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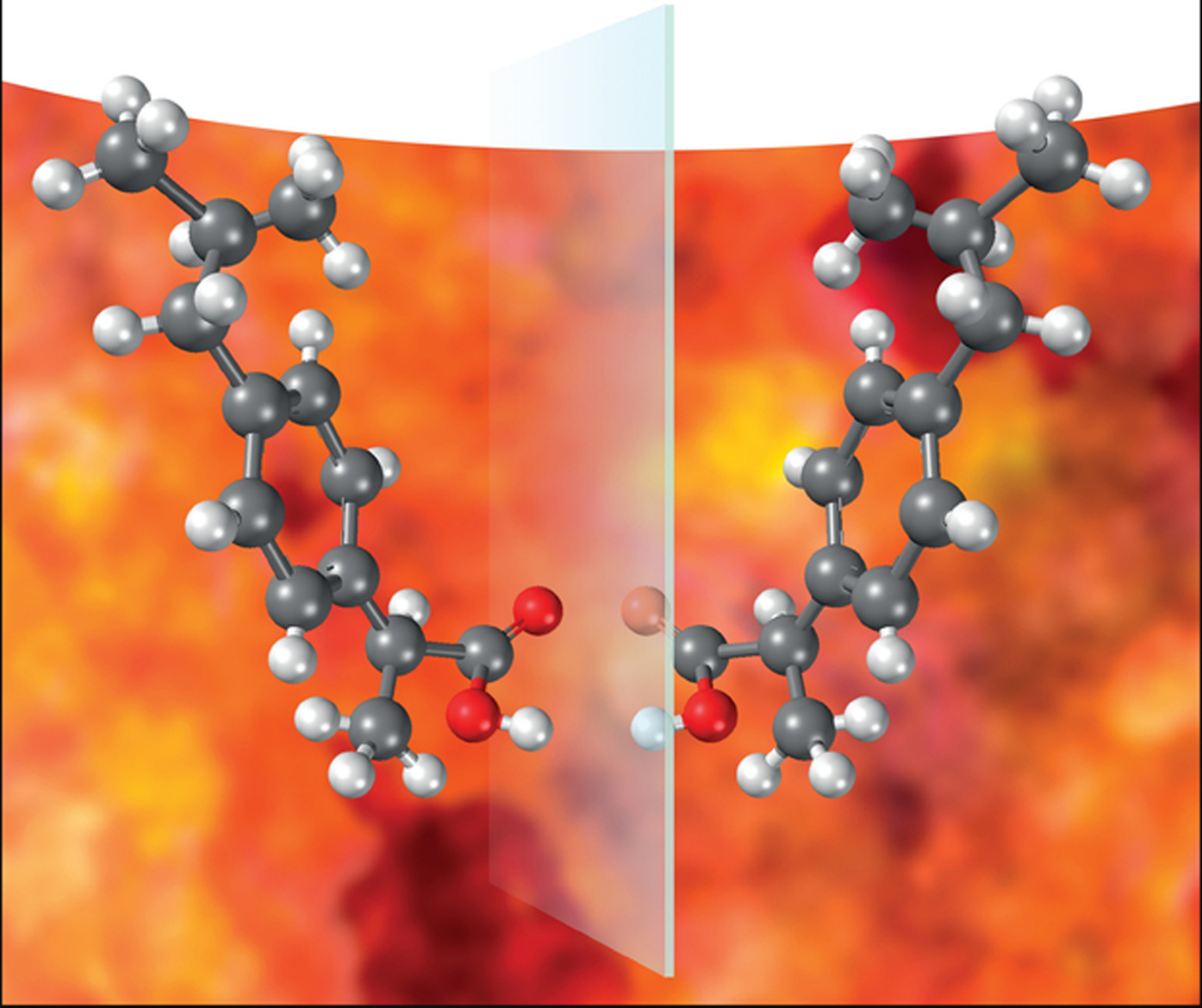
Eberhard Breitmaier

Efficiently Studying Organic Chemistry

Exam Training for Chemists, Biochemists, Pharmacists, Life and Health Scientists

Third, Revised Edition



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Contents

Preface

Reforms in Europe harmonized the conditions and curricula of the studies of chemistry and other natural sciences, improving the international compatibility of academic degrees (*bachelor* and *master*). Therefore, concise, sufficiently detailed, rounded textbooks are increasingly demanded, enabling students to efficiently prepare themselves for written and oral examinations.

This has been the driving force to structure and to draw up this volume which is not intended to be or to replace a comprehensive textbook. Rather, it has been written to facilitate an efficient learning, covering the *essentials of organic chemistry* in 86 short chapters in a total of about 300 pages, thus enforcing a very disciplined selection of the material and a succinct style of writing with a minimum of repetition. When adapted to different curricula of universities and individual demands of instructors, studying can be limited to a selection of the chapters presented in this text.

Based on the author's teaching and examination experience of more than 40 years, this book and its graphics have been developed from scripts of his lectures in organic chemistry and molecular spectroscopy held in the USA and in Germany. It comprises the molecular orbital model to explain *covalent bonding in organic molecules*, the *classes of organic compound*s including *natural products*, *polymers* and *biopolymers*, basic *concepts* (orbital hybridization, resonance, aromaticity), types and mechanisms of *organic reactions*, and essential aspects of *molecular structure* such as atom connectivities, skeletal isomerism, conformation, configuration, and chirality, including a very brief strategic introduction to structure elucidation by molecular spectroscopy. New chapters deal with *selectivity* and *specificity* of *organic reactions*, *prochirality and enantioselectivity*, *planning organic syntheses*, *two-dimensional* and *carbon-13 NMR* in the third revised edition.

Each chapter is designed as a *short learning unit*, presented *at one glance* on one or two pairs of pages (two-page view), ending with at least three *questions* very closely related to the chapter's contents. Thus, when *answers* cannot be given spontaneously, they are easily found by reading (and understanding) the text once again. These questions offer an *option of self-examination*. In few cases, obvious analogous conclusions, variations of reaction equations or the reader's own reflections are expected as the answers which are provided in the appendix "Working on Questions" and free of charge on the website *www.wiley-vch.de/ISBN9783527350568*.

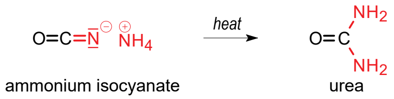
Many thanks are due to *Dr. Kay Greenfield* (Brisbane, Australia) for proofreading the first and second editions. - Any suggestions for corrections or improvement are very welcome for future electronic updating of this text.

Tübingen (Germany), summer 2021 *Eberhard Breitmaier*

for Stefanie

Organic Chemistry

Traditionally, chemistry is appropriately subdivided into *inorganic, organic* and *physical chemistry* as well as *biochemistry*. *Organic chemistry* deals with organic compounds. *Organic compounds* are not only metabolites and natural products isolated from living organisms and their fossil remains, as was assumed until the beginning of the 19th century, but can also be prepared by synthesis. WÖHLER´s 1828 preparation of *urea*, the physiological end-product of nitrogen excretion in mammals, exemplified the first synthesis of an organic compound from the inorganic salt ammonium isocyanate.



All organic compounds contain the element *carbon*. Thus, *organic chemistry* can be defined as the *chemistry of carbon compounds*, including their chemical *structure*, *properties*, *syntheses* and *reactions*.

Naturally occurring in the crystalline modifications *graphite* and *diamond*, *carbon* represents the *softest* and *hardest* solid element under normal conditions. Moreover, carbon is one of the most varied elements of the periodic table:

The *carbon atom* is *tetravalent*. It is able to form single, double and triple bonds with its own kind as well as with the atoms of many other elements. Carbon atoms are able to close rings with themselves and with other kinds of atoms, so-called heteroatoms, thus forming carbocycles and heterocycles. As many as 217 theoretical hydrocarbon structures can be written for the simple molecular formula C_6H_6. Bonds originating from the carbon atom are neither too weak nor too strong, meaning that organic compounds may undergo chemical reactions under moderate or physiological conditions. This explains the inexhaustibly large number of organic compounds. Several ten millions have already been documented. About 90 percent are synthetic substances; the remaining compounds have been isolated as *natural products* (Chapters 68-77), biosynthesized by microorganisms, fungi, plants, and animals.

Apart from carbon (C), organic compounds and natural products predominantly contain the *non-metal elements* hydrogen, oxygen, nitrogen, sulfur, phosphorus (H, O, N, S, P) and halogens. *Organometal compounds* (Chapter 32) characterized by carbon-metal bonds and useful as highly reactive reagents in organic synthesis are only synthetically available.

Organic compounds are divided into *classes*, each characterized by a *functional group*. A functional group is a particular arrangement of atoms which gives rise to a set of typical physical properties and chemical reactions. Hydroxy groups (–OH), for example, define the reactivity of alcohols (Chapter 33) and phenols (Chapter 52), and carboxy groups (–COOH) that of carboxylic acids (Chapter 41).

CH and CC bonds are the most prominent bonds of organic compounds. Both are *covalent bonds*. The formation, the geometry, the interactions, and the polarity of these bonds explain the structure, the properties, and the reactions of organic compounds. A clear picture of covalent single and multiple bonds is provided by the *molecular orbital model* (Chapters 1-4) which has been developed from quantum mechanical calculations.

This introduction permits answers to the following:

How is the field of organic chemistry defined?
Which elements are the predominant constituents of organic compounds?
What are the reasons behind the large number of organic compounds?
What is a functional group?

1 Atomic Orbitals, Electronic Configurations

1.1 Atomic Orbitals

Physical experiments (electron diffraction, COMPTON effect) provide evidence that *electrons* do not only behave as *particles* but as *standing waves* as well. Mathematically, the wave nature of the electron is described by the SCHRÖDINGER equation (1). This differential equation correlates the *wave function* ψ of the electron with its total energy E.

$$H\,\psi = E\,\psi \qquad (1)$$

(E: total energy, ψ: wave function, H: HAMILTON operator)

The SCHRÖDINGER equation (1) is only resolvable for *selected values of the energy E*. These values correspond to the *energy levels* of the electron in an atom, defined by the quantum numbers 1, 2, 3, ... Electronic energy is said to be *quantized*. The wave function ψ of an electron on a particular energy level E is the solution of the SCHRÖDINGER equation for that specific energy E. While this particular wave function ψ of the electron does not have any concrete meaning, its square, ψ^2, describes the space around the atomic nucleus where the electron is most likely to be found. This *"space of residence"* or simply the *"living room"* of an electron described by ψ^2 is referred to as the *atomic orbital* (electron cloud).

1.2 s and p Orbitals

Spherosymmetric atomic orbitals with the atomic nucleus as center are referred to as s orbitals (Fig. 1.1).

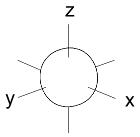


Fig. 1.1. s orbital: spherosymmetric distribution of the electron about the atomic nucleus

On the lowest energy level E_1 (quantum number n = 1) the electron occupies the 1s orbital; this applies for the hydrogen atom. The 2s orbital following at the second energy level E_2 (n = 2) concentrically envelops the 1s orbital. The 2s orbital is occupied by an electron in the lithium atom, following the helium atom of the first row of the periodic table (Table 1.1) with a doubly occupied 1s orbital.

Beginning with the second energy level E_2 (n = 2), there are *three* additional *dumpbell-shaped atomic orbitals* on energy levels slightly elevated relative to the 2s orbital (Fig. 1.2). In contrast to the spheric s orbitals, these orbitals are *directed*, extending along the axes *x*, *y* and *z*; therefore, they are called the $2p_x$, $2p_y$ and $2p_z$ orbitals. All three 2p orbitals possess the same energy and for this reason they are said to be *degenerate*.

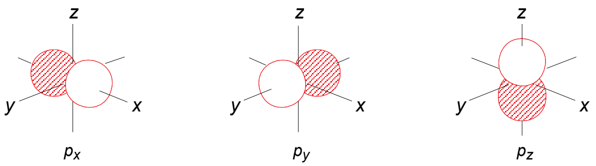


Fig. 1.2. p Orbitals (p_x, p_y, p_z) along the coordinate axes; p orbital halves in the range of negative sign are shaded

1.3 Electron Spin and PAULI Principle

In addition to their negative charge and their impulse to circumrotate the nucleus, electrons possess a *spin* (electron spin). They may spin either clockwise or counterclockwise. When two electrons spin in the same manner, they are said to have *parallel spins* and this situation is symbolized by two arrows in the same direction (↑↑). When, however, two elec-

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trons spin in opposite directions, they are said to have *antiparallel spins*, and this is symbolized by two arrows in opposite direction (↑↓). Electrons with antiparallel spin are also said to be *paired*.

Only two electrons can occupy the same orbital, provided they have antiparallel spins (↑↓). This restriction is known as the PAULI principle.

1.4 Electronic Configuration of Light Atoms

The distribution of electrons in the orbitals of an atom is called the *electronic configuration* of that atom. The electronic configuration represents the *ground state* of an atom, that is the state of lowest potential energy and highest stability. The main constituent atoms C, H, O, N of organic compounds are among the light elements of the periodic table. Their electrons occupy only s and p orbitals. Three rules regulate the occupation of orbitals by electrons:

- The orbitals are occupied in order of increasing energy: first 1s, then 2s, followed by $2p_x$, $2p_y$, $2p_z$.
- Only up to two electrons can occupy the same orbital. Double occupation requires electronic spins to be antiparallel (PAULI principle).
- When a set of degenerate orbitals is available, for instance the three 2p orbitals, single occupation takes place before any of these orbitals becomes doubly occupied (HUND rule, *cf.* the electronic configuration of the elements C, N, O in Table 1.1).

The electronic configuration of an atom (Table 1.1) is described by quoting the occupied orbitals in the order of increasing energy. The number of electrons in each orbital, 1 or 2, is indicated by the superscript ^{1} or ^{2} at the corresponding orbitals; the ^{1} for single occupation is usually omitted. Boron as an example has the electronic configuration $1s^2\ 2s^2\ 2p$ ($1s^2\ 2s^2\ 2p^1$), indicating double occupation for the 1s and 2s orbitals and single occupation for one 2p orbital.

Table 1.1. Electronic configuration of light atoms in the ground state

atom	occupation					representation
	1s	2s	$2p_x$	$2p_y$	$2p_z$	
H	↑					$1s$
He	↑↓					$1s^2$
Li	↑↓	↑	○	○	○	$1s^2\ 2s$
Be	↑↓	↑↓	○	○	○	$1s^2\ 2s^2$
B	↑↓	↑↓	↑	○	○	$1s^2\ 2s^2\ 2p$
C	↑↓	↑↓	↑	↑	○	$1s^2\ 2s^2\ 2p^2$
N	↑↓	↑↓	↑	↑	↑	$1s^2\ 2s^2\ 2p^3$
O	↑↓	↑↓	↑↓	↑	↑	$1s^2\ 2s^2\ 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2\ 2s^2\ 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2\ 2s^2\ 2p^6$ ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$)

Chapter 1 permits answers to the following:

(1.1) What is an atomic orbital?

(1.2) How do p orbitals differ from s orbitals?

(1.3) How do p orbitals differ among themselves?

(1.4) Write the orbital occupancy for the atoms in the first two rows of the periodic table.

(1.5) Is the tetravalency of carbon in accordance with the electronic configuration of carbon in Table 1.1?

2 Covalent Bonding

2.1 Kinds of Chemical Bond

Ionic and covalent bonds are the main types of chemical bonding. Instead of molecules, *ions* exist in inorganic salts such as sodium chloride in which the ions are held together by the ionic bond. *Ionic bonding* is the *electrostatic attraction of oppositely charged ions*. Thus, the sodium ion $Na^{\oplus}$ attracts and is attracted by the chloride anions $Cl^{\ominus}$ in the crystal lattice of sodium chloride.

In contrast, organic compounds do exist as molecules held together by covalent bonds. *Covalent bonding,* also referred to as *electron pair bonding*, arises from *sharing of electrons between two atoms*. This is exemplified by the hydrogen molecule in which two hydrogen nuclei, two protons $H^{\oplus}$, are held together by an *electron pair* between them:

electron pair or covalent bond

$H\bullet \qquad \bullet H \qquad\qquad H:H \qquad H{-}H$

two H atoms one H_2 molecule

2.2 Covalent Bonding by Overlapping of Atomic Orbitals

In terms of the orbital model, a *covalent bond* arises from *overlapping of atomic orbitals*. When two H atoms, for example, are brought closely enough together, their two singly occupied 1s atomic orbitals overlap (Fig. 2.1 b). A doubly occupied *molecular orbital* arises, enclosing both protons $H^{\oplus}$ in the hydrogen molecule (Fig. 2.1, HH bond length 74 pm, 1 pm = 1 picometer = 10^{-12} m).

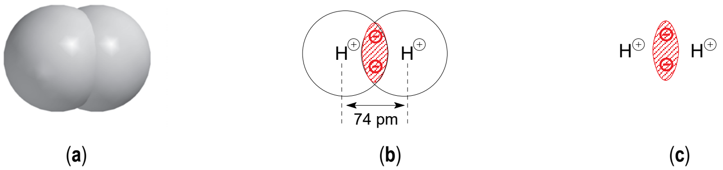

Fig. 2.1. σ Molecular orbital of the hydrogen molecule H_2: (**a**) shape; (**b**) cross section; (**c**) the bonding electrons are most likely to be found in the red shaded area of overlap

Mathematically, overlapping of atomic orbitals involves an *addition* and *subtraction* (linear combination) of the wave functions ψ_1 and ψ_2 attributed to the overlapping atomic orbitals:

$$\psi = N(\psi_1 + \psi_2) \qquad \psi^* = N(\psi_1 - \psi_2)$$

N is a factor for standardization. The resulting two wave functions are assigned to *two molecular orbitals*, one more stable *bonding* σ molecular orbital with lower energy and another less-stable *antibonding* σ* molecular orbital with higher energy (Fig. 2.2).

The square of the wave function, ψ^2, describes the shape of the electron cloud which is the distribution of electron density about the atomic nuclei. Squaring for the bonding molecular orbital ψ yields

$$\psi^2 = [N(\psi_1 + \psi_2)]^2 = N^2(\psi_1^2 + \psi_2^2 + 2\psi_1\psi_2)$$

and for the antibonding molecular orbital ψ^*

$$\psi^{*2} = [N(\psi_1 - \psi_2)]^2 = N^2(\psi_1^2 + \psi_2^2 - 2\psi_1\psi_2)\ .$$

To conclude, an amount of $2\psi_1\psi_2$ *increases the electron density* in the bonding σ molecular orbital relative to the total of the atomic orbitals, $\psi_1^2 + \psi_2^2$. The additional term $2\psi_1\psi_2$ adopts a maximum where ψ_1 and ψ_2 culminate. This is the area between the nuclei in the center of the bond where the atomic orbitals overlap (Fig. 2.1 c). The electron cloud accumu-

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lates there, thus overcompensating the electrostatic repulsion of the positively charged atomic nuclei. Overall, the electron density distribution in the bonding orbital referred to as a σ molecular orbital provides the amount of energy which stabilizes the hydrogen molecule H_2 relative to two hydrogen atoms (Fig. 2.2). The antibonding σ^* molecular orbital with the negative term $-2\psi_1\psi_2$, in contrast, destabilizes the hydrogen molecule in the excited state.

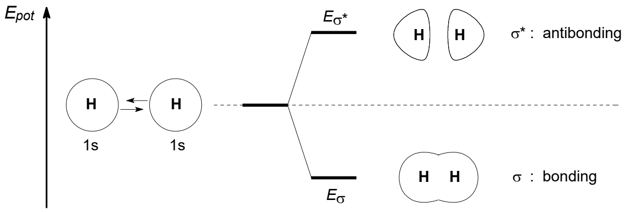


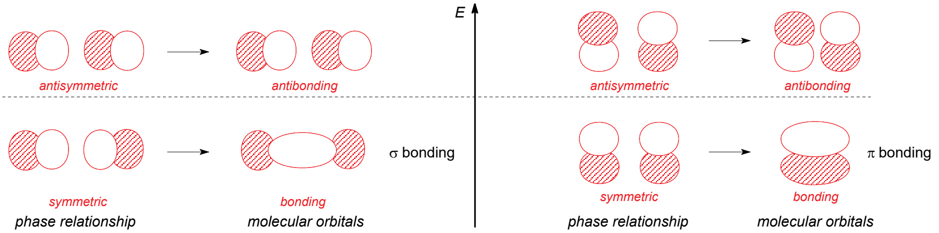
Fig. 2.2. Overlapping of 1s orbitals of two hydrogen atoms

Generally, two molecular orbitals (MOs) with different energies arise from the overlapping of atomic orbitals, the stable *bonding MO* with lower energy, and the *antibonding MO* on the higher energy level, corresponding to the excited state of a bonding electron attainable by supply of a defined quantum of energy.

2.3 Overlapping of p Orbitals

The overlapping of p orbitals and other *directed* atomic orbitals generates σ or π molecular orbitals depending on the manner of overlapping (Fig. 2.3). Molecular orbitals of the *σ type*, for example in the fluorine molecule F_2, arise from *endwise overlapping* of two singly occupied 2p atomic orbitals (Fig. 2.3 a). *Sidewise overlapping* of two singly occupied *coaxial* 2p atomic orbitals generates *π molecular orbitals* (Fig. 2.3 b); those explain the formation of multiple bonds in terms of the molecular orbital model (Chapters 4.2, 4.3).

Endwise or sidewise overlapping of p orbitals generates *bonding* and *antibonding* molecular orbitals, depending on the *phase relationship* (orbital symmetry) of these orbitals: *Bonding molecular orbitals* arise from *overlapping of lobes which have the same sign* (*symmetric* overlapping) while *overlapping of lobes with opposite sign* (*antisymmetric* overlapping) results in the formation of *antibonding* molecular orbitals (Fig 2.3).



(**a**) σ bonding by *endwise* overlapping of p orbitals (**b**) π bonding by *sidewise* overlapping of *coaxial* p orbitals

Fig. 2.3. (**a**) Endwise overlapping of two p orbitals resulting in two σ molecular orbitals (σ bonding); (**b**) sidewise overlapping of two coaxial p orbitals resulting in two π molecular orbitals (π bonding); p orbital lobes with negative sign are shaded

---

Chapter 2 permits answers to the following:

*(**2.1**)* What is a covalent bond?

*(**2.2**)* How is a molecular orbital (MO) generated?

*(**2.3**)* How can the covalent bond of the hydrogen molecule be explained?

*(**2.4**)* Calculate the particularly high electron density between covalently bonded atomic nuclei in terms of the MO model.

*(**2.5**)* Which options of overlapping exist for p orbitals? Which types of bonding are the result?

3 Hybridization of Atomic Orbitals

3.1 Geometry of the Methane Molecule

Methane, the simplest hydrocarbon, has the molecular formula CH_4. Spectroscopic data indicate the *four CH bonds* to be *equivalent* and directed to the corners of a regular tetrahedron (Fig. 3.1). All CH bonds are equal in length (109 pm, 1 pm = 1 picometer = 10^{-12} m) and pairwise enclose the *tetrahedral bond angle* of 109°28'.

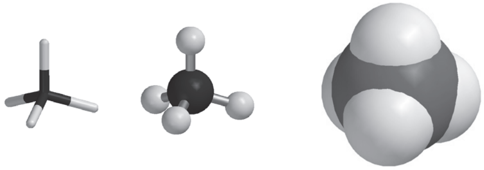


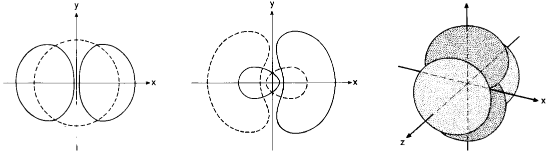
Fig. 3.1. Tetrahedral geometry of the methane molecule (tube, ball-spoke and space-filling molecular model)

The *equivalence and tetrahedral symmetry of all four CH bonds in methane* (CH_4) cannot be explained by the electronic configuration of the carbon atom in the ground state ($1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, Table 1.1). Its two singly occupied p orbitals could overlap with two s orbitals of two hydrogen atoms; the molecular formula of a hydrocarbon with bivalent carbon would be CH_2. Promotion of one 2s electron into the empty $2p_z$ orbital with the resultant electronic configuration $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$ would permit tetravalency and the correct molecular formula CH_4 but does not really solve the problem: two different kinds of CH bonds would arise, one bond by non-directed ss overlapping and three bonds by directed ps overlapping with bond angles of 90°.

3.2 Hybridization of Atomic Orbitals

The inadequacy of the atomic orbital model to explain the methane molecular structure has been removed by the concept of hybridization (PAULING, SLATER). *Hybridization of atomic orbitals* involves linear combination of different wave functions, for example those of s and p orbitals; the resulting equations describe the shapes and directions of hybrid orbitals. Simply, hybridization is a mixing of different atomic orbitals to form *hybrid orbitals* which are shaped differently from the parent atomic orbitals. Hybridization of s and p orbitals may generate sp, sp^2 and sp^3 hybrid orbitals, depending on the number of p orbitals ($^{1, 2, 3}$) involved in the hybridization.

Two sp hybrid orbitals arise from the crossing of one s with one p orbital (Fig. 3.2 a). Due to their origin, they have 50% s and 50% p character; like their parent p orbital they extend along an axis (*linear arrangement*), enclosing an *interorbital angle* of 180° (Fig. 3.2 b, Table 3.1). Two p orbitals perpendicular to the axis remain unhybridized (Fig. 3.2 c).



(**a**) (**b**) (**c**)

Fig. 3.2. sp hybrid orbitals: (**a**) hybridization of s and p_x atomic orbitals; (**b**) contours of the sp hybrid orbitals along the x axis; (**c**) remaining p orbitals, p_y and p_z

Three sp^2 hybrid orbitals arise from the combination of one s orbital with two p orbitals (Fig. 3.3 a). Due to their origin, they have 33.3% s and 66.7% p character. All three sp^2 hybrid orbitals are *coplanar* (Fig. 3.3 b); their axes enclose inter-

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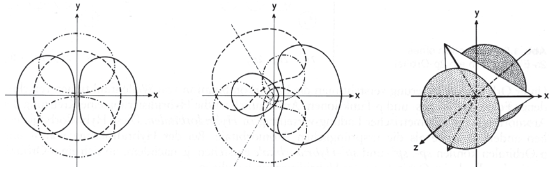
orbital angles of 120° (Table 3.1), forming the apexes of a regular triangle. One p orbital perpendicular to the plane of the sp^2 triangle remains unhybridized (Fig. 3.3 c).



(**a**) (**b**) (**c**)

Fig. 3.3. sp^2 hybrid orbitals: (**a**) hybridization of atomic orbitals s, p_x, p_y; (**b**) contours of the sp^2 hybrid orbitals in the xy plane; (**c**) remaining p_z orbital perpendicular to the plane of the sp^2 hybrid orbitals

Four sp^3 hybrid orbitals arise from the combination of an s orbital with all three p orbitals (Fig. 3.4). All of the four equivalent sp^3 hybrids have 25% s and 75% p character; they are directed towards the corners of a regular tetrahedron, pairwise enclosing the *tetrahedral angle* of 109°28' (Fig. 3.4, Table 3.1).

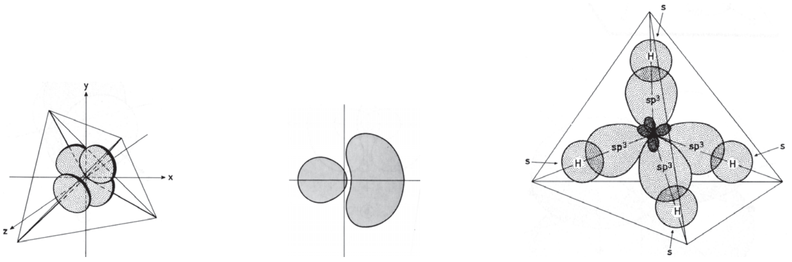
Table 3.1 compares the properties of sp, sp^2 and sp^3 hybrid orbitals. It turns out that the hybrid orbitals have a larger radial extension than s and p orbitals, increasing with their p character (sp < sp^2 < sp^3), and therefore offer better chances for overlapping than the parent orbitals.

Table 3.1. Properties of sp^x hybrid orbitals

hybridizing orbitals		hybrid orbitals	geometry	interorbital angle	character		remaining p orbitals	radius in relation to s = 1, p = 1.732
					% s	% p		
1 s	1 p	2 sp	linear	180°	50	50	2	1.93
1 s	2 p	3 sp^2	coplanar, trigonal	120°	33.3	66.7	1	1.99
1 s	3 p	4 sp^3	tetrahedral	109.5°	25	75	0	2.00

3.3 Carbon-Hydrogen Bonding in Methane

Provided bond angles in carbon compounds correspond to the angles formed by hybrid orbitals, the shape of organic molecules can be explained. Tetrahedral sp^3 hybrid orbitals exactly match the tetrahedral geometry of the methane molecule (Fig. 3.1): each one of the four CH bonds of methane arises from overlapping of an sp^3 hybrid orbital originating from the carbon atom with an s orbital of a hydrogen atom (Fig. 3.4 c).



(**a**) (**b**) (**c**)

Fig. 3.4. sp^3 hybrid orbitals: (**a**) all sp^3 hybrid orbitals in the x, y, z coordinate system; (**b**) cross section of an sp^3 hybrid orbital; (**c**) overlapping of four sp^3 hybrid orbitals of carbon and s orbitals of four hydrogens to the four CH σ bonds (σ molecular orbitals) of methane

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Chapter 3 permits answers to the following:

(3.1) Describe and draw the geometry of the methane molecule.

(3.2) The electronic configuration of the carbon atom does not explain the shape of the methane molecule. Why?

(3.3) What is hybridization of atomic orbitals? Hybrid orbitals offer better chances for overlapping. Why?

(3.4) What is the model explanation of the tetrahedral shape of the methane molecule and the genesis of its CH bonds?

4 Covalent Carbon-Carbon Bonding

4.1 Ethane, CC Single Bond

Similar to methane (Chapter 3.3), all bonds originating from both carbon atoms of the hydrocarbon *ethane* (C_2H_6, Chapter 5.1) are *tetrahedral*, enclosing bond angles of 109°28´, as illustrated by molecular models (Fig. 4.1).

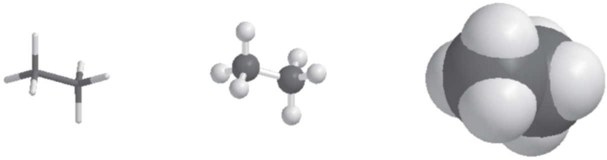

Fig. 4.1. Tube, ball-spoke and space-filling molecular model of ethane

The molecular orbital model explains the shape of the ethane molecule by invoking sp^3 hybridized C atoms. Six CH σ bonds arise from overlapping of sp^3 hybrid orbitals of carbon atoms with s orbitals of six hydrogens similar to the MO model of methane (Fig. 3.4 c). The CC σ bond (CC bond length 154 pm) results from an endwise overlapping of two sp^3 hybrid orbitals originating from the adjacent carbon atoms (Fig. 4.2).

bond lengths, bond angles

overlapping orbitals, σ bonds

Fig. 4.2. Bond lengths (nuclear distances), bond angles and σ bonds of ethane

4.2 Ethene, CC Double Bond

Ethene (ethylene, $H_2C{=}CH_2$, Chapter 14.1) is the simplest hydrocarbon that contains a CC double bond. It is a *planar molecule* with HCH and HCC bond angles of about 120°, as shown by the molecular models in Figs. 4.3 and 4.4 a. Consequently, hybrid orbitals which explain the shape of the ethene molecule must satisfy two conditions: they must be *coplanar* and must enclose *interorbital angles of 120°*.

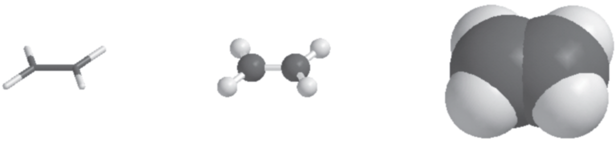

Fig. 4.3. Tube, ball-spoke and space-filling molecular model of ethene

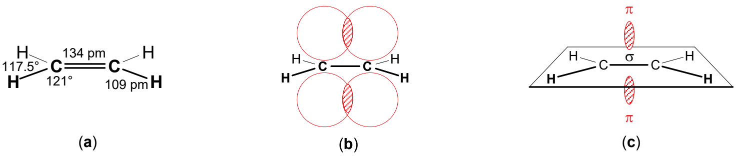

Fig. 4.4. Ethene molecule: (**a**) trigonal planar molecular shape with bond data; (**b**) overlapping p orbitals perpendicular to the plane of σ bonds; (**c**) areas where the π electrons are most likely to be found in the resultant π molecular orbital

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These requirements are met by sp^2 hybrid orbitals. Two sp^2 hybrid orbitals of the two adjacent carbon atoms overlap *endwise*, generating the CC σ bond of ethene. The four remaining sp^2 hybrid orbitals on the two C atoms overlap with four s orbitals of four hydrogen atoms, generating four CH σ bonds. When all five σ bonds are coplanar, the unhybridized 2p orbitals on both carbons are *coaxial* and this situation permits their *sidewise* overlapping. This overlapping generates a *π molecular orbital* and a *π bond* with the π electron cloud above and below the molecular plane (Fig. 4.4 b); π electrons are most likely to be found in the overlapping area of the original p orbitals above and below the center of the CC bond (Fig. 4.4 c). Thus, *a CC double bond arises from one σ and one π bond.*

4.3 Ethyne, CC Triple Bond

Ethyne (acetylene, $\mathrm{H{-}C{\equiv}C{-}H}$, Chapter 19.1), the simplest hydrocarbon with a CC triple bond, is a *linear molecule* forming HCC bond angles of 180° (Figs. 4.5, 4.6 a).

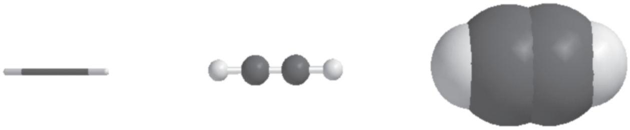
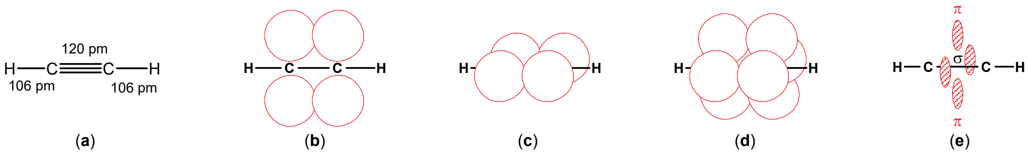


Fig. 4.5. Tube, ball-spoke and space-filling molecular model of ethyne

In the molecular orbital model, *linear sp hybrid orbitals* of carbon explain the *linear shape of ethyne*. The CC σ bond arises from endwise overlapping of two sp hybrid orbitals originating from the adjacent carbon atoms. Each of the two C atoms forms a CH σ bond by overlapping its sp hybrid orbital with an s orbital of hydrogen. *Sidewise* overlapping of the *coaxial* pairs of the remaining 2p orbitals at both carbon atoms generates *two π molecular orbitals* and *two CC π bonds* (Fig. 4.6 b-d); π electrons are most likely to be found in the overlapping areas of the original p orbitals above and below, and in front and behind, the center of the CC single bond (Fig. 4.6 e). Thus, *a CC triple bond arises from one σ bond and two additional π bonds*.



(**a**) (**b**) (**c**) (**d**) (**e**)

Fig. 4.6. Ethyne molecule: (**a**) linear molecular shape and bond lengths; (**b**) overlapping of p orbitals to the first, and (**c**) to the second π bond; (**d**) overlapping of both coaxial pairs of p orbitals to give two π bonds; (**e**) areas where the π electrons are most likely to be found in the resultant π molecular orbitals

Since the radial extension of hybrid orbitals decreases with growing s character (sp^3 > sp^2 > sp), the lengths of carbon-carbon single, double and triple bonds decrease with increasing bond order (single > double > triple).

C–C : 154 pm	C=C : 134 pm	C≡C : 120 pm
sp^3-sp^3	sp^2-sp^2	sp-sp

Chapter 4 permits answers to the following:

(4.1) What are the molecular shapes of ***(a)*** ethane, ***(b)*** ethene, and ***(c)*** ethyne?

(4.2) Explain the genesis of a CC single, a CC double and a CC triple bond in terms of the MO model.

(4.3) Draw the areas around a CC double bond where the π electrons are most likely to be found.

(4.4) Explain why CC multiple bonds are shorter than a CC single bond.

5 Alkanes

5.1 Homologous Series of Alkanes

Organic compounds that only contain carbon and hydrogen are called *hydrocarbons*. Hydrocarbons in which all carbon atoms are linked exclusively by CC single bonds are referred to as *alkanes*. All members of the alkane family possess the *general molecular formula* C_nH_{2n+2} , thus forming a *homologous series*. A homologous series includes chemically closely related compounds with a general molecular formula and common chemical properties; formally, homologues are constructed by insertion of a methylene group, $-CH_2-$ (*homologization*).

Table 5.1. Homologous series of alkanes (m.p.: melting point; b.p.: boiling point at normal pressure 1013 mbar)

n	C_nH_{2n+2}	abbreviated structure	name	m.p. °C	b.p. °C
1	CH_4	H_3C-H	methane	–183	–164
2	C_2H_6	H_3C-CH_3	ethane	–183	–89
3	C_3H_8	$H_3C-CH_2-CH_3$	propane	–190	–42
4	C_4H_{10}	$H_3C-(CH_2)_2-CH_3$	butane	–138	0
5	C_5H_{12}	$H_3C-(CH_2)_3-CH_3$	pentane	–130	36
6	C_6H_{14}	$H_3C-(CH_2)_4-CH_3$	hexane	–95	69
7	C_7H_{16}	$H_3C-(CH_2)_5-CH_3$	heptane	–90	98
8	C_8H_{18}	$H_3C-(CH_2)_6-CH_3$	octane	–59	126
9	C_9H_{20}	$H_3C-(CH_2)_7-CH_3$	nonane	–54	151
10	$C_{10}H_{22}$	$H_3C-(CH_2)_8-CH_3$	decane	–30	174
11	$C_{11}H_{24}$	$H_3C-(CH_2)_9-CH_3$	undecane	–26	196
12	$C_{12}H_{26}$	$H_3C-(CH_2)_{10}-CH_3$	dodecane	–10	216
13	$C_{13}H_{28}$	$H_3C-(CH_2)_{11}-CH_3$	tridecane	–6	230
14	$C_{14}H_{30}$	$H_3C-(CH_2)_{12}-CH_3$	tetradecane	6	251
15	$C_{15}H_{32}$	$H_3C-(CH_2)_{13}-CH_3$	pentadecane	10	268
20	$C_{20}H_{42}$	$H_3C-(CH_2)_{18}-CH_3$	eicosane	36	
30	$C_{30}H_{62}$	$H_3C-(CH_2)_{28}-CH_3$	triacontane	66	

5.2 Natural Sources and Preparation

5.2.1 Distillation of Petroleum

Coal, *natural gas*, and *petroleum* are the chief sources of alkanes and other hydrocarbons. These fossil sources of energy originated from anaerobic decomposition of microorganisms (plankton), plants, and animals in seas and oceans more than 100 million years ago. Due to their different boiling points (Table 5.1), alkanes and other components of petroleum can be separated by distillation. The petroleum fractions with their boiling point ranges and their use, predominantly for the production of energy and as raw materials in chemical industry (petrochemistry), are given in Table 5.2.

Table 5.2. Distillation fractions of refined petroleum

fraction	b.p. °C	hydrocarbons C_n	use
gas fraction	< 40	C_1 - C_6	fuel, heating
petroleum ether	30 - 60	C_5 - C_6	solvent, fuel
ligroin	60 - 100	C_6 - C_7	fuel
gasoline	40 - 200	C_5 - C_{10}	fuel
kerosine	180 - 230	C_{11} - C_{12}	fuel for jet engines
gas oil	230 - 300	C_{13} - C_{17}	diesel and furnace fuel
lubrication oils	300 - 400	C_{20} - C_{30}	lubrication
paraffin waxes	400 - 500	C_{20} - C_{30}	vaseline
asphalt	distillation	polycyclic structures	road building, roofing
petroleum coke	residues	carbon	fuel, carbon electrodes

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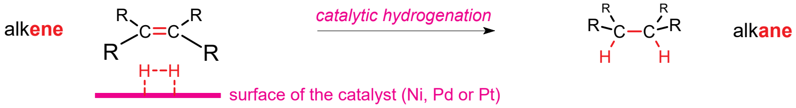
5.2.2 Catalytic Hydrogenation of Alkenes

Hydrogen adds to the double bonds of *alkenes* (hydrocarbons unsaturated with hydrogen, Chapter 14.1) in the presence of a metal (Ni, Pd, Pt) as catalyst which accelerates hydrogenation. *Alkanes*, saturated with hydrogen, are the products.



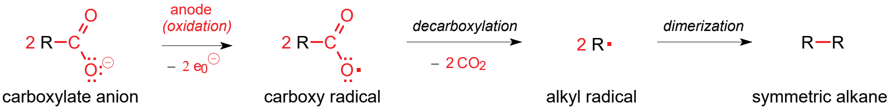
5.2.3 Wurtz Synthesis Involving Alkylsodium

Alkanes of the type R–R are obtained by reacting alkyl halides R–X with sodium metal. Initially formed alkylsodium R–Na, an organometal compound (Chapter 32), reacts with alkyl halide to yield the symmetric alkane. In this manner, hexane (R = $CH_3–CH_2–CH_2–$) can be prepared from 1-bromopropane (X = Br).

$$\underset{\text{alkyl halide}}{R{-}X} + 2\,Na \longrightarrow \underset{\text{alkylsodium}}{R{-}Na} + NaX \qquad R{-}Na + R{-}X \longrightarrow \underset{\text{symmetric alkane}}{R{-}R} + NaX \qquad X = Cl, Br, I$$

5.2.4 Kolbe Electrolysis of Carboxylates (Anodic Oxidation)

The electrolysis of carboxylates $RCOO^{\ominus}$, the salts of carboxylic acids (Chapter 41), also yields symmetric alkanes R–R. The anode abstracts an electron from the carboxylate anion, so that the reaction is an *anodic oxidation*. As an example, Kolbe electrolysis of propanoate (R = $CH_3–CH_2–CH_2–$) produces hexane.



5.3 Alkanes as an Energy Source

The alkanes of fuels (natural gas, gasoline, diesel oil, kerosine) can be oxidized by air oxygen to carbon dioxide and water, as exemplified for methane and ethane.

$$\begin{aligned} CH_4 + 2\,O_2 &\longrightarrow CO_2 + 2\,H_2O & \Delta H &= -883\ \text{kJ/mol} \\ 2\ H_3C{-}CH_3 + 7\,O_2 &\longrightarrow 4\,CO_2 + 6\,H_2O & \Delta H &= -1542\ \text{kJ/mol} \end{aligned}$$

However, combustion of alkanes requires ignition by a flame or a spark (Chapter 12.1); at room temperature and normal pressure a mixture of alkane and oxygen (air) does not react.

Combustion of alkanes produces energy because the oxidation is a strongly *exothermic reaction* (Chapter 12.1), delivering a high *heat of combustion* ΔH (reaction enthalpy) to the environment. Since energy is given away in an exothermic reaction, the sign of ΔH is negative.

This kind of *chemical production of energy* for heating, driving engines and jet propulsion produces tremendous amounts of the hothouse gas *carbon dioxide* (Chapter 56.1). For example, the combustion of 1 mol of methane (16 g / mol or 22.4 L) generates one mol of carbon dioxide (44 g / mol or 22.4 L).

Chapter 5 permits answers to the following:

(5.1) What is a homologous series of compounds?

(5.2) What natural sources of alkanes exist and how are alkanes produced industrially?

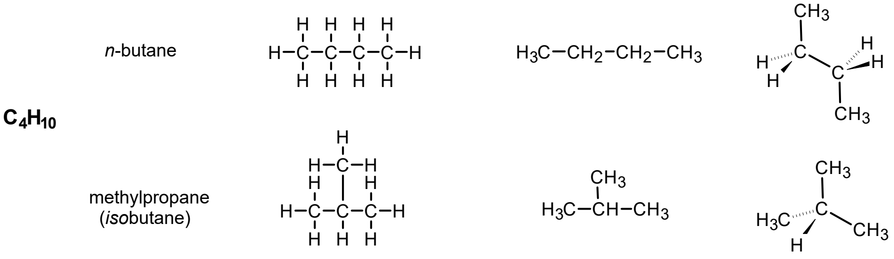
(5.3) Which reactions permit the preparation of specific alkanes?

(5.4) Alkanes are still an important source of energy. Why? Write the complete equation for an appropriate reaction.

6 Skeletal Structure, Structural Isomerism

6.1 Two and More Structures for One Molecular Formula

There are two different butanes, both with the same molecular formula C_4H_{10}: butane, more precisely *n*-butane (*n* for *normal*) has an *unbranched* (continuous) *chain* of carbon atoms with *elongated shape* (Fig. 6.1); *iso*butane also referred to as methylpropane belongs to the *branched-chain* alkanes, adopting a more spherical shape, as shown by molecular models (Fig. 6.1).



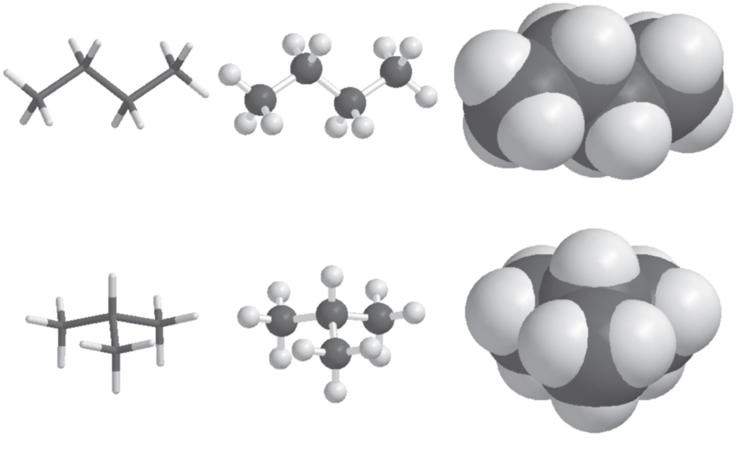


Fig. 6.1. Tube, ball-spoke and space-filling molecular model (from left to right) of unbranched butane (*n*-butane, top) and branched methylpropane (isobutane, bottom)

6.2 Skeletal Isomerism

Butane (*n*-butane) and methylpropane (isobutane) are referred to as *structural isomers* (from Greek *isos* = same, similar; *meros* = part). Structural isomers, also known as *skeletal isomers* or *constitutional isomers*, have the same molecular formula but different carbon skeletons (atom connectivities, skeletal structures, constitutions) as exemplified in Fig. 6.1 by the *unbranched n*-butane and the *branched* isobutane which has a methyl group in the *side chain*. Structural isomers exhibit different physical properties (melting points, boiling points, refractive indices, molecular spectra). At normal pressure, unbranched *n*-butane with elongated shape boils at 0 °C while branched isobutane with the more spherical shape boils at −12 °C. Due to their individual boiling points, structural isomers can be separated (purified) by distillation.

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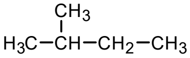
Three structural isomers exist for the molecular formula C_5H_{12}. These are the unbranched pentane (*n*-pentane), the singly branched methylbutane (isopentane), and doubly branched dimethylpropane (neopentane) with methyl groups as side chains:

unbranched — *singly branched* — *doubly branched*

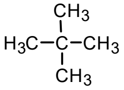
C_5H_{12}

$H_3C-CH_2-CH_2-CH_2-CH_3$

n-pentane


$H_3C-\overset{CH_3}{CH}-CH_2-CH_3$

methylbutane
(isopentane)


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

dimethylpropane
(neopentane)

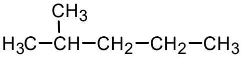
In going further to higher homologues of alkanes (Table 5.1), the number of isomers increases exponentially. Five structural isomers exist for hexane C_6H_{14}, 75 for decane $C_{10}H_{22}$, and more than four million for tridecane $C_{30}H_{62}$.

unbranched — *singly branched* — *multiply branched*

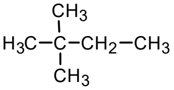
C_6H_{14}

$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$

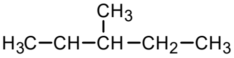
n-hexane


$H_3C-\overset{CH_3}{CH}-CH_2-CH_2-CH_3$

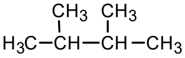
2-methylpentane


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

2,2-dimethylbutane


$H_3C-CH-\overset{CH_3}{CH}-CH_2-CH_3$

3-methylpentane


$H_3C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$

2,3-dimethylbutane

Chapter 6 permits answers to the following:

(6.1) What are structural (skeletal) isomers?

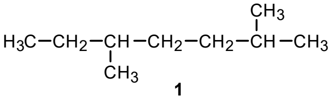
(6.2) Which structural isomers exist for ***(a)*** butane, ***(b)*** pentane, and ***(c)*** hexane?

(6.3) Which properties are individual (specific) for structural isomers?

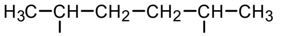
(6.4) Which one of these properties is the basis of a method for the separation and purification of structural isomers?

(6.5) Draw the structures of the skeletal isomers of heptane with ***(a)*** one methyl group and ***(b)*** two methyl groups in the side chain.

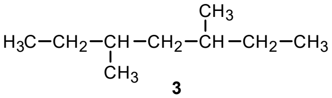
(6.6) Which of the following compounds (**1**-**6**) are structural isomers? Which ones are identical?


$H_3C-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-\overset{CH_3}{CH}-CH_3$

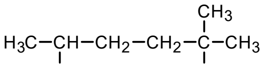
1


$H_3C-\underset{CH_3}{CH}-CH_2-CH_2-\underset{CH_2-CH_3}{CH}-CH_3$

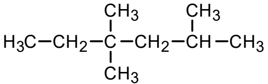
2


$H_3C-CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_2-CH_3$

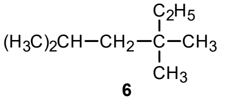
3


$H_3C-\underset{CH_3}{CH}-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

4


$H_3C-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$

5


$(H_3C)_2CH-CH_2-\overset{C_2H_5}{\underset{CH_3}{C}}-CH_3$

6

7 Basic Rules of Nomenclature

7.1 IUPAC Rules

Organic compounds are named systematically according to the rules established by IUPAC (International Union of Pure and Applied Chemistry). As shown in Tables 5.1 and 7.1, the first four alkanes have individual names partly derived from their natural origin (e.g. *butane*, C_4H_{10}, from *butyric acid*, $C_4H_8O_2$, in rancid *butter*). The names of higher members have Greek *prefixes* indicating the *number of carbon atoms* and the ending ***ane*** according to their membership in the alk*ane* family, exemplified by *pentane*, C_5H_{12}, with *five* carbon atoms (Greek *pente* = *five*). Endings ***ene*** and ***yne*** are given to hydrocarbons with CC *double* and *triple bonds*, belonging to the alk*ene* and alk*yne* family, respectively (Table 7.1, Chapters 14.1, 19.1).

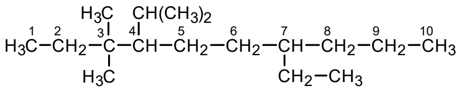
Following the IUPAC rules, the names of branched alkanes are derived from the names of the unbranched parent alkanes in Table 7.1, as demonstrated for a hydrocarbon with the structure drawn in the following manners (Chapter 8):

$H_3C-CH_2-C(CH_3)_2-CH(CH(CH_3)_2)-CH_2-CH_2-CH(CH_2-CH_3)-CH_2-CH_2-CH_3$

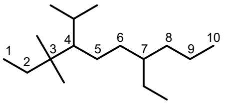
The IUPAC name is obtained as follows:

- The longest continuous carbon chain defines the *parent name*. Thus, *decane* is the parent name in this alkane example.
- The carbon atoms of the parent chain are numbered beginning from that end of the chain which will give the *smallest number to carbons carrying a substituent group* or atom other than H on a carbon of the chain; this is *3,4,7-* and not 4,7,8- (numbered from the opposite end of the chain) in the example.

- Substituents are named and their positions on the carbon chain indicated by *prefixes*, for example *7-ethyl-*.
- The names of substituents are ordered *alphabetically*; this is ***e**thyl* > ***i**sopropyl* > ***m**ethyl* in the example.
- Two, three, four, five identical substituents are indicated by the prefixes *di-*, *tri-*, *tetra-*, *penta-*; *dimethyl-* represents two CH_3 groups in the example.
- Branched alkyl groups are named according to Table 7.2, for example *isopropyl*.
- Thus, the correct IUPAC name is 7-ethyl-4-isopropyl-3,3-dimethyldecane.



7-ethyl-4-isopropyl-3,3-dimethyldecane



All branched structural isomers of pentane and hexane in Chapter 6.2 have been named accordingly.

The methyl group and other alkyl groups formally replacing (substituting) the H atoms in the parent skeleton are referred to as *substituents*. Their nomenclature follows Table 7.1.

7.2 Branched Alkyl Groups

When ranking alkyl groups and substituents named according to Table 7.2 alphabetically, *hyphenated prefixes* such as *sec-* and *tert-* = *t-* for branched alkyl groups (Table 7.2) are not taken into account.

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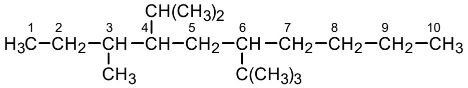
Therefore, *tert*-***b***utyl- (*t*-butyl-) is ranked before ***e***thyl and ***m***ethyl as exemplified:



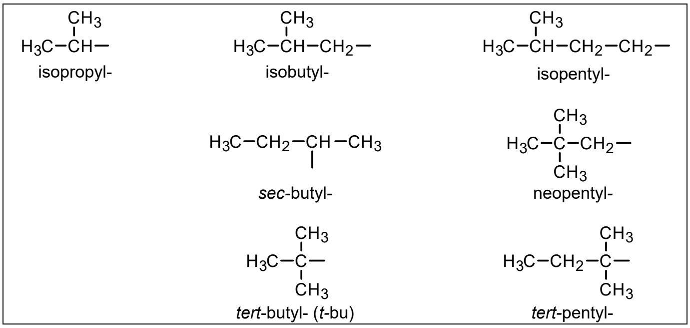
$H_3C-CH_2-CH(CH_3)-CH(CH(CH_3)_2)-CH_2-CH(C(CH_3)_3)-CH_2-CH_2-CH_2-CH_3$

6-*tert*-butyl-4-isopropyl-3-methyldecane

Table 7.1. Nomenclature of some parent hydrocarbons and derived alkyl and alkoxy groups (prefix: black, ending: red)

number of C atoms	hydrocarbon			substituent (group)	
	alkane (R–H)	alkene	alkyne	alkyl (R–)	alkoxy (R–O–)
1	methane			methyl	methoxy
2	ethane	ethene	ethyne	ethyl	ethoxy
3	propane	propene	propyne	propyl	propoxy
4	butane	butene	butyne	butyl	butoxy
5	pentane	pentene	pentyne	pentyl	pentoxy
6	hexane	hexene	hexyne	hexyl	hexoxy
7	heptane	heptene	heptyne	heptyl	heptoxy
8	octane	octene	octyne	octyl	octoxy
9	nonane	nonene	nonyne	nonyl	nonoxy
10	decane	decene	decyne	decyl	decoxy
11	undecane	undecene	undecyne	undecyl	undecoxy
12	dodecane	dodecene	dodecyne	dodecyl	dodecoxy
13	tridecane	tridecene	tridecyne	tridecyl	tridecoxy
14	tetradecane	tetradecene	tetradecyne	tetradecyl	tetradecoxy
15	pentadecane	pentadecene	pentadecyne	pentadecyl	pentadecoxy
20	eicosane	eicosene	eicosyne	eicosyl	eicosoxy

Table 7.2. Nomenclature of branched alkyl groups



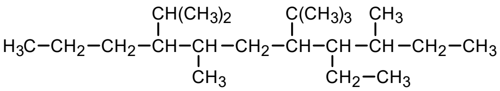
Chapter 7 permits answers to the following:

(7.1) What are the IUPAC names of all singly and doubly methyl branched isomers of heptane C_7H_{16}?

(7.2) Draw the structural formulas of ***(a)*** 2,2,4-trimethylhexane, and ***(b)*** 5-*t*-butyl-3,3-diethyloctane.

(7.3) Give the IUPAC names of the alkanes with structures drawn in question 6.6.

(7.4) What is the correct IUPAC name of the following alkane?



$H_3C-CH_2-CH_2-CH(CH(CH_3)_2)-CH(CH_3)-CH_2-CH(C(CH_3)_3)-CH(CH_2-CH_3)-CH(CH_3)-CH_2-CH_3$

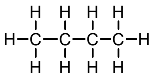
(7.5) What is the structural formula of 2,6,10-trimethyldodecane which occurs in slate oil?

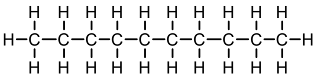
8 Drawing Molecular Structures

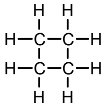
8.1 Structural Formulas

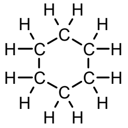
Planar projections of the three-dimensional (e.g. tetrahedral) molecules are generally drawn for convenience in several variations, depending on whether convenience, time saving, and clearness take preference or electronic configurations have to be presented in reaction equations.

The *structural* or *valence bond formula including all bonds* presents the *complete atom connectivities* of the molecule, as shown for the alkanes butane and decane and the cycloalkanes cyclobutane and cyclohexane.


butane


decane


cyclobutane


cyclohexane

Condensed structural formulas arise from removal of all CH bonds and permit reduced drawing time.

$H_3C-CH_2-CH_2-CH_3$

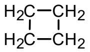
butane

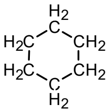
$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

or

$H_3C-(CH_2)_8-CH_3$

decane


cyclobutane


cyclohexane

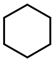
8.2 Skeletal Formulas

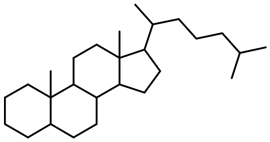
By not depicting all C and H atoms, the drawing is further shortened to the clear *skeletal formula*. Alkanes are simply represented as *zigzag* chains, and the six-membered ring of cyclohexane is a hexagon. Each corner represents a methylene group ($-CH_2-$); each open end corresponds to a methyl group ($-CH_3$). The skeletal formula is particularly useful for the presentation of larger organic molecules like cholestane, the parent hydrocarbon of cholesterol (Chapter 77.2).


butane


decane


cyclobutane

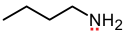

cyclohexane

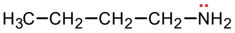

cholestane

Condensed and skeletal formulas are generally used to write reaction equations.

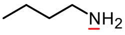
8.3 LEWIS Formulas

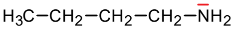
Non-bonding electron pairs at heteroatoms or functional groups frequently explain the reactivity and the origin of new bonds. Electron pairs are indicated by non-bonding lines (one line for each electron pair) or colons (one dot for each electron) in the *LEWIS formula* taking into account the octet rule.



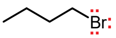

$H_3C-CH_2-CH_2-CH_2-\ddot{N}H_2$

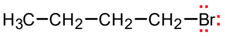
or



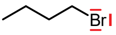

$H_3C-CH_2-CH_2-CH_2-\overline{N}H_2$

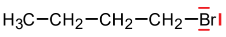
1-aminobutane (*n*-butylamine)




$H_3C-CH_2-CH_2-CH_2-\ddot{\underset{..}{Br}}:$

or




$H_3C-CH_2-CH_2-CH_2-\overline{\underline{Br}}|$

1-bromobutane (*n*-butyl bromide)

In reaction equations LEWIS formulas are frequently used to indicate the origin of newly formed bonds and non-bonding electron pairs. Nucleophilic substitution (Chapters 11.5, 31) of 1-bromobutane, for example, involves an attack of a non-

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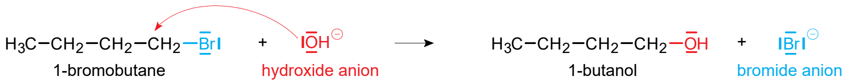
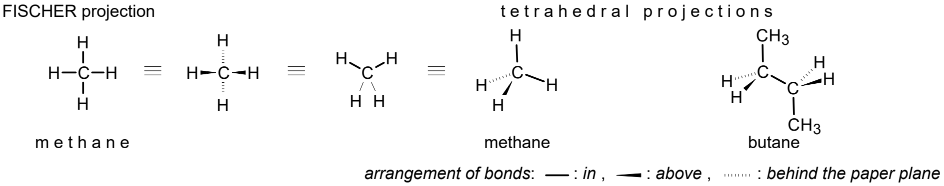
bonding electron pair of the hydroxide anion at the brominated carbon atom of 1-bromobutane, thus providing the bonding electron pair of the newly formed covalent bond. *Thereby, the arrow depicts the direction of electronic motion*: it points, by convention, from the donor of the electron pair (the hydroxide anion as the nucleophile, Chapters 11.5, 31) to the acceptor (the brominated C atom as the electrophile):



8.4 Projections

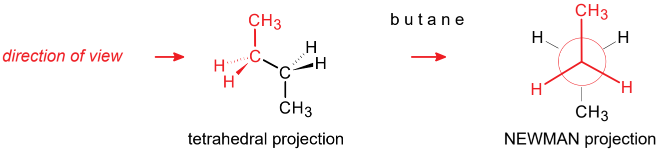
8.4.1 Fischer Projection

Two methods are suitable for drawing the spatial representation of a tetravalent carbon atom with tetrahedral bonds. In the planar *Fischer projection*, *horizontal* bonds are *above* and *vertical* bonds *behind* the paper plane. In the *tetrahedral projection*, *full lines* indicate bonds *in the plane*, *dotted lines* represent bonds *behind the plane*, and *wedge lines* emphasize bonds rising *above the plane* of the paper.



8.4.2 Newman Projection

The *Newman projection* clearly *visualizes the angular relationships* of groups attached to the carbons of a CC single bond. In this projection, the observer looks into the direction of the selected CC single bond so that one C atom lies behind the other. A circle surrounding the front carbon symbolizes both carbon atoms and the CC single bond connecting them. The additional three bonds originating from the front carbon atom enclose angles of 120° *in the projection*; the real tetrahedral angle is 109°28´ (Chapter 3.2). The three additional bonds connecting groups with the rear carbon atom originate from the circle line, also enclosing angles of 120° in the projection. The tetrahedral projection of butane is converted into the Newman projection of the central CC bond in this manner. As this drawing shows, the substituents of the tetrahedron in front and behind are *not eclipsed* but *staggered* (Chapter 9.1) and enclose *dihedral angles* (torsional angles) of 60° (CH_3 and H) and 180° (both CH_3 groups) in the projection:



Chapter 8 permits answers to the following:

(8.1) Draw the skeletal formulas for cyclopropane, cyclopentane, cycloheptane, and cyclooctane.

(8.2) Draw the condensed and skeletal structural formula of 2,6,10-trimethyldodecane.

(8.3) Draw the condensed and skeletal structural formula of 3-methylhexane and number the longest carbon chain.

(8.4) Draw one of the tetrahedral projections of the CH carbon (C-3) in 3-methylhexane.

(8.5) Write the reaction equation for 1-bromobutane with sodium hydroxide by means of Lewis formulas. What is the origin of the CO bond in the product 1-butanol?

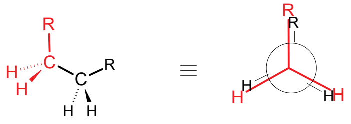
(8.6) Draw Newman projections of the central CC bond of hexane with staggered ethyl groups.

9 Conformation

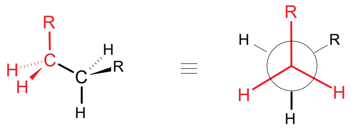
9.1 Conformation, Conformers

There is *free rotation about the CC single bonds* of alkanes; alkane molecules such as butane (R = CH_3 in the formulas to follow) can adopt an infinite number of arrangements of their atoms and groups (H and CH_3) in space resulting from rotation about CC single bonds (rotational states). The term *conformation* describes the total of these arrangements. A *conformer* is one specific arrangement.

The NEWMAN projection (Chapter 8.4.2) simply and precisely visualizes the spatial arrangement of groups in conformers. Two kinds of conformers can be distinguished as borderline cases: those with an *eclipsed* and those with a *staggered* arrangement of groups, such as H and CH_3 in butane. Conformers with groups arranged somewhere between eclipsed and staggered are called *skew*.



conformer with *eclipsed* alkyl groups and H atoms



conformer with *staggered* alkyl groups and H atoms

Clearly, repulsion because of crowding of groups is stronger for an eclipsed arrangement. To conclude, *conformers with staggered groups will be more stable*, occupying a lower energy level than those with eclipsed groups.

9.2 Energy Contents and Nomenclature of Conformers

Fig. 9.1 portrays the full rotation about a CC single bond, the relative energy contents, and the names of the conformers depending on the *dihedral angle* (torsional angle).

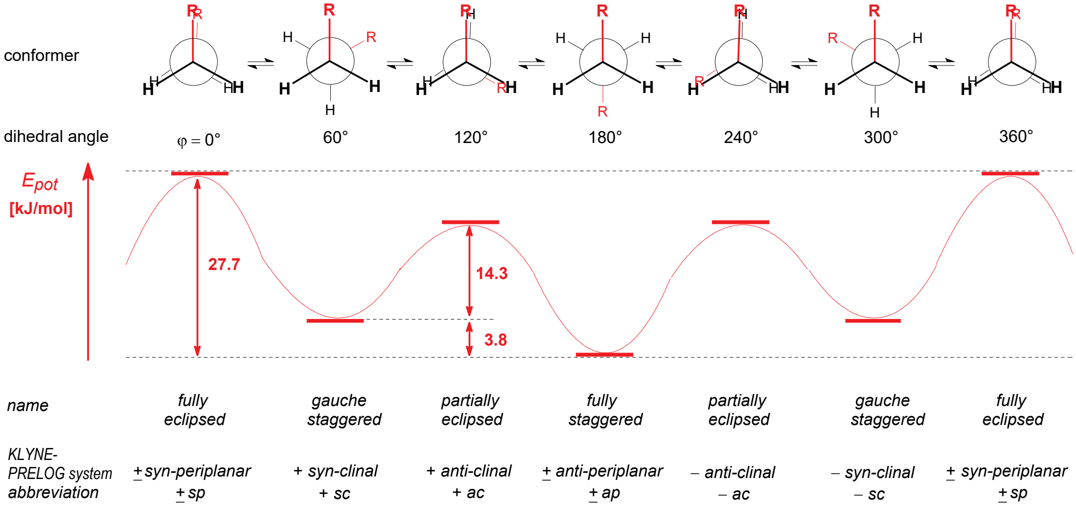


Fig. 9.1. Rotation about the C-2–C-3 bond of butane (R = CH_3): potential energy and nomenclature of conformers

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