (half-headed arrow or fish-hook arrow) following the same rules as for a regular curly arrow.

Definitions of Lewis acid and base

Lewis acid and Lewis base

A molecular or a chemical species that can coordinate with a Lewis base by accepting a pair of electrons from it and forming a Lewis adduct is called a **Lewis acid**.

A molecule or a chemical species that is able to coordinate with a Lewis acid by providing a pair of electrons, forming a Lewis adduct, is called a **Lewis base**.

In simple words, a Lewis is a lone pair acceptor, and a Lewis base is a lone pair donor in a chemical reaction forming a Lewis adduct. A Lewis acid has an empty orbital, usually the lowest unoccupied molecular orbital (LUMO), capable of accepting a lone pair from a Lewis base. For example, Al in $AlCl_3$ is octet incomplete, having LUMO, as shown in Figure 4.7.2 a), capable of accepting a lone pair to make a dative bond that completes its octet. The electron-deficiency on Al in $AlCl_3$ can be observed by $\delta+$ (blue) region in its electrostatic potential map, as shown in Figure 4.7.2 b).

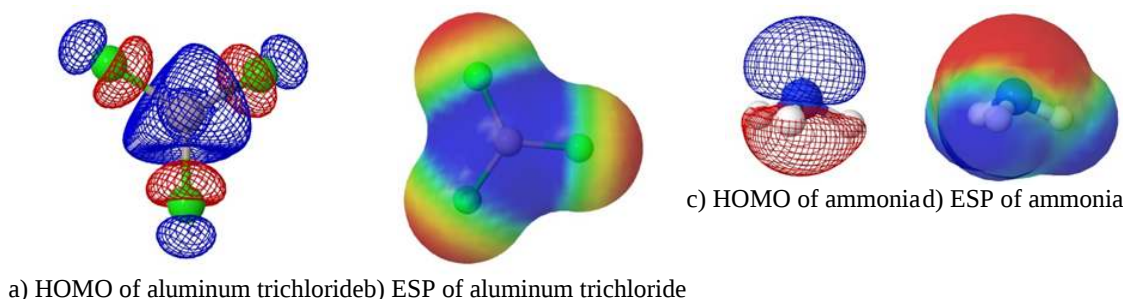
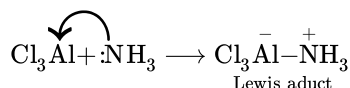


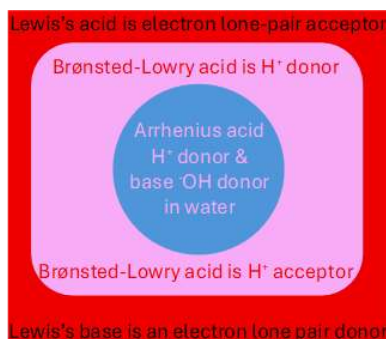
Figure 4.7.2: A is LUMO of a Lewis acid $AlCl_3$ and b) is its electrostatic potential map, c) HOMO of Lewis base $:NH_3$ and d) is its electrostatic potential map. The colors in the electrostatic potential map represent: blue $\delta+$, red is $\delta-$, and green is neutral (Copyright; Public domain).

Lewis bases have the highest occupied molecular orbital (HOMO) that is localized and capable of donating an electron pair to make a covalent bond. For example, N in $:NH_3$ has a lone pair in HOMO that is localized (lone pair) that it can donate. The HOMO of $:NH_3$ is shown in Figure 4.7.2 c), and its electrostatic potential map shows an electron-rich (red) region on N as shown in Figure 4.7.2 d). $AlCl_3$ is a Lewis acid and $:NH_3$ is a Lewis base: they react by Lewis acid-base reaction, shown below, producing Lewis adduct $Cl_3\overset{-}{Al}-\overset{+}{NH}_3$.

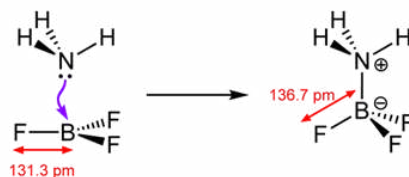


Boron trifluoride BF_3 is another example of a Lewis acid with octet incomplete on B that undergoes Lewis acid-base reaction with Lewis base $:NH_3$ as shown in the figure on the right margin.

All Brønsted-Lowry acids are Lewis acids in which the acidic H accepts a lone pair in its LUMO, and all Brønsted-Lowry bases are Lewis bases that donate a lone pair from their HOMO to the acids. Since H can not have two covalent bonds, it breaks its previous covalent bond, leaving the bonding electrons as a lone pair on the conjugate base. Lewis acid-base reactions are a much



broader category of reactions that include Brønsted-Lowry acid-base reactions, nearly all polar organic reactions, and the formation of coordination compounds of transition metals. The figure on the left margin shows that Arrhenius acid-base pairs are a subclass of Brønsted-Lowry acid-base pairs, which, in turn, are a subclass of Lewis acid-base pairs.

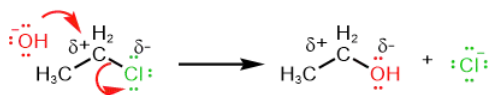


Electrophile and nucleophile

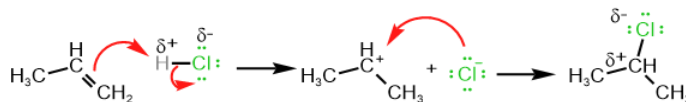
Most organic reactions are polar reactions in which a positively charged region of a species receives an electron pair from a negatively charged or partially negatively charged region of another species that has a lone pair to donate.

The electron recipient in the polar reactions is called an **electrophile**, meaning electron lover, and the electron donor is called a **nucleophile** or nucleus lover.

For example, in the reaction shown below $\text{CH}_3\text{--H}_2\text{C}^{\delta+}\text{--}\ddot{\text{Cl}}^{\delta-}$ is an electrophile receiving electrons on $\text{C}^{\delta+}$ and $:\ddot{\text{O}}\text{H}^-$ is a nucleophile donating a lone pair to make a new bond. Since $\text{C}^{\delta+}$ of the electrophile can not have five bonds, it breaks a polar covalent bond $\text{C}^{\delta+}\text{--}\text{Cl}^{\delta-}$ leaving electron on the departing nucleophile $:\ddot{\text{Cl}}^{\delta-}$ as it makes a new bond with the incoming nucleophile. Overall reaction is called a nucleophilic substitution reaction.



Below is another example where $\text{CH}_3\text{CH}=\text{CH}_2$ is a nucleophile donating π electrons to $\text{H}^{\delta+}$ end of the electrophile $\text{H}^{\delta+}\text{--}\ddot{\text{Cl}}^{\delta-}$. Since $\text{H}^{\delta+}$ of the electrophile can not have two bonds, it breaks a polar covalent bond $\text{H}^{\delta+}\text{--}\text{Cl}^{\delta-}$ leaving electron on the departing nucleophile $:\ddot{\text{Cl}}^{\delta-}$ as it makes a new bond with the incoming nucleophile.



This is a two-step reaction, in which the products of the first step are reactants of the second step. In the second step, $\text{CH}_3\text{CH}^+\text{--CH}_3$ is an electrophile and $:\ddot{\text{Cl}}^{\delta-}$ is a nucleophile. The electrophile and the nucleophile add in the second step. The overall reaction is an electrophilic addition reaction.

$\text{CH}_3\text{--H}_2\text{C}^{\delta+}\text{--}\ddot{\text{Cl}}^{\delta-}$ in the first reaction above is a Lewis acid and $\text{CH}_3\text{CH}=\text{CH}_2$ in the second reaction is a Lewis base. Similarly, $\text{H}^{\delta+}\text{--}\ddot{\text{Cl}}^{\delta-}$ and $:\ddot{\text{O}}\text{H}^-$ are Brønsted-Lowry acid and base, respectively, which can also be called Lewis acid and Lewis base. The question is, what term should be used for electron donors and acceptors, and when? The answer to this question is addressed in the next section.

What should electron donors and acceptors in organic reactions be called?

Brønsted-Lowry acid-base reactions, Lewis acid-base reactions, and polar reactions between electrophile and nucleophile are all reactions between electron pair acceptors and donors. The terms Brønsted-Lowry acid, Lewis acid, and electrophile, referring to electron pair acceptors, have diffused boundaries and in some situations are used interchangeably. Same is true about Brønsted-

Lowry base, Lewis base, and nucleophile, referring to electron pair donors. However, a distinction can be made between them in most cases. The following conventions can specify which term to use where, in most cases.

1. When an electron pair acceptor is a proton, the electron pair acceptor is Brønsted-Lowry acid and the donor is Brønsted-Lowry base, which are usually termed as an **acid** and a **base**. The acid-base reactions are inherently fast. Therefore, acidity is related to thermodynamic properties, i.e., stability. For example, if the products are more stable than the reactants, the acid is stronger, K_{eq} is more than one, ΔG° is negative, and the reaction is product-favored. In other words, the acidity properties are related to proton exchange reactions, and they are about the thermodynamic aspects of the reactions.

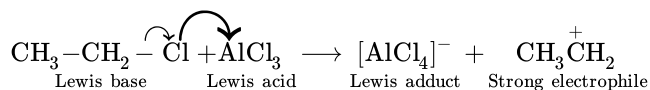
- When an electron pair acceptor is a proton receiving lone-pair from a heteroatom of an organic compound, the reaction is termed an acid-base reaction, or a proton-exchange reaction, or a protonation and deprotonation reaction.
- However, when the electron donor is a carbon species, it is usually termed a nucleophile. For example, $\text{CH}_3\text{CH}=\text{CH}_2$

donating its π -electron pair to the proton of $\overset{\delta+}{\text{H}}-\overset{\delta-}{\underset{\cdot\cdot}{\text{Cl}}}$, $\text{CH}_3\text{CH}=\text{CH}_2$ is an electrophile and $\text{CH}_3\text{CH}=\text{CH}_2$ donating its π -

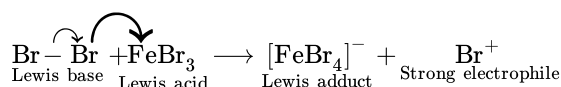
electron pair to the proton of $\overset{\delta+}{\text{H}}-\overset{\delta-}{\underset{\cdot\cdot}{\text{Cl}}}$ is a nucleophile.

2. When an electron-pair acceptor is a specie other than a proton, often a C in polar organic reactions, the electron-pair recipient is called an **electrophile** and the electron donor a **nucleophile**. The electrophile-nucleophile reactions are not necessarily equilibrium reactions; they are often a one-way reaction, and the properties refer to kinetic aspects of the reaction. For example, a stronger electrophile is the one that reacts faster with a reference nucleophile and vice versa.
3. Lewis acid-base is a broader term that encompasses Brønsted-Lowry acid bases, nucleophiles, and electrophiles. It is **specifically** used when the electron pair acceptor is not a proton or a carbon, and the reference pertains to the thermodynamic aspect of the reaction. The electron lone-pair donors to transition metals in inorganic chemistry are usually called chelates, and the products of the reaction are usually called coordination compounds. So, Lewis acid-base terms are usually limited to electron-deficient metal compounds like AlCl_3 or transition metal complexes like FeBr_3 that are employed as catalysts in

organic reactions. For example, alkyl halides like $\text{CH}_3-\text{H}_2\overset{\delta+}{\text{C}}-\overset{\delta-}{\underset{\cdot\cdot}{\text{Cl}}}$, are electrophiles, as shown in one reaction above, but not enough reactive to accept π -electrons of an aromatic ring. AlCl_3 is employed as a Lewis acid catalyst to convert it into a strong electrophile by the following reaction.



Similarly, FeBr_3 is employed as a Lewis acid catalyst to convert weak electrophile Br_2 into a strong electrophile by the following reaction.



4.7: Lewis acids and bases is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

Index

D

dire

Detailed Licensing

Overview

Title: Organic Chemistry -Part 1 Fundamentals (Malik)

Webpages: 43

All licenses found:

- **Public Domain:** 60.5% (26 pages)
- **Undeclared:** 39.5% (17 pages)

By Page

- Organic Chemistry -Part 1 Fundamentals (Malik) - *Public Domain*
 - Front Matter - *Public Domain*
 - TitlePage - *Public Domain*
 - InfoPage - *Public Domain*
 - Table of Contents - *Public Domain*
 - Licensing - *Public Domain*
 - 1: Bonding and structure - *Public Domain*
 - 1.1: What is organic chemistry - *Public Domain*
 - 1.2: Structure of an atom - *Public Domain*
 - 1.3: Chemical bonds - *Public Domain*
 - 1.4: Bonding theories and geometries of molecules - *Public Domain*
 - 1.5: Polarity of bonds and molecules - *Public Domain*
 - 2: Representing organic structures - *Public Domain*
 - 2.1: Drawing organic structures - *Public Domain*
 - 2.2: Resonance - *Public Domain*
 - 2.3: Organic nomenclature -alkanes - *Public Domain*
 - 2.4: Organic nomenclature -functional group containing compounds - *Undeclared*
 - 3: Stereochemistry - *Undeclared*
 - 3.1: Introduction to stereochemistry - *Public Domain*
 - 3.2: Conformational analyses - *Public Domain*
 - 3.3: Conformational analysis of cyclohexanes - *Undeclared*
 - 3.4: Configurational stereoisomerism - *Public Domain*
 - 3.5: Assigning R/S stereodescriptors to chirally center - *Undeclared*
 - 3.6: Optical activity - *Undeclared*
 - 3.7: Types of chiral molecules - *Undeclared*
 - 3.8: Chirality related topics - *Undeclared*
 - 4: Acids and bases - *Public Domain*
 - 4.1: Importance of acids, bases and their reactions - *Undeclared*
 - 4.2: Arrhenius Acids and Bases - *Undeclared*
 - 4.3: Brønsted-Lowry Acids and Bases - *Undeclared*
 - 4.4: Predicting the direction of acid-base reactions - *Undeclared*
 - 4.5: Thermochemistry of acid-base reactions - *Undeclared*
 - 4.6: Factors affecting the strength of an acid - *Undeclared*
 - 4.7: Lewis acids and bases - *Undeclared*
 - 5: Alkanes and Free radical reaction mechanisms - *Undeclared*
 - 6: Alkenes, alkynes and electrophilic addition reactions - *Undeclared*
 - 7: Alkyl halides and Nucleophilic substitutions and eliminations - *Public Domain*
 - 8: Aromaticity and electrophilic aromatic substitution reactions - *Public Domain*
 - Back Matter - *Public Domain*
 - Index - *Public Domain*
 - Glossary - *Public Domain*
 - Detailed Licensing - *Public Domain*
 - Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: Organic Chemistry -Part 1 Fundamentals (Malik)

Webpages: 43

All licenses found:

- **Public Domain:** 60.5% (26 pages)
- **Undeclared:** 39.5% (17 pages)

By Page

- Organic Chemistry -Part 1 Fundamentals (Malik) - *Public Domain*
 - Front Matter - *Public Domain*
 - TitlePage - *Public Domain*
 - InfoPage - *Public Domain*
 - Table of Contents - *Public Domain*
 - Licensing - *Public Domain*
 - 1: Bonding and structure - *Public Domain*
 - 1.1: What is organic chemistry - *Public Domain*
 - 1.2: Structure of an atom - *Public Domain*
 - 1.3: Chemical bonds - *Public Domain*
 - 1.4: Bonding theories and geometries of molecules - *Public Domain*
 - 1.5: Polarity of bonds and molecules - *Public Domain*
 - 2: Representing organic structures - *Public Domain*
 - 2.1: Drawing organic structures - *Public Domain*
 - 2.2: Resonance - *Public Domain*
 - 2.3: Organic nomenclature -alkanes - *Public Domain*
 - 2.4: Organic nomenclature -functional group containing compounds - *Undeclared*
 - 3: Stereochemistry - *Undeclared*
 - 3.1: Introduction to stereochemistry - *Public Domain*
 - 3.2: Conformational analyses - *Public Domain*
 - 3.3: Conformational analysis of cyclohexanes - *Undeclared*
 - 3.4: Configurational stereoisomerism - *Public Domain*
 - 3.5: Assigning R/S stereodescriptors to chirally center - *Undeclared*
 - 3.6: Optical activity - *Undeclared*
 - 3.7: Types of chiral molecules - *Undeclared*
 - 3.8: Chirality related topics - *Undeclared*
 - 4: Acids and bases - *Public Domain*
 - 4.1: Importance of acids, bases and their reactions - *Undeclared*
 - 4.2: Arrhenius Acids and Bases - *Undeclared*
 - 4.3: Brønsted-Lowry Acids and Bases - *Undeclared*
 - 4.4: Predicting the direction of acid-base reactions - *Undeclared*
 - 4.5: Thermochemistry of acid-base reactions - *Undeclared*
 - 4.6: Factors affecting the strength of an acid - *Undeclared*
 - 4.7: Lewis acids and bases - *Undeclared*
 - 5: Alkanes and Free radical reaction mechanisms - *Undeclared*
 - 6: Alkenes, alkynes and electrophilic addition reactions - *Undeclared*
 - 7: Alkyl halides and Nucleophilic substitutions and eliminations - *Public Domain*
 - 8: Aromaticity and electrophilic aromatic substitution reactions - *Public Domain*
 - Back Matter - *Public Domain*
 - Index - *Public Domain*
 - Glossary - *Public Domain*
 - Detailed Licensing - *Public Domain*
 - Detailed Licensing - *Undeclared*