普通高等教育“十三五”规划教材

河南省“十二五”普通高等教育规划教材

双语版

高等有机化学

Advanced Organic Chemistry 2nd

第二版

谢普会　胡思前　徐翠莲　主编
Puhui Xie　Siqian Hu　Cuilian Xu　Edit-in-Chief

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·北京·

《高等有机化学（双语版）第二版（Advanced Organic Chemistry 2nd）》第 1 章介绍了分子结构和化学键与反应活性的定性关系。第 2 章为立体化学，主要介绍了立体异构、消旋化合物的拆分、立体选择性和立体特异性反应、不对称合成等。第 3 章主要介绍有机反应的类型，通过举例来解释反应机理，并结合机理讨论反应中间体的结构、稳定性和化学性质。第 4 章讨论亲核取代反应的机理、立体化学和影响因素。第 5 章讨论加成和消除反应的机理和立体化学。第 6 章主要介绍羰基化合物的亲核加成反应。第 7 章介绍重排反应。第 8 章讨论芳香亲核和亲电取代反应，同时介绍定位效应。第 9 章介绍各类氧化和还原反应及歧化反应。第 10 章介绍周环反应。每章后附有相关习题、专业术语词汇表。为方便学生理解，每章后有中文列出的知识要点。

《高等有机化学（双语版）第二版（Advanced Organic Chemistry 2nd）》可供化学类专业高年级本科生和研究生使用，亦可供从事高等有机化学教学的教师参考。

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前　言

Advanced Organic Chemistry 是河南省高等学校双语教学示范课程，目前市场上还没有一本适合该门课程课时及内容难易适中的双语教材。由于国外原版教材内容多、难度大、价格高，因此编写一本适合国内化学相关专业高年级本科生或研究生用的双语教材势在必行。这样可使学生融会贯通地深入学习有机化学的理论与反应机理，同时提高英语阅读水平和应用能力。

《高等有机化学（双语版）第二版（Advanced Organic Chemistry 2nd）》共分10章，前3章主要讨论有机化合物结构、立体化学与有机反应活性的关系，简单概述了反应机理的基础知识。后7章具体介绍了各类重要的有机反应机理，探讨了不同影响因素对这些反应机理、反应活性及产物的立体化学的影响。每章后附有相关习题、专业术语词汇表，专业术语词汇表中的词汇在文中以斜体表示以方便查阅。最后附有三套高等有机化学测试题及答案。

《高等有机化学（双语版）第二版（Advanced Organic Chemistry 2nd）》修改了第一版中的错误，将各级标题补充了中文，并在主要内容的章节后面用中文知识点加以概括以帮助理解。第1章、第3章由杨国玉编写，第2章由徐翠莲编写，第4章、第6章由潘振良编写，第5章由金秋编写，第7章、第9章由鲍峰玉编写，第8章由胡思前、彭望明、王亮编写，第10章由谢普会编写，附录由高光芹编写。全书由谢普会统稿、定稿。

《高等有机化学（双语版）第二版（Advanced Organic Chemistry 2nd）》得到河南省省级教学质量工程《高等有机化学》双语教学示范课程（豫教高〔2011〕173号）、河南农业大学校级教学质量工程《高等有机化学》双语教学示范课程、河南农业大学校级教学改革研究项目、江汉大学高等有机化学研究生教材立项的经费资助，并经河南省普通高等教育教材建设指导委员会审定。感谢河南省“十二五”规划教材评审专家对本教材编写提出的宝贵意见！

由于笔者水平有限，书中疏漏之处在所难免，诚恳希望读者批评指正。

编　者

2019年4月于河南农业大学

Contents

Chapter 1

Chemical Bonding and Molecular Structure（化学键与分子结构）

Information about molecular structure and ideas about bonds can be used to interpret and predict physical properties and chemical reactivities. Molecular structure specifies the relative position of all atoms (bond lengths and bond angles) in a molecule in quantitative terms. Structural information and interpretation can also be provided by computational chemistry. In this chapter, molecular orbital theory is applied to the interpretation of molecular structure and properties.

1.1 Localized chemical bonding（定域化学键）

Valence bond theory was the first structural theory applied to the empirical information about organic chemistry. In this theory, carbon almost always formed four bonds, nitrogen three, oxygen two, and the halogen one. Kekule's structure for benzene, published in 1865, was a highlight of this period. However, the structural formulas were developed without understanding of the nature of the chemical bond that is represented by the lines in the formulas. The key advance in understanding the concept of origin of chemical bonds was the introducing of the concept of electron-pair and the octet rule proposed by G. N. Lewis in 1916. The concept of bonds as electron pairs gave a fuller meaning to the traditional structural formulas, since the lines then specifically represent single, double, and triple bonds. However, Lewis structures convey relatively little information about molecular structure. The hybridization concept developed by Linus Pauling provided an approximate molecular geometry. The Pauling hybridization scheme provides an effective structural framework for most molecules. However, a particular hybridization scheme does not provide a unique description of molecular structure. Valence bond theory is neither a unique nor a complete description of *electron density*. Qualitative information about electron distribution can be deduced by applying the concepts of polarity and resonance.

Molecular orbital (MO) theory is an alternative way of describing molecular structure and electron density. In the molecular-orbital method, bonding is considered to arise from the overlap of atomic orbitals. When atomic orbitals overlap in a molecule, they combine to form new molecular orbitals with an equal number of atomic orbitals. Molecular orbitals (MOs) differ from atomic orbitals in that there are electron clouds that surround the nuclei of two or more atoms, rather than just one atom. MOs that involve only two atoms are called *localized molecular orbitals*. In localized bonding, the number of atomic orbitals that overlap is two (each containing one electron), so that two molecular orbitals are generated. One of them, called a *bonding orbital*, has lower energy than the original atomic orbitals, and the other, called an *antibonding orbital*, has higher energy than the original atomic orbitals. Bonding orbitals are filled first. Since the two original atomic orbitals each held one electron, both of these electrons can now go into the new molecular bonding orbital, since any orbital can hold two electrons. The antibonding orbital remains empty in the *ground state*. The greater the overlap is, the stronger the bond is. Fig 1.1 shows the bonding and antibonding orbitals that arise by the overlap of two 1s orbitals. Since the antibonding orbital has a node between the nuclei, there is practically no electron density in that area, so that this orbital cannot bond very well.

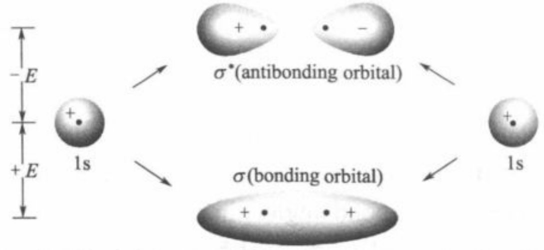


Fig 1.1 Overlap of two 1s orbitals gives rise to a σ and a σ* orbital.

Molecular orbitals formed by the overlap of two atomic orbitals are called σ (sigma) orbitals when most of its electron density is centered along the line connecting the two nuclei, and the bonds are called σ bonds. Corresponding antibonding orbitals are designated as σ*. Sigma orbitals are formed not only by the overlap of two s orbitals, but also by the overlap of any two atomic orbitals of s, p, d, or f. But the two *lobes* of the two atomic orbitals that can overlap must have the same signs: a positive s orbital can form a bond only by overlapping with another positive s orbital or with a positive lobe of a p, d, or f orbital. Any σ orbital may be represented as approximately ellipsoidal in shape.

A pi bond (π bond) results from overlap between two p orbitals oriented perpendicular to the line connecting the nuclei. These parallel orbitals overlap sideways, with most of the electron density centered above and below the line connecting the nuclei. This overlap is parallel, not linear (as in a sigma bond), so a π molecular orbital is not cylindrically symmetrical.

When ethylene forms, the combination of a σ bond and a π bond between the two carbons is involved. The two p orbitals of the two carbon atoms overlap and form a π bonding and a π antibonding (π*) molecular orbital, as shown in Fig 1.2. The π bonding molecular orbital of ethylene forms when the p atomic orbitals overlap with the same signs of the *wave function* in the bonding region between the two nuclei. This type of overlap is called a *constructive overlap*. Formation of the π antibonding molecular orbital occurs when the p atomic orbitals with opposite signs for the wave functions overlap in the bonding region. This type of overlap is called a *destructive overlap*. In the ground state of ethylene, two electrons are in the bonding MO, but the antibonding MO is vacant.

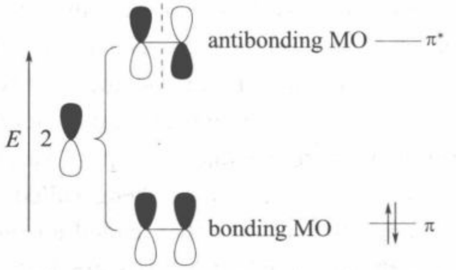


Fig 1.2 The formation of π molecular orbitals in ethylene from p atomic orbitals

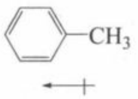
The distances between atoms in a molecule (bond lengths) are characteristic properties of the molecule and can give us information if we compare the same bond in different molecules. There is a correlation of bond strengths with bond lengths. In general, shorter bonds are stronger bonds. Bonds become weaker as we move down the periodic table. Compare C—O and C—S, or the carbon–halogen bonds C—F, C—Cl, C—Br, C—I, since bond distances must increase as we go down the periodic table because the number of inner electrons increases. Double bonds are both shorter and stronger than the corresponding single bonds, but not twice as strong, because π overlap is weaker than σ overlap. This means that a σ bond is stronger than a π bond.

原子轨道在线性组合成分子轨道时（即两个波函数相加得到的分子轨道），得到的分子轨道的能量比组合前的原子轨道能量低的分子轨道叫成键轨道。组合得到的分子轨道的能量比组合前的原子轨道能量高的分子轨道叫作反键轨道。成键轨道与反键轨道总是成对出现。成键轨道是由两个原子轨道符号相同的部分相加重叠而成。成键轨道中，核间的电子的概率密度大。电子在成键轨道中可以使两个原子核结合在一起，形成稳定分子。成键轨道有 σ 成键轨道和 π 成键轨道(以符号 σ 和 π 标记)。反键轨道有 σ*反键轨道和 π*反键轨道(以符号 σ*和 π*标记)。

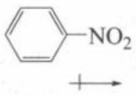
定域共价键只存在于两个原子之间。只包含定域键的多原子分子可以看成由相对独立的两个原子之间的化学键把原子连接起来形成的，而忽略相邻化学键的影响，把描述双原子分子中化学键的方法用到多原子分子的定域键上。如：乙烯中有一个 C—C、四个 C—H σ 键和一个 C—Cπ 键。定域键具有比较恒定的键性质。例如：一定类型定域键的键长、键偶极矩、键极化度、键力常数、键能等在不同分子中近似保持不变。

1.2 Dipole moments（偶极矩）

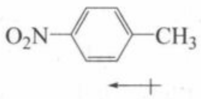
A bond with the electrons shared equally between two atoms is a nonpolar covalent bond. In most bonds between two different elements, the bonding electrons are attracted more strongly to one of the two nuclei. An unequally shared pair of bonding electrons is a polar covalent bond. The bond polarity is measured by dipole moment (μ), defined to be the product of charge separations (δ^+ and δ^-) and the bond length. The total dipole moment of the molecule is the vector sum of the individual bond moments. This vector sum reflects both the magnitude and the direction of each individual bond dipole moment.



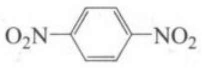
μ=0.43D



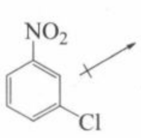
μ=3.93D

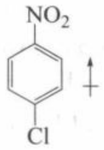


μ=4.39D

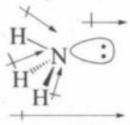


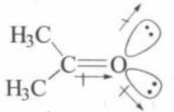
μ=0D

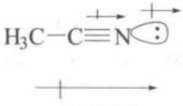




Lone pairs of electrons contribute to the dipole moments of bonds and molecules. Each lone pair corresponds to a charge separation, with the nucleus having a partial positive charge balanced by the negative charge of lone pair.


$\mu = 1.5\ \mathrm{D}$

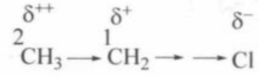

$\mu = 2.9\ \mathrm{D}$


$\mu = 3.9\ \mathrm{D}$

由不同原子形成的共价键，由于成键原子电负性不同，成键电子云偏向电负性较大的原子，该原子带上部分负电荷，而电负性较小的原子带部分正电荷。这种共价键具有极性。共价键的极性主要决定于成键原子的相对电负性大小。电负性差别越大，键的极性越大。还受相邻键和不相邻原子或基团的影响。共价键的偶极矩表示键的极性大小。偶极矩 $\mu=qd$，方向：正电中心指向负电中心。分子的偶极矩为所有共价键偶极矩的矢量和。

1.3 Inductive effects and field effects（诱导效应和场效应）

The C—C bond in ethane has no polarity because it connects two equivalent carbon atoms. However, the C—C bond in chloroethane is polarized by the presence of the more *electronegative* chlorine atom. Electronegativity differences are the origin of polar bonds. The C1 atom in chloroethane, having been deprived of some of its electron density by Cl with the greater electronegativity, is partially compensated by drawing the C—C electrons closer to itself, resulting in a polarization of this bond and a slightly positive charge on the C1 atom. This polarization of a bond caused by the polarization of an adjacent bond is called the *inductive effect*. The effect is greatest for adjacent bonds but may also be felt farther away; thus the polarization of the C—C bond causes a (slight) polarization of the three methyl C—H bonds.

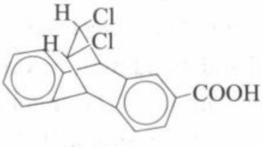

$$\overset{\delta^{++}}{\overset{2}{CH_3}} \longrightarrow \overset{\delta^{+}}{\overset{1}{CH_2}} \longrightarrow\!\longrightarrow \overset{\delta^{-}}{Cl}$$

Functional groups can be classified as *electron-withdrawing* (*–I*) or *electron-donating* (*+I*) groups relative to hydrogen. The most common *–I* groups include $—NR_3^+$, $—SR_2^+$, $—NH_3^+$, $—NO_2$, $—SO_2R$, —CN, $—SO_2Ar$, —COOH, —F, —Cl, —Br, —I, —OAr, —COOR, —OR, —COR, —SH, —SR, —OH, —C≡CR, —Ar and $—C{=}CR_2$. The most common *+I* groups include $—O^-$, $—COO^-$, $—CR_3$, $—CHR_2$, $—CH_2R$, $—CH_3$ and D. The groups are listed approximately in order of decreasing strength for both *–I* and *+I* groups. It can be seen that most groups are electron withdrawing. The *+I* groups are groups with a formal negative charge, or atoms with low electronegativity (Si, Mg, etc., and alkyl groups). Deuterium is electrondonating with respect to hydrogen. Atoms with sp hybridization orbital generally have a greater electron-withdrawing power than those with sp^2 hybridization orbital, which in turn have more electron-withdrawing power than those with sp^3 hybridization orbital. Inductive effects always decrease with increasing distance, and in most cases (except when a very powerful *+I* or *–I* group is involved), cause very little difference in four bonds away or more.

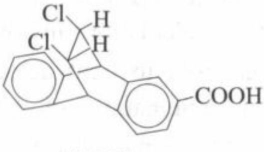
Typical order of *–I* groups: —F > —OH > $—NH_2$ > $—CH_3$ (central atom in the same period), F > Cl > Br > I (in the same group), —C≡CR > $—C{=}CR_2$ > $—CR_2CR_3$.

Typical order of *+I* groups: $—CR_3$ > $—CHR_2$ > $—CH_2R$ > $—CH_3$

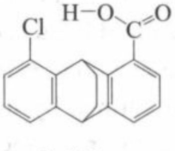
The *field effect* operates not through bonds, but directly through space or solvent molecules. The field effect depends on the geometry of the molecule. But the inductive effect depends only on the nature of the bonds. For example, in isomers **1** and **2**, the inductive effect of the chlorine atoms on the position of the electrons in the COOH group should be the same since the bonds intervene is the same. But the field effect is different because the chloro groups are closer in space to the COOH in **1** than they are in **2**. Thus a comparison of the acidity of **1** and **2** should reveal whether a field effect is truly operating. The *–I* effect of the chloro group in **3** should cause a stronger acidity than **4.** The result is reverse because of the field effect between Cl and —COOH, leading to less ability of releasing H^+ in **3** than in **4**.


$\mathrm{p}K_a$=6.07

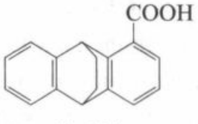
1


$\mathrm{p}K_a$=5.67

2


$\mathrm{p}K_a$ 6.25

3


$\mathrm{p}K_a$ 6.04

4

因分子中某一原子或基团的电负性不同引起分子中 σ 电子云向一个方向传递的效应叫诱导效应。通常以 H 的电负性作为衡量标准。凡是比 H 电负性大的原子或基团叫吸电子基，其诱导效应叫吸电子诱导效应（*–I*），反之叫供电子基和供电子诱导效应（*+I*）。

诱导效应的特点如下：

① 诱导效应以静电诱导方式沿键（包括 σ 和 π 键）进行传递，只涉及电子云分布状况的改变和键极性的改变。一般不引起整个电荷的转移和价态的变化；

② 诱导效应沿键迅速减小，其影响一般在三个原子内起作用；

③ 传递方向具有单一性。

诱导效应的相对强度如下：

电负性越大的原子或基团，其*–I* 越大。电负性越小，原子或基团的*+I* 效应越大。同主族元素，从上到下，电负性降低，*–I* 作用降低（*+I* 增加）。*–I* 效应：—F>—Cl>—Br>—I。

同周期元素的基团或原子，从左到右，电负性增加，*–I* 增加（*+I* 降低）。–I 效应：—F>—OH>—NH_2>—CH_3。

当烷基与不饱和碳原子或电负性原子(基团)相连时为*+I* 效应。*+I* 效应：—CR_3>—CHR_2>—CH_2R>—CH_3。

原子或基团带正电荷时具有相对较强的*–I* 效应，原子或基团带负电荷时具有相对较强的*+I* 效应。

诱导效应对物质性质的影响如下：

（1）对反应活性中间体稳定性的影响

中心碳原子上连的烷基越多的碳正离子和碳自由基的稳定性越大，而碳负离子的稳定性正相反。

（2）对羧酸酸性的影响

羧酸的酸性主要取决于 O—H 键离解的倾向以及共轭碱的稳定性，而诱导效应对两者均有影响。凡是烃基上带吸电基时将增加羧酸的酸性，带供电基时减小其酸性。

场效应：分子中的极性基团通过空间电场的传递的静电作用叫场效应。场效应依赖分子的几何构型。场效应也会对物质的酸碱性产生影响。

1.4 Delocalized chemical bonding（离域共价键）

Some compounds contain one or more bonding orbitals that are not restricted to two atoms, but spread out over three or more atoms. Such bonding is said to be delocalized. Delocalized bonding can not be adequately described by a single Lewis structure.

For planar unsaturated and aromatic molecules, many molecular-orbital calculations (MO calculations) have been made by treating σ and π electrons separately. It is assumed that the σ orbitals can be treated as localized bonds and the calculations involve only the π electrons. Hückel molecular-orbital (HMO) calculations is often used to treat delocalized bonding. According to HMO, a molecular orbital is formed by linear combinations of atomic orbitals. The number of π molecular orbitals is always the same as the number of p atomic orbitals used to form π MOs. These MOs have energies that are symmetrically distributed above and below the energy of the starting p orbitals. Half of the MOs are bonding MOs. Half of the MOs are antibonding MOs.

The construction of the π molecular orbitals for a conjugated diene requires that four p atomic orbitals from the four carbon atoms overlap. The overlap of these orbitals leads to four π MOs, each MO encompasses all four atoms that contributed the p orbitals. In the molecular orbital picture (Fig. 1.3), the overlap of four p orbitals gives two bonding orbitals that contain the four electrons and two vacant antibonding orbitals. It can be seen that each orbital has one more *node* than the one of next lower energy. The nodes in a molecular orbital are always symmetrically distributed. For example, the π_3 molecular orbital has two nodes equidistant from the center and the two ends of the orbital. Each of the two lower energy π MOs is filled with two electrons, whereas the two higher energy π MOs remain empty.

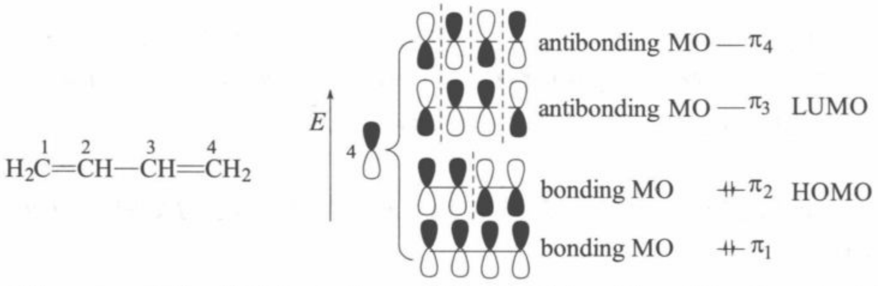


Fig 1.3 The energy relationship between the constituent p orbitals and the π MOs of a conjugated diene.

As shown in Fig 1.3, The π_1 molecular orbital consists only of bonding overlaps between the constituent atomic orbitals of 1,3-butadiene. As a result, the π_1 molecular orbital is very stable. The $\pi_{1\text{-}4}$ MOs of a conjugated diene are called *delocalized molecular orbitals* because they extend over more than two atoms.

The π_1 molecular orbital of a conjugated diene is lower in energy than the π_1 molecular orbital of an unconjugated diene or alkene. The π_1 molecular orbital of a conjugated system also exhibits the other two characteristics of a conjugated system: planar conformation and a shorter single bond between C2—C3 than typical single bond. This MO has the lowest energy among the four MOs formed in a conjugated system, so it fills with electrons before any other levels.

The π_2 MO involves bonding overlap between C1—C2 and C3—C4 along with an antibonding overlap (node) between C2 and C3. The π_2 MO is higher in energy than the π_1 MO because of the node between C2 and C3. After the π_1 MO fills with electrons, the π_2 MO then fills. The π_2 MO is *the highest occupied molecular orbital* (abbreviated HOMO) of 1,3-butadiene.

The π_3 MO involves a bonding overlap between C2—C3 and an antibonding overlap between C1—C2 and C3—C4. The π_3 molecular orbital is *the lowest unoccupied molecular orbital* (LUMO) of 1,3-butadiene. The π_4 MO involves all antibonding overlaps between adjacent carbons. The π_4 MO is the highest unoccupied molecular orbital.

Where a p orbital is on an atom adjacent to a double bond, there are three parallel p orbitals that overlap. As previously noted, it is a general rule that the overlap of *n* atomic orbitals creates *n* molecular orbitals, so overlap of a p orbital with an adjacent double bond gives rise to three new orbitals, as shown in Fig 1.4. The middle orbital is a *nonbonding molecular orbital* of zero bonding energy. The central carbon atom does not participate in the nonbonding orbital. Electrons in this orbital have the same energy as an isolated p orbital.

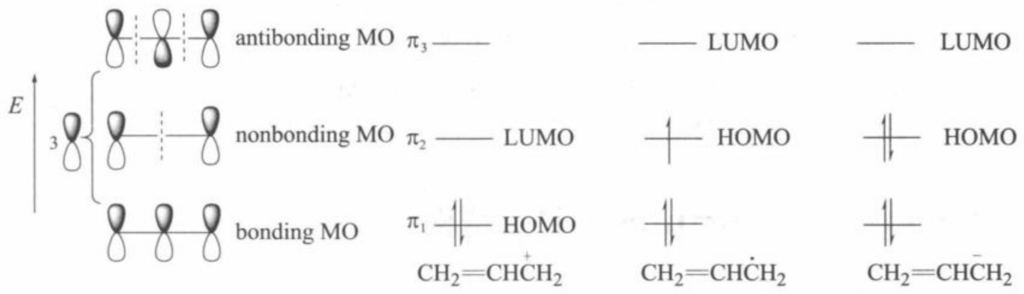


Fig 1.4 The energy relationship between the constituent p orbitals and the MOs of allylic cation, free radical, and carbanion.

There are three cases: the original p orbital may have contained no, one, or two electrons. Since the original double bond contributes two electrons, the total number of electrons accommodated by the new molecular orbitals is two, three, or four respectively. For example, the orbital structures of the allylic cation, free radical, and carbanion differ from each other, therefore, only in that the nonbonding orbital is empty, half-filled, or filled. The electrons in the nonbonding orbital do not contribute to the bonding energy, positively or negatively. The two cases, where the original p orbital contains only one or no electron, are generally found only in free radicals and cations, respectively. Allylic free radicals have one electron in the nonbonding orbital. In allylic cations, this orbital is vacant and only the bonding orbital is occupied. An allylic carbocation is more stable than an ordinary carbocation. The case where the original p orbital contains two electrons are found in allylic carbanions as well as any system containing an atom that has an unshared pair and that is directly attached to a multiple-bond atom, e.g. $CH_2=CH-Cl$, $CH_2=CH-Cl$, $CH_2=CH-OCH_3$, etc.

分子轨道理论：描述共价键形成的一种理论。包括以下要点：

① 分子中任何电子都可看成在所有核和其余电子所构成的势场中运动，描述分子中电子运动状态的波函数称为分子轨道。

② 分子轨道由能量相同/相近的原子轨道的线性组合而构成。对于离域 π 键，π 分子轨道是由原子的 P_z 原子轨道线性组合而成。

$$\Psi=C_1\phi_1+C_2\phi_2+\cdots+C_n\phi_n。$$

式中，C_1，C_2，C_n 为原子轨道系数；$\phi_1, \phi_2\cdots\phi_n$ 为原子轨道，Ψ 为分子轨道。

③ 每个分子轨道的能量：$E=\int\Psi H\Psi\mathrm{d}\tau$ 分子的总能量等于被电子占据的分子轨道能量

的总和。

④ 分子中电子的填充：Pauli 不相容原理和 Hund 规则。

每个分子轨道最多能容纳两个电子，且电子自旋反平行。对于能量相等的分子轨道，电子将尽可能分占不同的轨道，且自旋平行。

分子轨道的基本特点如下：

① 分子轨道数目等于参与线性组合的原子轨道数目。

② 离域 π 键分子轨道分为成键轨道、非键轨道和反键轨道。

能量低于原子轨道的分子轨道叫成键轨道（有利于共价键的形成），能量等于原子轨道的分子轨道叫非键轨道（对共价键的形成没有任何作用），能量高于原子轨道的分子轨道叫反键轨道（不利于共价键的形成）。

前线轨道理论：日本诺贝尔化学奖获得者福井谦一提出了前线轨道理论。其要点如下：有电子占据的能量最高的分子轨道叫最高已占分子轨道（HOMO）。没有电子占据的能量最低的分子轨道叫最低未占分子轨道（LUMO）。HOMO 与 LUMO 统称为前线轨道（FMO）。前线轨道中的电子是化学反应中最活泼的电子，是有机化学反应的核心。

1.5 Resonance structures（共振结构）

A resonance structure may be drawn for any conjugated structure by moving electrons from one place to another, so long as the rules of Lewis structures are followed. The electron delocalization described by resonance enhances the stability of the molecules, and compounds or ions composed of such molecules often show exceptional stability. Resonance structures are not different compounds, but different ways of drawing the same compound. The actual molecule is said to be a resonance hybrid of its resonance forms.

In drawing resonance structures, we try to draw structures that are as low in energy as possible. The best candidates are those that have the maximum number of octets and the maximum number of bonds. Only electrons can be delocalized. Nuclei cannot be delocalized. They must remain in the same places, with the same bond lengths and angles in all the resonance contributors. The following general rules will help us to draw realistic resonance structures:

(1) All the resonance structures must be valid Lewis structures for the compound.

(2) Only the placement of electrons may be shifted from one structure to another (electrons in double bonds and lone pairs are the ones that are most commonly shifted.). Nuclei cannot be moved, and the bond angles must remain the same.

(3) All the *canonical forms* must have the same number of paired and unpaired electrons. Most stable compounds have no unpaired electrons, and all the electrons must remain paired in all the resonance structures.

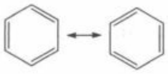
(4) The major resonance contributor is the one with the lowest energy. Good contributors generally have all octets satisfied, as many bonds as possible, and as little charge separation as possible. Positive charge is best accommodated on atoms of low electronegativity, and negative charge on high electronegative atoms.

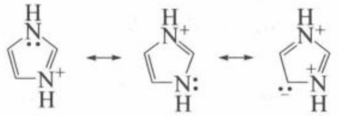
(5) Resonance stabilization is most important when it serves to delocalize a charge over two or more atoms.

$$CH_2{=}CH{-}\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2{-}CH{=}CH_2$$

$$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$$

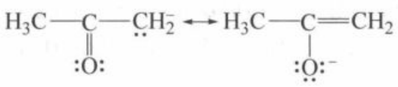
$$CH_2{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2$$





$$H_2\overset{+}{C}{-}CH{=}CH{-}CH{=}CH{-}CH_3 \longleftrightarrow H_2C{=}CH{-}CH{=}CH{-}\overset{+}{C}H{-}CH_3 \longleftrightarrow H_2C{=}CH{-}\overset{+}{C}H{-}CH{=}CH{-}CH_3$$

$$H_3C{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}{-}CH_2^+ \longleftrightarrow H_3C{-}\underset{\cdot\cdot}{\overset{+}{S}}{=}CH_2$$



$$H_3C{-}\underset{\|\atop :O:}{C}{-}\underset{\cdot\cdot}{C}H_2^- \longleftrightarrow H_3C{-}\underset{|\atop :\ddot{O}:^-}{C}{=}CH_2$$

当一个分子、离子或自由基的结构不能用路易斯结构式正确地描述时，可以用多个路易斯式表示，这些路易斯式称为共振结构（又称极限式或正则结构）。在共振结构之间用双箭头“↔”联系，以表示它们的共振关系。要正确写出共振结构式，应符合下列几条规则：

① 共振结构式之间只允许键和电子的移动，而不允许原子核位置的改变。

② 所有的共振结构式必须符合 Lewis 结构式。

③ 所有的共振结构式必须具有相同数目的未成对电子。

④ 共振结构式中所有的原子都具有完整的价电子层，是较为稳定的。

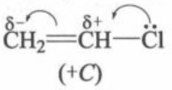
⑤ 有电荷分离的共振结构式稳定性较低。

⑥ 负电荷在电负性较大的原子上的共振结构式较稳定。

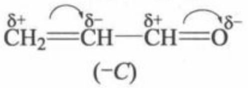
1.6 Conjugative effect（共轭效应）

Multiple bonds that alternate with single bonds are said to be conjugated. In the conjugated systems, many p orbitals overlap to form a more stable π bond where the π electrons are delocalized than similar systems with isolated double bonds.

The interaction effect of atoms on the electronic density in conjugated systems is called conjugative effect (C). Conjugative effect from the overlap and interaction of p orbitals whose axis are parallel to each other is a characteristic of conjugative systems. Compared with inductive effect, conjugative effect only exists in the conjugative systems. The intensity of conjugative effect is not weakened along with the increase of the distance. Conjugative effect can be divided into electron withdrawing conjugative effect (–*C*) and electron donating conjugative effect (+*C*).



(+*C*)



(−*C*)

Common +*C* and –*C* groups:

+*C* groups: O^-, S^{2-}, —NR_2, —NHR, —NH_2, —NHCOR, —OR, —OCOR, —SR, —SH, —F, —Cl, —Br, —I, —R, —Ar.

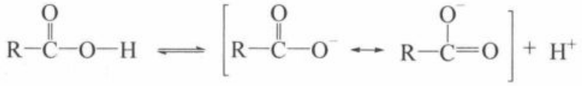
–*C* groups: —NO_2, —CN, —COOH, —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —CHO, —COR, —SO_3R, —SO_2R, —NO, —Ar.

+*C* groups decrease in order: —F > —Cl > —Br > —I, —OR > —SR > —SeR, —O^- > —OR> —O^+R_2.

In π-π conjugative systems, –*C* groups decrease in order: —C=O > —C=N > —C=C, —$C{=}N^+HR_2$ > —C=NR.

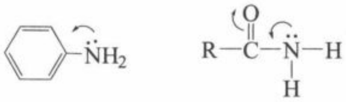
In p-π conjugative systems, +*C* decreases in the order: —NR_2> —OR > —F.

The conjugative effect can affect the chemical properties of some compounds. The conjugative effect can affect on the acidity of compounds. For example, carboxylic acids are more acidic than alcohols owing to the conjugative effect of hydroxy group in carboxylic acids. Let's look at the stabilities of *carboxylate anions*, the negative charge in the carboxylate is shared by both oxygen atoms. In other words, a carboxylate anion is a resonance *hybrid* of two equivalent structures. Since a carboxylate anion is more stable than an *alkoxide anion*, a carboxylate anion is lower in energy and is present in greater amount at equilibrium than an alkoxide anion.

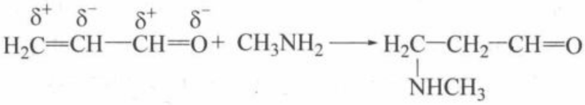


$$R{-}\overset{O}{\overset{\|}{C}}{-}O{-}H \rightleftharpoons \left[R{-}\overset{O}{\overset{\|}{C}}{-}O^- \longleftrightarrow R{-}\overset{O^-}{\overset{|}{C}}{=}O\right] + H^+$$

The conjugative effect can also affect the basicity of compounds. Arylamines, such as aniline, are weaker bases than alkylamines by a factor of about 10^6. The nitrogen lone-pair electrons in an *arylamine* are shared by orbital overlap with the π orbitals of the aromatic ring, and they are therefore less available for bonding to an acid. In contrast to amines, amides ($RCONH_2$) are nearly neutral. The main reason for the decreased basicity of amides relative to amines is that the lone-pair electrons on nitrogen atom of amides are shared by orbital overlap with the adjacent carbonyl group π orbital. The electrons are therefore much less available for bonding to an acid.



The conjugative effect can affect the type of some addition reactions. The reaction of ethylene with HCl is an *electrophilic* addition because the electrons in the π bond are accessible to electrophiles. In *acrylaldehyde*, however, the π electrons in the C=C bond are accessible to *nucleophiles* because the electronegative oxygen atom of α, β-unsaturated carbonyl compound withdraws electrons from the β carbon, thereby making it more electron-poor and more electrophilic than a typical C=C bond in an alkene.



$$\overset{\delta^+}{H_2C}{=}\overset{\delta^-}{CH}{-}\overset{\delta^+}{CH}{=}\overset{\delta^-}{O} + CH_3NH_2 \longrightarrow \underset{NHCH_3}{\underset{|}{H_2C}}{-}CH_2{-}CH{=}O$$

包含三个或三个以上原子的 π 键叫共轭 π 键，这样的体系叫共轭体系。共轭体系中的电子云是离域的而不是定域的，使得所涉及的化学键平均化，这种体现在共轭体系中原子之间的相互影响的电子效应叫共轭效应。

基本特点如下：共轭效应只存在于共轭体系中，只沿共轭体系传递；无论共轭体系有多