Chapter 1 Electrons and Chemical Bonds

Contents

In order to understand organic chemistry, you have to learn first of all the electron configuration of atoms constructing organic molecules, and the way atoms combine to form chemical bonds. Such concepts as quantum number will be an important part of the basis of organic chemistry.

Hybridization of atomic orbitals of carbon atoms forms the fundamentals, not only of physical chemistry, but also of organic chemistry. In organic chemistry, knowledge of hybridization is essential to understand the reaction of organic chemistry and the shape of molecules.

The relation between the hybridization state of carbon atoms forming methane, ethane, ethylene and acetylene, and their structures may be regarded as the starting point of organic chemistry.

1.1 Electron configuration of atoms

The first step of basic chemistry is to understand the atomic structure and the combination of atoms, *i.e.*, the chemical bonds. The situation is the same for organic chemistry. The image of an atom that consists in central nucleus and electrons surrounding it was established in the beginning of the 20th century by Rutherford, and this concept was combined with the quantum theory by Bohr. Then there arose quantum mechanics. Electrons were so far regarded as a kind of particles with definite position and velocity. According to quantum mechanics, electrons are now regarded as a kind of cloud spreading outside the nucleus.

In other words, we can only define the probability of finding an electron at a certain position. The area where the probability of finding the electron is highest corresponds to so-called electron shell.

Each electron shell consists of a certain number of atomic orbitals or atomic orbital function. Each atomic orbital is characterized by three quantum numbers, **principal quantum number** (n), **azimuthal quantum number** (l), and **magnetic quantum number** (m). Each atomic orbital can accommodate two electrons at maximum with different **spin magnetic quantum number** (m_S), the fourth quantum number. The number of electrons which each atomic orbital can accommodate is determined by these quantum numbers as is shown in Table 1.1.

Electrons with the same principal quantum number form one electron shell. Electron shells are named K, L, M… from the one nearest to the nucleus. There is a limitation as for the number of electrons that an electron shell can accommodate. The nearer to the nucleus, the lower the energy of electrons in each electron shell (named as the energy level of the electron shell), and the energy will increase as the distance becomes larger.

Table 1.1 covers sufficient range of quantum numbers. The figures in the table is determined by the **Pauli's exclusion principle**, which tells there is no electron in one atom which has the same combination of quantum numbers with the other electrons.

Table 1.1 Four quantum numbers

characteristics	quantum number	symbol	possible figures
distance from the nucleus	principal	n	1, 2, 3, …
shape of electron cloud	azimuthal	l	0, 1, 2, 3, ..., n-1
orientation in the space	magnetic	m	0, ±1, ±2, ±3,…, ±l
electron spin	spin magnetic	m_s	+½, -½

Table 1.2 Electron shell and quantum number

electron shells	K	L	M	N
corresponding principal quantum number (n)	1	2	3	4
number of atomic orbitals	1	4	16	32
maximum number of electrons to be accommodated	2	8	18	32

1.2 Electron configuration of the carbon atoms

If you paint out the area where the probability of finding electrons is high, you will obtain a figure, which may be approximated as the shape of atomic orbital. For instance, the shape of an atomic orbital with the principal quantum number of 1 and azimuthal quantum number of 0 is a sphere, which is named as **1s orbital**. The K shell consists in solely s orbitals.

The atomic orbital with the principal quantum number of 2 and the azimuthal quantum number of 0 is also a sphere, and is named as **2s orbital**. The energy associated with the electrons in 2s orbital (the energy level of atomic orbital) is higher than that in 1s orbital. There are other atomic orbitals with the principal quantum number of 2 which have the azimuthal quantum number of 1. These are named as **2p orbital**. Three magnetic quantum numbers, +1, 0 and -1, are possible for 2p orbital. In other words there are three types of p orbital. This means that there are three 2p orbitals. These orbitals have a dumbbell shape and are perpendicular and intersect each other at the nucleus. The energy level of these three orbitals is the same and called **degenerated**. It is higher than that of 2s orbital. By coinciding the three orbitals with the Cartesian coordinate, these may be called as $2p_x$, $2p_y$, and $2p_z$ orbitals, respectively (Figure 1.1). Four orbitals, 2s and three 2p, form the L electron shell.

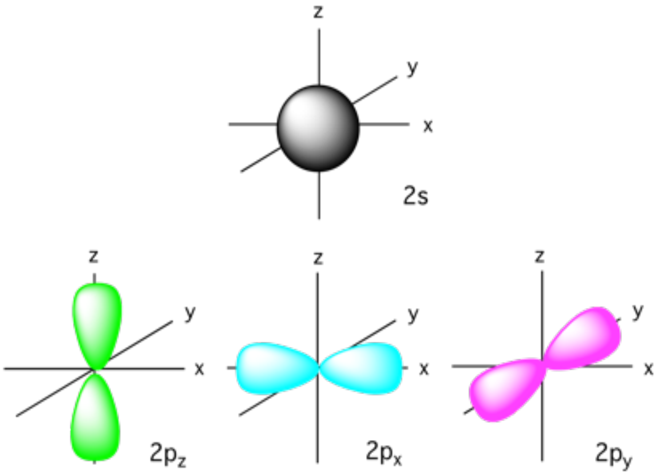


Figure 1.1 The shape of orbitals

You must notice that each orbital is defined by a unique combination of quantum numbers. The relation for carbon atoms is summarized in Table 1.3. The combination of postscripts *x*, *y* and *z* which represent the direction of orbitals and the values of magnetic quantum number (-1, 0, +1) is arbitrary. Usually $2p_z$ is assigned to 0, and $2p_x$ and $2p_y$ to ±1. If $2p_x$ is assigned to +1, $2p_y$ is assigned to -1.

According to Pauli’s exclusion principle, two electrons in maximum with different spin magnetic quantum number can be accommodated in one atomic orbital. In other words, one atomic orbital can accommodate one electron with either + or – magnetic quantum number, or two electrons with + and – spin magnetic quantum numbers. It cannot accommodate, however, two electrons with the same sign of spin two electrons with + and – spin magnetic quantum numbers. It cannot accommodate, however, two electrons with the same sign of spin magnetic quantum number.

Table 1.3 Quantum numbers for the atomic orbitals of a carbon atom

name of atomic orbital	principal quantum number	azimuthal quantum number	magnetic quantum number
1s	1	0	0
2s	2	0	0
$2p_x$	2	1	±1*
$2p_y$	2	1	±1*
$2p_z$	2	1	0

*One of + or – is chosen.

Now let us discuss about the electron configuration of a carbon atom. If the atom is in a stable state (**ground state**), the electrons will occupy orbitals with lower energy. Accordingly, four out of six electrons will be used to occupy 1s (2 electrons) and 2s (2 electrons) orbitals.

The crucial point is the fate of the rest. It is natural to expect the fifth electron to occupy, say, $2p_x$ orbital. The sixth electron will occupy either $2p_y$ or $2p_z$ (not $2p_x$) with the spin quantum number of the same sign. The rule for occupying degenerate orbitals is named as **Hund's rule**. When degenerate orbitals are involved, Hund' rule is always to be applied. The second electron can occupy $2p_x$ orbital only after both $2p_y$ or $2p_z$ orbitals accommodate one electron with the same sign. Two rules, Pauli's exclusion principle and Hund' rule, are put together and referred to as **Aufbau principle**. Table 1.4 shows the electron configuration of carbon atoms by Aufbau principle.

Table 1.4 Quantum numbers associated with each electron of a carbon atom

electron shell	principal quantum number	azimuthal quantum number	magnetic quantum number	spin magnetic quantum number	symbol
K	1	0	0	+½	1s
K	1	0	0	-½	1s
L	2	0	0	+½	2s
L	2	0	0	-½	2s
L	2	1	±1	±½	$2p_x$
L	2	1	±1	±½	$2p_y$

Instead of indicating all quantum numbers for each electron, expressions such as $1s^22s^22p^2$ or $1s^22s^22p_x^{\,1}2p_y^{\,1}$ are conventionally used.

The superscript figures indicate the number of electrons in the atomic orbital.

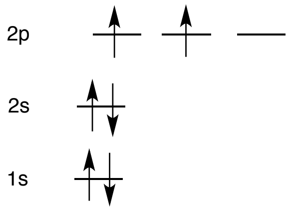


Figure 1.2 Electron configuration of carbon atom

The expression used in Figure 1.2 indicates the electron spin. The directions of arrows for $2p_x$ and $2p_y$ have no meaning. Only the point that these have the same sign is significant. You may draw two downward arrows instead.

Point: Aufbau principle

The electron configuration of an atom is determined by Aufbau principle, a combination of two basic rules.

Pauli's principle: There are no electrons with the same set of quantum numbers.

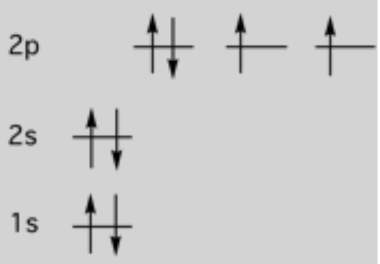
Hund's rule: Each of degenerate orbitals with the same energy firstly accommodates one electron with the same spin. After all orbitals accommodate one electron, they can accommodate the second electron.

Exercise 1.1 Electron configuration of an oxygen atom

Show the electron configuration of an oxygen atom, copying after Fig. 1.2.

Answer

An oxygen atom (atomic number 8) has eight electrons.



1.3 Covalent bonds

The electron configuration of a hydrogen atom is 1s and that of a helium atom is $1s^2$. Helium belongs to a group of elements named as noble gas, and very stable. The stability is due to the fact that its K shell is filled with electrons. A shell filled with electrons is called as a closed shell. It is the cause of stability of molecules and atoms. A hydrogen atom is unstable and under the normal condition it cannot remain as an atom: two hydrogen atoms approach, make their orbitals overlap and share electrons. Thus, a covalent bond is formed and the result is a hydrogen molecule.

In a hydrogen molecule, each atom possesses two electrons in its orbital to achieve the closed shell structure like rare gases. A combination of two atoms due to the sharing of electrons is named as the **covalent bond**. The electron pair which is the basis of the covalent bond is named as the **shared electron pair**. It must be noted that the sign of spins of electrons in the shared electron pair should be different.

The right side of Figure 1.3(a) is a Lewis structural formula of a hydrogen molecule, and the shared electron pair is represented by : or a short line representing a chemical bond. In Fig. 1.3(b), the formation of the covalent bond is represented by the overlap of orbitals.

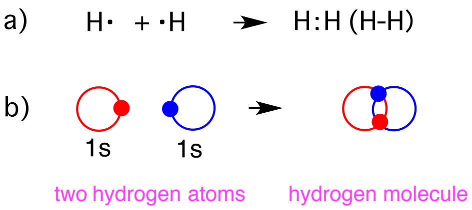
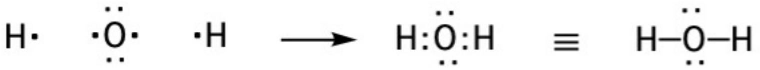


Figure 1.3 Formation of a hydrogen molecule

Since the formation of a covalent bond is equivalent to the formation of a shared electron pair, the existence electrons that are not participated in a shared electron pair, *i.e.*, an **unpaired electron**, is necessary. An atom can form bonds equal to the number of unpaired electrons. Since an oxygen atom has two unpaired electrons, it can make bonds with two hydrogen atoms to form a molecule of water. The process is shown in Eq. 1.1.



$$\mathrm{H}\cdot \quad \cdot\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\cdot \quad \cdot\mathrm{H} \longrightarrow \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H} \equiv \mathrm{H}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-\mathrm{H} \tag{1.1}$$

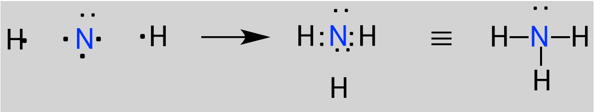
The number of bonds, which an atom can newly form, is named as the **valence** of that atom. The valence of a hydrogen atom and an oxygen atom is 1 and 2, respectively.

Exercise 1.2 Formation of ammonia

Explain the formation of ammonia from one nitrogen atom and three hydrogen atoms in a manner exemplified in Eq (1.1).

Answer

Three hydrogen atoms are bonded to the nitrogen atom, where one pair of lone pair remains unused.



You will find, however, that it is not appropriate to apply the way used for water or ammonia to the bonding between a carbon atom and hydrogen atoms. The reason is as follows. Since a carbon atom has two unpaired electrons, its valence is 2, and the compound between carbon and hydrogen will be CH_2.

carbene (a divalent compound)

Certainly CH_2 (named as carbene or methylene) does exist, but in fact carbene is very unstable, and it is impossible to isolate as such at ordinary temperate and pressure. Tetravalent compounds as methane are stable. The stable compound of carbon and hydrogen is, for example, methane where the carbon atom is tetravalent. How we can solve this discrepancy?

1.4 Hybridized orbitals of carbon atoms

(a) Structure of alkanes

The electron configuration of a carbon atom in its ground state is $1s^2 2s^2 2p_x^1 2p_y^1$ (Figure 1/4(a)). From this electron configuration、formation of a divalent species carbene is expected by the overlap of $2p_x$ and $2p_y$ orbitals with 1s orbitals of two hydrogen atoms. However, what does exist is a tetravalent carbon compounds such as methane. In these compounds, it is clear that the carbon atom does not have $1s^2 2s^2 2p_x^1 2p_y^1$ electron configuration.

(1) sp^3 hybridization

Linus C. Pauling (1901-1994) successfully explained this discrepancy by introducing a new concept, **hybridization**, a mixing of 2s and 2p orbitals. In general, hybridization is defined as a process in which two or more than two orbitals are mixed to form new orbitals. New orbitals thus formed have the same energy (**degenerated**) and shapes and directions different from the original ones.

The first step of hybridization of a carbon atom is elevation of one 2s electron to 2p orbital (Figure

1.4(b)). Then one 2s and three 2p orbitals, each with one electron, are mixed to form four sp^3 hybridized orbitals. These four orbitals are oriented to the four apexes of tetrahedron with the carbon atom in its center (Figure 1.4(b)). This can be predicted by the valence shell electron pair repulsion (VSEPR) theory that is described in the "*Fundamentals of Chemistry* (Ch. 4.1)", which is the first volume of this series. The shape of sp^3 orbital is an asymmetric water drop as is shown in Figure 1.4(e). In this book, however, the smaller parts will be omitted for simplicity (Figure 1.4 (f)).

Let us examine the energetics of the hybridization process. The 1st step (elevation of a 2s electron to 2p orbital) is clearly an endothermic process (*ca*. 400 kJ mol^{-1}). By absorbing energy, the carbon atom in the excited state now has four unpaired electrons with the same spin. The carbon atom is now tetravalent, and is now ready to form four bonds. The bond-forming step is exothermic. Since the bond energy of a C-H bond is 413.4 kJ mol^{-1}, by hybridization and by forming methane, a carbon atom can stabilize by 2 x 413.4 = 826.8 kJ mol^{-1}. This is much larger than the energy required for excitation of a 2s electron to 2p orbital, and hence, hybridization is more favorable than forming carbene.

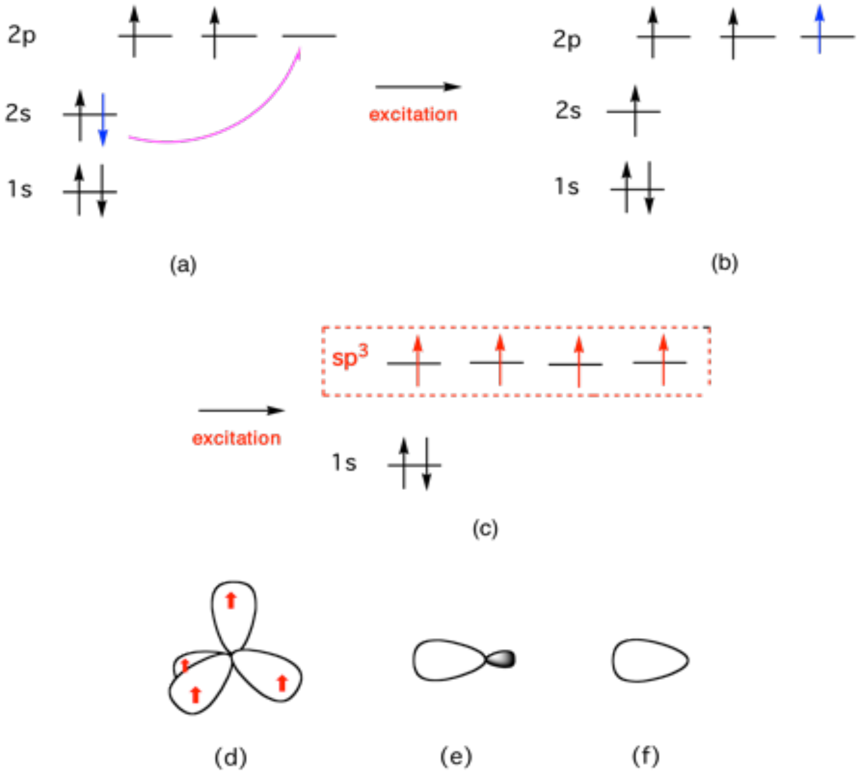


Figure 1.4 Formation of sp^3 hybridized orbital of a carbon atom
(a) electron configuration of the ground state
(b) electron configuration of the excited state
(c) electron configuration of sp^3 hybridized state
(d) sp^3 hybridized orbital
(e) the shape of hybridized orbital
(f) simplified shape of a hybridized orbital

(2) Structure of methane

In methane, each sp^3 hybridized orbital of the carbon atom overlaps with a 1s orbital of hydrogen atom. Two electrons distribute nearly equally in the axis connecting two atoms, forming a C-H bond.

The shape of methane thus formed keeps the shape of four sp^3 hybridized orbitals. Methane is tetrahedral with the carbon atom in its center and four hydrogen atoms at each of four apexes (Figure1.5).

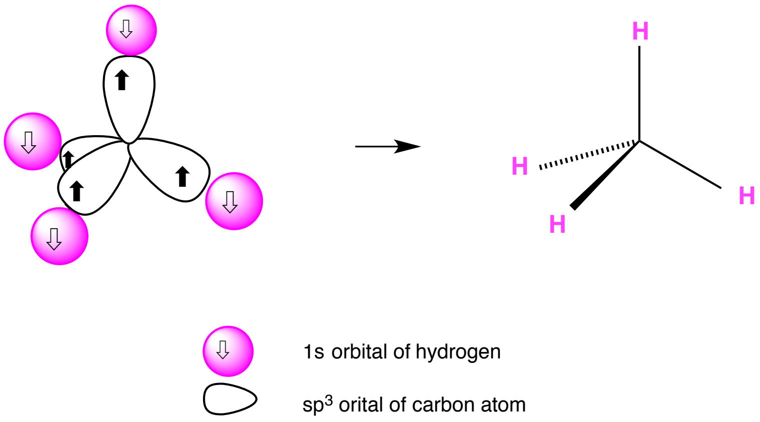


Figure 1.5 Structure of methane

There are several methods of demonstrating a three-dimensional molecule in a two- dimensional front side of a paper. The right structure of Figure 1.5 is a **perspective drawing**, which is the simplest representation. The solid line represents the bond on the front of the paper, and hence the two ends of the line correspond two atoms. A wedge sticks out from the front side of a paper to the reader. Hence an atom at the broader tip of the wedge is floating in the space between the paper and the reader. A broken line represents a bond which is leaving from the reader. Hence the atom at the end of the broken line is below the paper.

(3) Structure of ethane

The C-C bond of ethane is formed from two sp^3 orbitals donated by each carbon atom which overlap along the bond axis. The bonding electrons symmetrically distribute along the bond axis. Bonds of this type are named as an **σ bond**. The type of a bond made from a σ bond is a single bond. Details will be discussed in Ch. 2. Because it has a symmetric distribution of electrons, the two parts of the molecule at both ends (in ethane, two CH_3 groups) can rotate about the bond almost freely. Details will be discussed in Ch.5.2(b). The remaining six sp^3 orbitals are overlapping with 1s orbitals of hydrogen atoms (Figure 1.6).

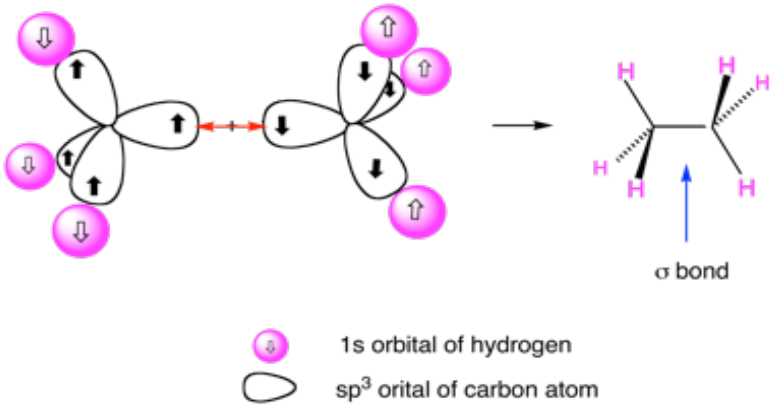


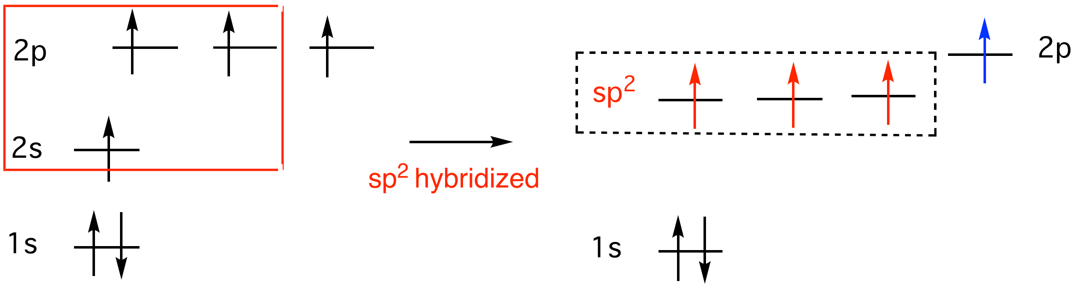
Figure 1.6 Structure of ethane

(b) Structure of ethylene

Four sp^3 hybridized orbitals are obtained by mixing one 2s orbital and three 2p orbitals. When 2s, $2p_x$ and $2p_y$ orbitals are mixed, three degenerate sp^2 orbitals are obtained. These three sp^2 orbitals are coplanar, and two of the bonds form an angle of 120°. The remaining $2p_z$ orbital is perpendicular to the plane (Figure 1.7).

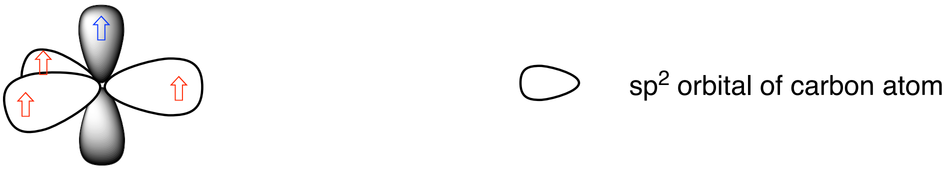
(1) sp^2 hybridization

The C-C bond of ethylene (ethene) is formed by a σ bond made from two sp^2 hybridized orbitals from each carbon atom overlapping along the bond and an another kind of bond made from two $2p_z$ orbitals perpendicular to the bond axis. The new type of bond is named as a **π bond** since its origin of the latter is p orbital. The type of a bond made from a σ bond and a π bond is a double bond. Details will be discussed in Ch. 2. The remaining four sp^2 orbitals are overlapping with 1s orbitals of hydrogen atoms.



(a) electron configuration of an excited carbon atom

(b) electron configuration of sp^2 hybridizedx carbon atom



c) sp^2 hybridized orbital

Figure 1.7 Formation of sp^2 hybridized orbital of a carbon atom
(a) electron configuration of the excited state
(b) electron configuration of sp^2 hybridized state
(c) sp^2 hybridized orbital

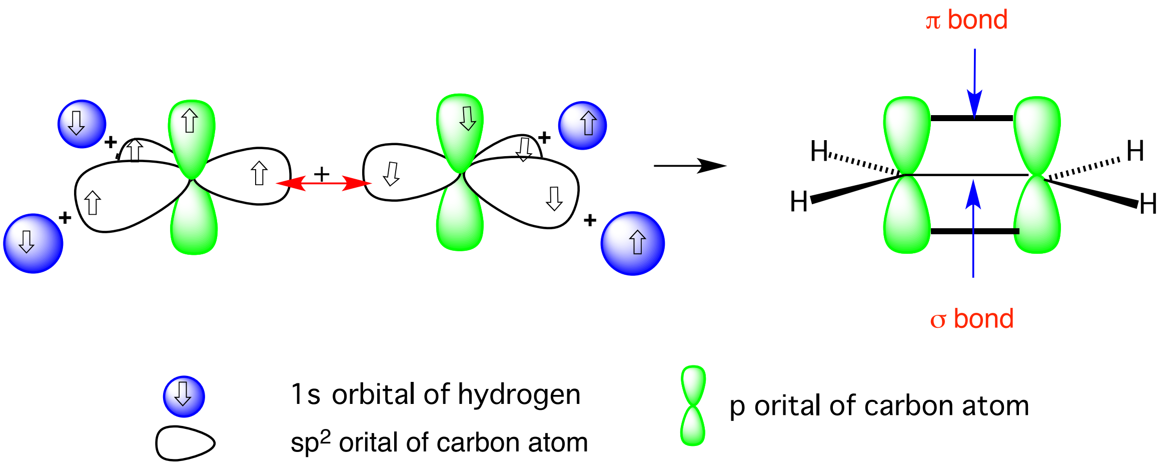


Figure 1.8 Structure of ethylene

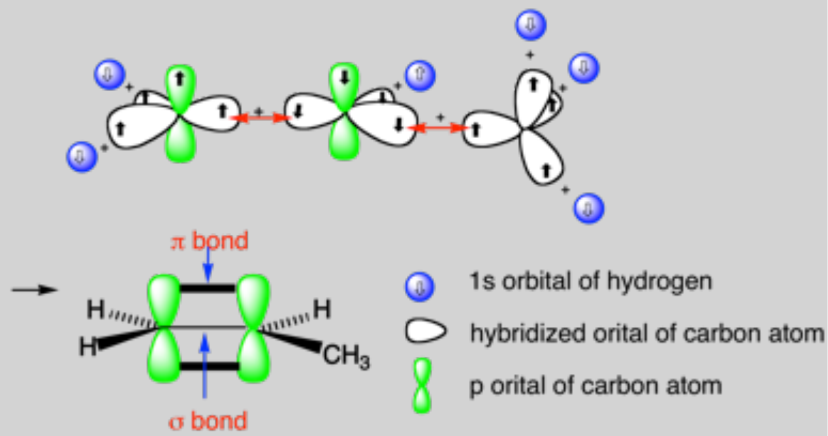
The electron distribution about the C-C bond of ethylene is devoid of symmetry which is different from the case of ethane. If the two parts of the molecule at both ends (in ethylene, two CH_2 groups) rotate about the bond, the cleavage of π bond must accompany. A bond cleavage process is highly endothermic, and the thermal energy that the ethylene molecule has at ambient temperature is not enough for bond cleavage. So, for ethylene rotation about the C-C bond is difficult to occur, and the six atoms of ethylene remain in one plane. Figure 1.8 schematically represents the process of formation of ethylene by overlapping of orbitals. In it, the π bond formed by overlapping of p orbitals is featured.

Exercise 1.3 Structure of propene

Indicate the structure of propene $CH_3CH=CH_2$. Follow the style shown in Figs. 1.5-1.8.

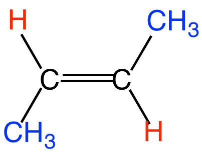
Answer

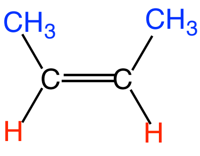
Propene is obtained by substituting one hydrogen of ethylene with a methyl group. In practice, one of the sp^2 hybridized orbital overlaps with the sp^3 hybridized orbital of the third carbon.



(2) Geometrical isomers[1]

There are two kinds of 2-butenes $CH_3-CH=CH-CH_3$, formally obtained by substituting two hydrogens of ethylene bonded to each end of the molecule with two methyl groups; one is the ***trans*** isomer in which two methyl groups are located at the opposite sides of the double bond, and the other is the ***cis*** isomer in which two methyl groups are located at the same side. Sometimes the *trans* isomer is referred to as ***E*** (entgegen) isomer and the *cis* isomer to ***Z*** (zusammen). The *trans* and *cis* isomers have an identical molecular formula, and the way of connection of atoms is identical, but the relative position of atoms is different. Hence these are called **stereoisomers**. The stereoisomer related to the position of substituents related to the double bond is sometimes called **geometrical isomers**.


trans-2-butene


cis-2-butene

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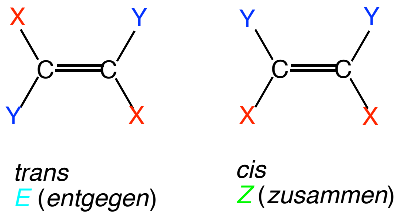
[1] According to IUPAC recommendation, the term geometrical isomer is not recommended. IUPAC recommends *cis-trans* isomer instead.

Point: Geometrical isomer (*cis-trans* isomer)



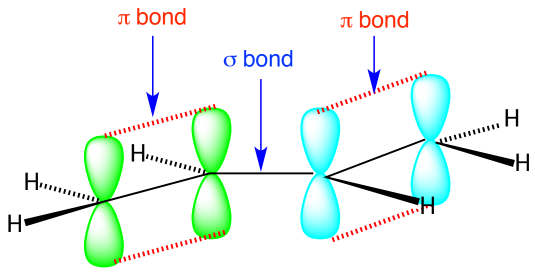
(3) Conjugated system

In 1,3-butadiene $CH_2=CH-CH=CH_2$, formed by linking two ethylene moieties with a single bond, two double bonds are connected with one single bond. Such a combination of double and single bonds is called a **conjugated double bond**. A system in which multiple bonds are connected with single bond in such a manner is called as a **conjugated system**.

In Figure 1.9(a), 1,3-butadiene is represented as a compound with two ethylene moieties. In other words, two π electrons are accommodated in each double bond without any interaction among them. Such a situation is referred to as **localization** of electrons.

Different from ethylene, the p orbitals belonging to the two middle carbon atoms can overlap with the p orbitals belonging to two edge carbon atoms. Consequently, π electrons in each double bond does not localize in a specific bond, but spread over the whole molecule. Such is named as **delocalization** of π electrons.

(a) π electrons are localllized



(b) π electrons are delocallized

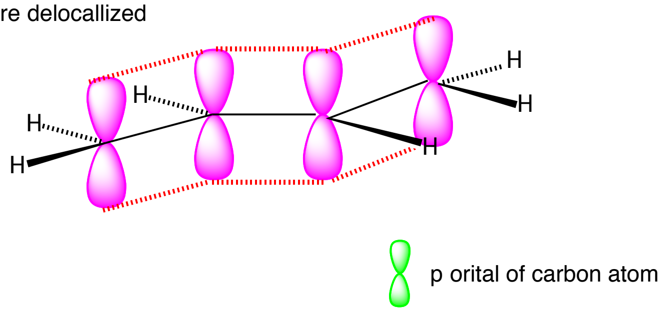


Figure 1.9 Structure of 1,3-butadiene

(c) Structure of benzene

Commonly benzene is represented as a hexagon in which double and single bonds are alternatively connected (Figure 1.10(a)). This structure is referred to as a **Kekulé structure** after F. A. Kekulé von Stradonitz (1829-1896) who proposed this structure first.

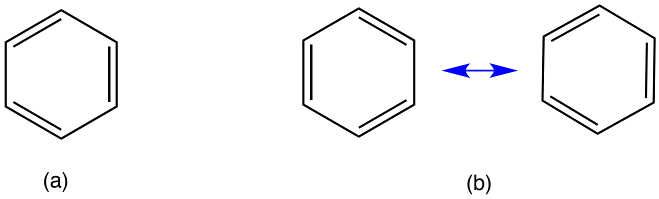


Figure 1.10 Kekulé structure of benzene. (a) Kekulé structure, (b) resonance between two Kekulé structures

Since ethylene readily decolorizes bromine water, but benzene does not possess such property, it is understood that even at that time the simple Kekulé structure does not represent the true structure of benzene. Hence Kekulé assumed a rapid oscillation between two benzene structures and named this phenomenon resonance to explain the low reactivity of benzene. According to this theory, each of the Kekulé structure is named resonance structure (often referred to as canonical formula. In this book、however simpler naming, resonance structure, will be used. Compounds with resonance structures are generally more stable than those without these.

Resonance is not equivalent to equilibrium. There is a high energy state between the left and right sides of the equation for an equilibrium reaction. No such high energy state is involved in the resonance. To distinguish two processes, a symbol ⇌ is used for an equilibrium, and ↔ for a resonance.

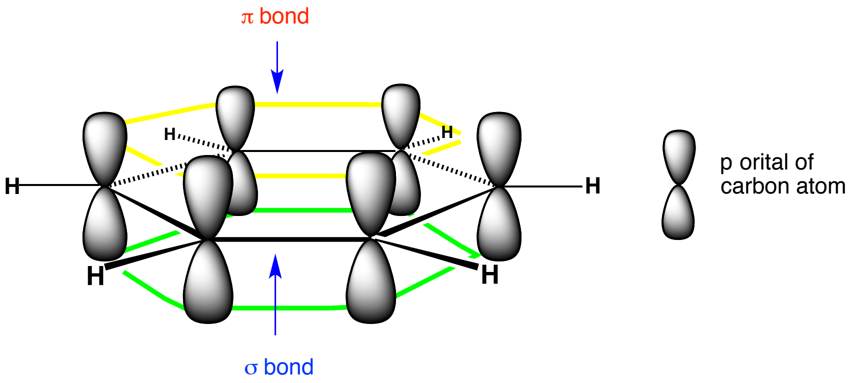
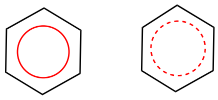


Figure 1.11 Structure of benzene

The Kekulé structure corresponds to the state where π electrons are localized in the respective bonds. On the other hand, a benzene molecule is a conjugate system, and π electrons are delocalized (Figure 1.11). If π electrons are fully delocalized, there would be no difference between a double and a single bond and six bonds will become equal. Hence a benzene molecule should be a regular hexagon. It is proved by experiments (*e.g.*, X-ray crystallographic analysis) that a benzene molecule is a regular hexagon. It is still common to use Kekulé structures for benzene, but such structures as shown below is sometimes used to emphasize the delocalization.



Point: Structure of benzene
Kekulé structure:
a structure in which C-C double and single bonds are joined alternatively.
experimentally obtained structure:
a regular hexagon: all six bonds have an identical length, which is explained by the resonance theory or delocalization of π electrons.

(d) Structure of acetylene

(1) sp hybridization

When 2s and $2p_x$ orbitals are mixed, two degenerate sp orbitals are obtained. These two sp orbitals are linearly oriented, and two bonds form an angle of 180°. The remaining $2p_y$ and $2p_z$ orbitals are perpendicular to sp hybridized orbital (Figure 1.12).

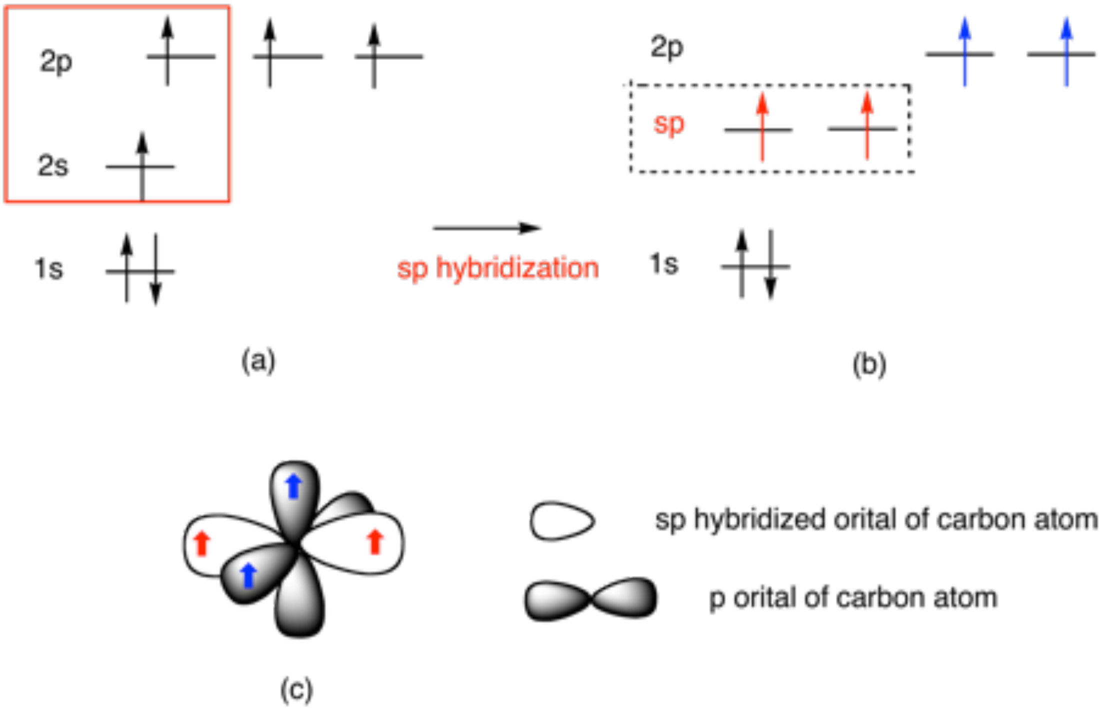


Figure 1.12 Formation of sp hybridized orbital of a carbon atom
(a) electron configuration of the excited state
(b) electron configuration of sp hybridized state
(c) sp hybridized orbital

(2) Acetylene

The C-C bond of HC≡CH is formed by a σ bond made from two sp hybridized orbitals from each carbon atom overlapping along the bond and two π orbitals are formed from the vertical overlap of $2p_x$ and $2p_z$ orbitals. The new type of bond is named as a **π bond** since its origin of the latter is p orbital. The remaining two sp orbitals are overlapping with 1s orbitals of hydrogen atoms. Hence, four atoms of an acetylene molecule are linearly arranged (Figure 1.13).

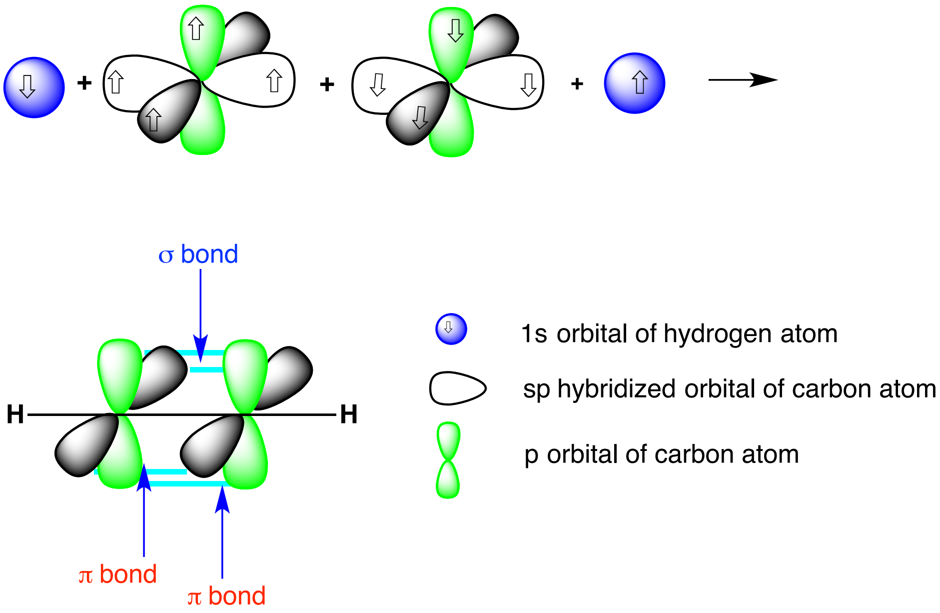
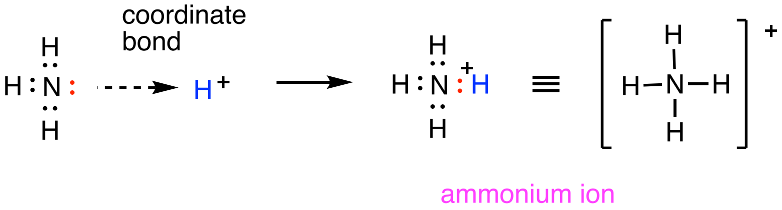


Figure 1.13 Structure of acetylene

Point: Structure of fundamental organic compounds
methane: sp^3 hybridized; tetrahedral with bond angles 109.5°
ethane: sp^3 hybridized; two fused tetrahedron; rotation about C-C bond is possible
ethylene: sp^2 hybridized; planar; rotation about C-C bond is prohibited
benzene: sp^2 hybridized; hexagonal; planar
acetylene: sp hybridized; linear

1.5 Coordinate Bond

When a covalent bond is formed, each of two atoms donates one electron. However, when an atom, a nitrogen atom as an example, which has an unshared electron pair not involved in bonding, will form a covalent bond, it can donate an unshared electron pair. In other words, an atom may donate two electrons when a covalent bond is formed.



The bond thus formed is nothing other than a covalent bond, but is referred to as a **coordinate bond** to indicate the different way of formation. Once an ammonium ion is formed, the four hydrogen atoms are all equivalent, and undistinguishable. This indicates that all four bonds are identical.

Problems

1.1

Write the electron configuration of a fluorine atom modeled after Figure 1.2.

1.2

Show all the orbitals which form 1-butene $CH_2=CHCH_2CH_3$ modeled after Figures 1.5-1.8.

1.3

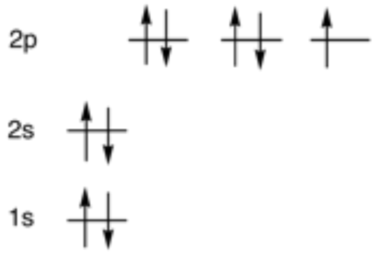
Show all the orbitals which form propyne $H-C\equiv C-CH_3$ modeled after Figures 1.5-1.13.

1.4

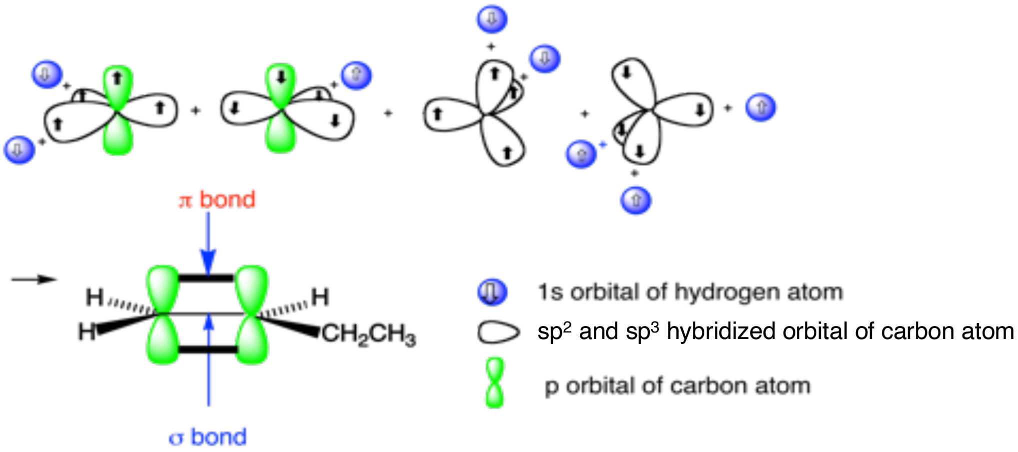
Show all the orbitals which form allene $CH_2=C=CH_2$ modeled after Figures 1.5-1.8. Find out the state of hybridization of the central atom.

Answers

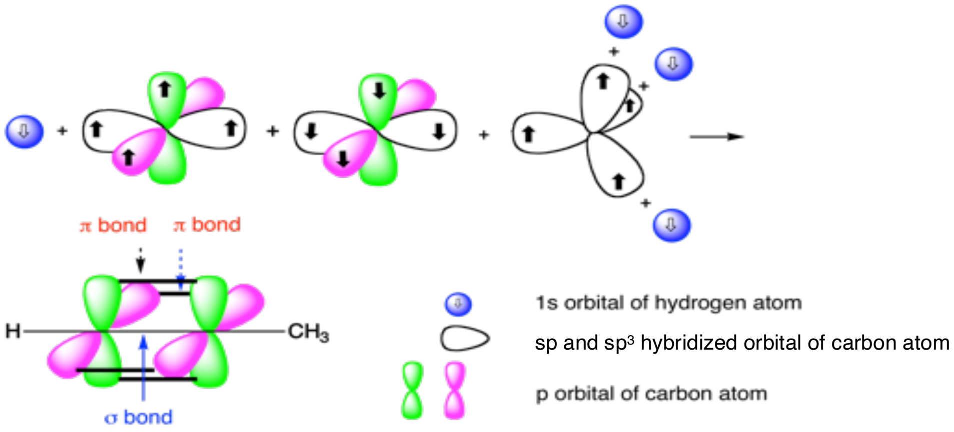
1.1



1.2

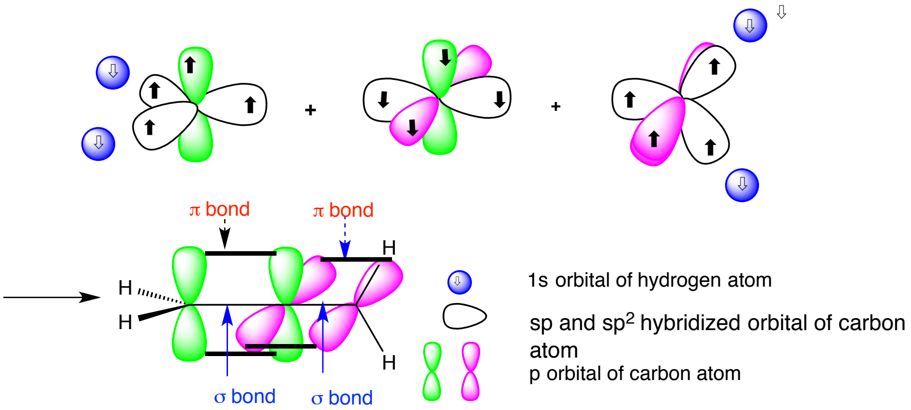


1.3



1.4

The central carbon atom of allene is sp hybridized. Notice that the plane formed by the left half of the molecule is perpendicular to the one formed by the right half.


+
+
π bond
π bond
H
H
H
H
σ bond
σ bond
1s orbital of hydrogen atom
sp and sp2 hybridized orbital of carbon atom
p orbital of carbon atom