Advanced Organic Chemistry

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About this course

Polymer science or macromolecular science is a subfield of materials science concerned with polymers, primarily synthetic polymers such as plastics and elastomers. The field of polymer science includes researchers in multiple disciplines including chemistry, physics, and engineering

Polymer science comprises three main sub-disciplines:

- Polymer chemistry or macromolecular chemistry, concerned with the chemical synthesis and chemical properties of polymers.
- Polymer physics, concerned with the bulk properties of polymer materials and engineering applications.
- Polymer characterization is concerned with the analysis of chemical structure and morphology as well as the determination of physical properties in relation to compositional and structural parameters.

Polymer chemistry

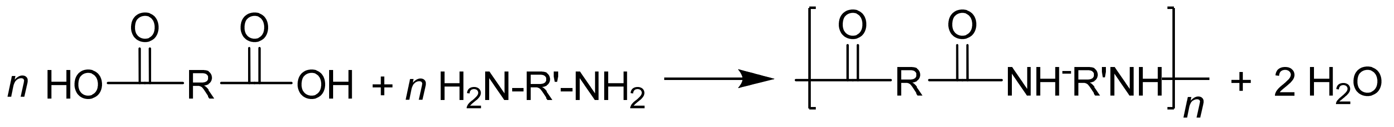
— the foundation of polymer science .

Goal:

- New polymerization reactions, new polymerization techniques, new catalysts, new monomers…
- Synthesis with controllability of polymeric chain structures, stereoregularity, functionality…
- Synthesis techniques for polymeric materials with specific massed structure…
- The synthesis of new polymeric materials with high performance using common monomers…

…….

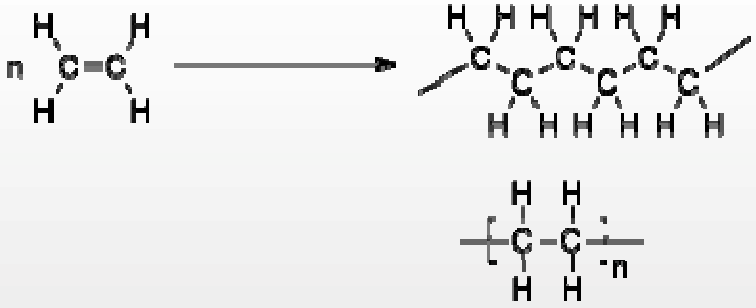
Polycondensation



$$n\ \mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}OH} + n\ \mathrm{H_2N{-}R'{-}NH_2} \longrightarrow \left[\mathrm{C({=}O){-}R{-}C({=}O){-}NH{-}R'NH}\right]_n + 2\ \mathrm{H_2O}$$

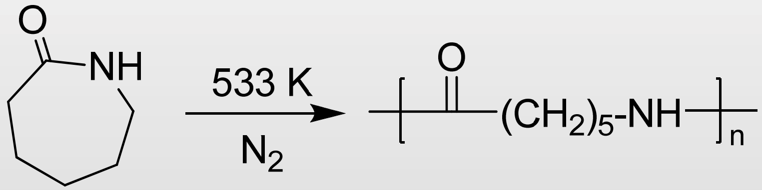
Nylon-66

Radical Polymerization



High-pressure polyethylene

Ring-opening polymerization



Nylon-6

Coordination polymerization
(Ziegler-Natta Catalyst)

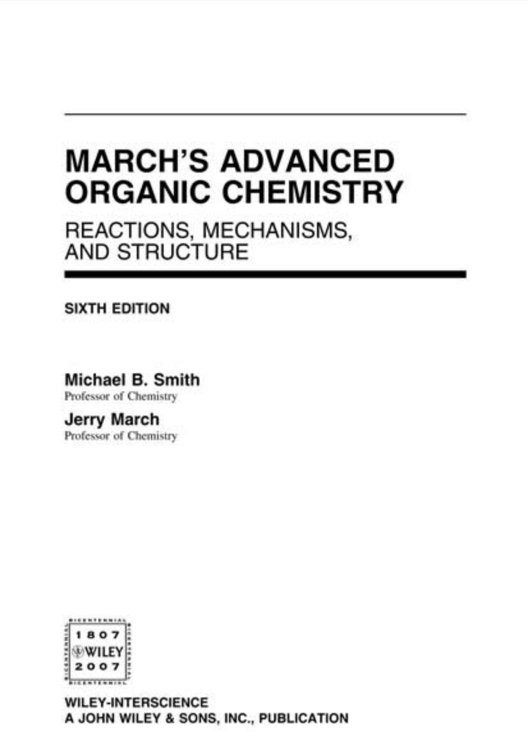
→

Stereoregular polyolefin:
i-PP, *s*-PSt…

CONTENTS:

Reference:

Michael B. Smith, Jerry March, "Advanced Organic Chemistry", 6th ed., John Wiley & Son (2006).



MARCH'S ADVANCED ORGANIC CHEMISTRY

REACTIONS, MECHANISMS, AND STRUCTURE

SIXTH EDITION

Michael B. Smith
Professor of Chemistry
Jerry March
Professor of Chemistry

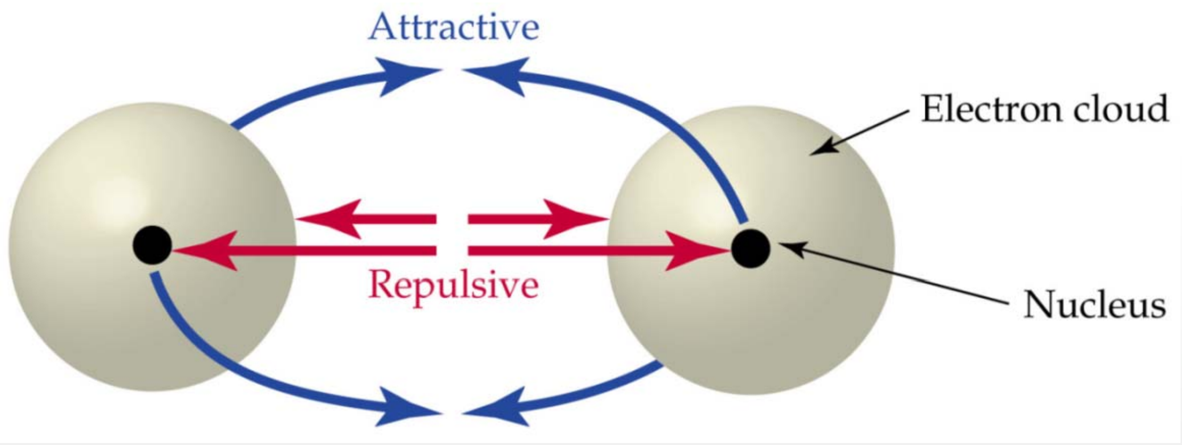
WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

Chapter 1

Chemical Bonding

- Localized Chemical Bonding
- Delocalized Chemical Bonding
- Bonding weaker than covalent bond

1.0 Theories of chemical bonding: Overview



A **chemical bond** is the physical process responsible for the attractive interactions between atoms and molecules, and that which confers stability to diatomic and polyatomic chemical compounds.

- Valence Bond Theory (VB) 价键理论
- Molecular Orbital Theory (MO) 分子轨道理论
- Ligand Field Theory (LFT) describes the bonding, orbital arrangement, and other characteristics of coordination complexes (配位化合物).

1.0.1 Valence Bond Theory (VB)

According to this theory a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.

F_2: F - F bond p_z-p_z

HF: H-F bond 1s-2p_z

- 1916, **G.N. Lewis**: a chemical bond forms by the interaction of two shared bonding electrons (共享键合电子)
- 1927, **Heitler-London**: calculation of bonding properties of H_2 based on quantum mechanical considerations
- **Walter Heitler**: used Schrödinger’s wave equation to show how two hydrogen atom wave functions join together, with plus, minus, and exchange terms, to form a covalent bond.

Linus Pauling (1901-1994)

resonance (1928); orbital hybridization (1930).

"The Nature of the Chemical Bond"

Cornell University Press, Ithaca New York,
1939 (3rd Edition, 1960).

- the "bible" of modern chemistry, helping experimental chemists to understand the impact of quantum theory on chemistry
- the Nobel Prize in Chemistry (1954, 1962).

As a biochemist, Pauling conducted research with X-ray crystallography and modeling in crystal and protein structures. This type of approach was used by Rosalind Franklin, James Watson and Francis Crick in the U.K to discover the double helix structure of the DNA molecule.

1.0.2 Molecular Orbital Theory (MO)

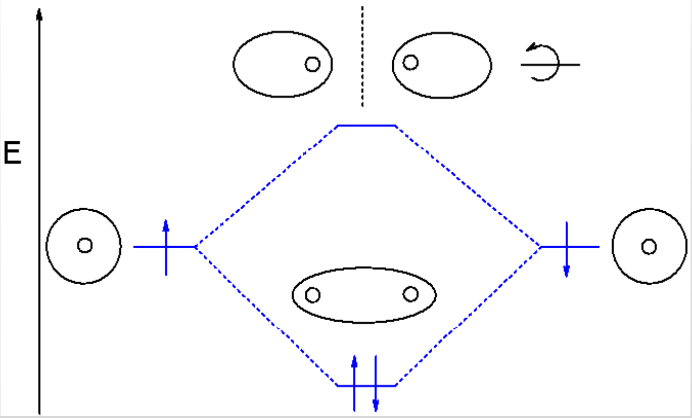
Molecular orbital theory (MO theory) is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.

- MO theory uses a *linear combination of atomic orbitals* (LCAO) to form molecular orbitals which cover the whole molecule.
- These molecular orbitals are results of electron-nucleus interactions that are caused by the fundamental force of electromagnetism.
- These orbitals are often divided into:

  bonding orbitals,

  anti-bonding orbitals, and

  non-bonding orbitals.



Dihydrogen MO diagram

Frontier Molecular Orbital Theory

Kenichi Fukui (福井谦一, Kyoto University, 1918-1998)
Roald Hoffmann (Cornell University, 1937-)
The Nobel Prize in Chemistry (1981)

The role of frontier orbitals in chemical reactions: molecules share loosely bonded electrons which occupy the frontier orbitals, that is the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO).

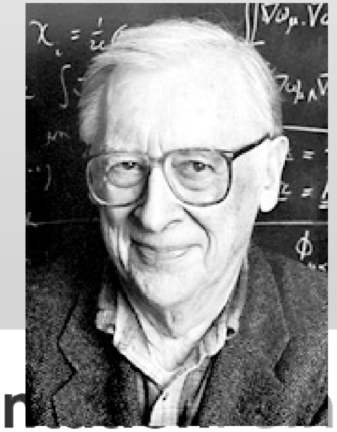
Walter Kohn (1923-), for his development of the

Density-Functional Theory

John Pople (1925-2004)

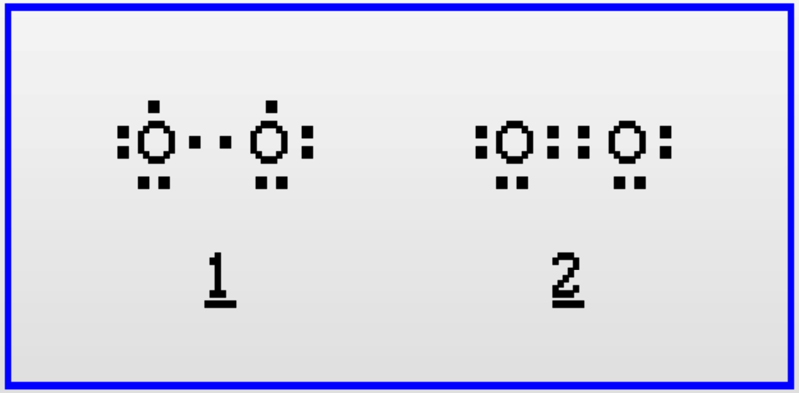
"for his development of computational methods in quantum chemistry"

The Nobel Prize in Chemistry (1998)



1.1 Localized Chemical Bonding(定域化学键)

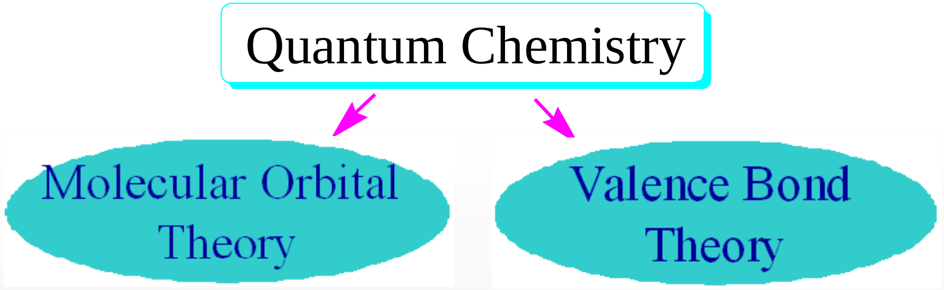
Localized chemical bonding may be defined as bonding in which the electrons are shared by two and only two nuclei.



Two Lewis Structures for O_2
O: $1s^2 2s^2 2p^4$

Which of the alternatives best represents the structure of dioxygen?

1.1.1 Covalent Bonding (共价键)

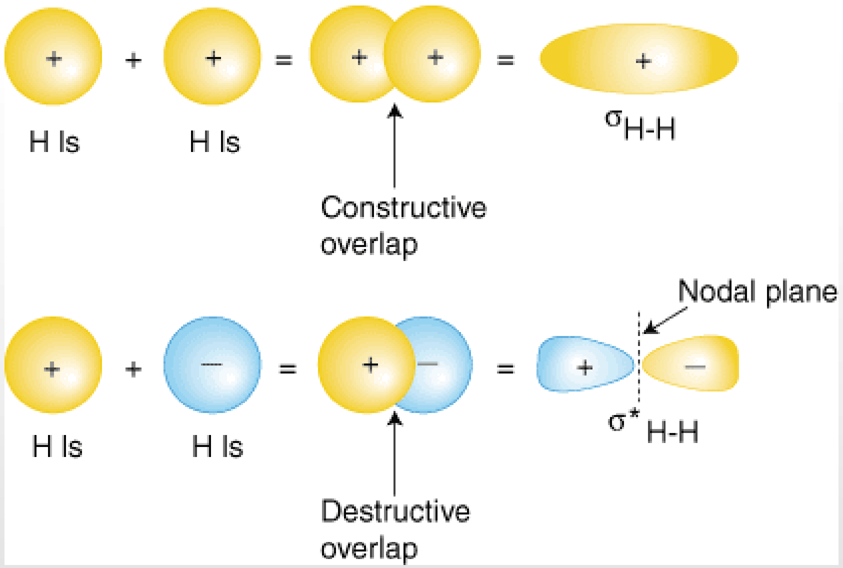


Quantum Chemistry

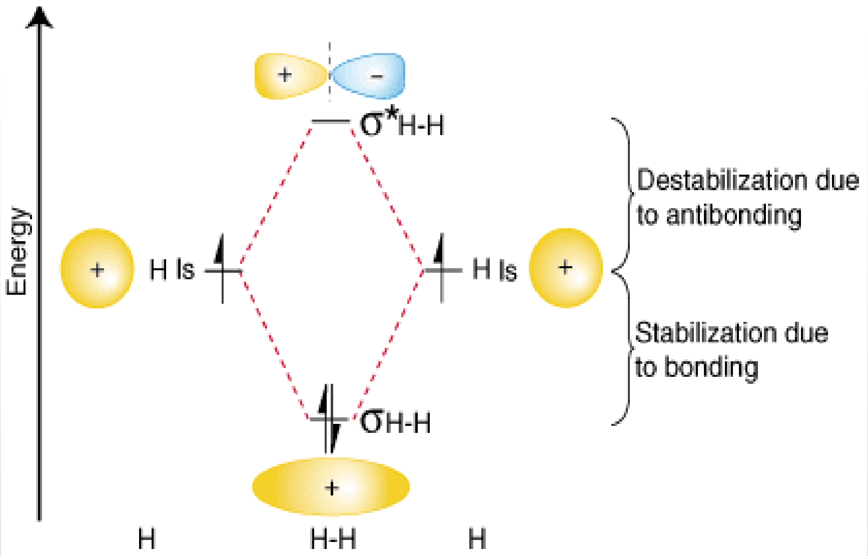
Molecular Orbital Theory

Valence Bond Theory

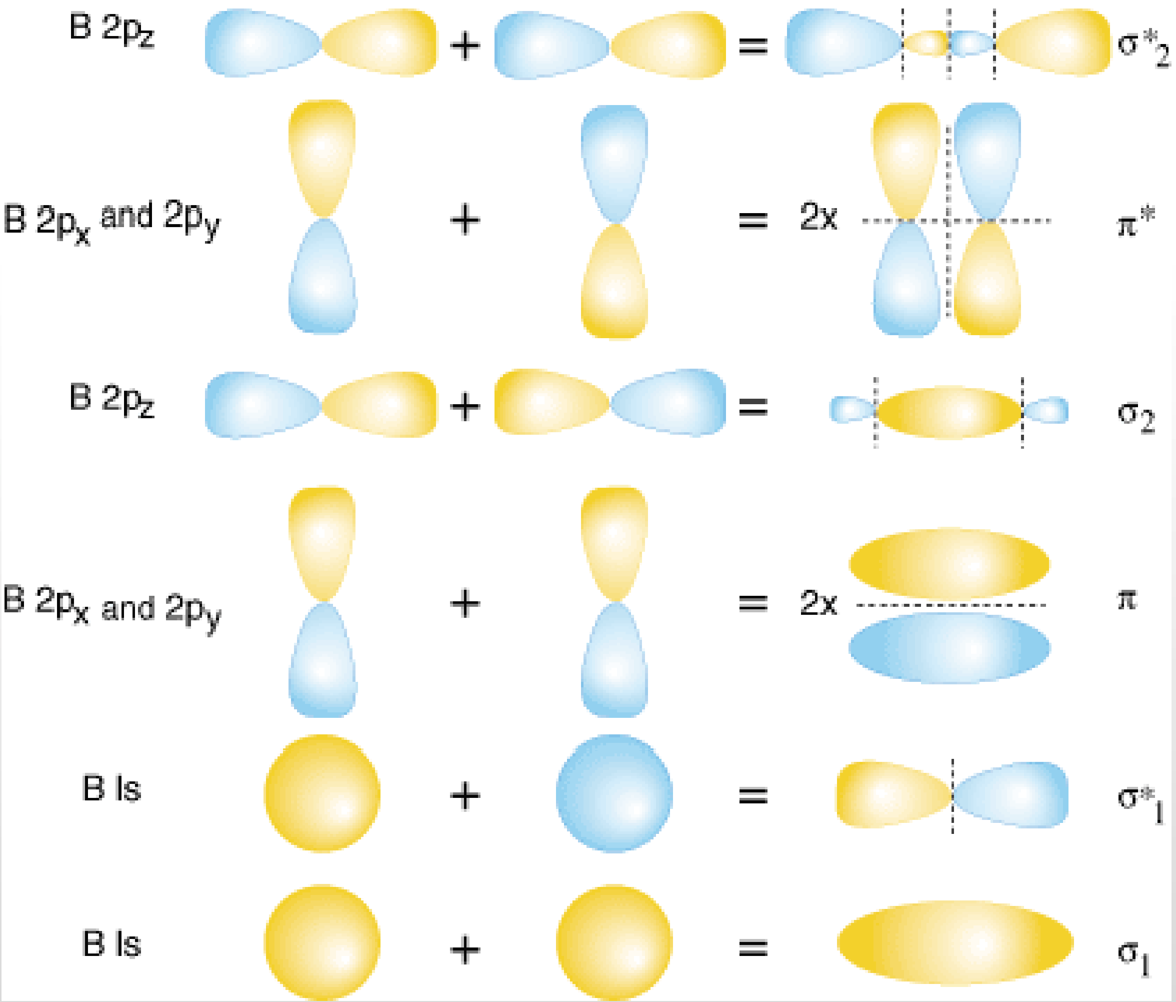
- In atoms, electrons reside in orbitals of differing energy levels such as 1s, 2s, 2p, 3d, etc. These orbitals represent the probability distribution for finding an electron anywhere around the atom. **Molecular orbital theory** posits the notion that electrons in molecules likewise exist in different orbitals that give the probability of finding the electron at particular points around the molecule.
- In the molecular orbital theory, **bonding** is considered to arise from the overlap of atomic orbitals. When any number of atomic orbitals overlap, they combine to form an equal number of new orbitals, called molecular orbitals.



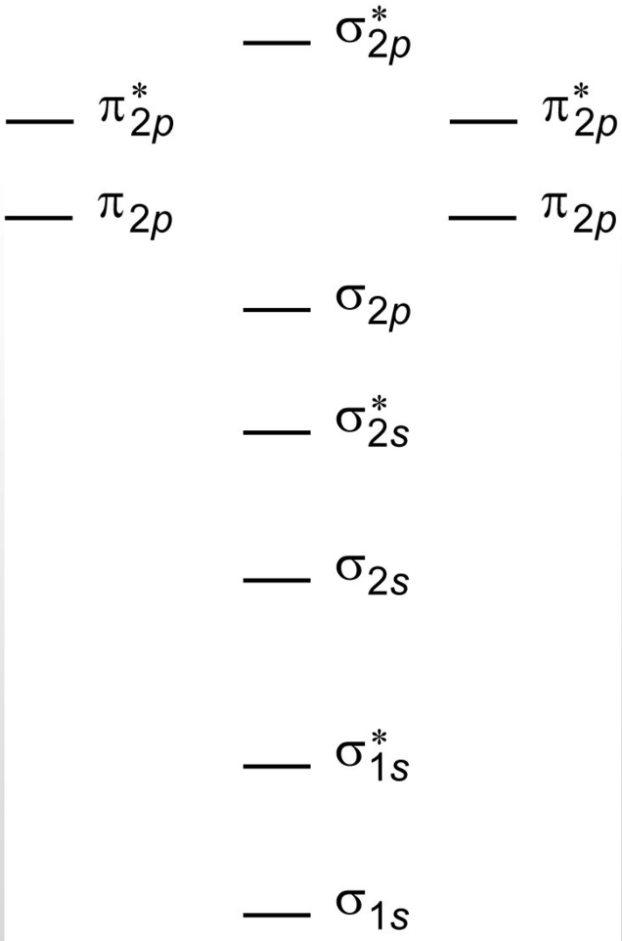
Two *1s* orbitals combine to form a bonding and an anti-bonding M.O.



An orbital correlation diagram for hydrogen.

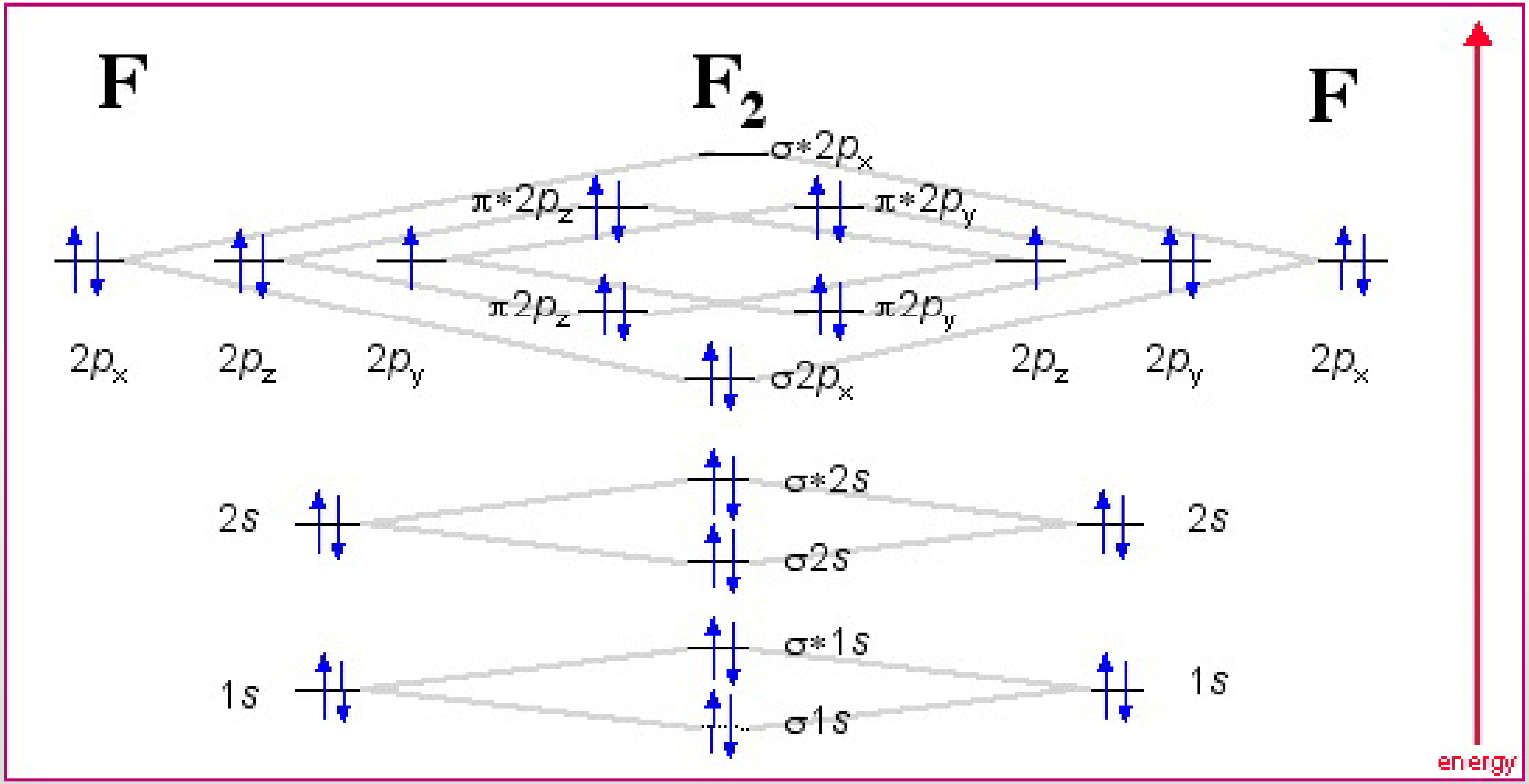


The molecular orbitals of diboron (B_2)



The expected molecular orbital diagram for O_2, F_2, Ne_2, CO, and NO.

- Determine the number of electrons in the molecule. We get the number of electrons per atom from their atomic number on the periodic table. (Remember to determine the total number of electrons, not just the valence electrons.)
- Fill the molecular orbitals from bottom to top until all the electrons are added. Describe the electrons with arrows. Put two arrows in each molecular orbital, with the first arrow pointing up and the second pointing down.
- Orbitals of equal energy are half filled with parallel spin before they begin to pair up.



Orbital correlation diagram for F_2 (homonuclear diatomic molecules).

Bond order = 1/2 (#e-in bonding MO's – #e-in antibonding MO's)

the stability of molecules?

◆ If the bond order for a molecule is equal to zero, the molecule is unstable. A bond order of greater than zero suggests a stable molecule.

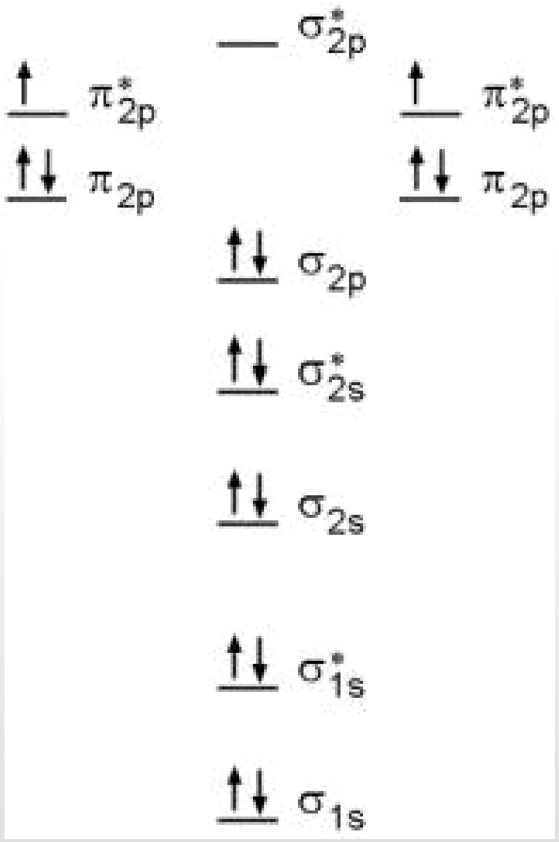
◆ The higher the bond order is, the more stable the bond.

Predicting whether a molecule is paramagnetic or diamagnetic based on the molecular orbital diagram:

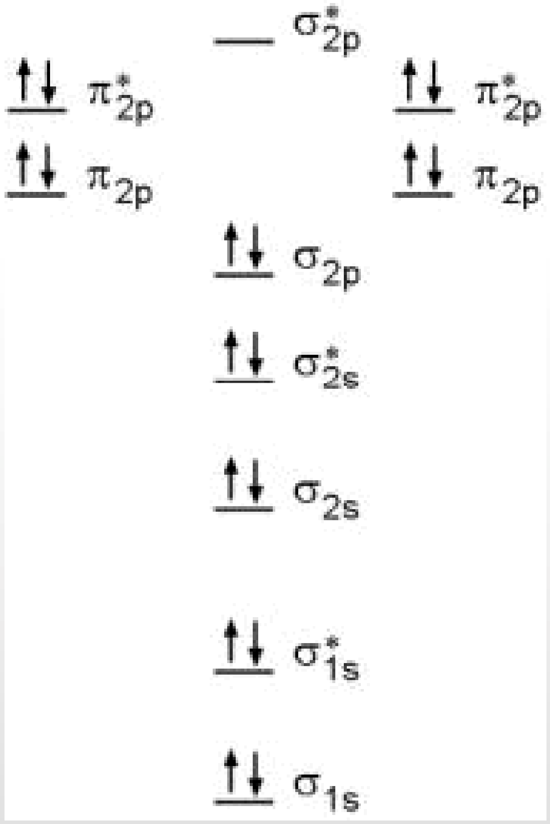
If all the electrons are paired, the molecule is ***diamagnetic****. If one or more electrons are unpaired, the molecule is* ***paramagnetic****.*

抗磁性：在有外加磁场的情况下,物质获得一个对抗该外加磁场的磁矩的现象。放在外磁场中的物质,若其磁化强度*M*方向与外加磁场强度*H*方向相反,则称这种物质具有**抗磁性**.

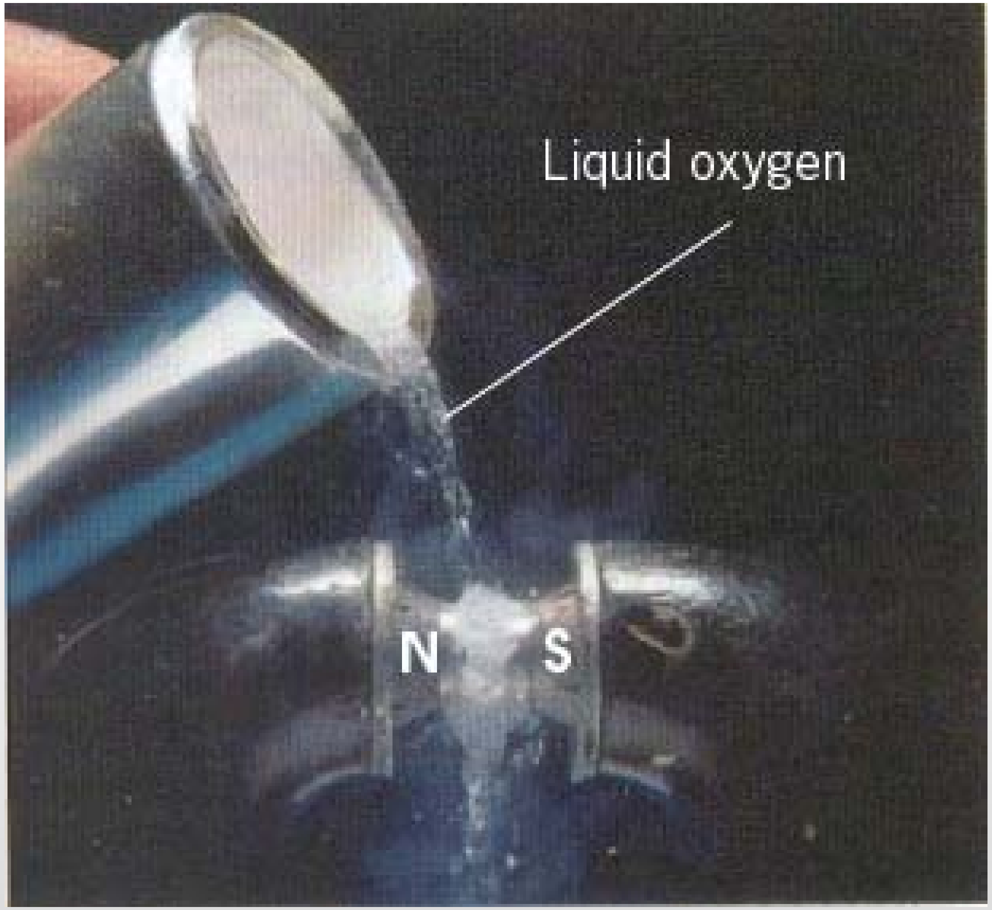
顺磁性：即磁化强度*M*的方向与磁场强度*H*的相同,数量级在室温时一般为10^{-2}～10^{-5} emu



The molecular orbital diagram for $\mathbf{O_2}$.
Bond order = 2 (stable)
paramagnetic



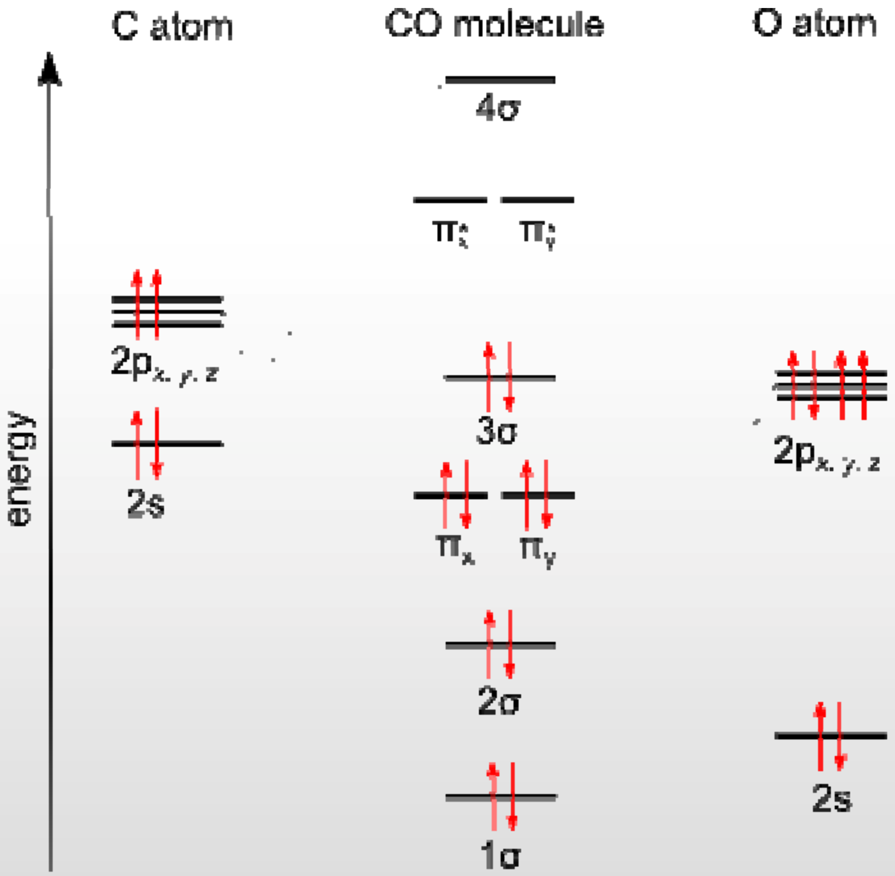
The molecular orbital diagram for $\mathbf{F_2}$.
Bond order = 1 (stable)
diamagnetic



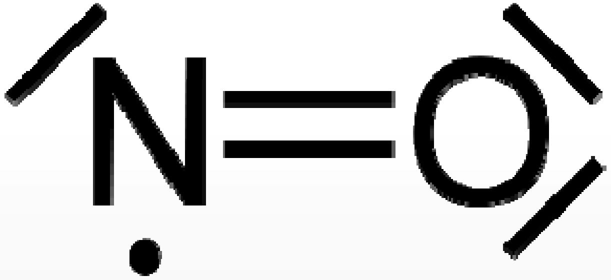
The paramagnetism of oxygen can readily be demonstrated by pouring liquid O_2 between the poles of a strong permanent magnet; the liquid stream is trapped by the field and fills up the space between the poles.

- We can describe diatomic molecules composed of atoms of different elements in a similar way. The bond between the carbon and oxygen in carbon monoxide is very strong despite what looks like a strange and perhaps unstable Lewis Structure.

the plus formal charge on the **O** and the minus formal charge on the **C**, Suggesting instability



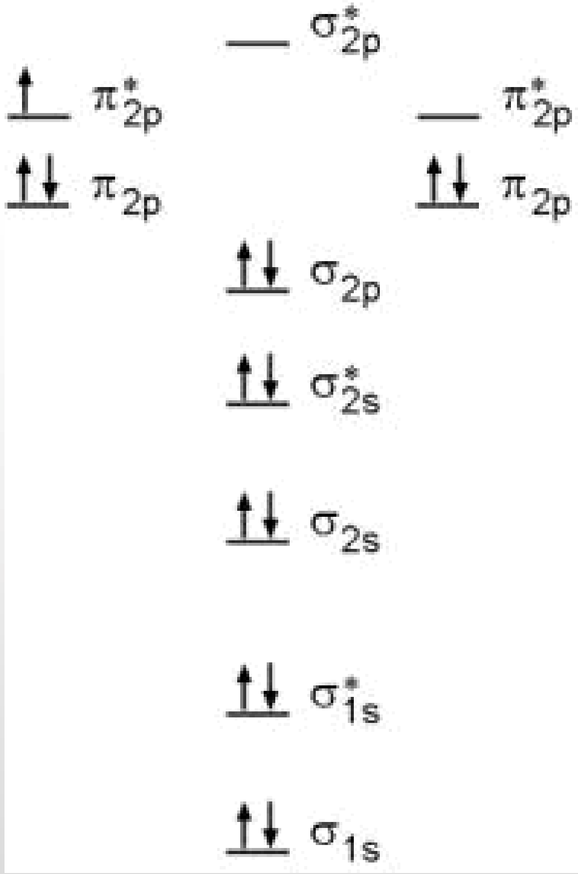
The molecular orbital diagram for carbon monooxide.
Bond order = 3



N $1s^22s^22p^3$

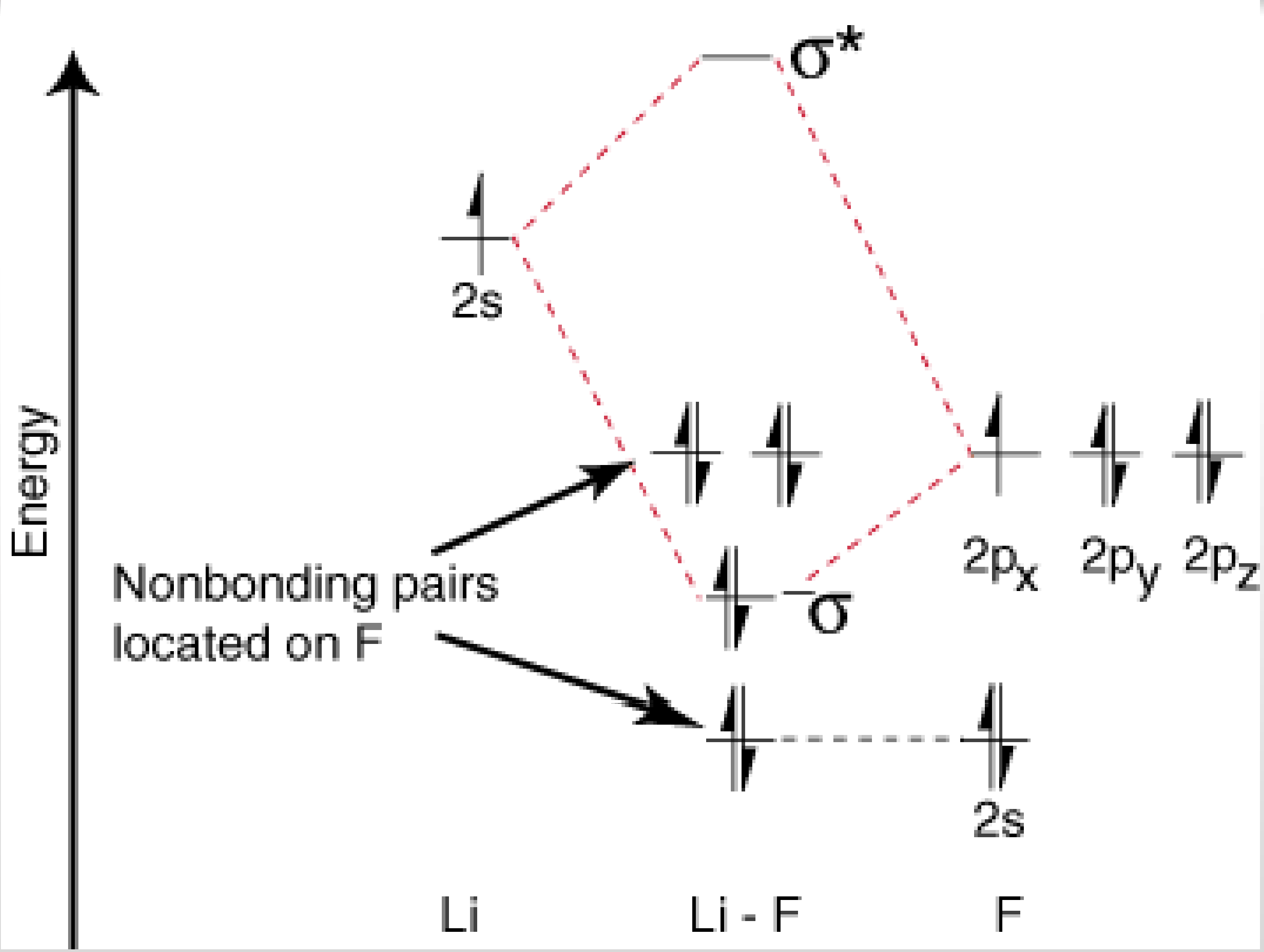
O $1s^22s^22p^4$

The unpaired electron and the lack of an octet of electrons around nitrogen would suggest an unstable molecule.

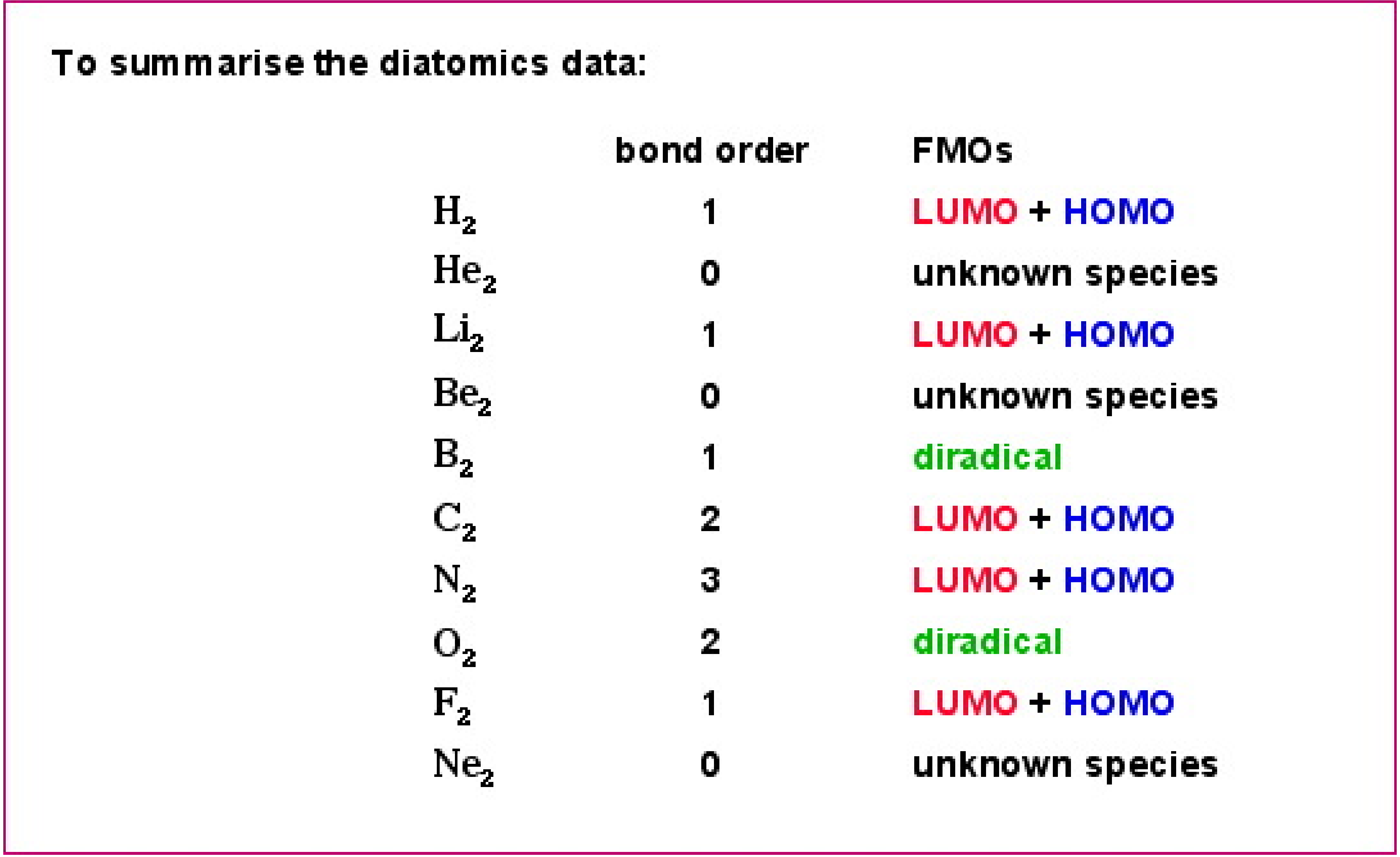


The molecular orbital diagram for NO.

Bond order = 2.5



Orbital correlation diagram for LiF.



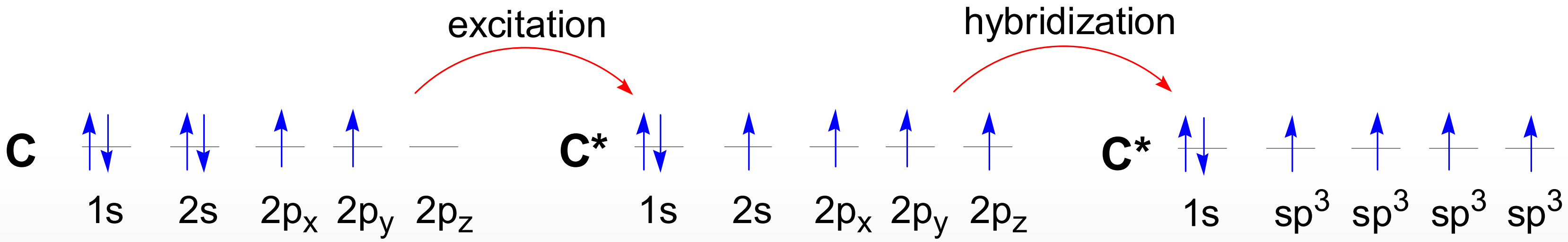
To summarise the diatomics data:

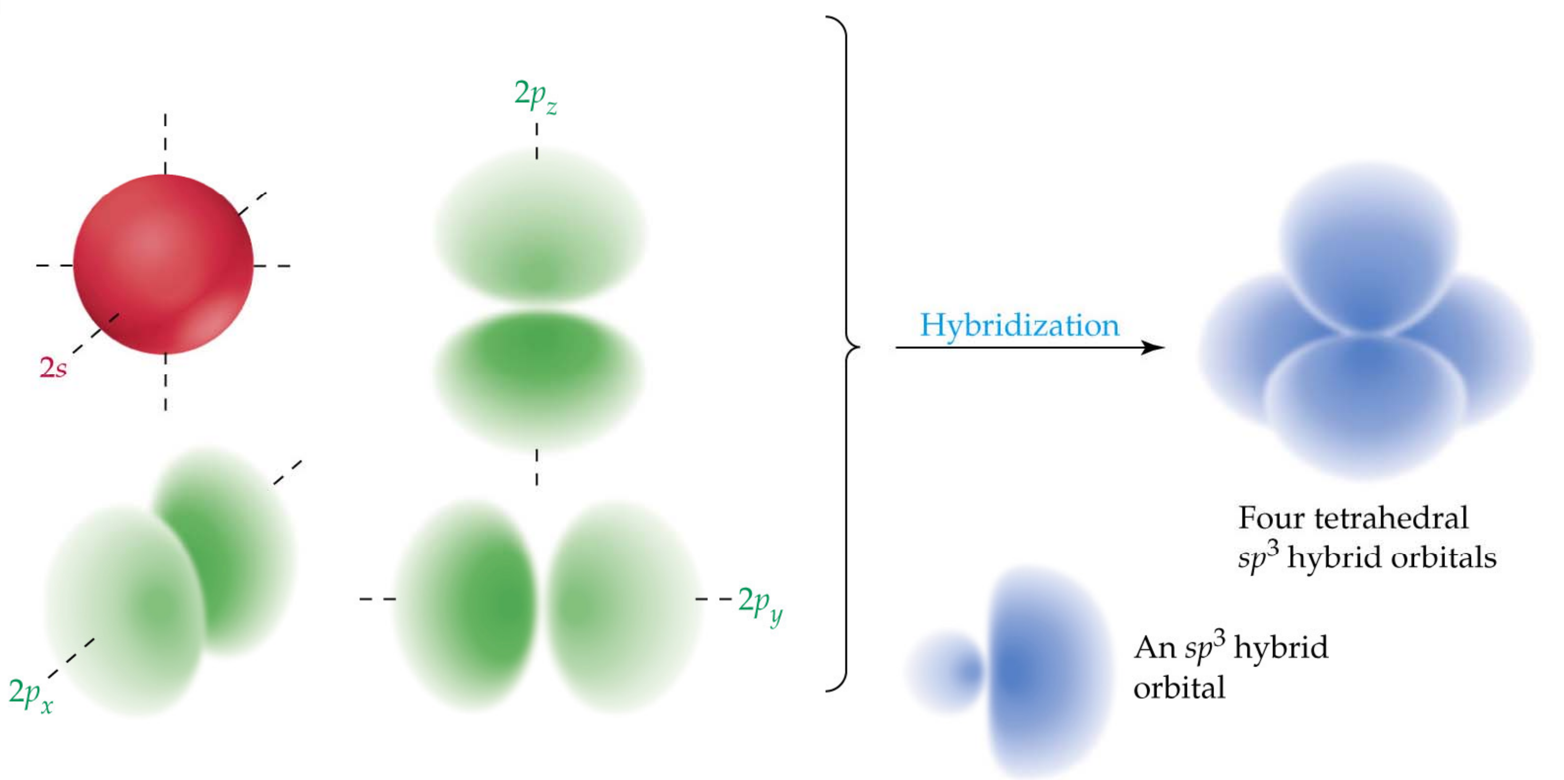
	bond order	FMOs
H_2	1	LUMO + HOMO
He_2	0	unknown species
Li_2	1	LUMO + HOMO
Be_2	0	unknown species
B_2	1	diradical
C_2	2	LUMO + HOMO
N_2	3	LUMO + HOMO
O_2	2	diradical
F_2	1	LUMO + HOMO
Ne_2	0	unknown species

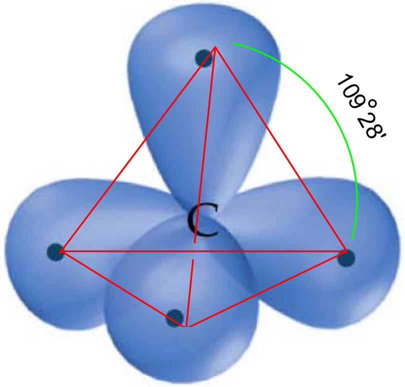
1.1.2 Multiple Valence and Hybridization（多价态　杂化）

- A univalent atom has only one orbital available for bonding. But atoms with a valence of 2 or more must form bonds by using at least two orbitals.
- In chemistry, **hybridization** is the concept of mixing atomic orbitals to form new **hybrid orbitals** suitable for the qualitative description of atomic bonding properties. Hybridised orbitals are very useful in the explanation of the shape of molecular orbitals for molecules. It is an integral part of valence bond theory.
- The hybridization theory finds its use mainly in organic chemistry, and mostly concerns **C**, **N** and **O** (and to a lesser extent **P** and **S**). Its explanation starts with the way bonding is organized in methane.

sp^3 hybrids

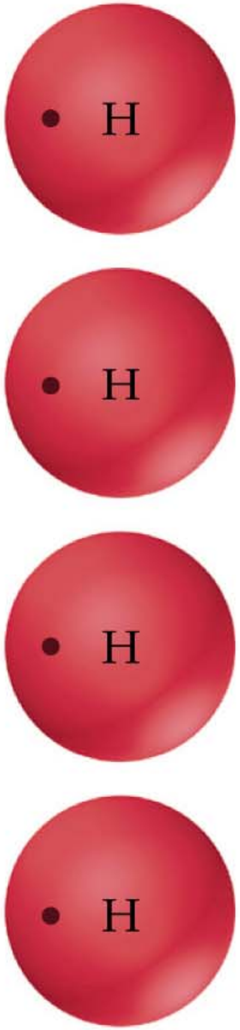

excitation
hybridization
C
1s
2s
2px
2py
2pz
C*
1s
2s
2px
2py
2pz
C*
1s
sp3
sp3
sp3
sp3


2s
2pz
2px
2py
Hybridization
Four tetrahedral sp3 hybrid orbitals
An sp3 hybrid orbital

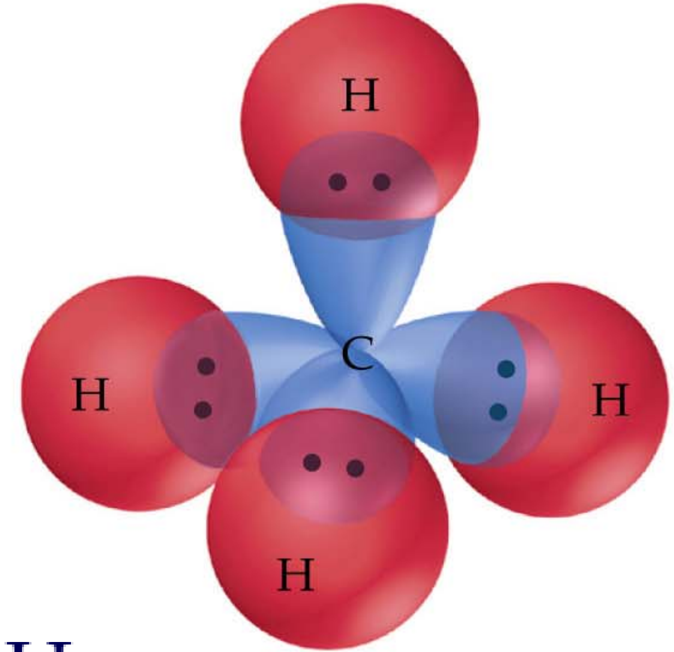


Four carbon sp^3
hybrid orbitals

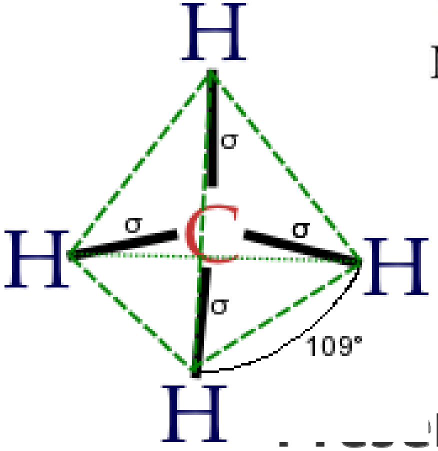
+

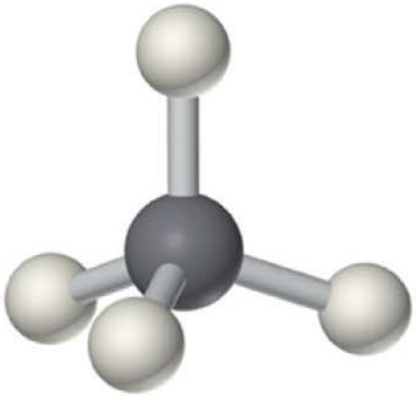


Four hydrogen 1*s*
atomic orbitals

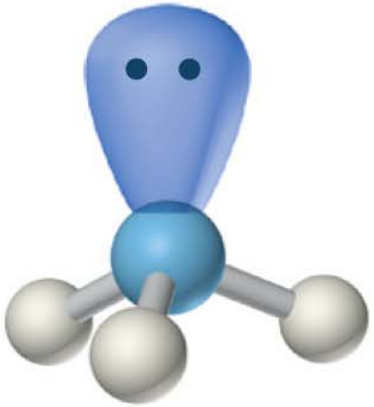


Methane

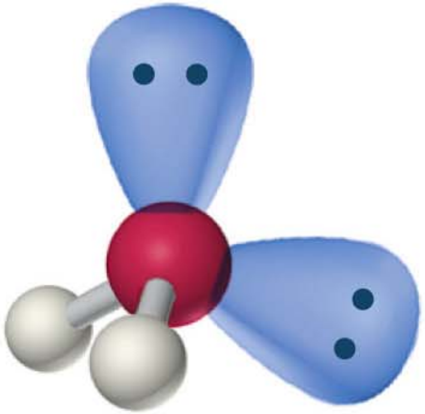




Methane, CH_4

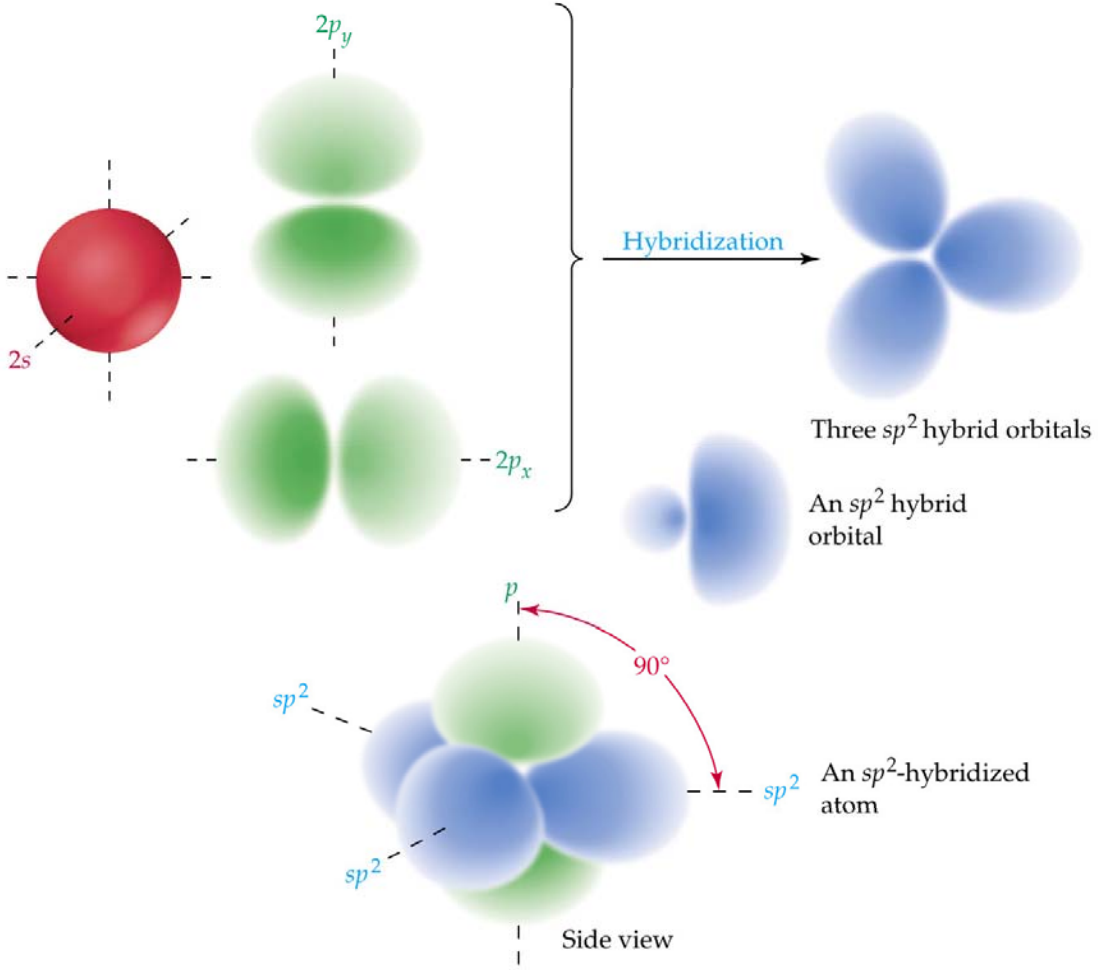


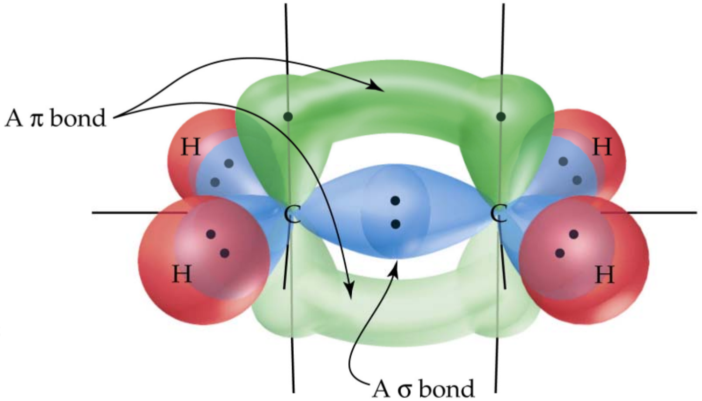
Ammonia, NH_3

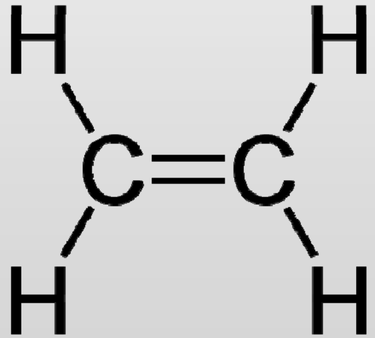


Water, H_2O

sp^2 hybrids

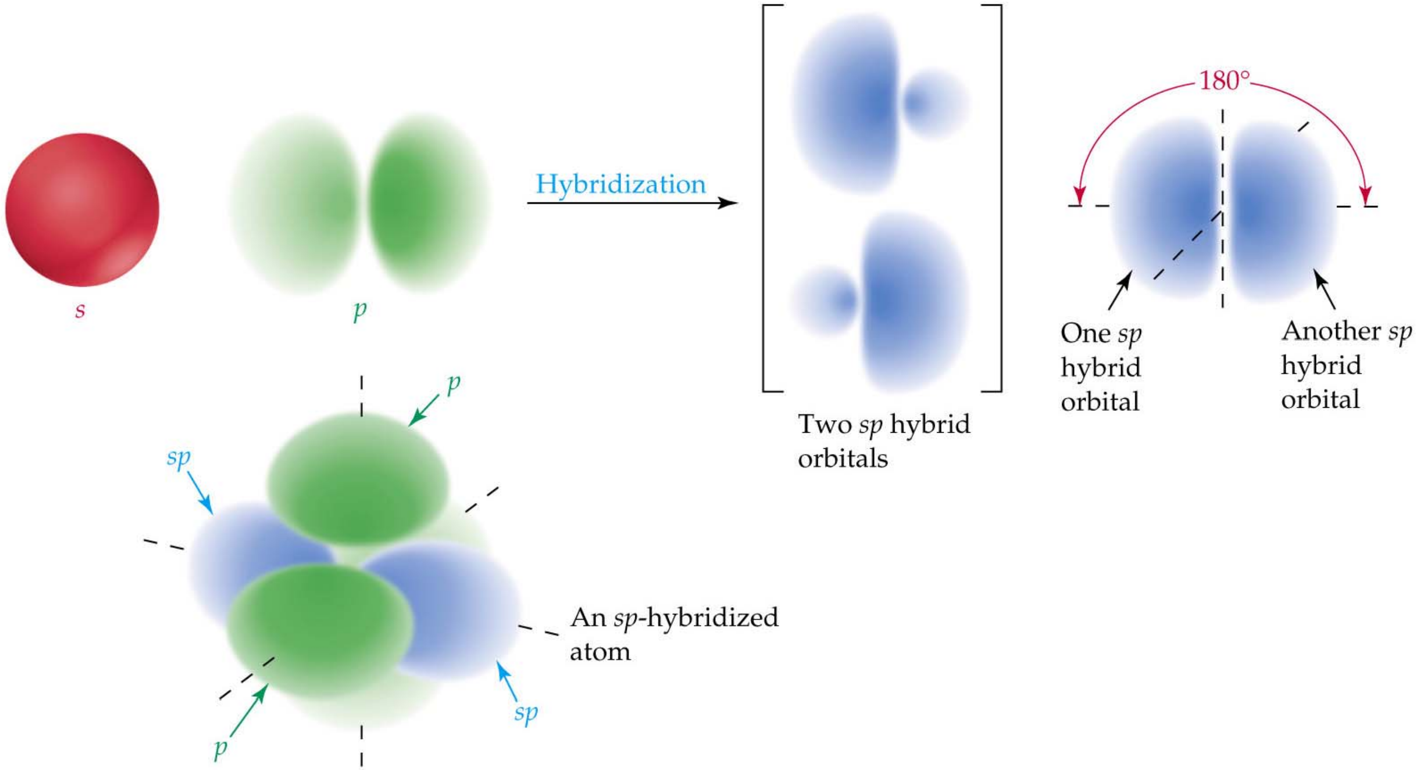

2py
2s
2px
Hybridization
Three sp2 hybrid orbitals
An sp2 hybrid orbital
p
90°
sp2
sp2
sp2
An sp2-hybridized atom
Side view

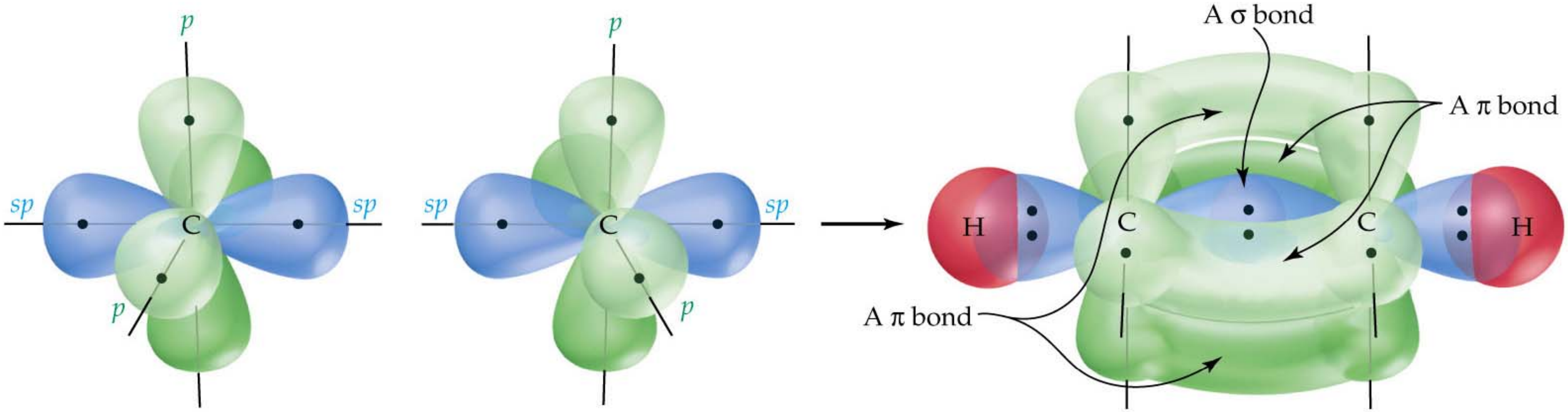

A π bond
H
H
C
C
H
H
A σ bond


H
H
C=C
H
H

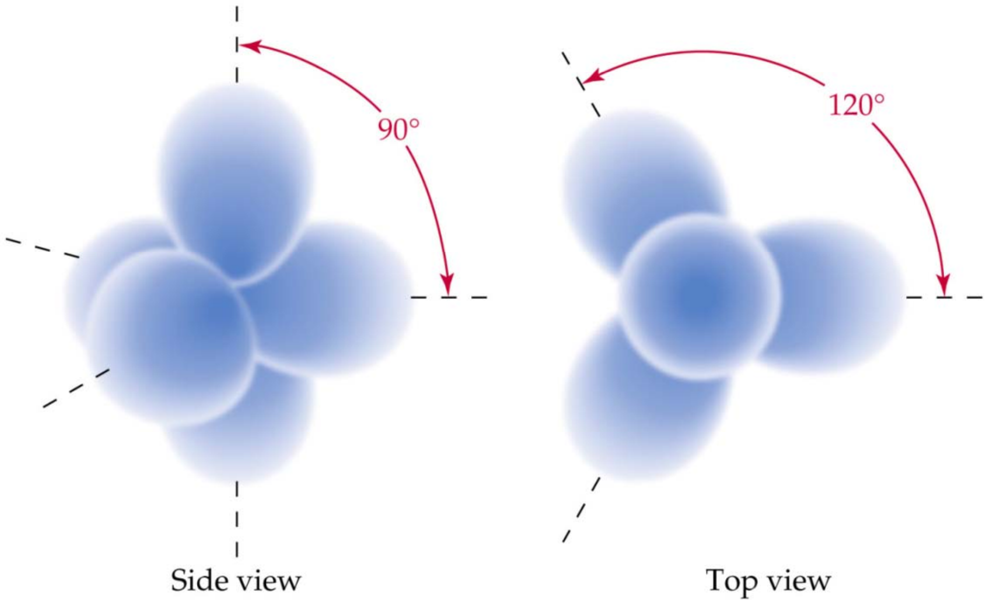
sp hybrids

CH≡CH

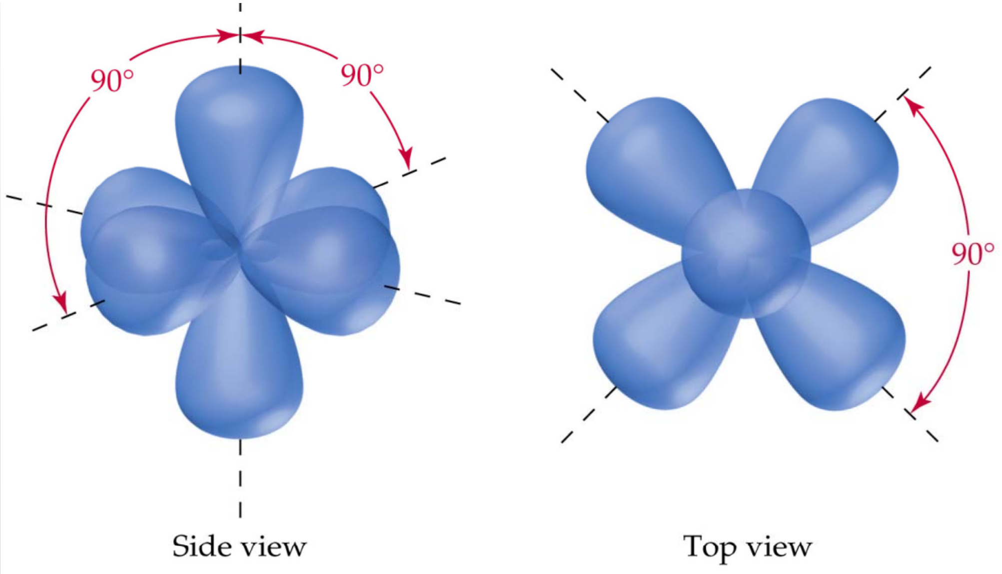


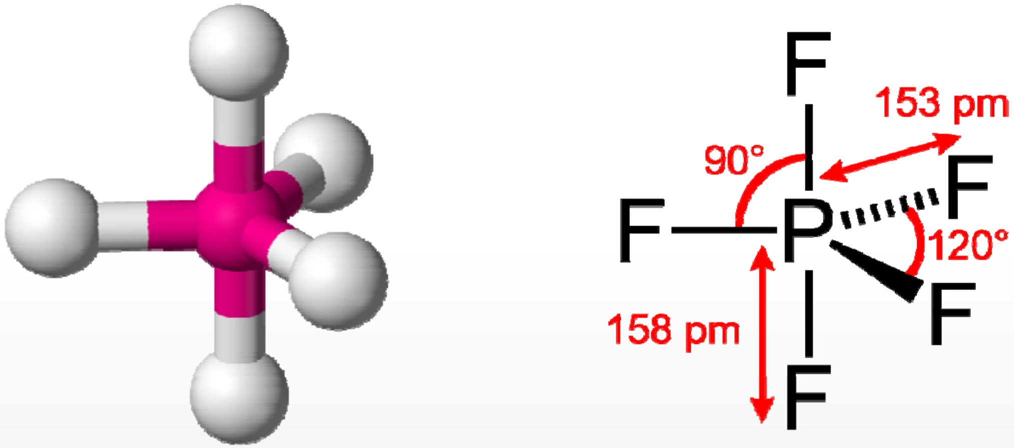


sp^3d

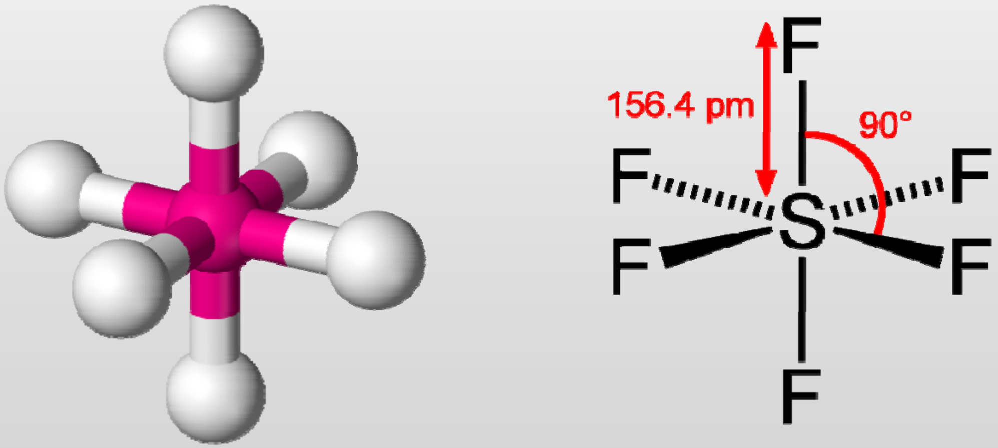


sp^3d^2





sp^{3}d: Trigonal bipyramidal molecular geometry

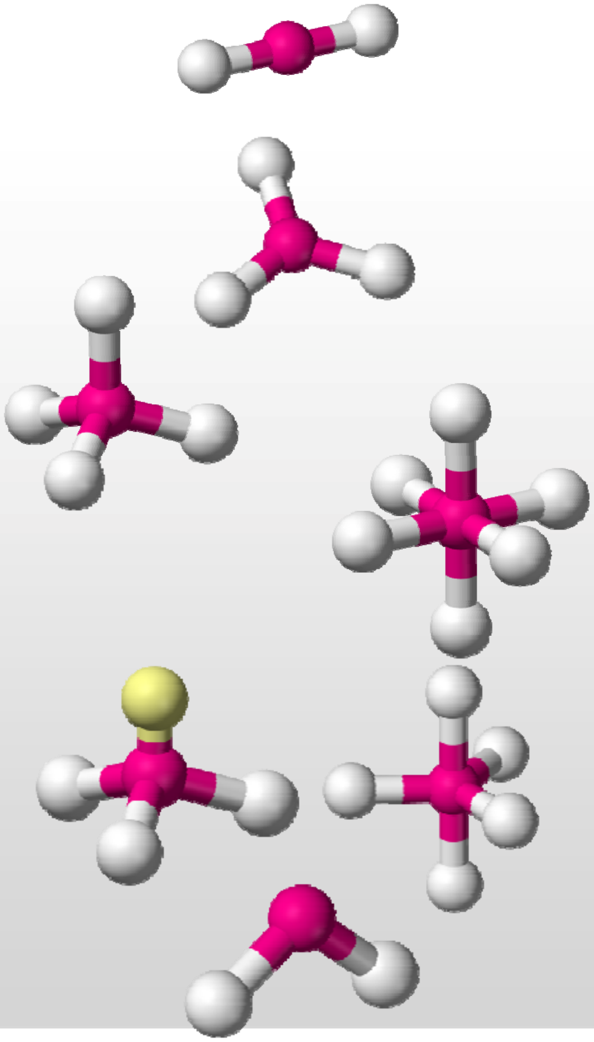


sp^{3}d^2: Octahedral molecular geometry

VSEPR (valence-shell electron pair repulsion theory)

There are six basic shape types for molecules:

- **Linear**: In a linear model, atoms are connected in a straight line. The bond angles are set at 180°. $BeCl_2$
- **Trigonal planar**: Molecules with the trigonal planar shape are somewhat triangular and in one plane. Bond angles are set at 120°. BF_3.
- **Tetrahedral**: *Tetra-* signifies four, and *-hedral* relates to a surface, so tetrahedral almost literally means "four surfaces." Bond angles are 109.5°. CH_4.
- **Octahedral**: *Octa-* signifies eight, and *-hedral* relates to a surface, so octahedral almost literally means "eight surfaces." The bond angle is 90°. SF_6.
- **Pyramidal**: Pyramidal-shaped molecules have pyramid-like shapes. Lone pair-bond pair repulsions change the angle from the tetrahedral angle to a slightly lower value. NH_3, PCl_5.
- **Bent**: H_2O, Lone pair-bond pair repulsions push the angle from the tetrahedral angle down to around 106°.



1.1.3 VB *vs* MO

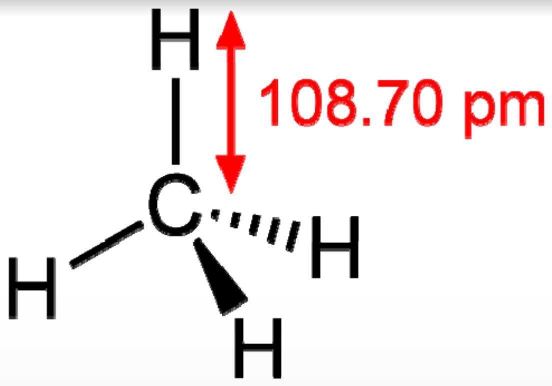
Which approach is better ?

There is no straightforward answer to this question - neither approach is exact.

◇ In some instances, such as in the description of bonding in diatomic molecules, the two approaches give essentially identical results.

◇ **The VB approach** is the approach with which you will be most familiar — it is conceptually simpler and is widely used in organic chemistry, but it fails to adequately explain the bonding in certain classes of molecules, including aromatic compounds.

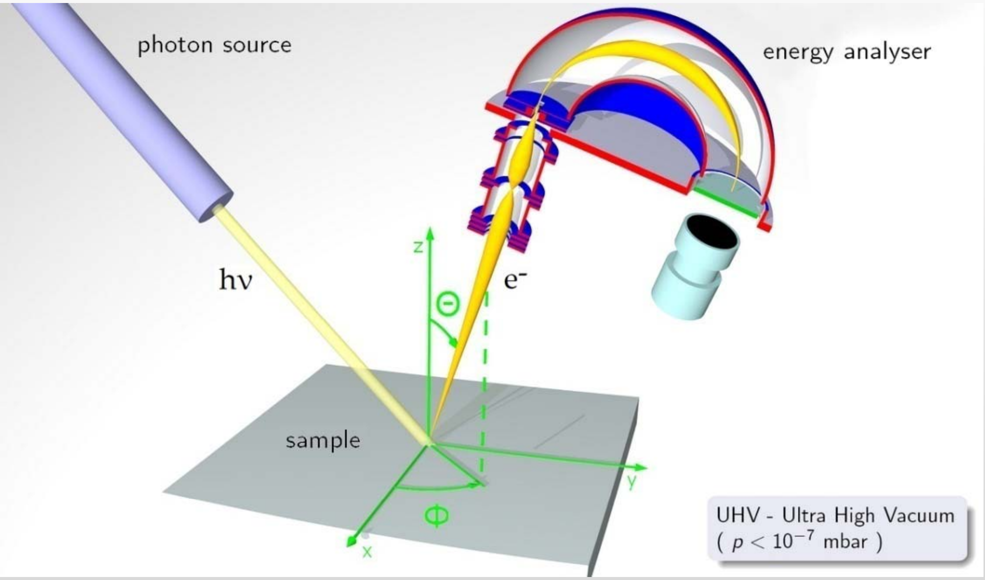
◇ **The MO approach** is generally harder to implement but better explains the bonding in those molecules where the VB approach fails, and is generally more consistent with the results of spectroscopic measurements.



QUESTION:

Photoelectron Spectroscopy

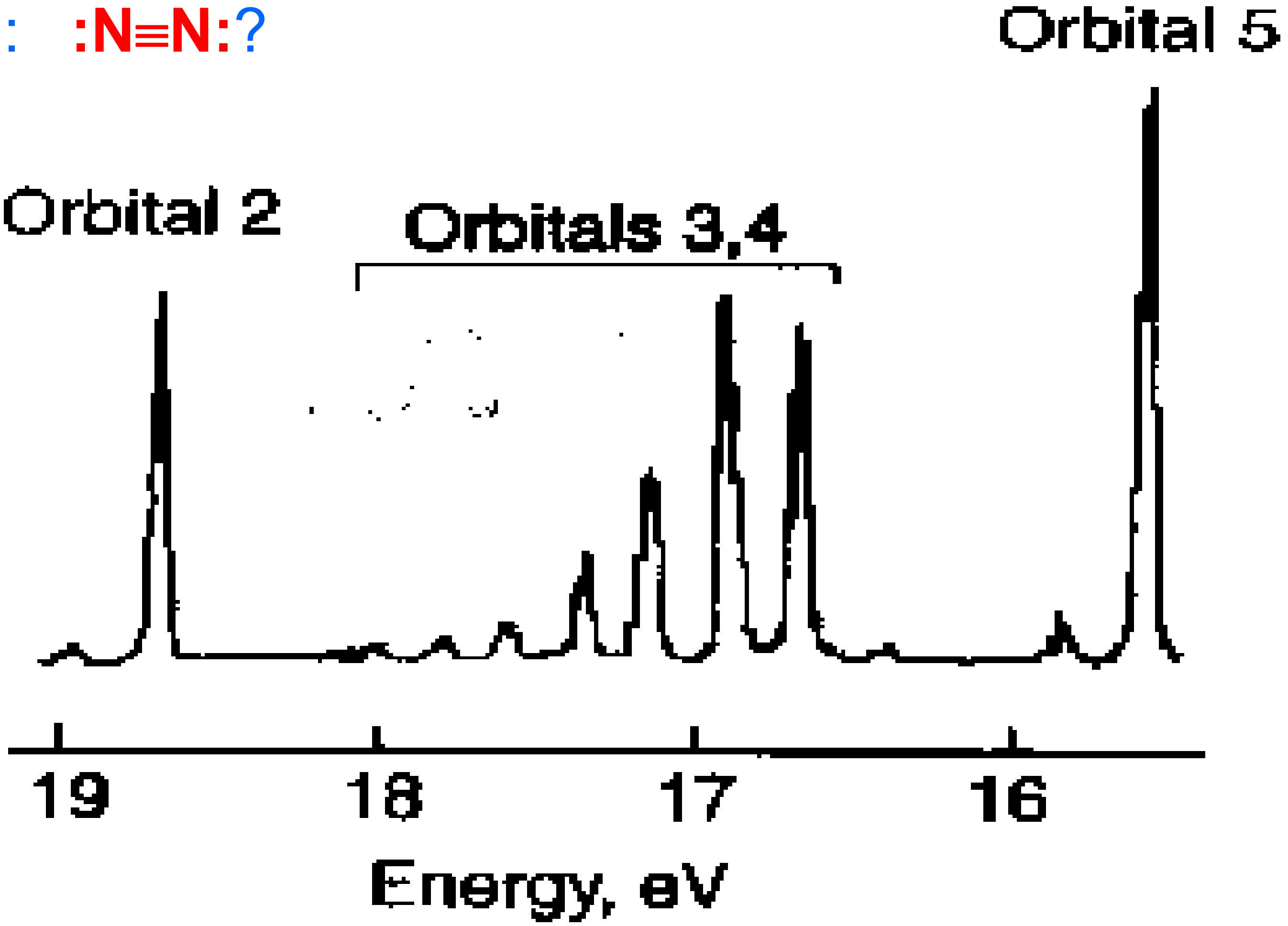
In photoelectron spectroscopy, a molecule or atom is bombarded with vacuum UV radiation, causing an electron to be ejected. The energy of the ejected electron can be measured, and the difference between the energy of the radiation used and that of the ejected electron is the **ionization potential** of that electron.



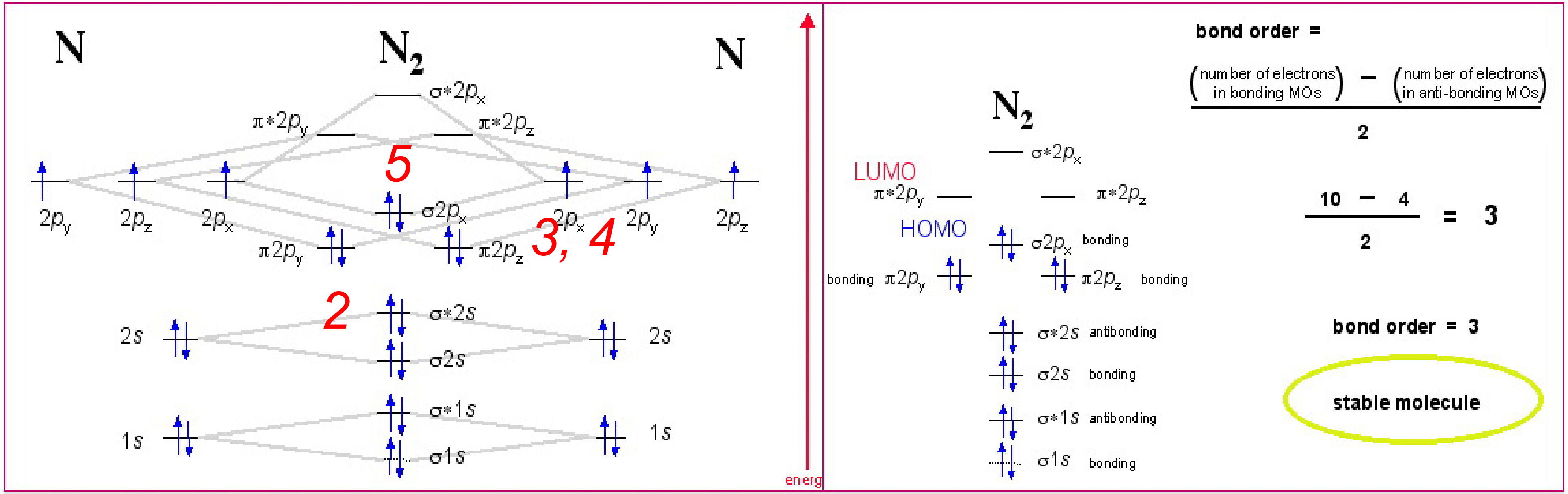
Principle of angle resolved PES.

Question: N_2? N: $1s^22s^22p^3$

VB: **:N≡N:**?



Photoelectron spectrum of N_2.



bond order =

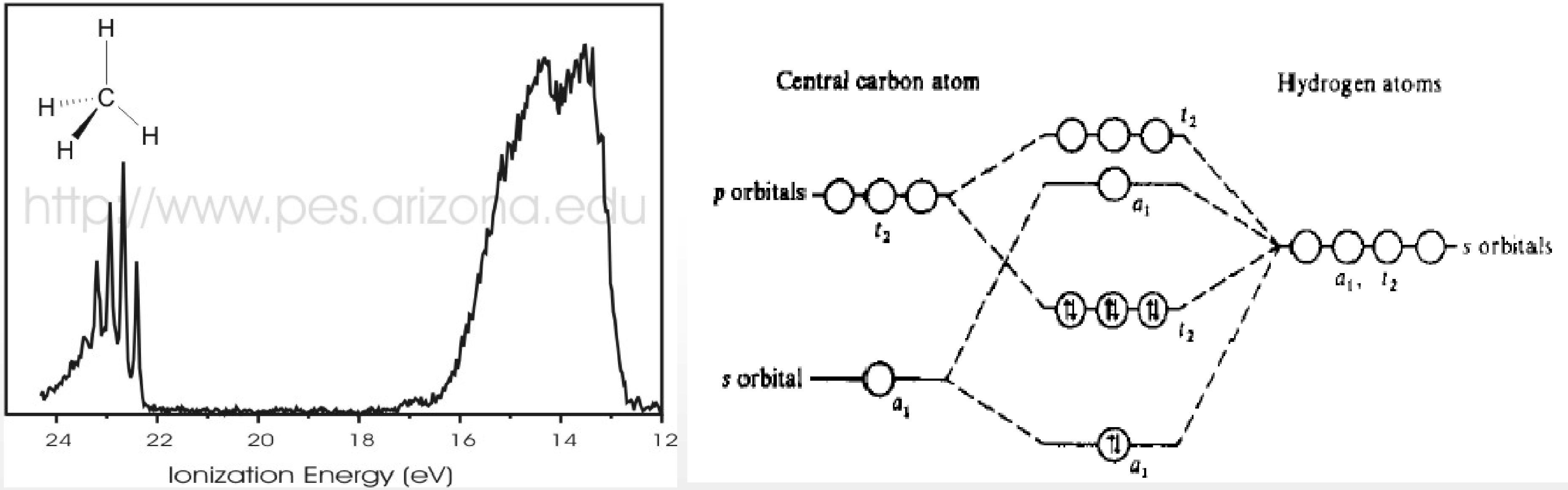
$$\frac{\left(\text{number of electrons in bonding MOs}\right) - \left(\text{number of electrons in anti-bonding MOs}\right)}{2}$$

$$\frac{10 - 4}{2} = 3$$

bond order = 3

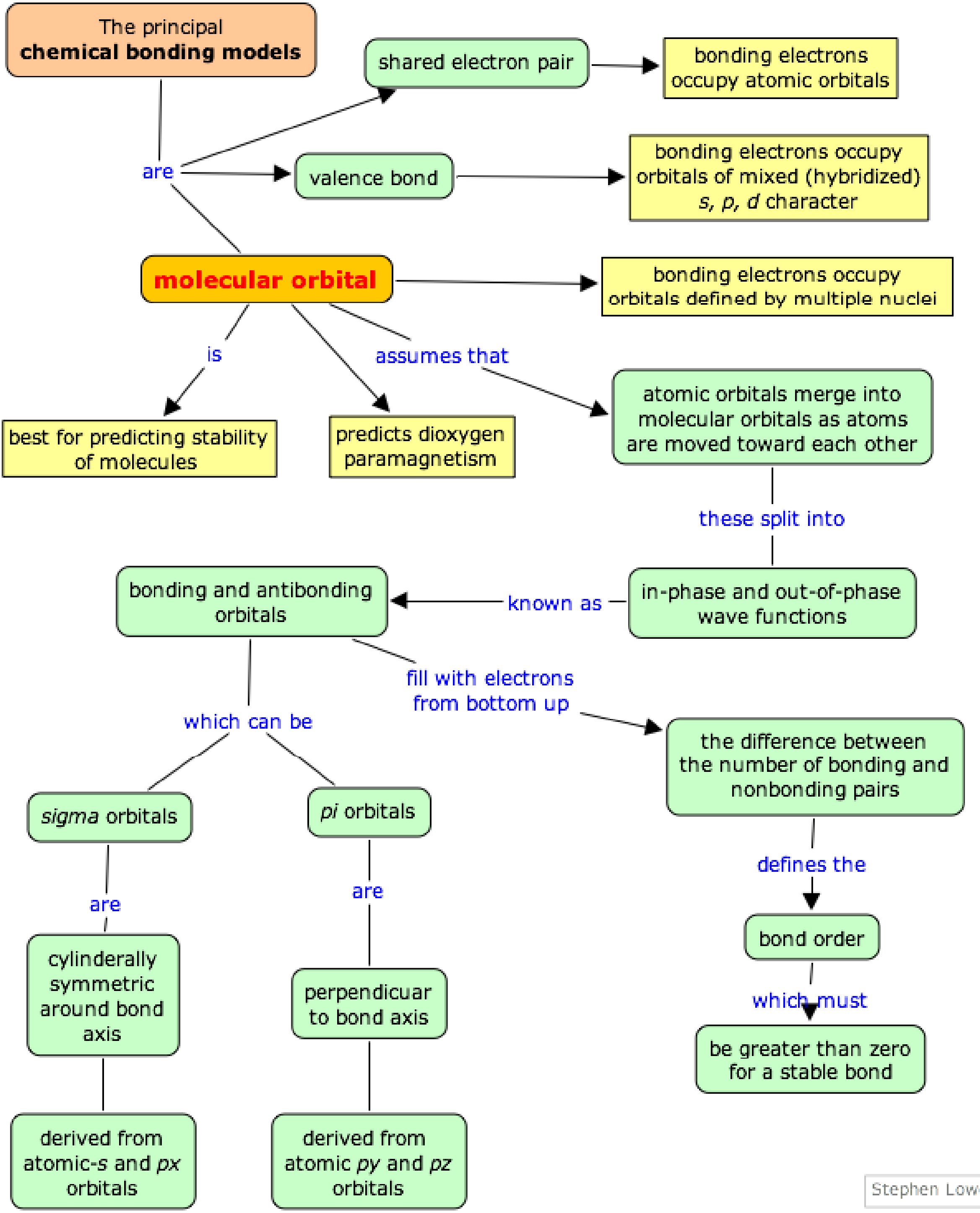
stable molecule

Electron structure of N_2



Photoelectron spectrum of CH_4 and MO.

According to the orbital hybridisation theory the valence electrons in methane should be equal in energy but its photoelectron spectrum shows two bands, one at **23** eV (one electron pair) and one at **12.7** eV (three electron pairs). This apparent inconsistency can be explained when one considers additional orbital mixing taking place when the *sp*^{3} orbitals mix with the 4 hydrogen orbitals.



The principal **chemical bonding models**

are

shared electron pair

bonding electrons occupy atomic orbitals

valence bond

bonding electrons occupy orbitals of mixed (hybridized) *s, p, d* character

molecular orbital

bonding electrons occupy orbitals defined by multiple nuclei

is

best for predicting stability of molecules

predicts dioxygen paramagnetism

assumes that

atomic orbitals merge into molecular orbitals as atoms are moved toward each other

these split into

in-phase and out-of-phase wave functions

known as

bonding and antibonding orbitals

which can be

sigma orbitals

are

cylinderally symmetric around bond axis

derived from atomic-*s* and *px* orbitals

pi orbitals

are

perpendicuar to bond axis

derived from atomic *py* and *pz* orbitals

fill with electrons from bottom up

the difference between the number of bonding and nonbonding pairs

defines the

bond order

which must

be greater than zero for a stable bond

Point

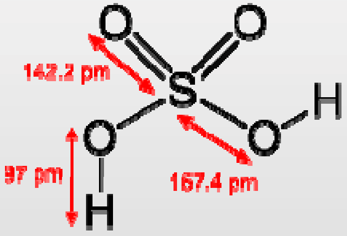
Stephen Lower

1.1.4 Electronic Structures of Molecules

- **Lewis structure** are diagrams that show the bonding between atoms of a molecule, and the lone pairs of electrons that may exist in the molecule. For each molecule, ion, or free radical that has only localized electrons, *it is possible to draw an* ***electron formula*** *that shows the location of these electrons*.
- Only the valence electrons are shown. Valence electrons may be found in covalent bonds connecting two atoms or they may be unshared.

Rules for Lewis structures

1. The total number of **valence electrons** in the molecule (or ion, or free radical) must be the sum of all outer-shell electrons “contributed” to the molecule by each atom plus the negative charge or minus the positive charge, for the case of ions.



H_2SO_4

2 (one for each hydrogen)
6 (for the sulfur)
+) 24 (6 for each oxygen)

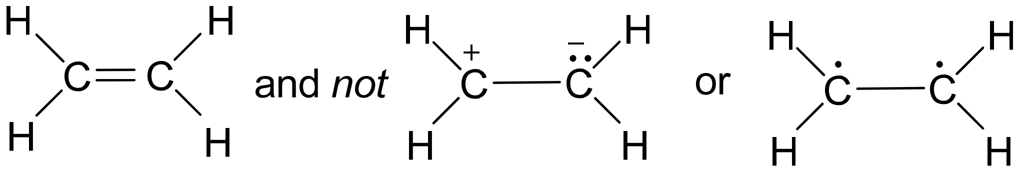
32

2. Once the number of valence electrons has been ascertained, it is necessary to determine which of them are found in covalent bonds and which are unshared.

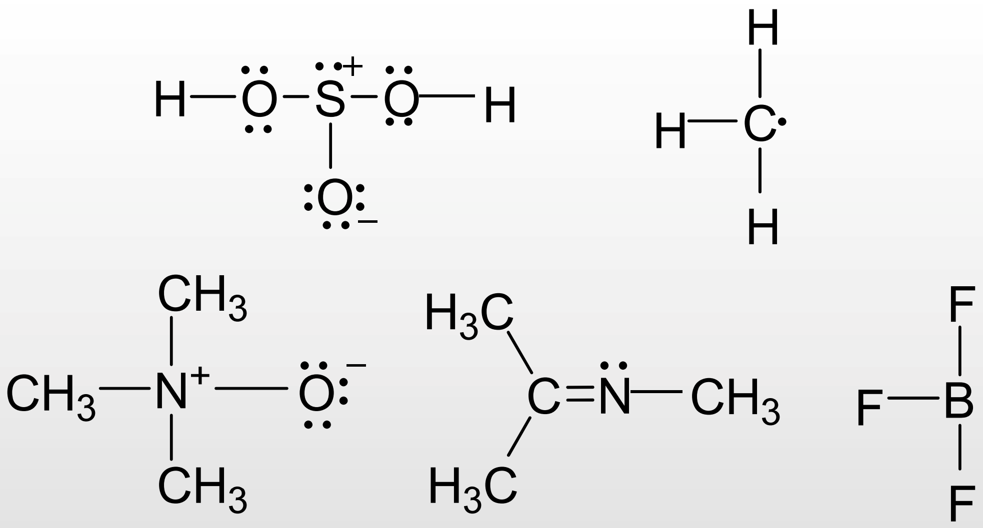
Note: First-row atoms (B, C, N, O, F) can have a maximum of eight valence electrons.

3. It is customary to show the formal charge on each atom.

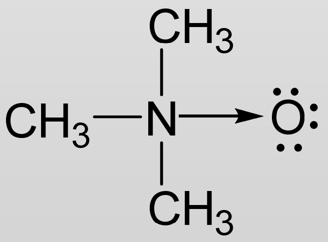
4. A coordinate-covalent bond, represented by an arrow, is one in which both electrons from the same atom.



(1)



(2)



(3)

1.1.5 Electronegativity 电负性

- The attraction of atom or group to the electron cloud is called **electronegativity**.
- Pauling scale: $\chi_A - \chi_B = (\text{eV})^{-1/2}\,(E_d(AB) - [E_d(AA) + E_d(BB)]/2)^{1/2}$

dissociation energies (E_d); E_d(H-Br) 3.79, E_d(H-H) 4.52, E_d(Br-Br) 2.0 eV. So, the difference in Pauling electronegativity between hydrogen and bromine is 0.53

$$x_A - x_B = \sqrt{\frac{\Delta}{23.06}}$$

x_A and x_B are the electronegativities of the known and unknown atoms and 23.06 is an arbitrary constant.

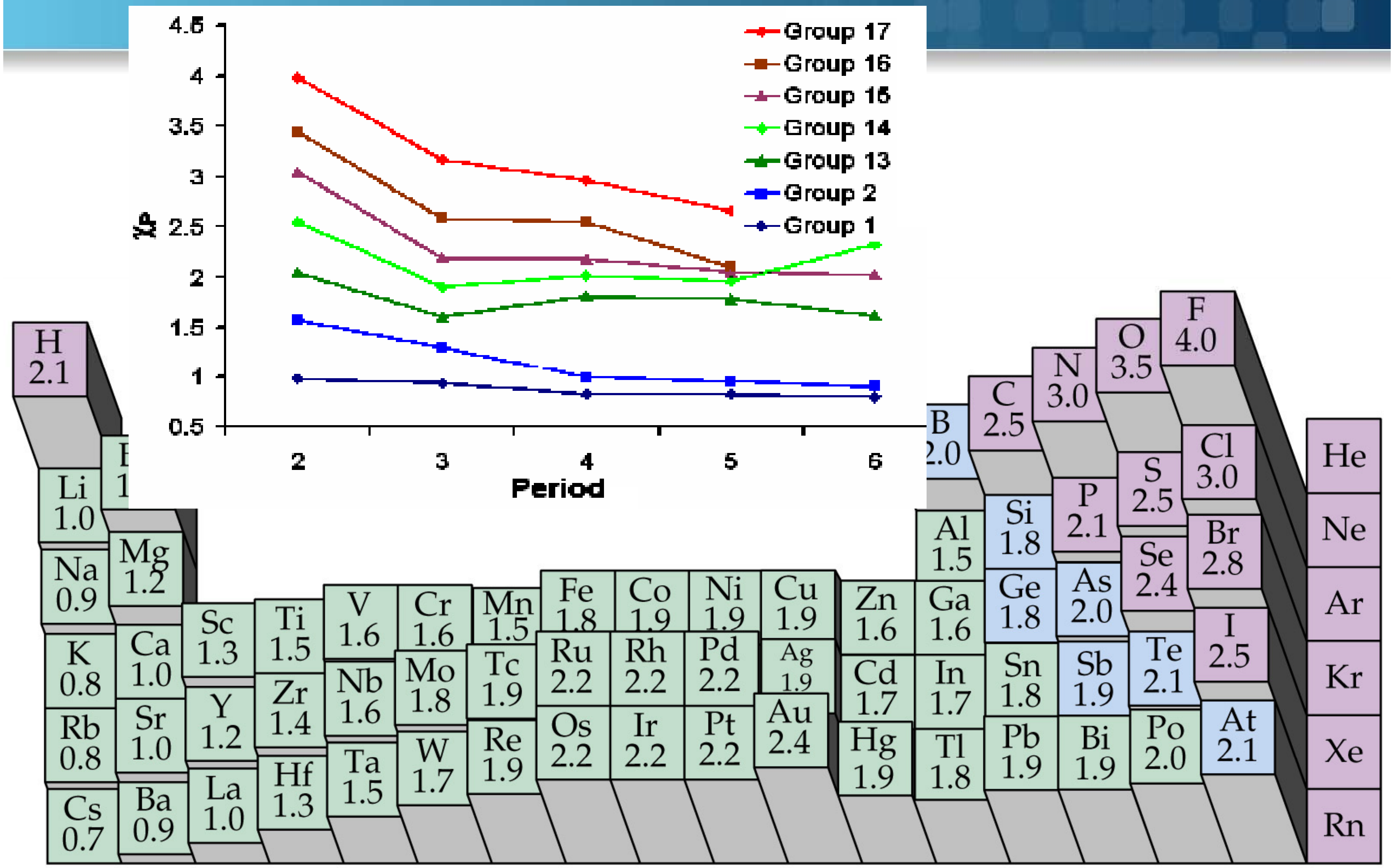
Electronegativity, as it is usually calculated, is not strictly an atomic property, but rather a property of an atom in a molecule: the equivalent property of a free atom is its electron affinity.

Table 1. Electronegativities of some atoms on the Pauling scales

F	4.0	**S**	2.5	**B**	2.0
O	3.5	**I**	2.5	**Si**	1.8
Cl	3.0	**C**	2.5	**Mg**	1.2
N	3.0	**H**	2.1	**Na**	0.9
Br	2.8	**P**	2.1	**Cs**	0.7

Table 2. Some group electroneativities relative to H = 2.176

CH_3	2.472	CCl_3	2.666
CH_3CH_2	2.482	C_6H_5	2.717
CH_2Cl	2.538	CF_3	2.985
CBr_3	2.561	$C\equiv N$	3.208
$CHCl_2$	2.602	NO_2	3.421



The variation of Pauling electronegativity in the periodic table

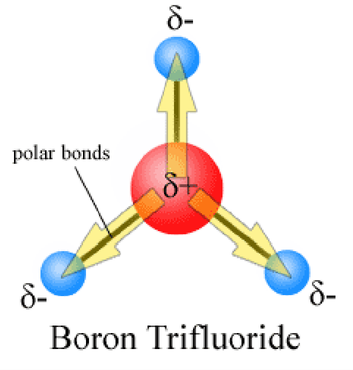
1.1.6 Dipole Moment 偶极矩

◆ The dipole moment is a property of the molecule that results from charge separation. The unequal sharing of electrons within a bond leads to the formation of an electric dipole: a separation of positive and negative electric charge. Example:

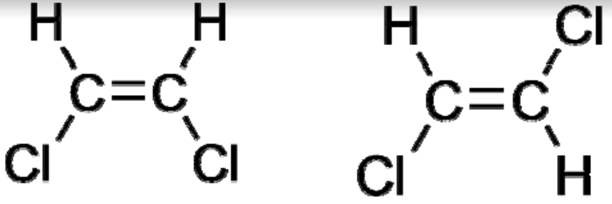
(positive) H–Cl (negative)

◆ It is not possible to measure the dipole moment of an individual bond within a molecule; we can measure only the total of the molecule, which is the vector sum of the individual bond moment.

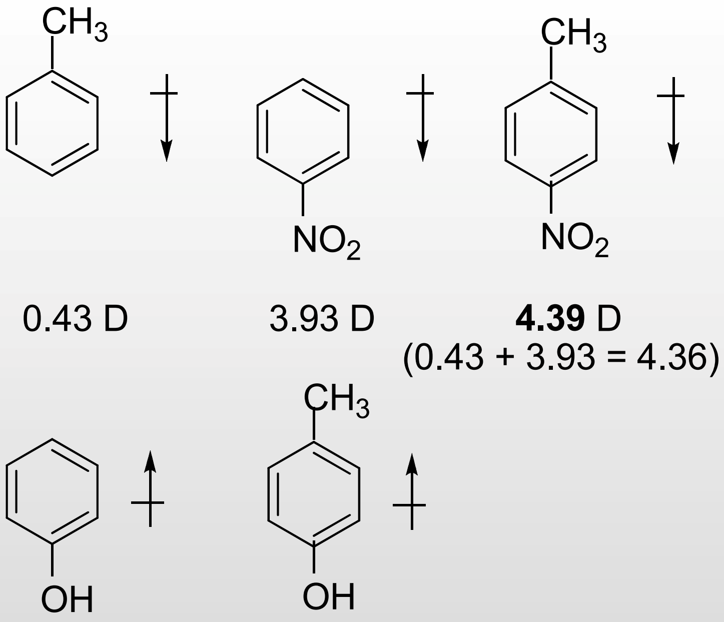
◆ From the dipole moment information can be deduced about the molecular geometry of the molecule.



Dipole moment (gas phase, debye)	
carbon dioxide	0
carbon monoxide	0.112
ozone	0.53
phosgene	1.17
water vapor	1.85
hydrogen cyanide	2.98
cyanamide	4.27
potassium bromide	10.41



Dipole moment : 1.90 **D** 0



0.43 D

3.93 D

4.39 D
(0.43 + 3.93 = 4.36)

1.54 D

1.57 D, (1.54 - 0.43 = 1.11)

Some dipole moments, in debye, measured in benzene. The arrow points to the negative part of the molecule.

NOTE:

The **debye** (symbol: **D**) is a CGS unit (a non-SI metric unit) of electric dipole moment named in honour of the physicist Peter J. W. Debye. It is defined as 1×10^{-18} statcoulomb-centimetre

1 **D** = 10^{-18} statC·cm

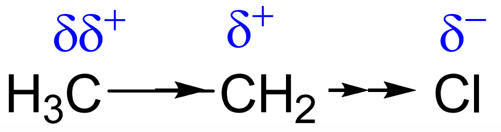
= 10^{-10} esu·Å

esu: electrostatic unit

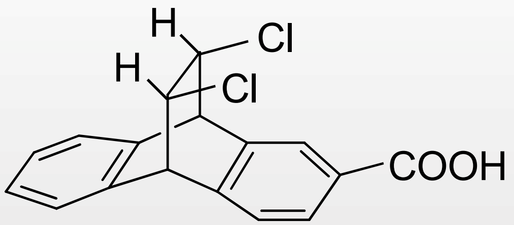
1Å = 10^{-8} cm

1.1.7 Inductive and Field Effects

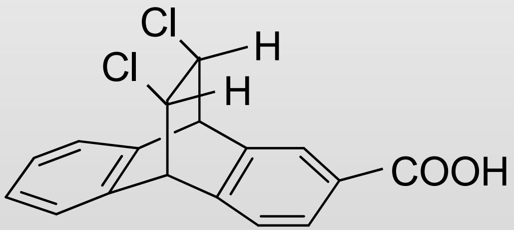
- The polarity induced in adjacent bonds due to polarity of a specific bond is known as the inductive effect. The electron cloud in a σ-bond between two unlike atoms is not uniform and is slightly displaced towards the more electronegative of the two atoms.
- **Field effect**: an experimentally observable effect of intramolecular coulombic interaction between the centre of interest and a remote unipole or dipole, by direct action through space rather than through bonds. The magnitude of the field effect depends on unipolar charge/dipole moment, orientation of dipole, shortest distance between the centre of interest and the remote unipole or dipole, and on the effective dielectric constant.



$$\overset{\delta\delta^+}{H_3C}\longrightarrow\overset{\delta^+}{CH_2}\twoheadrightarrow\overset{\delta^-}{Cl}$$



(1) pKa = 6.07



(2) pKa = 5.67

Table 3. Field effects of various groups relative to hydrogen

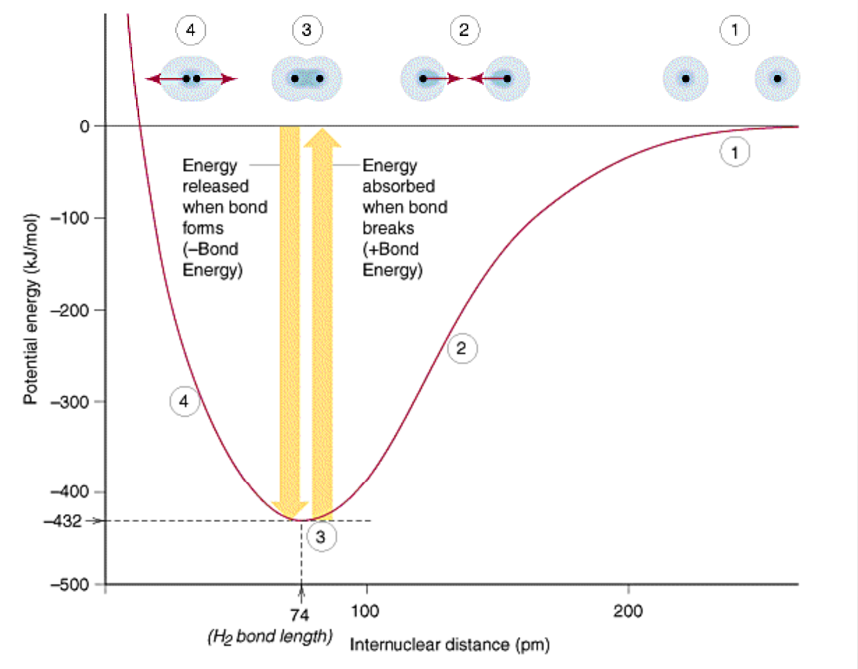
+ *I*	–*I*		
O^-	NR_3^+	COOH	OR
COO^-	SR_2^+	F	COR
CR_3	NH_3^+	Cl	SH
CHR_2	NO_2	Br	SR
CH_2R	SO_2R	I	OH
CH_3	CN	OAr	$C\equiv CR$
D	SO_2Ar	COOR	Ar
			$CH=CR_2$

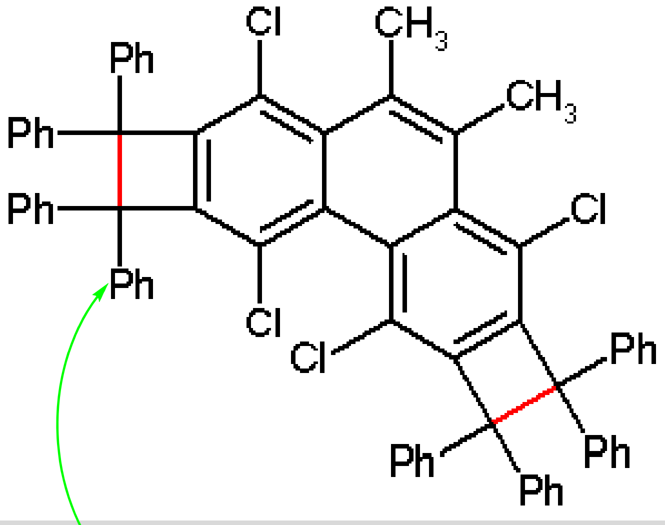
The groups are listed approximately in order of decreasing strength for both –*I* and +*I* groups.

1.1.8 Bond Characteristics

Bond Length

Bond length defined as the internuclear distance when energy is at a minimum. Bond lengths are measured in molecules by means of x-ray diffraction. *The actual bond length between two atoms in a molecule depends on such factors as the orbital hybridization and the electronic and steric nature of the substituents.*





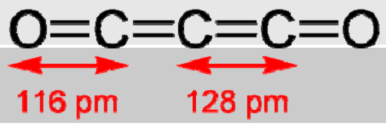
1.74 Å

cyclobutabenzene

Table 4. Bond lengths between sp^3 carbons in some compounds

C–C bond in	Bond length (Å)
Diamond 金刚石	1.544
C_2H_6	1.5324
C_2H_5Cl	1.5495
C_3H_8	1.532
Cyclohexane	1.54
tert-Butyl chloride	1.532
n-Butane to *n*-heptane	1.531-1.534
isobutane	1.535

Table 5. Bond distances

Bond type		Length (Å)	Typical compounds
C–C	sp^3–sp^3	1.53	
	sp^3–sp^2	1.51	acetaldehyde, toluene, propene
	sp^3–sp	1.47	acetonitrile, propyne
	sp^2–sp^2	1.48	butadiene, glyoxal, biphenyl
	sp^2–sp	1.43	acrylonitrile, vinylacetylene
	sp–sp	1.38	cyanoacetylene, butadiyne
C=C	sp^2–sp^2	1.32	ethylene
	sp^2–sp	1.31	ketene, allenes
	sp–sp	1.28	Butatriene (CH_2=C=C=CH_2), carbon suboxide 
C≡C	sp–sp	1.18	acetylene
C–H	sp^3–H	1.09	methane
	sp^2–H	1.08	benzene, ethylene
	sp–H	1.08	HCN, acetylene

(continued)			
C–O	sp^3–O	1.43	CH_3OCH_3, CH_3OH
	sp^2–O	1.34	HCOOH
C=O	sp^2=O	1.21	HCHO, HCOOH
	sp=O	1.16	CO_2
C–N	sp^3–N	1.47	CH_3NH_2
	sp^2–N	1.38	formamide
C=N	sp^2–N	1.28	Oximes, imines
C≡N	sp–N	1.14	HCN
C–S	sp^3–S	1.82	CH_3SH
	sp^2–S	1.75	Diphenyl sulfide
	sp–S	1.68	CH_3SCN
C=S	sp–S	1.67	CS_2

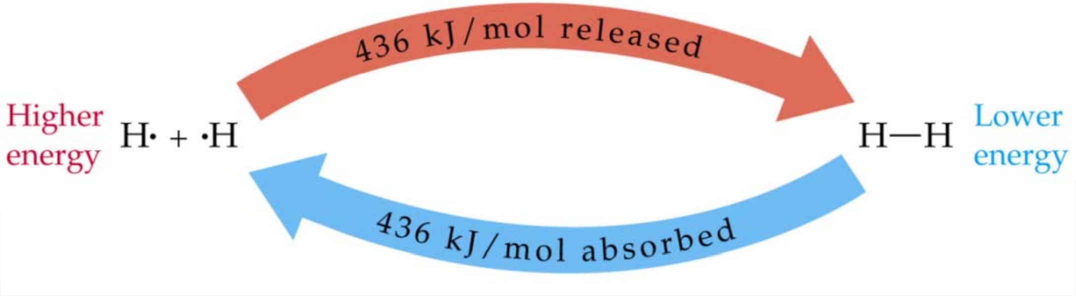
C–X	sp^3–	sp^2–	sp–
C–F	1.40	1.34	1.27
C–Cl	1.79	1.73	1.63
C–Br	1.97	1.88	1.79
C–I	2.16	2.10	1.99

Bond Angles

Table 6. Oxygen, sulfur, and nitrogen bond angles in some compounds

Angle	Value	compound	Note
H–O–H	104°27’	H_2O	◆ Bond angles of oxygen and nitrogen compounds are much closer to the tetrahedral angle of 109˚28’ than to 90˚. ◆ An unshared pair may be considered to be an “atom” of the lowest possible electronegativity, since there is no attracting power at all. Consequently, the unshared pairs have more *s* and the bonds more *p* character than pure orbitals, making the bonds somewhat more like p^2 bonds and reducing the angle.
C–O–H	107–109°	CH_3OH	
C–O–C	111°43’	CH_3OCH_3	
C–O–C	124°±5°	$C_6H_5OC_6H_5$	
H–S–H	92.1°	H_2S	
C–S–H	99.4°	CH_3SH	
C–S–C	99.1°	CH_3SCH_3	
H–N–H	106°46’	NH_3	
H–N–H	106°	CH_3NH_2	
C–N–H	112°	CH_3NH_2	
C–N–C	108.7°	$(CH_3)_3N$	

Bond Energies



Bond energy (*E*) is a measure of bond strength in a chemical bond.
Bond dissociation energy (*D*)
Bond energy (*E*)

Example	*D* (kJ/mol)
$H_2O \rightarrow HO + H$	494
$H—O \rightarrow H + O$	418

the bond energy *E* = (494+418)/2=456

- In diatomic molecules, *D* = *E*
- the method to calculate *E* : from the *heat of combustion*

Table 7. Bond energy *E* values at 25°C for some important bond types

Bond	**kJ mol^{-1}**	**Bond**	**kJ mol^{-1}**
O–H	460–464	C–S	255
C–H	400–415	C–I	220
N–H	390		
S–H	340	C≡C	
C–F	451–485	C=C	
C–H	400–415	C–C	
C–O	355–380		
C–C	345–355	C≡N	854
C–Cl	330	C=O	724–757
C–N	290–315	C=N	598
C–Br	275		

a) The *E* values are arranged within each group in order of decreasing strength. The values are averaged over a large series of compounds.

DISCUSSION

- *There is a direct correlation of bond strengths with bond distances. Shorter bonds are stronger bonds.*

For example:

the *covalent* radius of boron = 0.83Å,

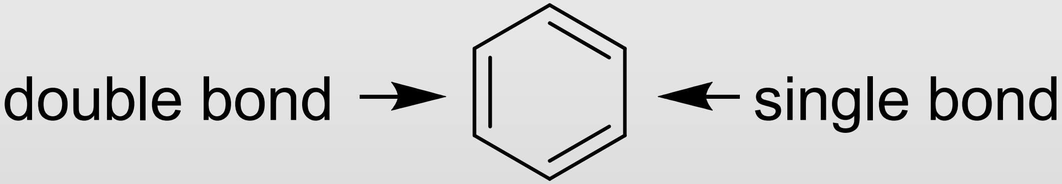
the bond length of **B–B** in **B_2Cl_4 = 1.75Å** (a significantly larger value). This would indicate that the bond between the two boron atoms is a rather *weak* single bond. This method of determination is most useful for covalently bonded compounds.

- *Bonds become weaker as we move down the periodic table*. See: C—O, C—S, and four C—X bonds;
- *Double bonds are both shorter and stronger than the corresponding single bonds, but not twice as strong, because π overlap is less than σ overlap.*

1.2 Delocalized Chemical Bonding (离域化学键)

Delocalized chemical bonding may be defined as bonding in which the electrons are shared by more than two nuclei. Delocalized electrons are contained within an orbital that extends over several adjacent atoms.

In valence bond theory, delocalization in benzene is represented by resonance structures.

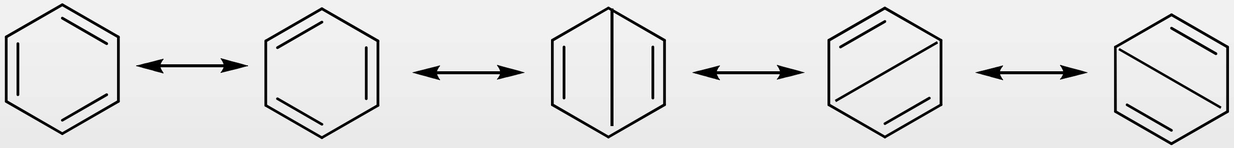


Benzene
(Lewis formula)

1.2.1 General description

A. The valence-bond method → **resonance concept** (Pauling, 1928)

Several possible Lewis structures are drawn and the molecule is taken to be a weighted average of them. This representation of a real structure as a weighted average of two or more canonical forms is called *resonance* (共振)



The different structures contributing to the resonance hybrid are referred to as CANONICAL FORMS of the molecule. The more stable a canonical form, the more it contributes to the RESONANCE HYBRID（共振杂化体）.

True nature of resonance

When a molecule cannot be represented by the standard tools of valence bond theory (promotion, hybridisation, orbital overlap, sigma and π bond formation) because no single structure predicted by VB can account for all the properties of the molecule, one invokes the concept of resonance.

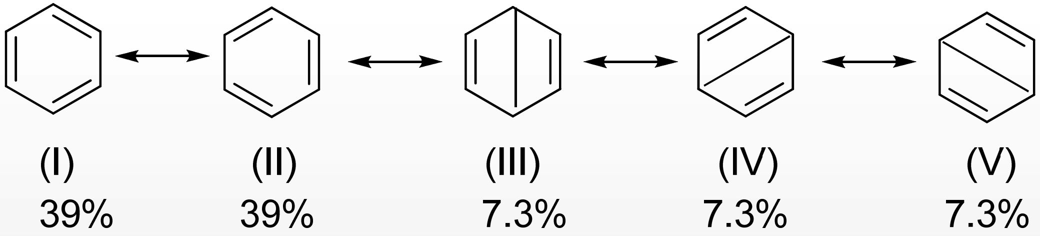
G. W. Wheland（芝加哥大学教授，L. Pauling的学生）的比喻：如把骡子看作是马和驴杂交后生下的动物，是一种生物杂化体。这并不是说骡子是几分之几的马和几分之几的驴，也不能说骡子有时候是马，有时候是驴，只能说骡子是与马和驴都有关系的动物。因而可用两种熟知的动物马和驴来很好地说明骡子。

J.D.Roberts 教授（加利福尼亚工艺学院）的比喻：在中世纪，欧洲有一个旅行者从印度回来，他把犀牛描绘成龙和独角兽的生物杂化体。用两种熟知的、但完全是想像中的动物来很好地描绘一种真实的动物。 Kerber, Robert C. *If It's Resonance, What Is Resonating?*

J. Chem. Educ. **83**,223 (2006)

The bond order (键级) of a particular bond is the sum of the weights of those canonical forms *in which the bonds is double* plus 1 for the single bond that is present in all of them.

- The C-C bond order of benzene = 1.463 (0.39+0.073+1)



The magnitude of the bond order is associated with the bond length. According to Pauling, the bond order is experimentally described by:

$$\boxed{S_{ij} = e^{\left(\frac{R_{ij} + d_{ij}}{b}\right)}}$$

Where R_{ij} is the bond length experimentally measured, d_{ij} is the single bond length, and *b* is a constant, depending on the atoms. A good approximation for *b* use to be 0.37.

B. The molecular-orbital method → Hückel molecular-orbital (HMO) Method (1931)

For planar unsaturated and aromatic molecules, many molecular-orbital calculations (*MO calculations*) have been made by treating the 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 method (**HMO**): a very simple linear combination of atomic orbitals to molecular orbitals (LCAO MO) method for the determination of energies of molecular orbitals of π electrons in conjugated hydrocarbon systems, such as ethylene, benzene and butadiene.

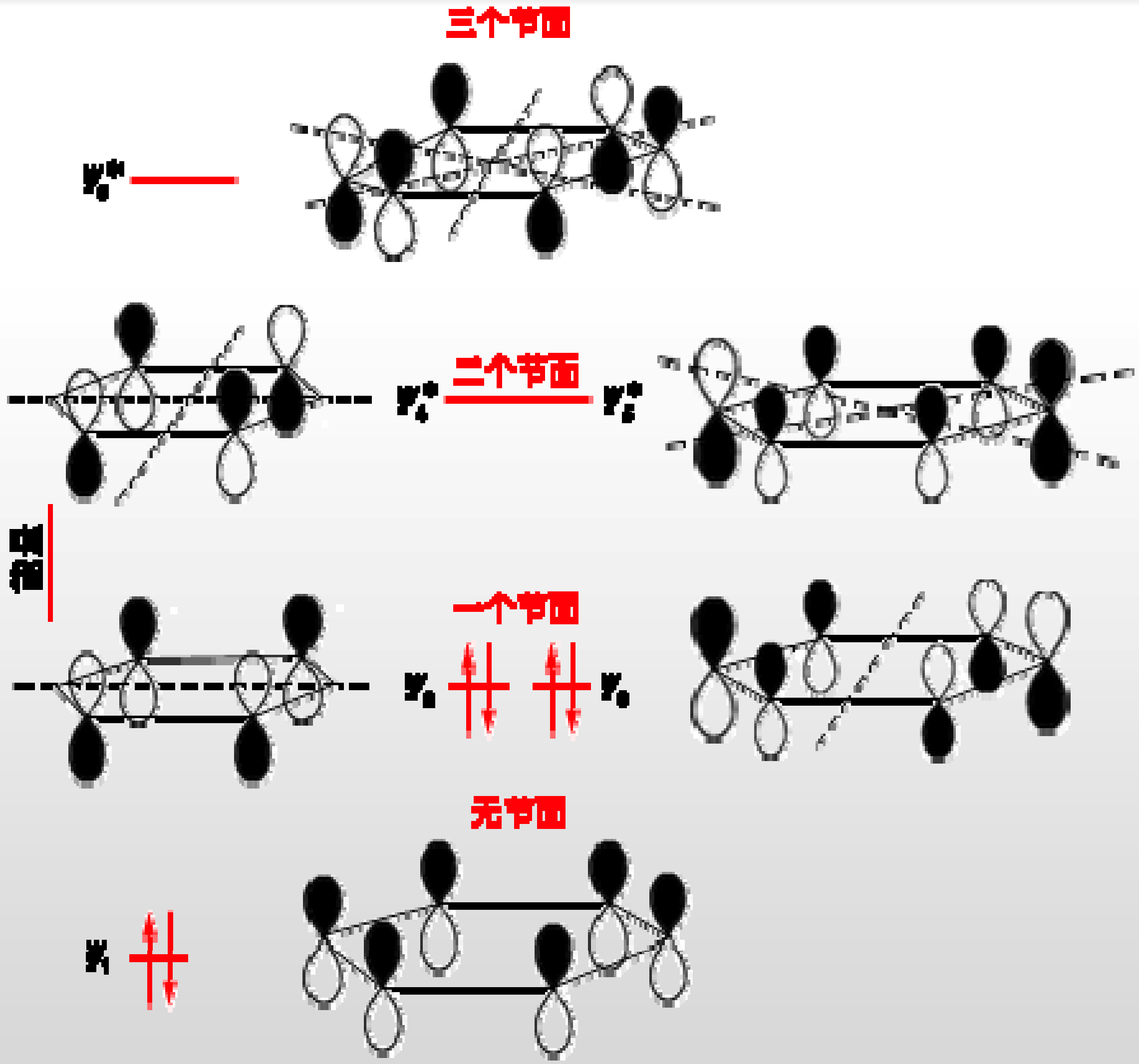
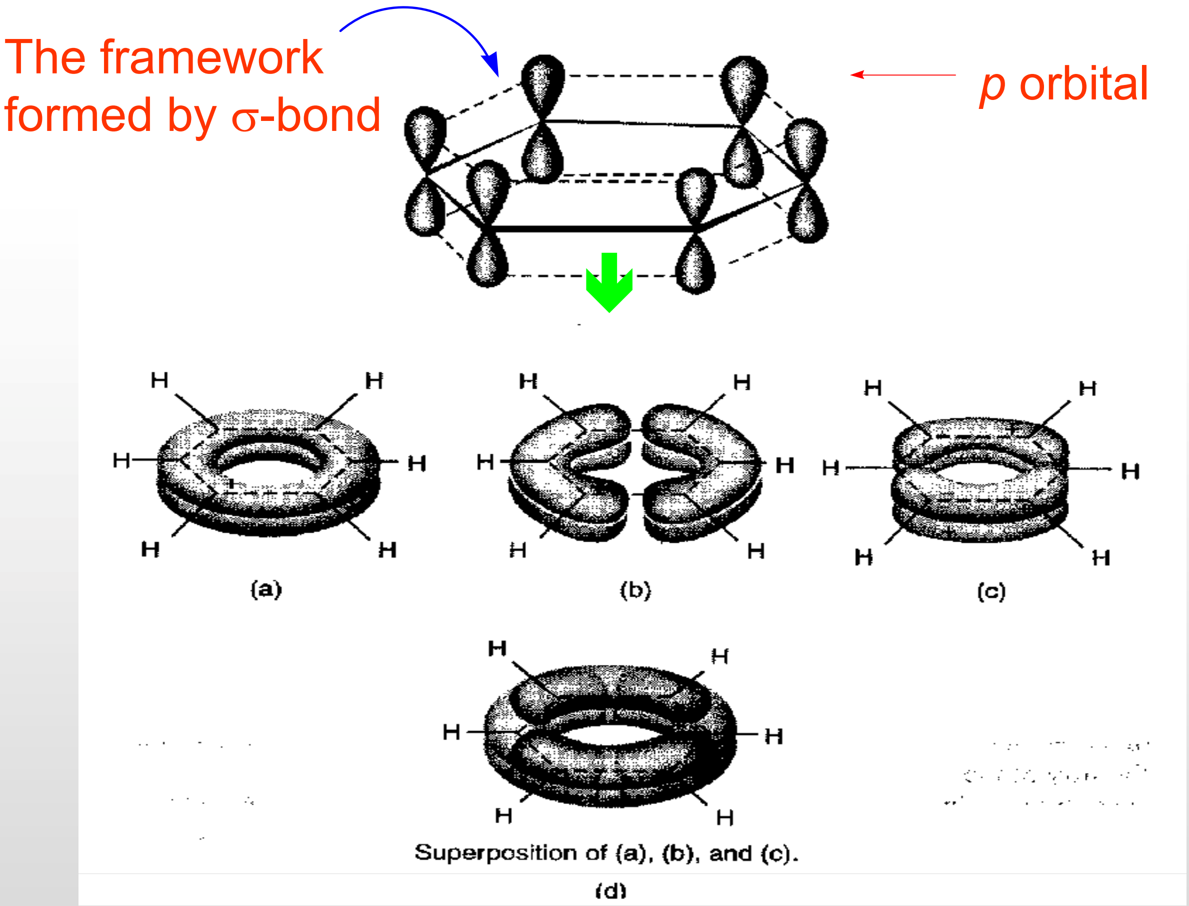


图6-2 苯的 π 分子轨道能级图


The framework formed by σ-bond

p orbital

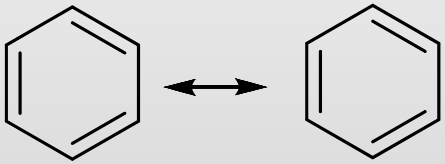
The six *p* orbitals of benzene overlap to form three bonding orbitals, (a), (b), and (c). (d) is the superimposed three orbitals.

1.2.2 Bond Energies and Distances in Compounds Containing Delocalized Bonds

Resonance hybrids are always more stable than any of the canonical structures would be, if they existed. The delocalization of the electrons lowers the orbital energies, imparting this stability. The gain in stability of the resonance hybrid over the most stable of the (non-existent) canonical structures is called the RESONANCE ENERGY （共振能） or DELOCALISATION ENERGY.

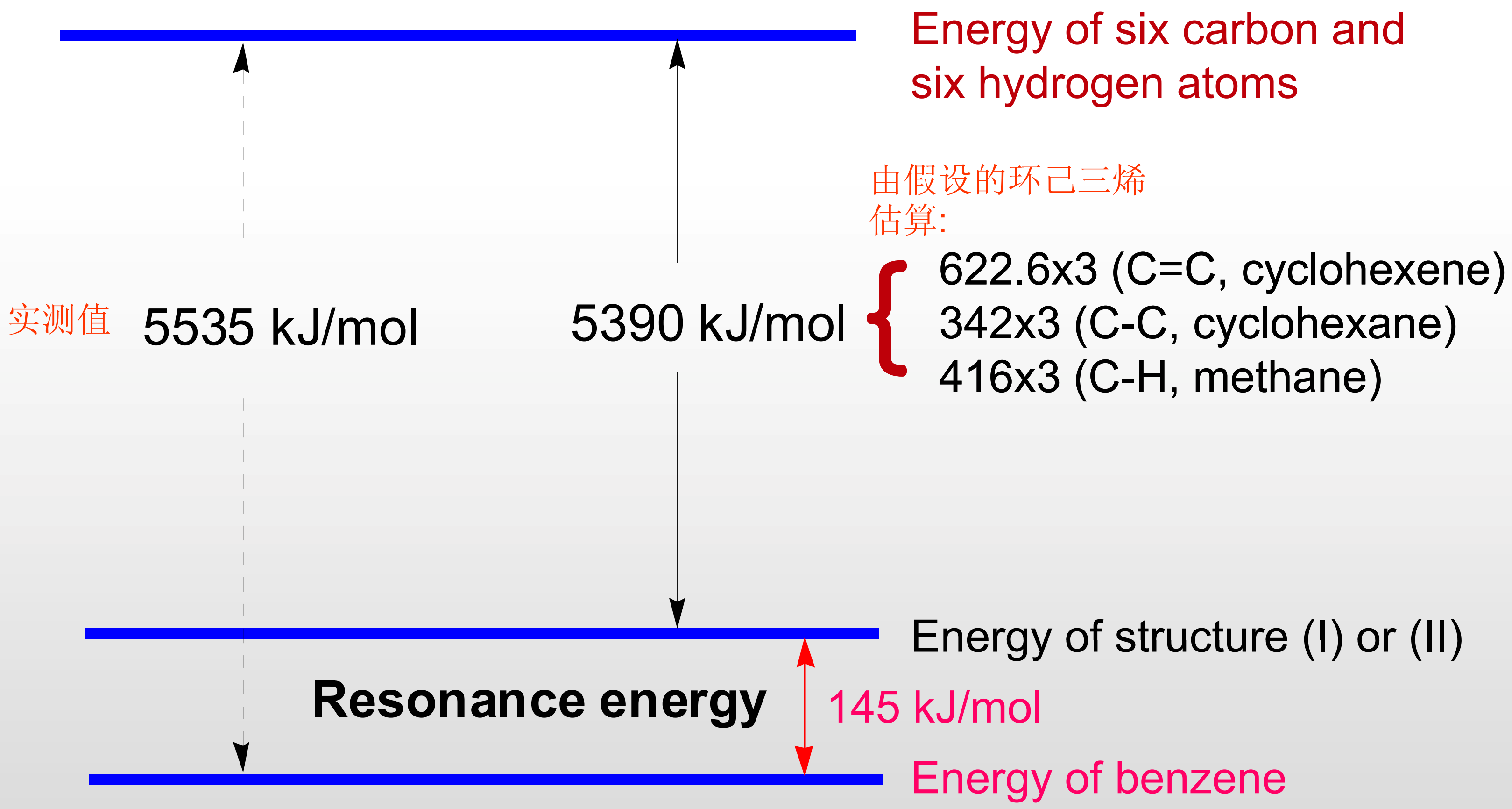
Estimation of resonance energy from

- the heat of atomization (原子化热)
- the heat of hydrogenation (氢化热)
- HMO theory



(I) (II)

The most stable canonical structures of benzene



Energy of six carbon and six hydrogen atoms

由假设的环己三烯
估算:

622.6x3 (C=C, cyclohexene)
342x3 (C-C, cyclohexane)
416x3 (C-H, methane)

实测值 5535 kJ/mol

5390 kJ/mol

Energy of structure (I) or (II)

Resonance energy

145 kJ/mol

Energy of benzene

Resonance energy of benzene

- Resonance energy from the heat of hydrogenation:

the heat of hydrogenation (kJ/mol)

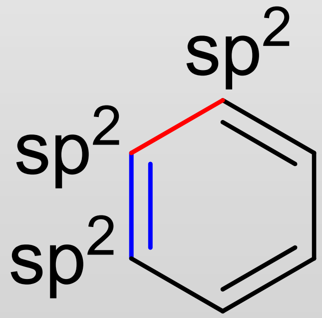
cyclohexene: 120
the hypothetical (I) or (II): 360
the real benzene: 208

---

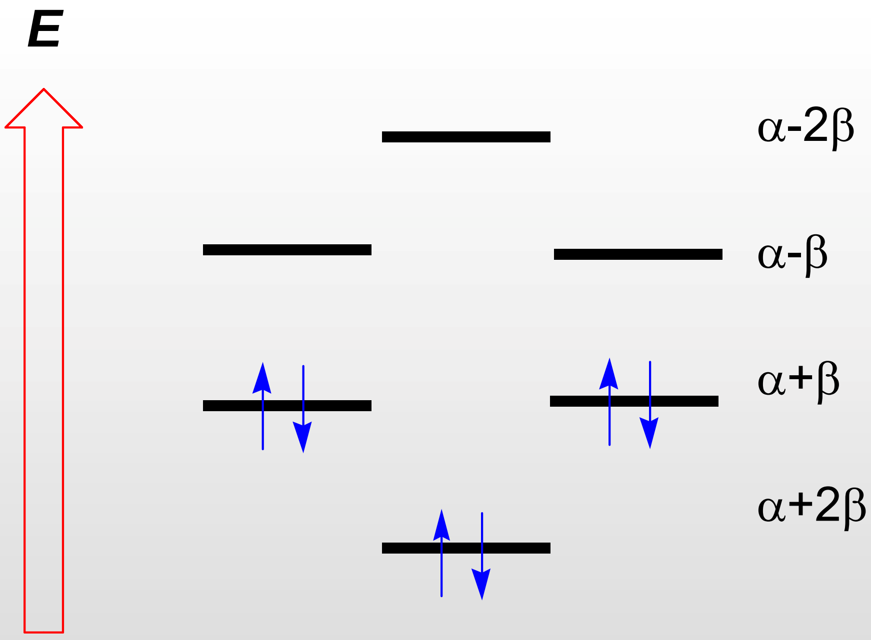
the resonance energy: 152 kJ/mol

NOTE: One must bear in mind again that resonance structures have no physical existence. So, even though the term 'resonance energy' is quite meaningless, it offers an insight into how different the VB picture of a molecule is from the actual molecule itself.

Bond length
sp^2-sp^2 C—C: 1.48 Å
sp^2-sp^2 C=C: 1.32 Å
C-C bond distance in benzene: **1.40 Å**



- The energies of six benzene orbitals can be calculated from HMO theory in terms of two quantities, α and β.



Energy level of benzene

α is the amount of possessed by an isolated 2*p* orbital before overlap

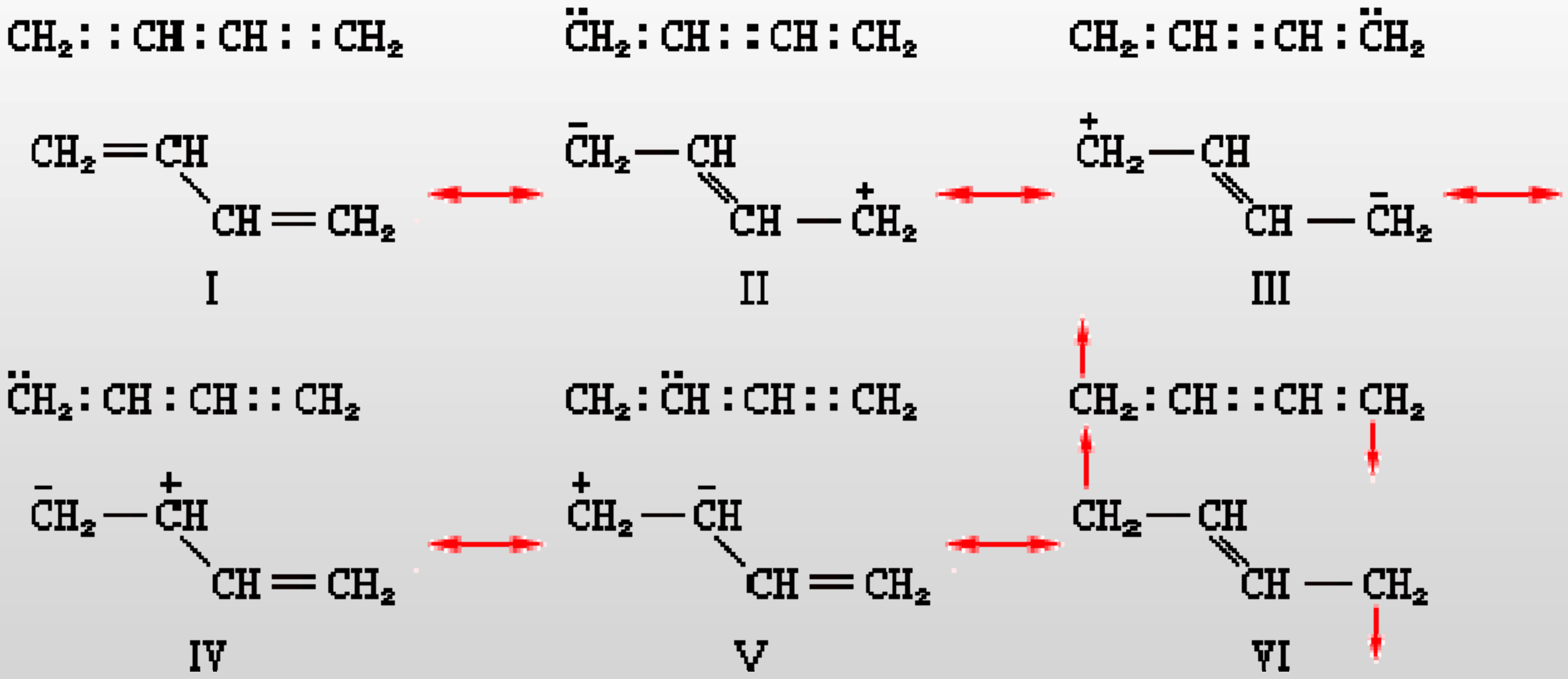
β (*resonance integral*) is an energy unit expressing the degree of stabilization resulting from π-orbital overlap

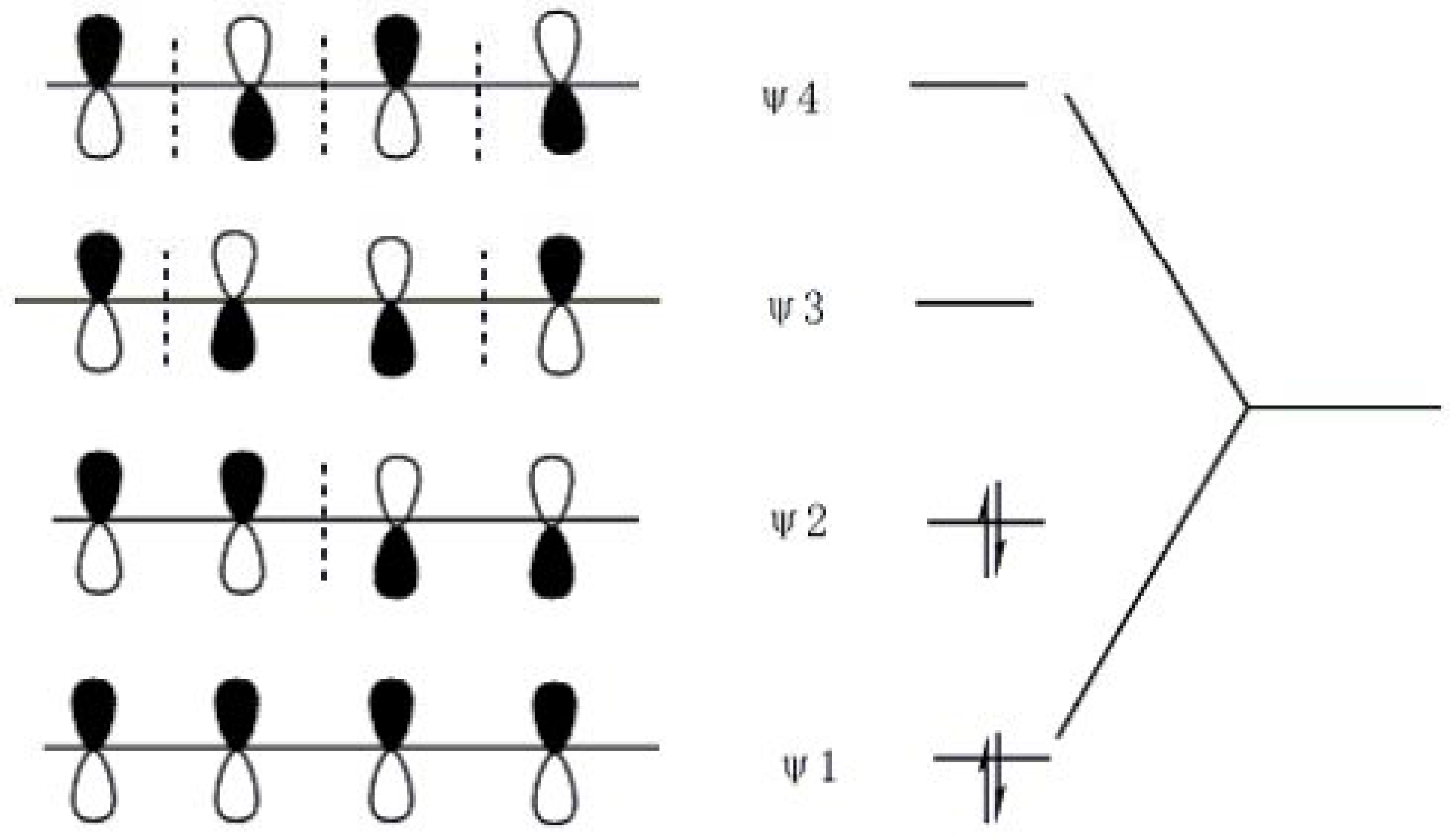
The resonance energy= $(6\alpha+8\beta)-(6\alpha+6\beta) = 2\beta$

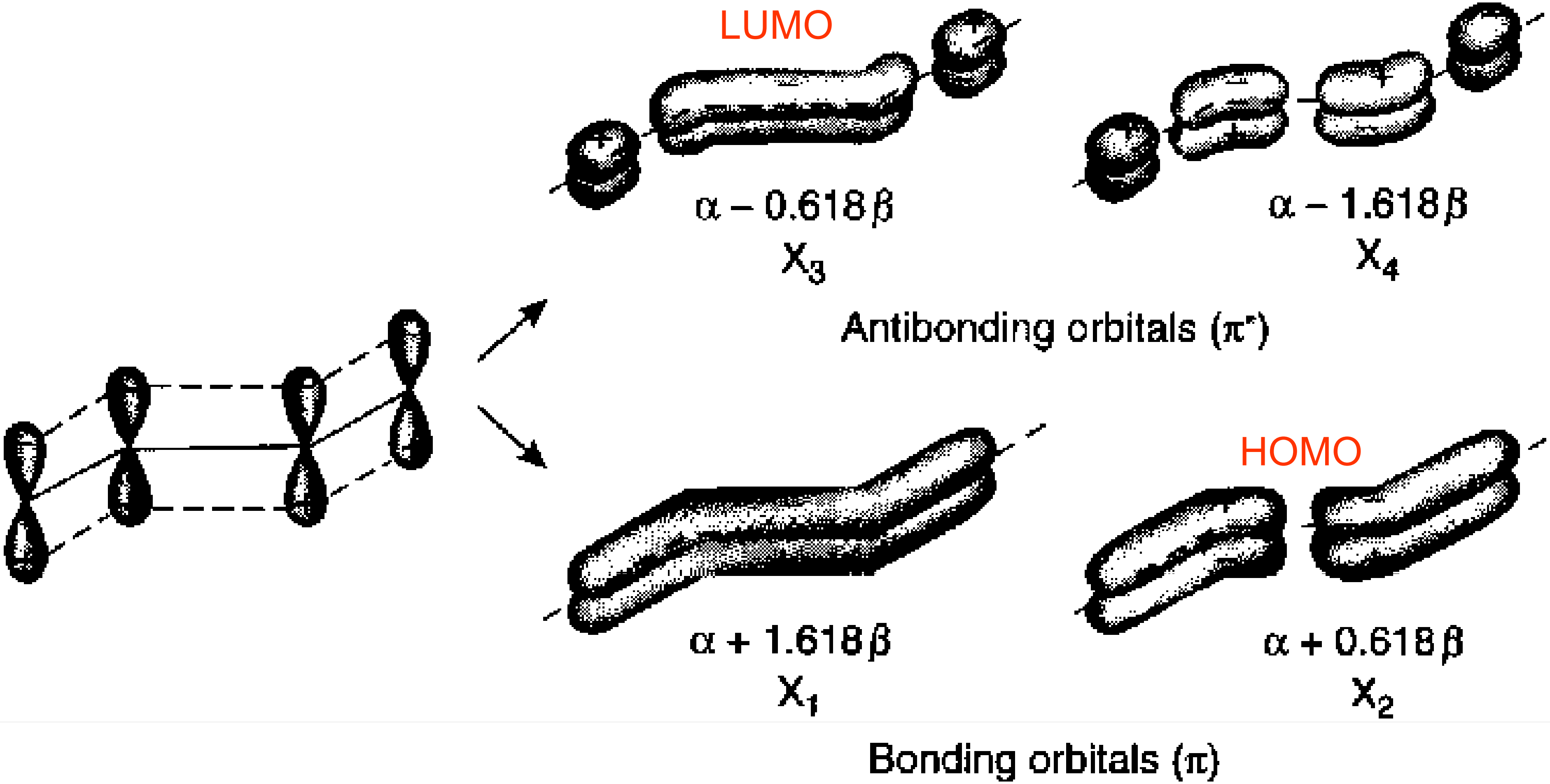
1.2.3 Kinds of molecules that have delocalized bonds

1.2.3.1 Double or triple bonds in conjugation

A system of atoms covalently bonded with alternating single and multiple bonds is a conjugated system.



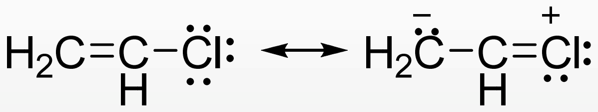

ψ 4
ψ 3
ψ 2
ψ 1



The four π orbitals of butadiene, formed by overlap of four *p* orbitals

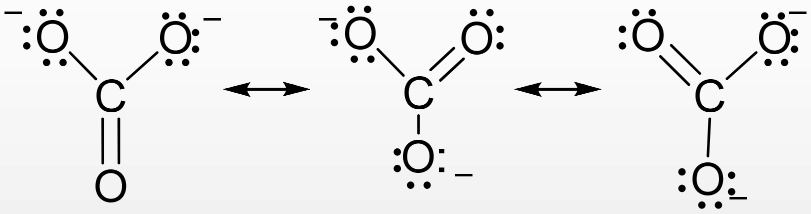
1.2.3.2 Double or triple bonds in conjugation with a p orbital on an adjacent atom

There are three cases: the original *p* orbital may have contained two, one, or no electrons.



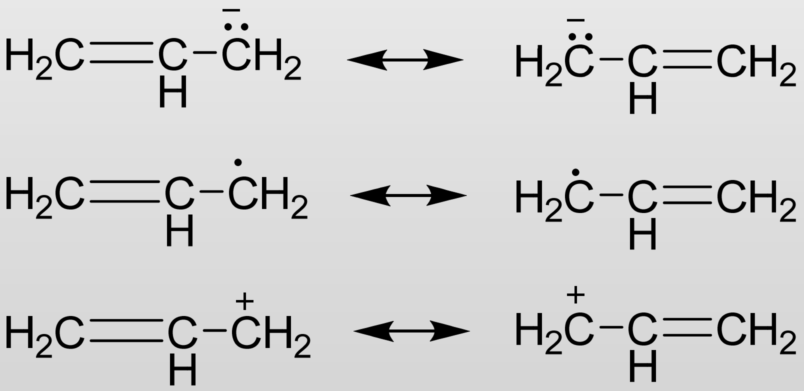
(I) (II)

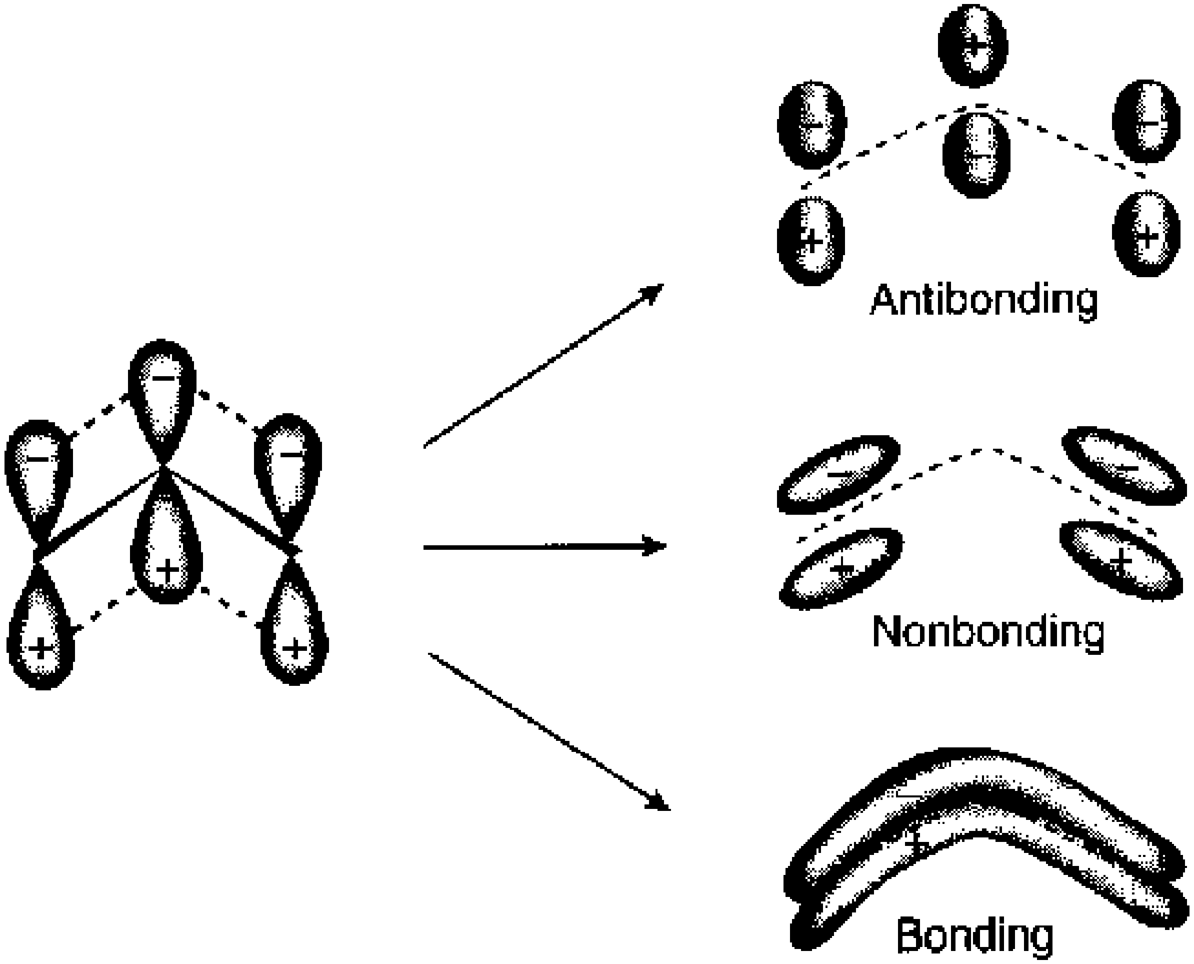
vinyl chloride



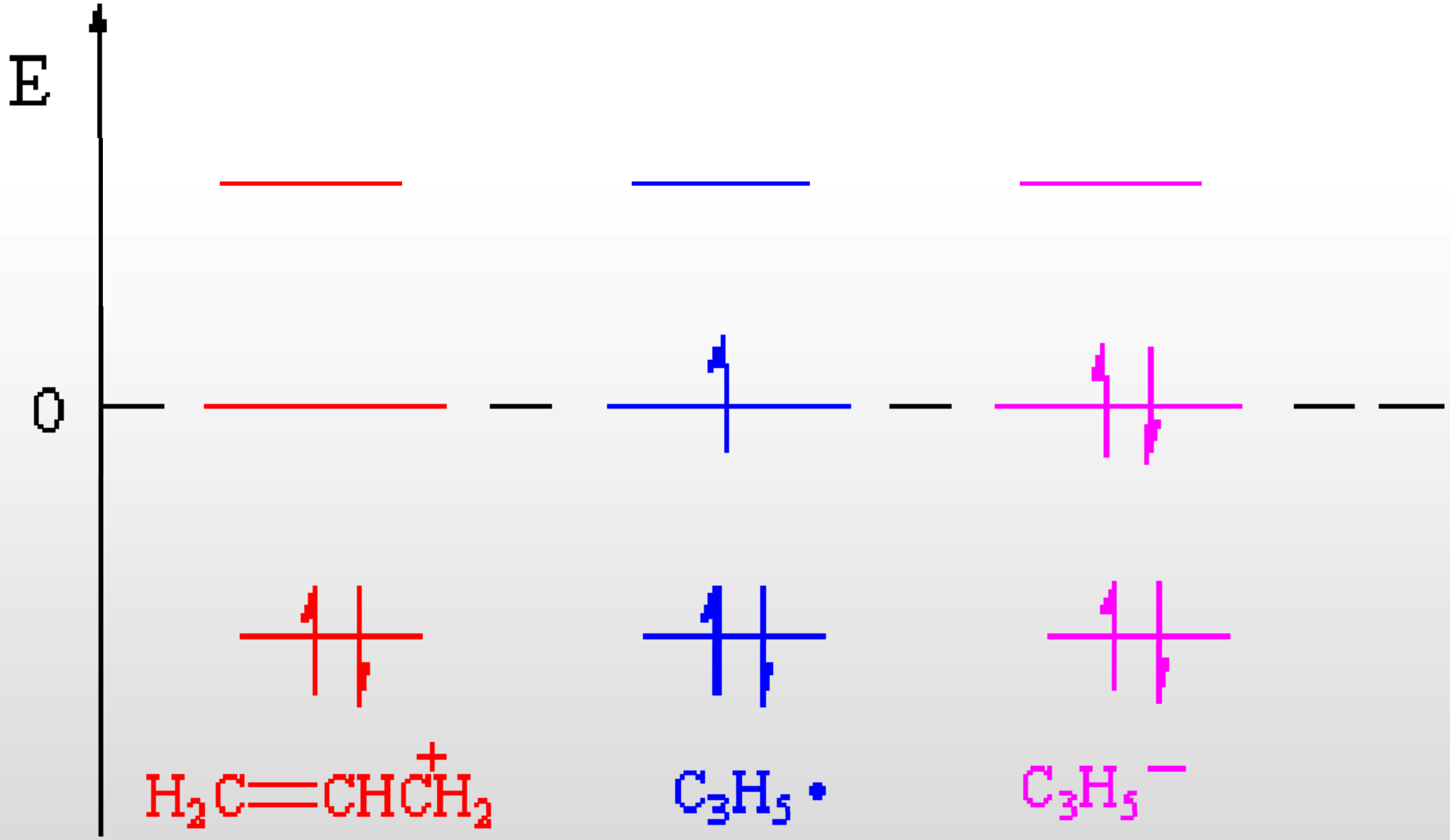
(III) (IV) (V)

carbonate ion



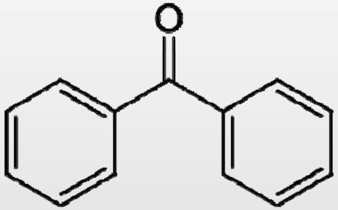


The three orbitals of an allylic system, formed by overlap of three *p* orbitals.

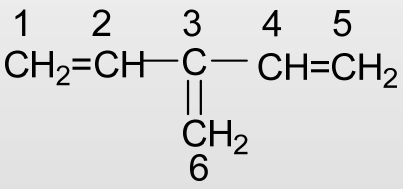

E
0
$H_2C{=}CH\overset{+}{C}H_2$
$C_3H_5\bullet$
$C_3H_5^-$

1.2.3.3 Cross-Conjugation

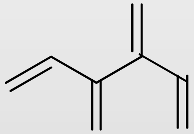
In a cross-conjugation compound, three groups are present, two of which are not conjugated with each other, although each is conjugated with the third. The type of conjugation has an impact on reactivity and molecular electronic transitions.

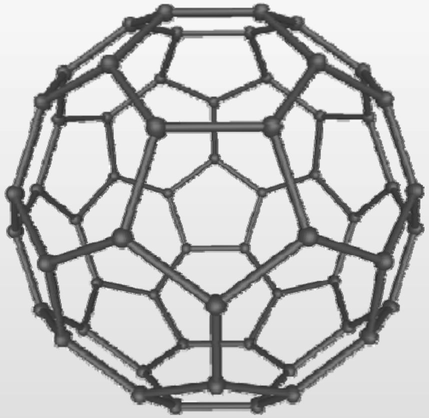


$CH_2=CH-O-CH=CH_2$



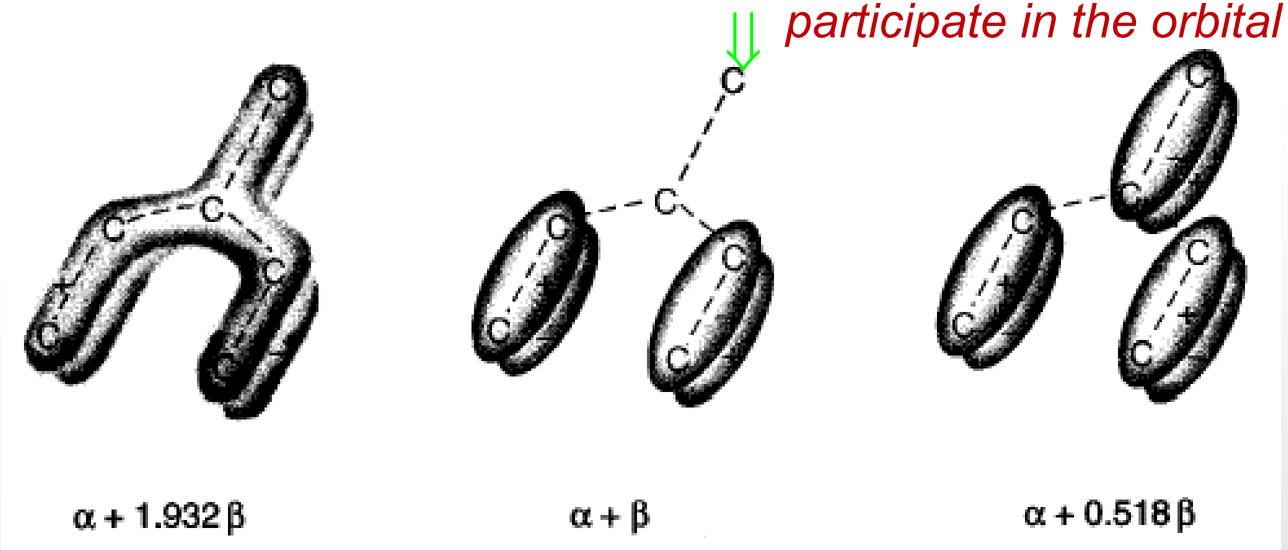
$$\overset{1}{CH_2}=\overset{2}{CH}-\underset{\substack{\| \\ CH_2 \\ 6}}{\overset{3}{C}}-\overset{4}{CH}=\overset{5}{CH_2}$$





benzophenone, divinylether, dendralenes and Buckminsterfullerene C_{60}

MO treatment: 6 *p* orbitals ⇒ 6 molecular orbitals (3 bonding orbitals shown below)



2 carbon atoms do not participate in the orbital

The three bonding orbitals of 3-methylene-1,4-pentadiene

The total energy of the occupied orbitals = 6α + 6.900β
The resonance energy = 0.900 β

QUESTION: Please draw the resonance picture of 3-methylene-1,4-pentadiene and discuss the bonding of the molecule.

1.2.3.4 Hyperconjugation 超共轭

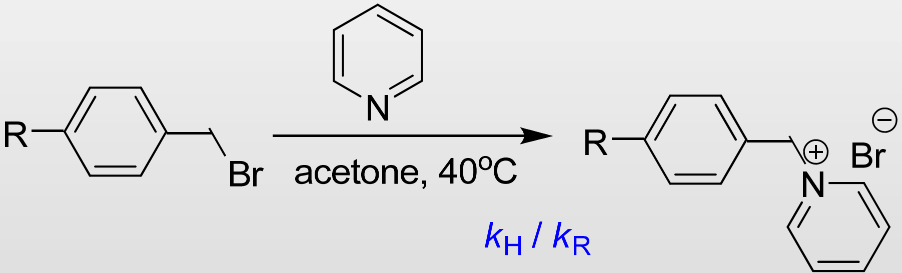
By the field effect alone, the order of electron-release for alkyl groups connected to an unsaturated system:

t-butyl > isopropyl > ethyl > methyl

The dipole moments in the gas phase (*D*):

$PhCH_3(0.37) < PhC_2H_5\ (0.58) < PhCH(CH_3)_2(0.65) < PhC(CH_3)_3\ (0.70)$

Baker and Nathan (1935):

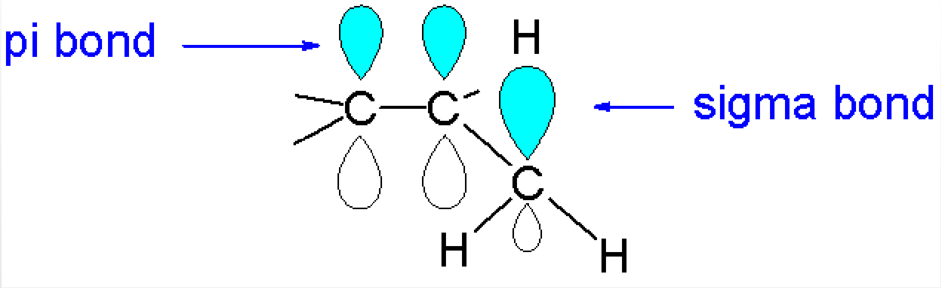


	k_H / k_R
R = Me	1.66
R = Et	1.40
R = i-Pr	1.35
R = t-Bu	1.34
R = H	1

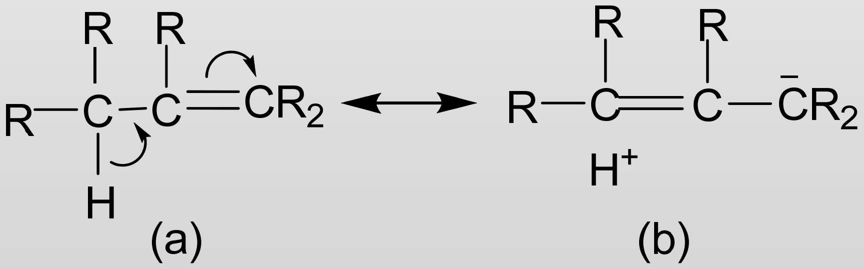
It seems to be +*I:*
methyl >
Ethyl >
isopropyl >
tert-butyl

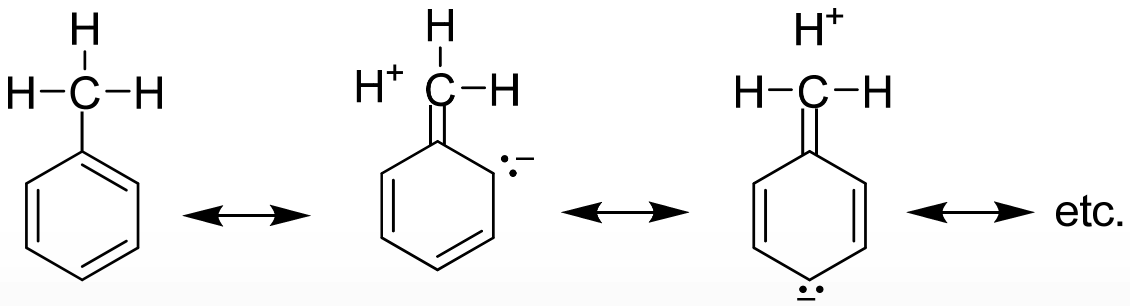
What is the Hyperconjugation?

Hyperconjugation is the stabilizing interaction that results from the interaction of the electrons in a sigma bond (usually C-H or C-C) with an adjacent empty (or partially filled) non-bonding *p*-orbital or antibonding π orbital or filled π orbital to give an extended molecular orbital that increases the stability of the system.



When a carbon attached to at least one hydrogen is attached to an unsaturated atom or one with an ***unshared orbital****, canonical forms such as (b) can be drawn.*





For the other alkyl groups, hyperconjugation is diminished because the number of C—H bonds is diminished and in *t*-butyl there are none; hence, with respect to this effect, methyl is the strongest electron donor and *t*-butyl the weakest. So,

Hyperconjugation:

methyl > ethyl > isopropyl > *t*-butyl

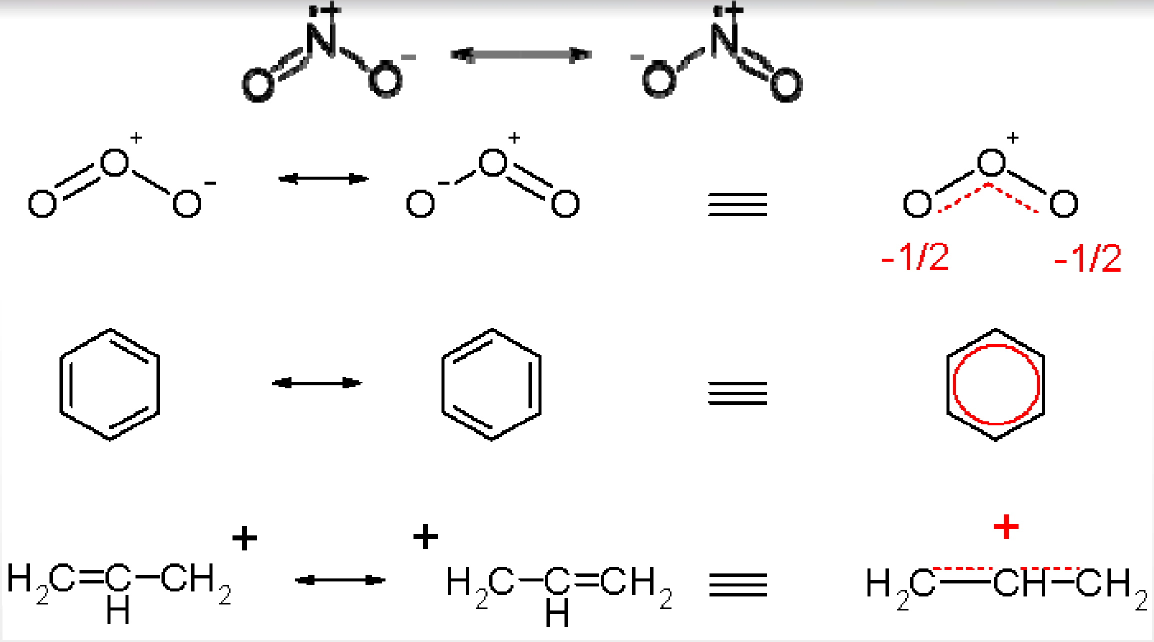
Hyperconjugation effect: stability of carbocations

$$(CH_3)_3C^+ > (CH_3)_2CH^+ > (CH_3)CH_2^+ > CH_3^+$$

1.2.4 The Rules of Resonance 共振规则

- We have seen that one way of expressing the actual structure of a molecule containing delocalized bonds is to draw several possible structures and to assume that the actual molecule is a hybrid of them. These canonical forms have no existence except in our imaginations. The molecule does not rapidly shift between them. It is not the case that some molecules have one canonical form and some another. All the molecules of the substance have the same structure. **That structure is always the same all the time and is a weighted average of all the canonical forms.**

1. All the canonical forms must be bona fide Lewis structures. For instance, none of them may have a carbon with five bonds.
2. The positions of the nuclei must be the same in all the structures. This means that all we are doing when we draw the various canonical forms is putting the electrons in different ways.

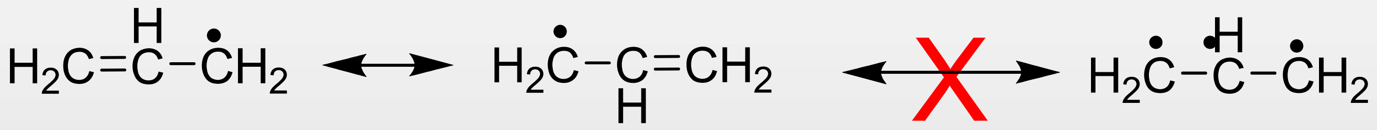


Examples of resonance –nitrogen dioxide, ozone, benzene and allyl cation.

Note: In most resonance, σ bonds are not involved, and only the π or unshared electrons are put in different ways. This means that if we write one canonical form for a molecule, we can then write the others by merely moving π and unshared electrons.

3. All atoms taking part in the resonance, i.e., covered by delocalized electrons, must lie in a plane or nearly so. This, of course, does not apply to atoms that have the same bonding in all the canonical forms. The reason for planarity is maximum overlap of the *p* orbitals.

4. All canonical forms must have the same number of unpaired electrons.



$$H_2C=\overset{H}{C}-\dot{C}H_2 \longleftrightarrow H_2\dot{C}-\underset{H}{C}=CH_2 \quad \not\longleftrightarrow \quad H_2\dot{C}-\overset{H}{\dot{C}}-\dot{C}H_2$$

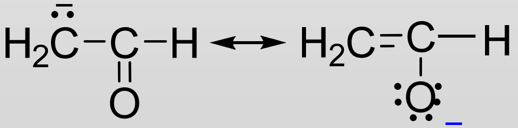
5. The energy of the actual molecule is lower than that of any canonical form, obviously. Therefore, delocalization is a stabilizing phenomenon.

6. All canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most.

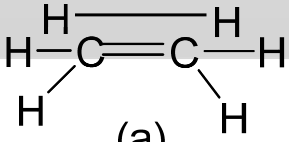
♦ The greater the number of significant structures that can be written and the more nearly equal they are, the greater the resonance energy, other things being equal.

The helpful rules for deciding relative stabilities of imaginary structures:

a. Structures with **more covalent bonds** are ordinarily more stable than those with fewer.
b. Stability is decreased by an increase in **charge separation**. Structures with formal charges are less stable than uncharged structures.
c. obeying as much as possible the octet rule (8 valence electrons around each atom rather than having deficiencies or surplus). Structures that carry **a negative charge on a more electronegative atom** are more stable than those in which the charge is on a less electronegative atom. Similarly, positive charges are best carried on atoms of low elctronegativity.
d. Structures with **distorted bond angles or lengths** are unstable, e.g., the structure (a) for ethane.



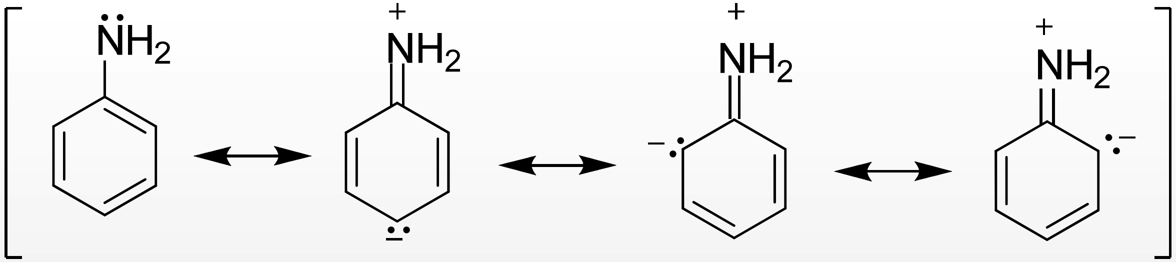
$$H_2\overset{\ddot{-}}{C}-\underset{\overset{\|}{O}}{C}-H \longleftrightarrow H_2C=\underset{\overset{|}{:\ddot{O}:^{-}}}{C}-H$$



(a)

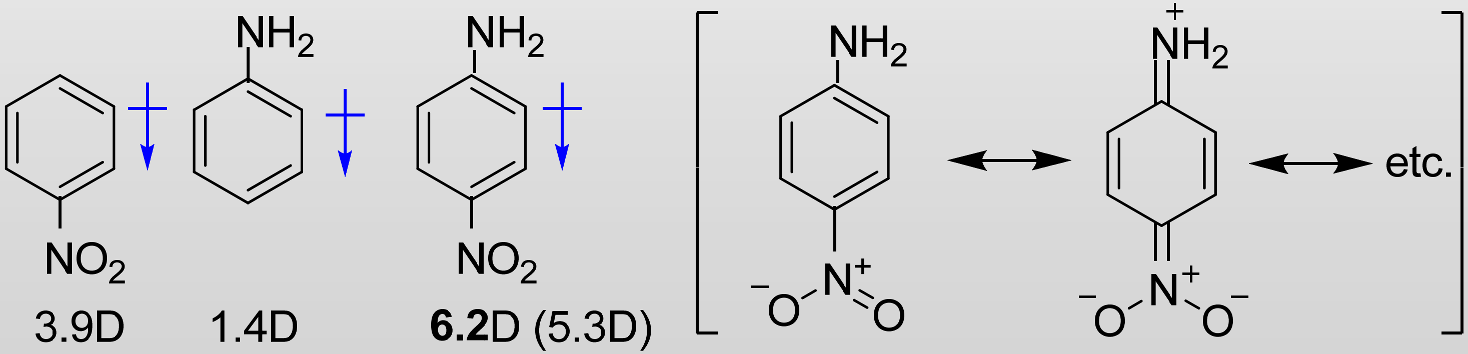
1.2.5 The Resonance Effect (共振效应)

Resonance always results in a different distribution of electron density than would be the case if there were no resonance.

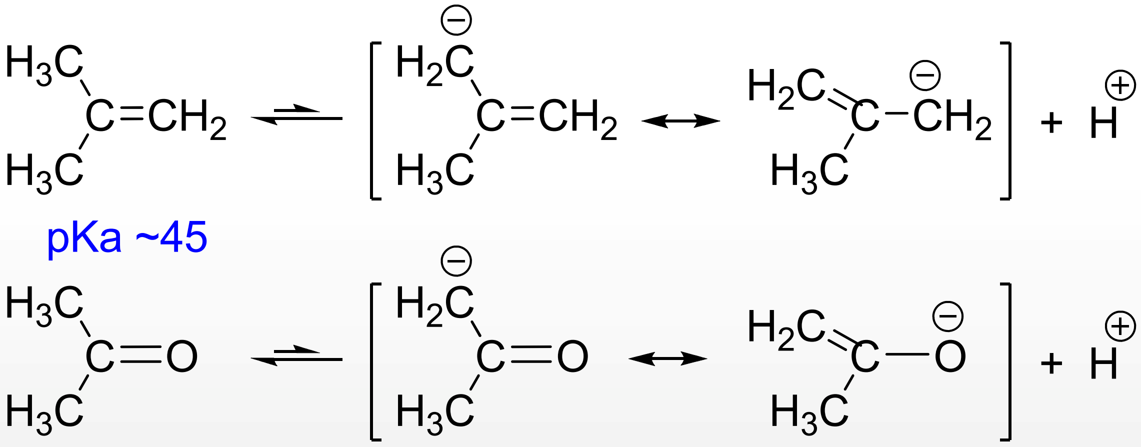


This decrease in electron density at one position (and corresponding increase elsewhere) is called the **resonance effect**.

A. Dipole moment



B. Acidity and basicity

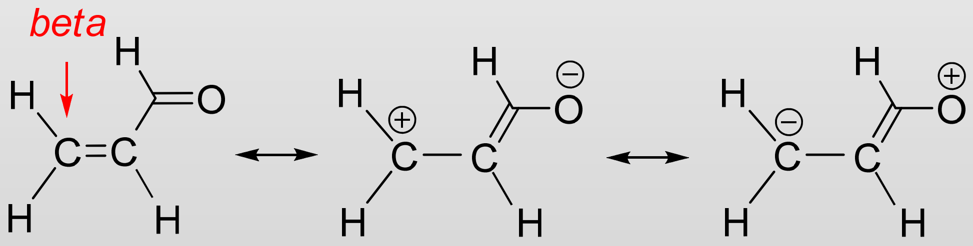


pKa ~45

pKa ~25

conjugated base

C. Spectrographic behavior and reactivity



major contributor

significant contributor

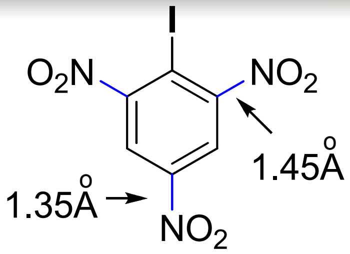
minor contributor

i) IR: C=O ~1690 cm^{-1}
(1730 cm^{-1} for saturated compounds)

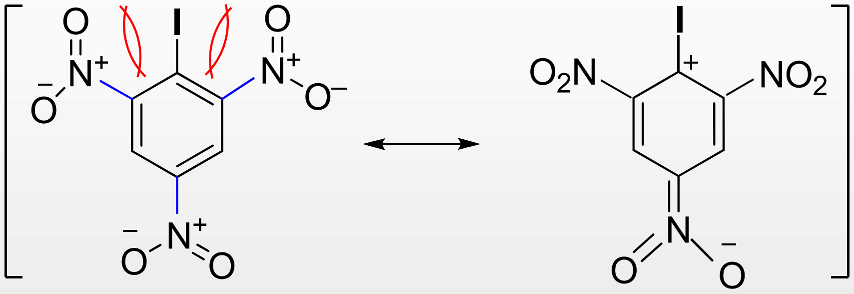
ii) ^{13}C NMR: β-C is less shielded, chemical shift (δ)↑

iii) nuclear attack at β-C

Steric inhibition of resonance

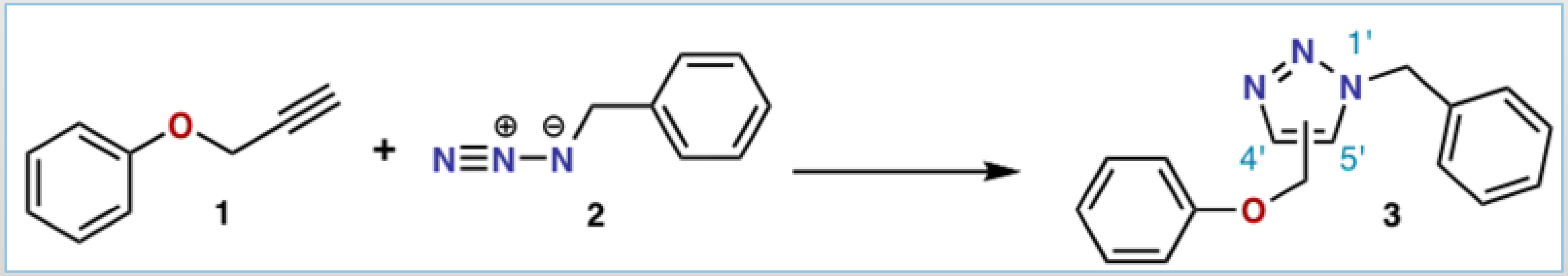


2,4,6-Trinitroiodobenzene
(picryl iodide)



(a) (b)

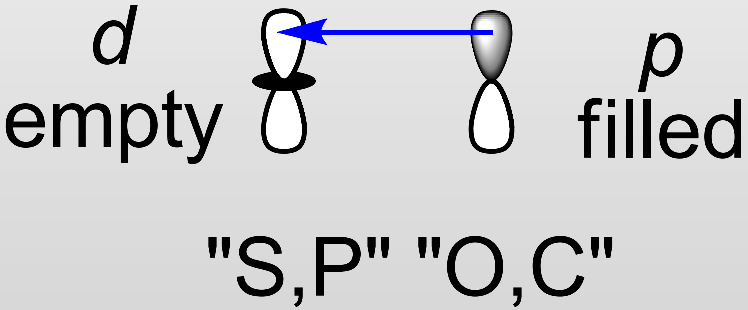
Question:



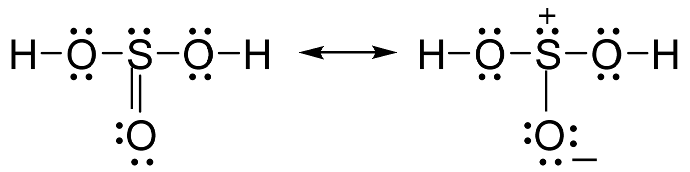
Azide-Alkyne Huisgen Cycloaddition: 1,4- or 1,5-123-triazole ?

1.2.6 *p*π-*d*π Bonding. Ylide (叶立德)

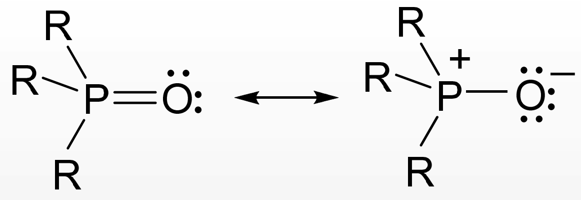
- Usually, π bonds formed by overlap of parallel *p* orbitals.
- Another type of double bond contains one σ orbital, the second orbital is not a π orbital by overlap of half-filled *p* orbitals; instead it is formed by overlap of a filled *p* orbital from the oxygen with an empty *d* orbital from the sulfur. It is called ***p*π-*d*π orbital**, which is particularly common for the second-row atoms: sulfur and phosphorus.



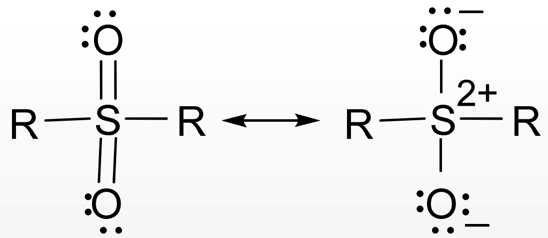
Examples:



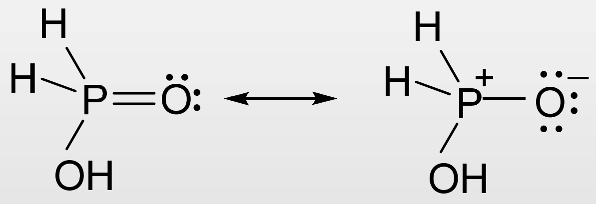
p-pi *d*-pi canonical form



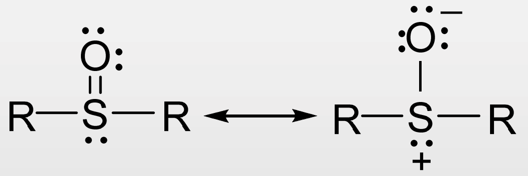
phosphine oxide



sulfones

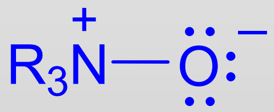


hypophosphorus acid



sulfoxides

- *This type of molecules can be represented by two canonical forms but the bond is nevertheless localized.*
- *Nitrogen analogs are less stable because the resonance is lacking.*



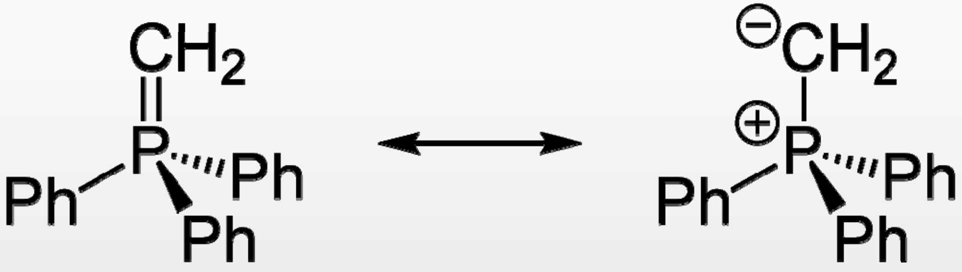
$R_3\overset{+}{N}-\ddot{\underset{..}{O}}:^{-}$

amine oxide

Ylide

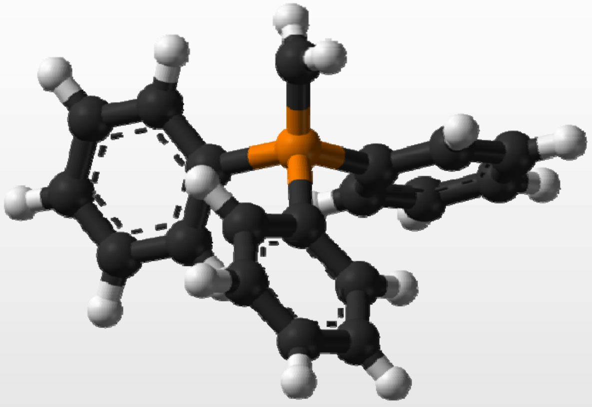
An ylid or ylide (US) is a neutral dipolar molecule, in which a positively charged atom from group VA or VIA of the periodic table is connected to a carbon atom carrying an unshared pair of electrons.

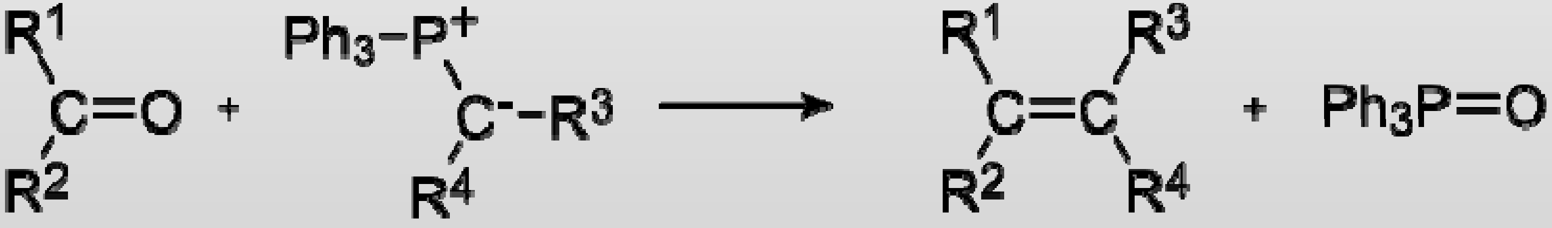
phosphonium ylids



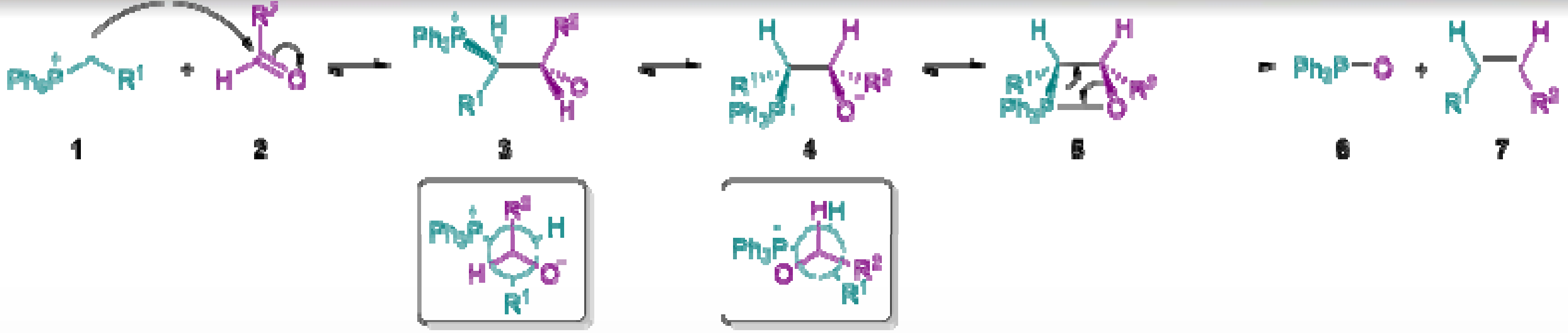
Phosphorane form

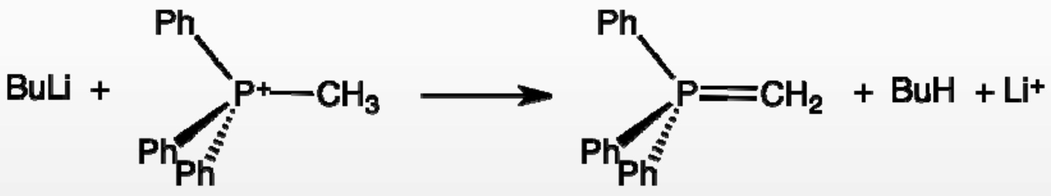
ylide form

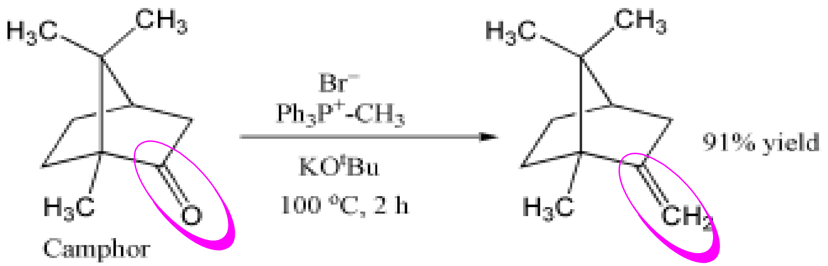


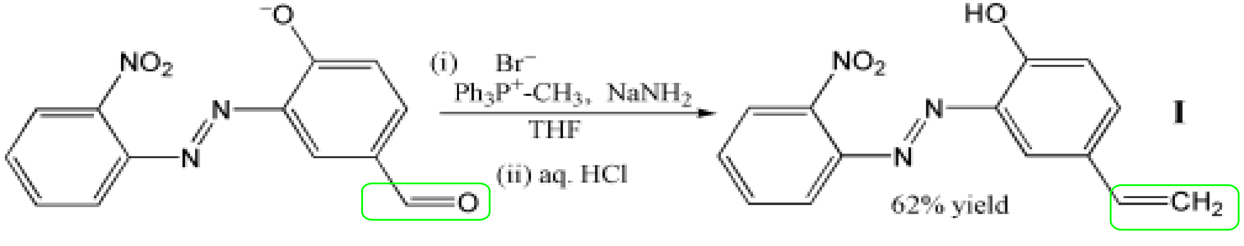


Wittig Reaction

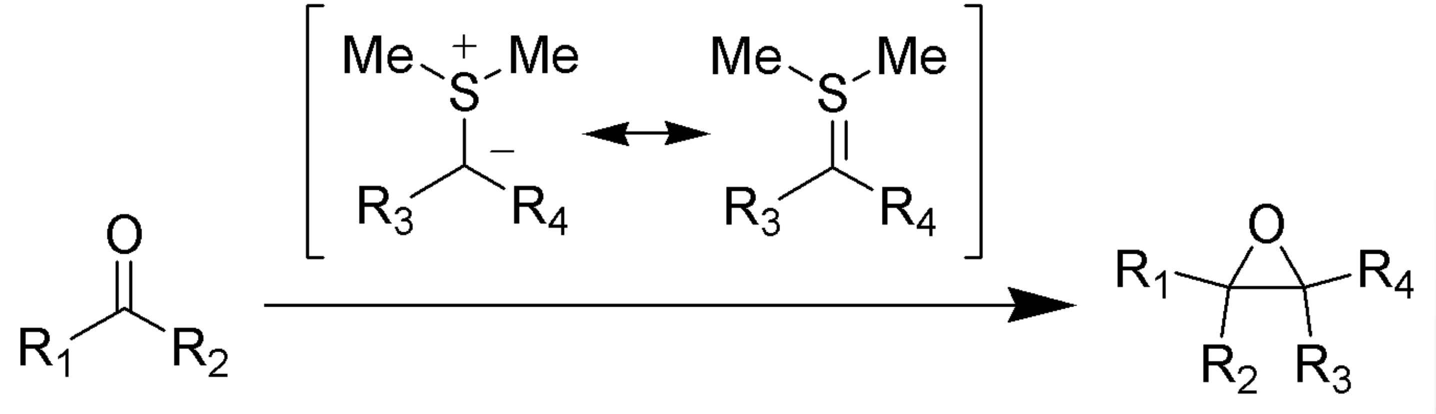

Ph3P+
R1
H
R2
O
Ph3P
R1
R2
Ph3P−O
1
2
3
4
5
6
7


BuLi +
Ph
P+—CH3
Ph
Ph
P=CH2
+ BuH + Li+


Camphor
H3C
CH3
O
Br−
Ph3P+-CH3
KOtBu
100 °C, 2 h
CH2
91% yield


−O
NO2
N
N
O
(i) Br−
Ph3P+-CH3, NaNH2
THF
(ii) aq. HCl
HO
CH2
62% yield
I

Sulfonium ylide



i. In almost all compounds that have *p*π-*d*π bonds, the central atom is connected to four atoms or three atoms and an unshared pair and the bonding is approximately tetrahedral. The *p*π-*d*π bond, therefore, does not greatly change the geometry of the molecule in contrast to the normal π bond, which changes an atom from tetrahedral to trigonal.

ii. There are three main types of ylids: phosphorus, nitrogen, and sulfur ylids are also known.

Stability: *P*-ylids>*S*-ylids>*N*-ylids

1.2.7 Aromaticity 芳香性

Characteristics of aromatic (aryl) compounds:

1) A delocalized conjugated π system, most commonly an arrangement of alternating single and double bonds

2) Coplanar structure, with all the contributing atoms in the same plane

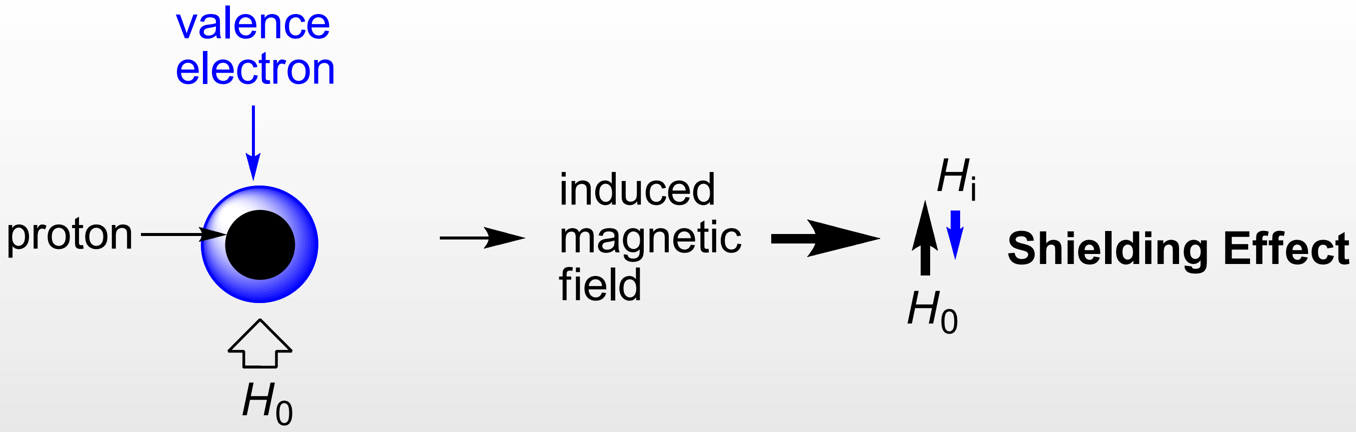
3) Contributing atoms arranged in one or more rings

4) A number of π delocalized electrons that is even, but not a multiple of 4. That is, **4n + 2** number of π electrons, where n=0, 1, 2, 3, and so on. This is known as Hückel's Rule.

- In organic chemistry, aromaticity is a chemical property describing the way in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibits a stabilization stronger than would be expected by the stabilization of conjugation alone.
- 1925, Armit and Robinson: the aromatic properties of the benzene —— the presence of a closed loop of electrons .

闭合的电子回路

NMR: determine experimentally whether or not a compound has a closed ring of electron.



valence electron

proton

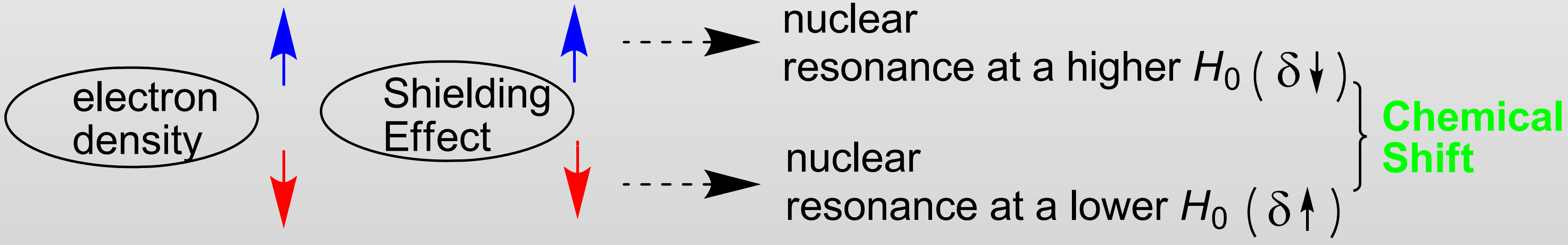
H_0

induced magnetic field

H_i

H_0

Shielding Effect



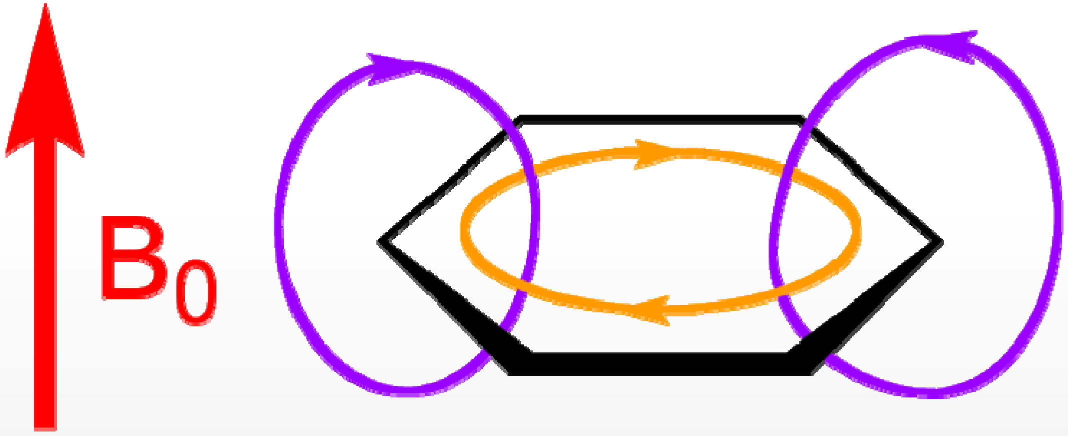
electron density

Shielding Effect

nuclear resonance at a higher H_0 ($\delta\downarrow$)

nuclear resonance at a lower H_0 ($\delta\uparrow$)

Chemical Shift



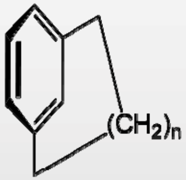
A diagram of an aromatic ring current. B_0 is the applied magnetic field, the red arrow indicating its direction. The orange ring shows the direction of the ring current, and the purple rings show the direction of the induced magnetic field.

i. ^{1}H NMR: the greater the density of the electron cloud surrounding a proton, the more upfield is its chemical shift (a lower δ value).

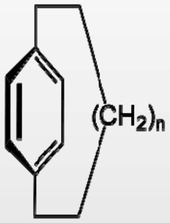
ii. The field "seen" by the aromatic protons is greater than it would have been in the absence of the diamagnetic ring current. The protons are moved downfield (to higher δ) compared to they would be if electron density were the only factor.

Aromaticity can be defined as the ability to sustain an induced ring current. A compound with this ability is called diatropic.

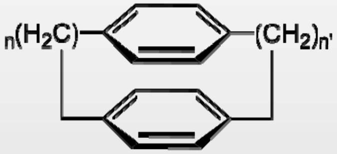
- Ordinary alkene hydrogens: **~ 5–6 δ**; cyclohexene 5.6
- The hydrogen atoms of benzene rings: **~ 7.3 δ**
- If there were protons located above or within the ring, they would be subjected a decreased field and should appear at lower δ values than normal CH_2 groups (normal δ for CH_2 is ~1-2).



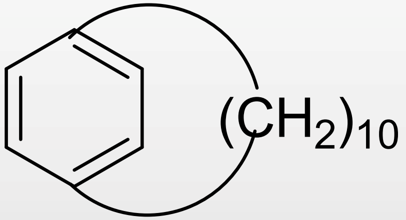
I



II



III

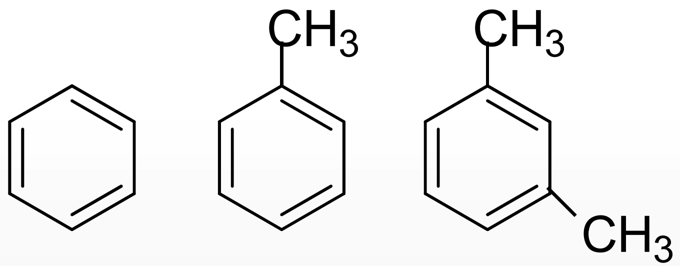


(对环芳烷)

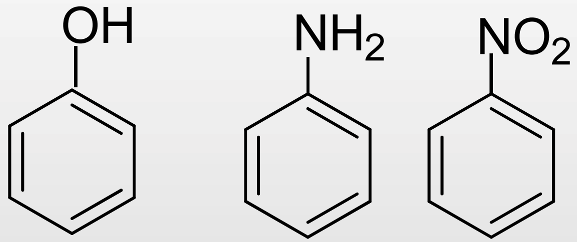
[10]paracyclophane

It follows that aromaticity can be determined from an nmr spectrum. If the protons attached to the ring are shifted downfield from the normal olefinic region, we can conclude that the molecule is diatropic and hence aromatic.

i. Six-member rings



benzene toluene meta-xylene



phenol aniline nitrobenzene

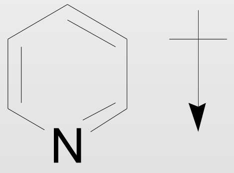
(Representative aromatic compounds)

NOTE

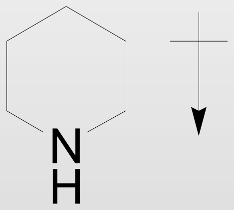
For nitrogen heterocyclics there are more significant canonical forms than for benzene.

QUESTIONS

1) Dipole moment?



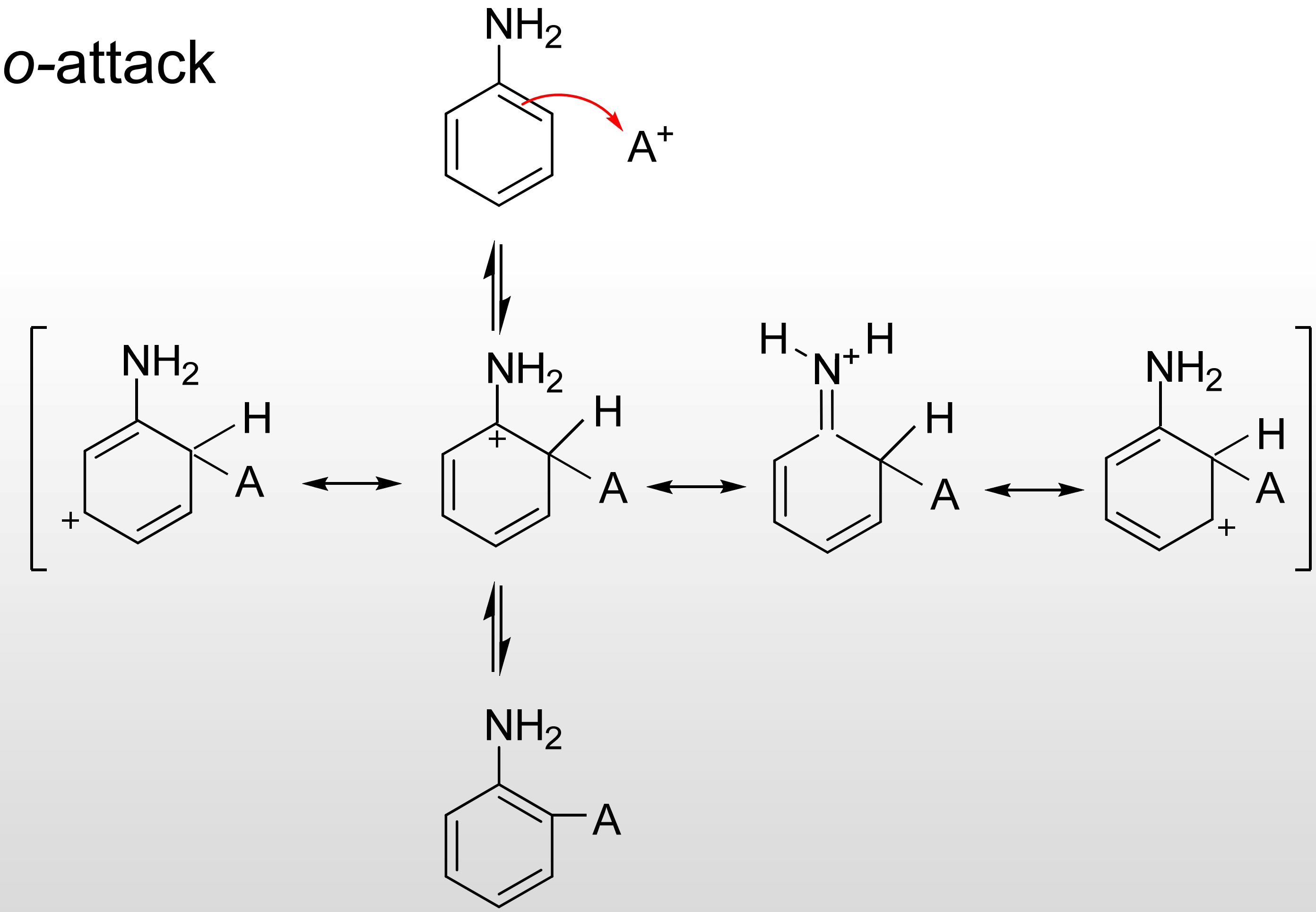
2.22D



1.17D

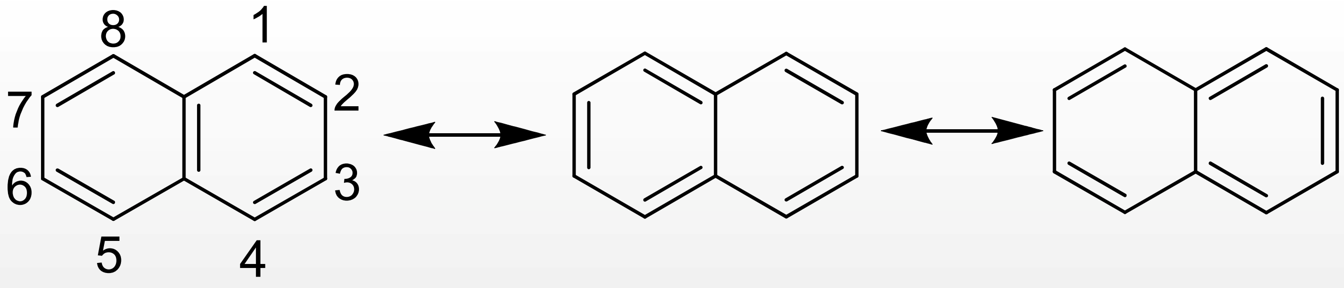
2) Reactivity of pyridine in electrophilic aromatic substitution?

Ortho-attack



How about the *para*- or *meta*-attack?

Polycyclic aromatic hydrocarbon

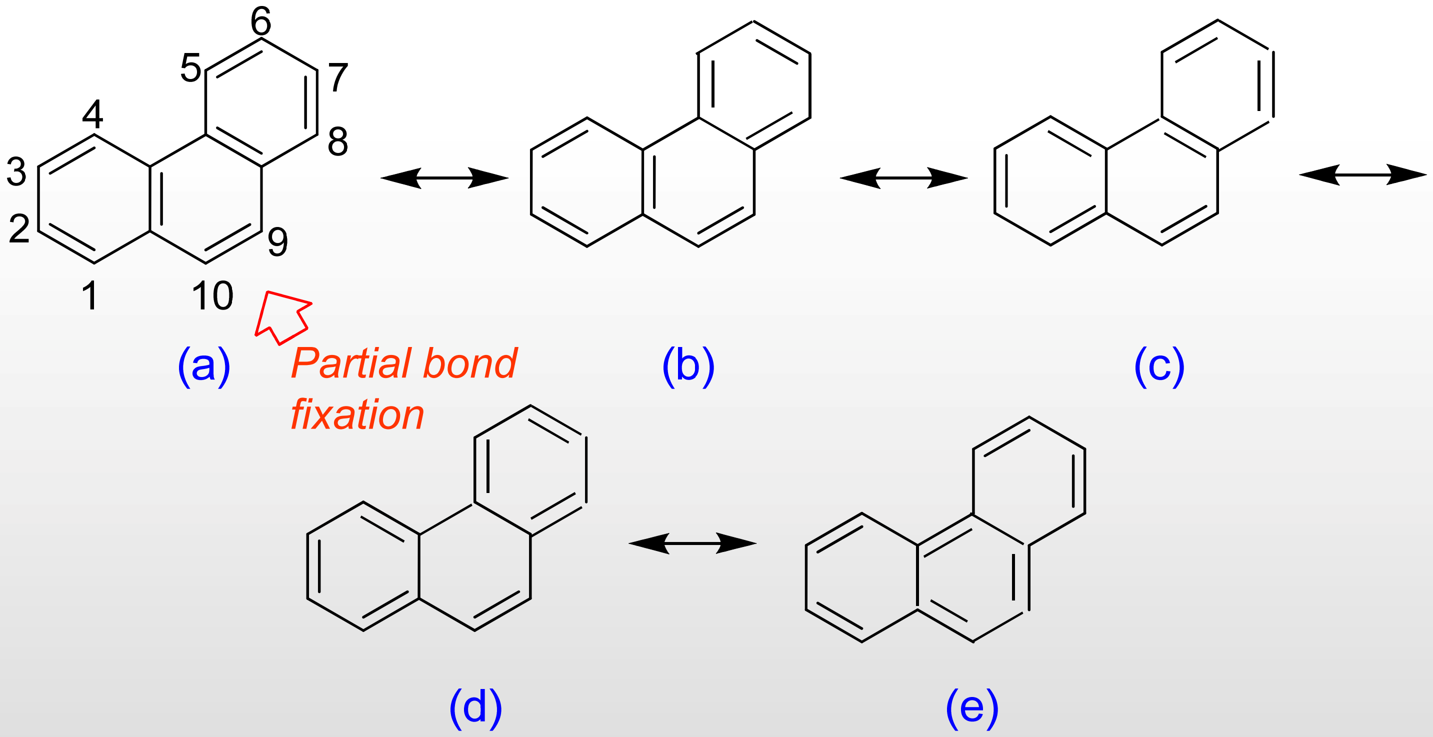


(a) (b) (c)

	bond order	bond distance (Å)
1,2-bond	1.724	1.36
2,3-bond	1.603	1.415

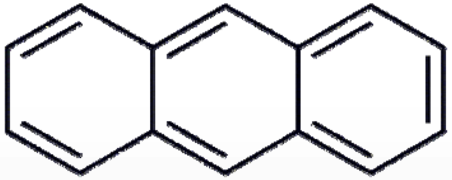
The principal canonical forms are usually not all equivalent. This nonequivalency of bonds, called partial-bond fixation 部份键固定.

b. Phenanthrene

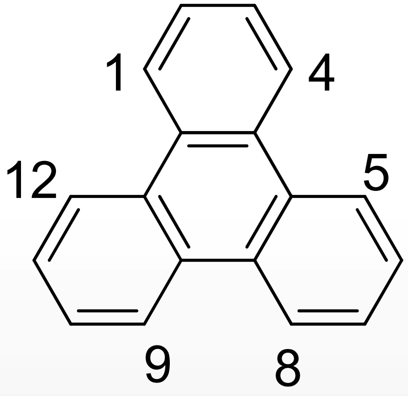


Partial bond fixation

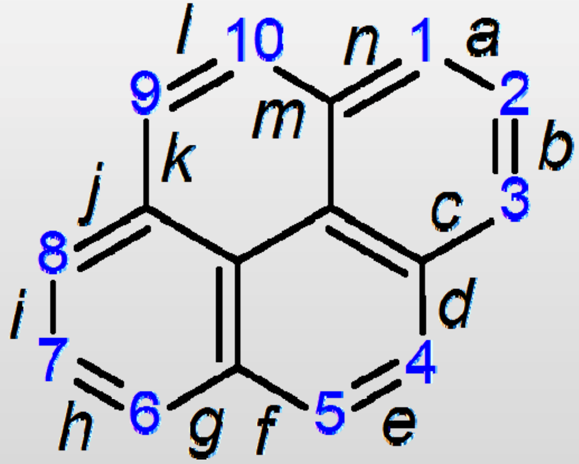
In phenanthrene, where the 9,10 bond is a single bond in only one of five forms, bond fixation becomes extreme and this bond is readily attacked by many reagents.



Anthracene



Triphenylene



Pyrene

Pyrene and its derivatives are valuable molecular probes via fluorescence spectroscopy, having a high quantum yield and lifetime (0.65 and 410 nanosecond, respectively, in ethanol at 293K).

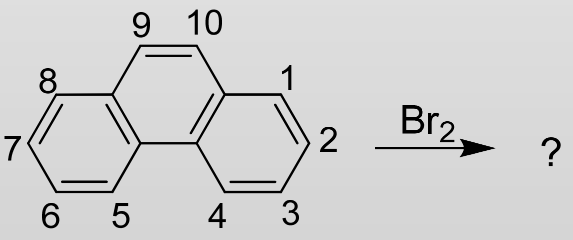
Summary

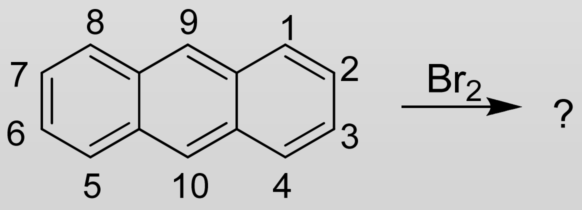
	canonical forms	resonance energy (kJ/mol)
benzene	2	152
naphthalene	3	255
anthracene	4	351
phenanthrene	5	385

NOTE:

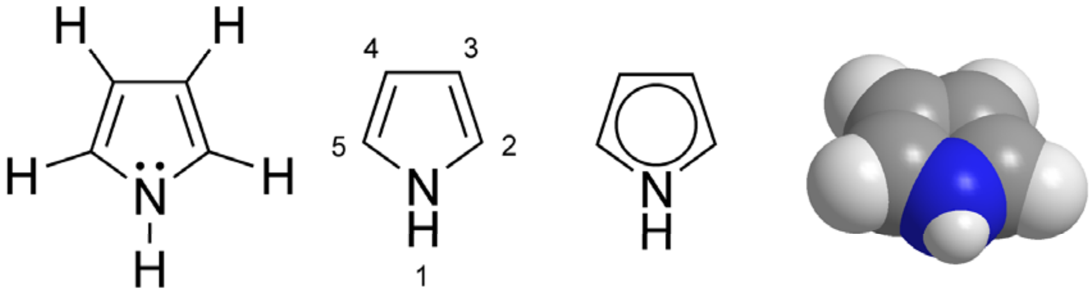
Phenanthrene loses the 9,10 bond by attack of a reagent such as ozone or bromine, two complete benzene rings remain, each with 152 kJ/mol that would be lost if benzene was similarly attacked.

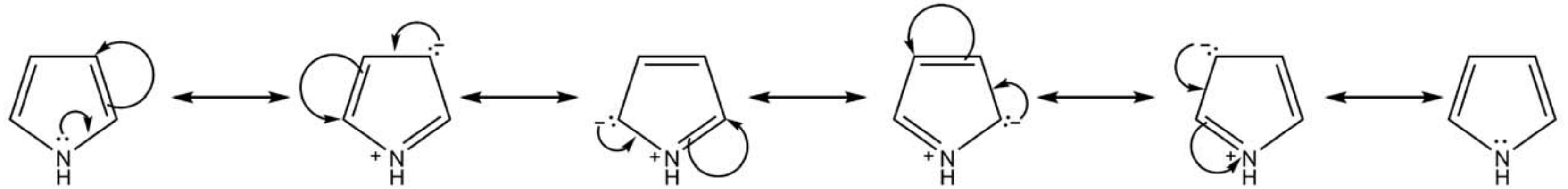
QUESTION:





ii. Five-member rings

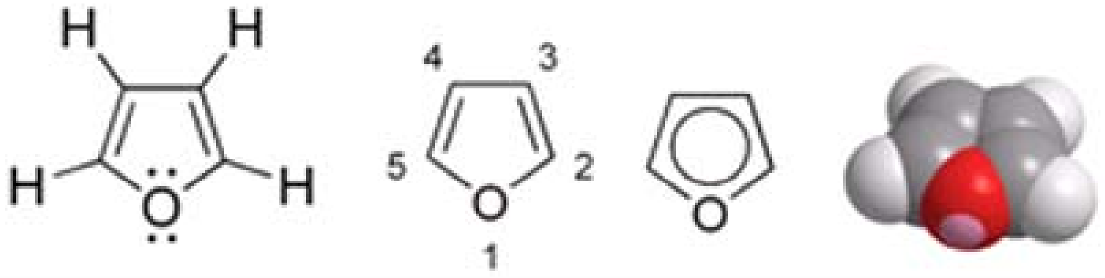


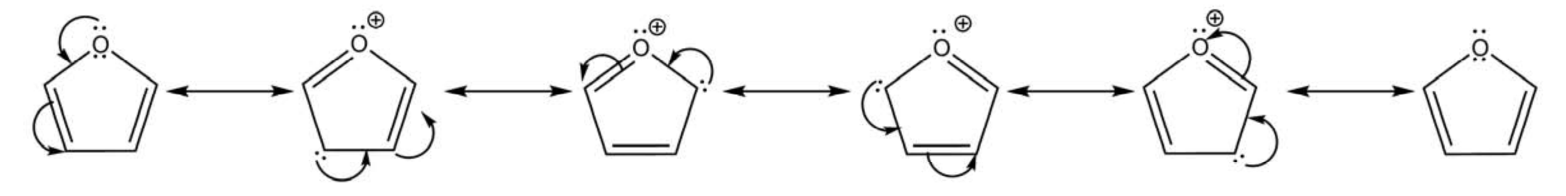


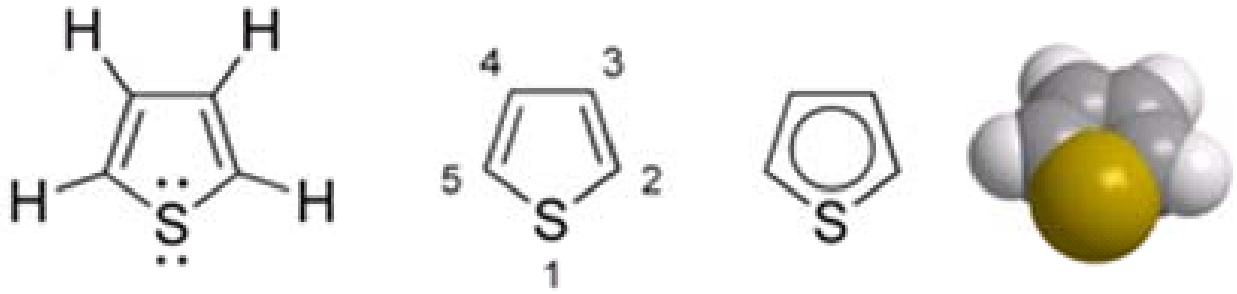
Resonance contributors of pyrrole

◆The N**H** proton in pyrroles is moderately acidic with a pK_a of 17.5.

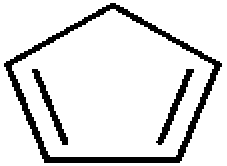
◆Pyrrole undergoes electrophilic aromatic substitution predominantly at the 2 and 5 positions.

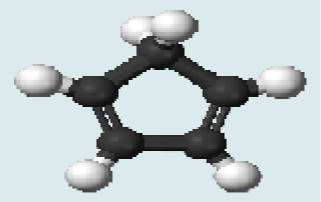

H
H
H
H
O
4
3
5
2
O
1
O

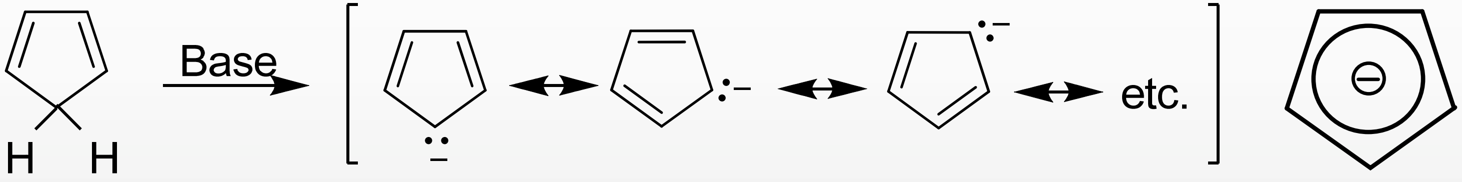

O
O
O
O
O
O


H
H
H
H
S
4
3
5
2
S
1
S

Cyclopentadiene

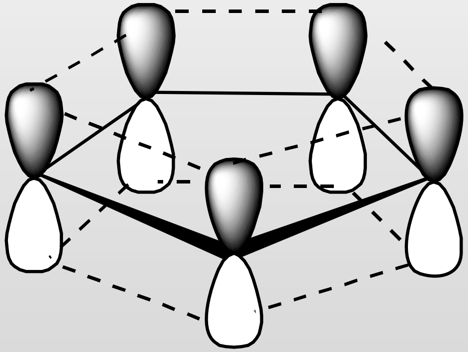






pKa = 16

Cyclopentadienide ion (Cp)



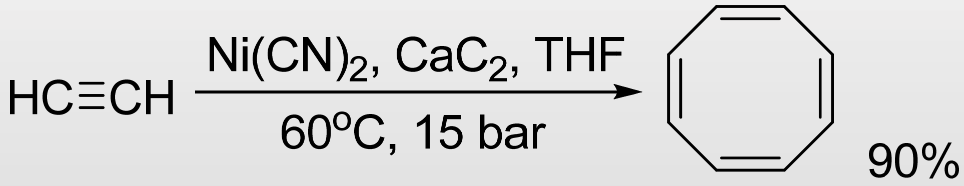
Overlap of five *p* orbitals in molecules such as pyrrole, thiophene, and the cyclopentadienide ion

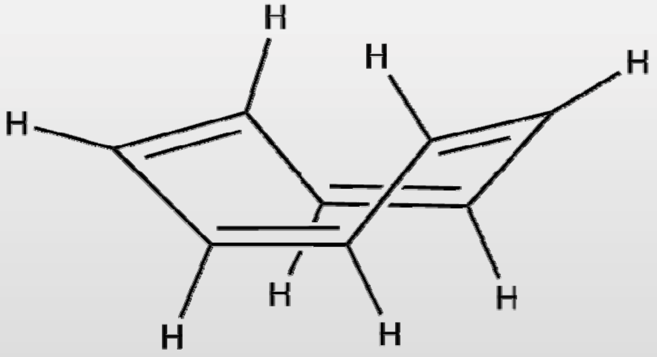
1.2.8 Aromatic systems with electron numbers other than 6

- **Annulene** (轮烯) are completely conjugated monocyclic hydrocarbons. They have the general formula C_nH_n (when *n* is an even number) or C_nH_{n+1} (when *n* is an odd number).

Cyclooctatetraene is also known as [8]annulene.

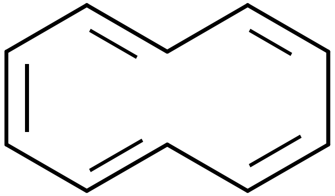
Reppe's synthesis:



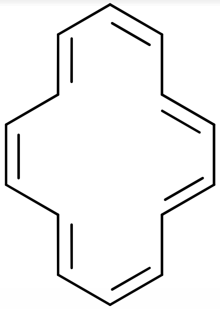


- ♦ not aromatic
- ♦ addition reaction

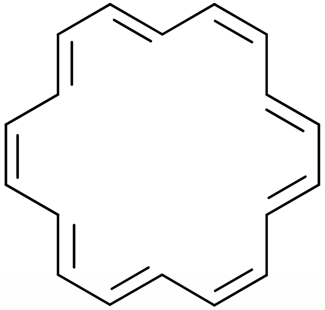
Cyclooctatetraene in its native "tub-shaped" conformation.



Cyclodecapentaene
[10]annulene, $C_{10}H_{10}$
aromatic ?



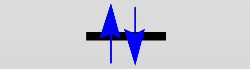
[14]annulene
aromatic



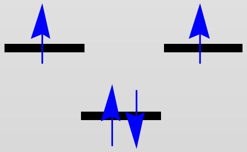
Cyclooctadecanonaene
[18]annulene, $C_{18}H_{18}$
aromatic

Hückel's rule

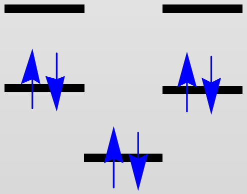
Electron rings will constitute an aromatic system only if the number of electrons in the ring is of the form 4n+2, where *n* is zero or any position integer.



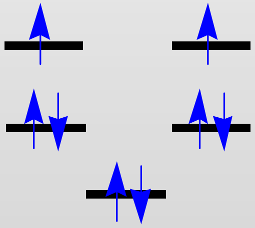
Duet
(aromatic)



Quartet
(diradical)



Sextet
(aromatic)



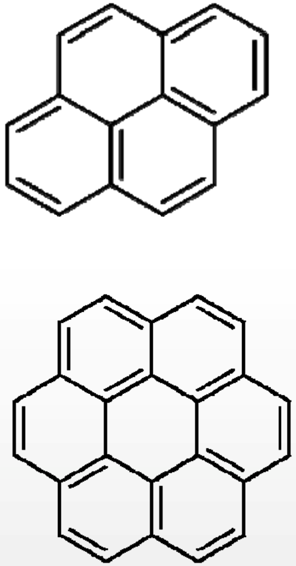
Octet
(diradical)

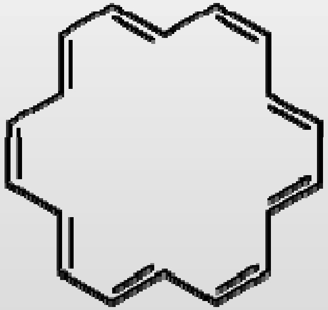
Hückel‘s rule is not valid for many compounds containing more than three fused aromatic nuclei in a cyclic fashion. For example, pyrene contains 16 conjugated electrons (8 bonds), and coronene contains 24 conjugated electrons (12 bonds). Both of these polycyclic molecules are aromatic even though they fail the $4n+2$ rule.

Look for aromaticity:

a) the presence of a diamagnetic ring current;
b) equal or approximately equal bond distances, except when the symmetry is disturbed by a hetero atom or other way;
c) planarity;
d) chemical stability;
e) the ability to undergo aromatic substitution.

Hückel’s rule can only be theoretically justified for monocyclic systems.

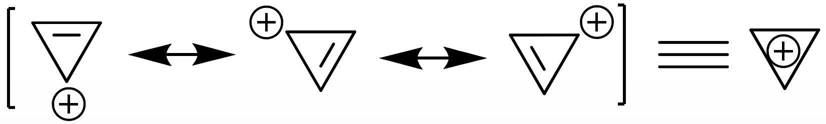


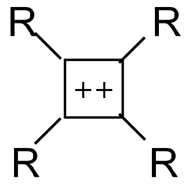


[18]annulene

Shiefing effect:
6 inner protons at −3 ppm

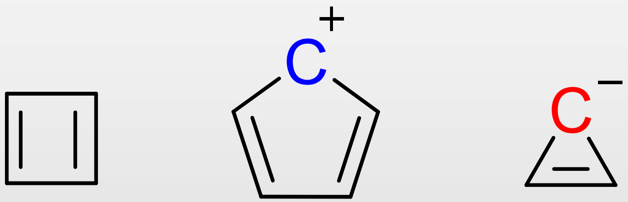
i. System of two electrons, $4n+2$ (n =0)



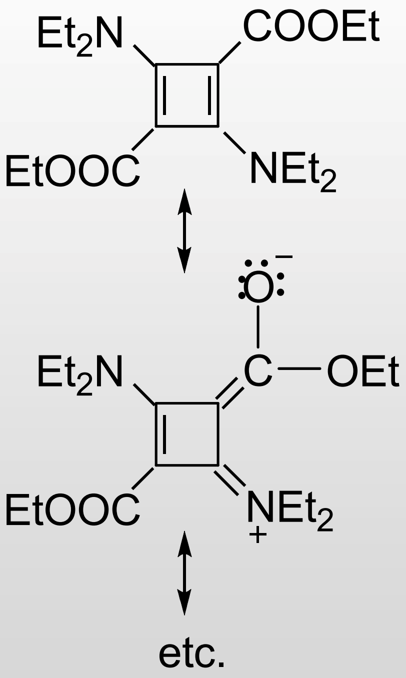


(R = Me, Ph)

ii. Systems of four electrons. Antiaromaticity



Antiaromatic molecules are cyclic systems containing alternating single and double bonds, where the pi electron energy of antiaromatic compounds is higher than that of its open-chain counterpart. IUPAC criteria: $4n$ π electrons, cyclic, planar, and a conjugated pi electron system.

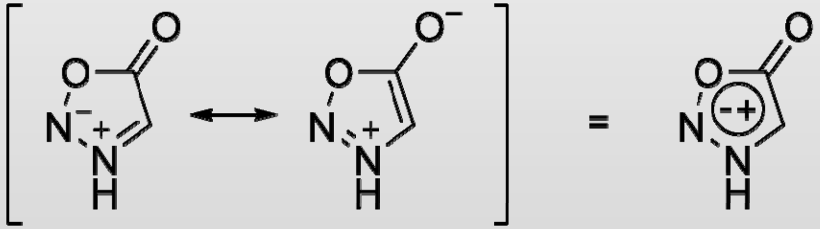


Push-pull effect

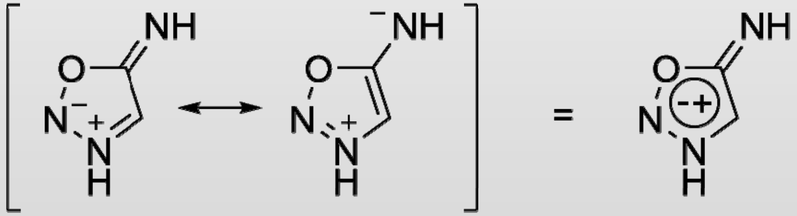
1.2.9 Other aromatic compounds

i) Mesoionic compounds (介离子化合物)

Mesoionic chemical compounds are dipolar five- or six- membered heterocyclic compounds in which both the negative and the positive charges are delocalized. A completely uncharged structure cannot be written and mesoionic compounds cannot be represented satisfactorily by any one mesomeric structure.

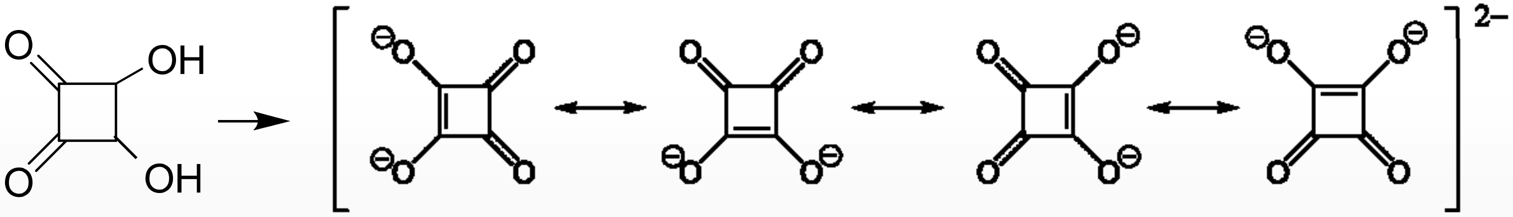


Sydnone 斯德酮



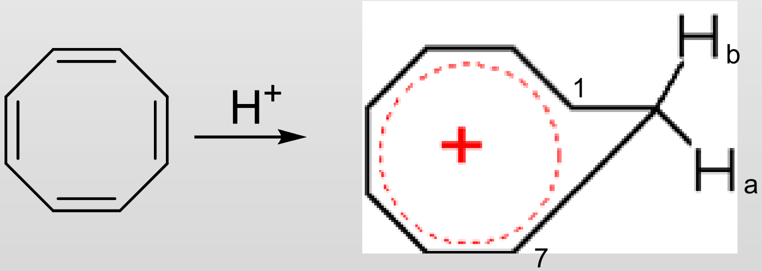
Sydnone imine

ii) The dianion of squaric acid 方酸



pK_1 = ~1.5; pK_2= ~3.5, which means that even the second proton is given up much more readily than the proton of acetic acid.

iii) Homoaromatic compounds 同芳香化合物



NMR: H_b -0.3 ppm; H_a 5.1 ppm; H_1 and H_7 6.4 ppm; H_2-H_6 8.5 ppm

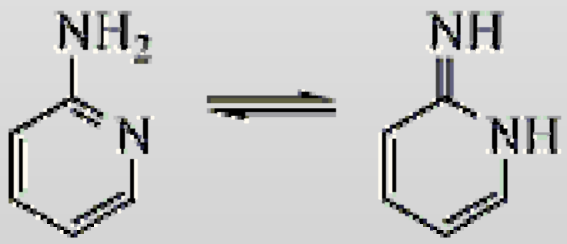
1.2.10 Tautomerism 互变异构

Tautomers are isomers of organic compounds that readily interconvert by a chemical reaction called tautomerization. Commonly this reaction results in the formal migration of a **hydrogen atom or proton**, accompanied by a switch of a single bond and adjacent double bond.

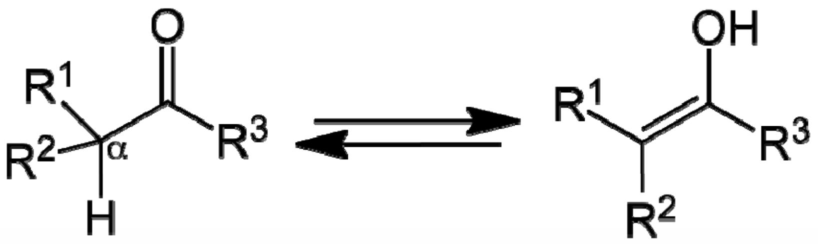
Enol form Keto form

Lactam form Lactim form

Amide form Imidic acid form



Amine form Imine form

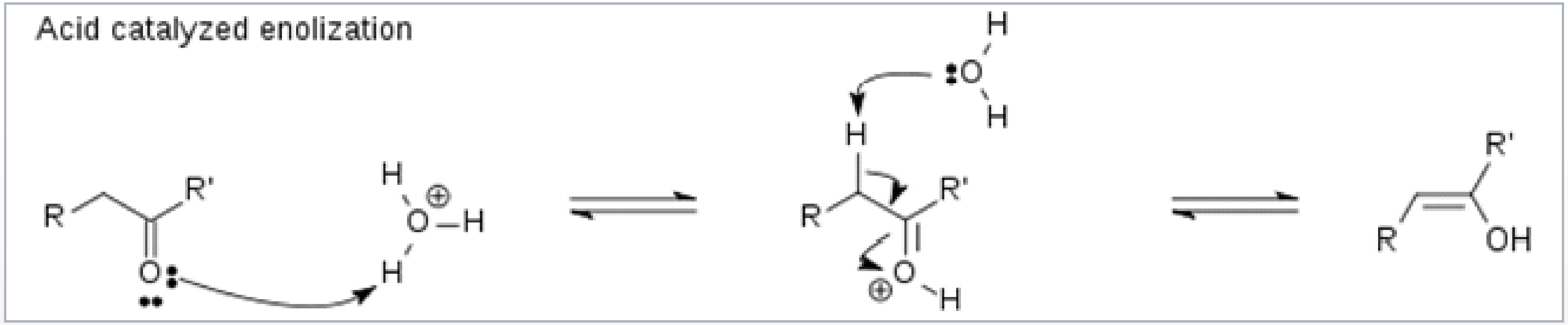


Keto-enol tautomerism. keto form (left); enol (right).

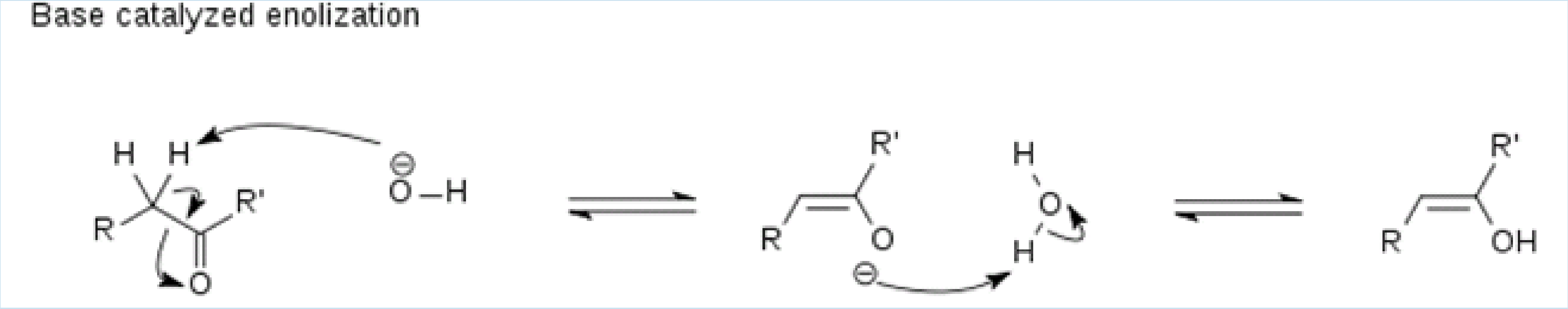
The enol content of some carbonyl compounds

Compound	Enol content/%	Compound	Enol content/%
Acetone	6×10^{-7}	$CH_3COOC_2H_5$	No enol found
$PhCOC\mathbf{H}_3$	1.1×10^{-6}	$CH_3COC\mathbf{H}_2COOC_2H_5$	8.4
Cyclopentanone	1×10^{-6}	$CH_3COC\mathbf{H}_2COCH_3$	80
$C\mathbf{H}_3CHO$	6×10^{-5}	$PhCOCH_2COCH_3$	**89.2**
Cyclohexanone	4×10^{-5}	$C_2H_5OOCH_2COOC_2H_5$	7.7×10^{-3}
butanal	5.5×10^{-4}	$NCCH_2COOC_2H_5$	2.5×10^{-1}
$(CH_3)_2CHCHO$	1.4×10^{-2}	Indane-1-one	3.3×10^{-8}
$Ph_2C\mathbf{H}CHO$	**9.1**	$CH_2(COONH_2)_2$	No enol found

Acid catalyzed enolization



Base catalyzed enolization

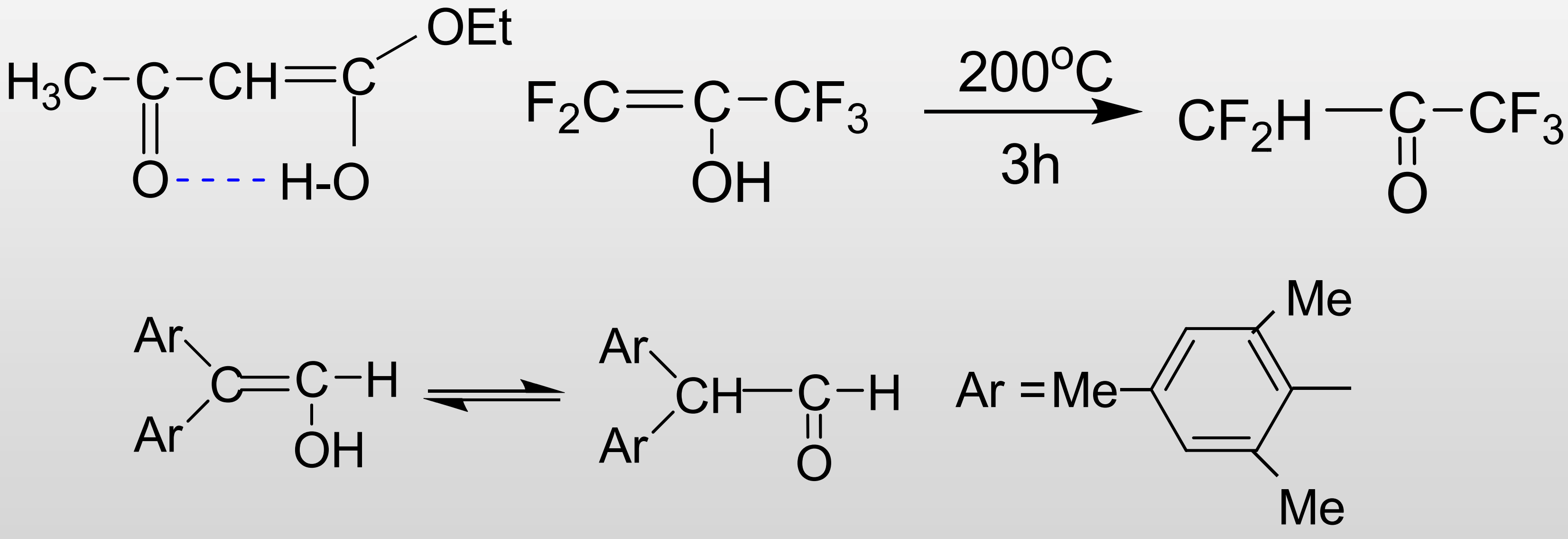


Three main types of the more stable enoles

i. Molecules in which the enolic double bond is in conjugation with another double bond. The enol is also stabilized by internal hydrogen bonding.

ii. Molecules that contain two or three bulky aryl groups.

iii. Highly fluorinated enols

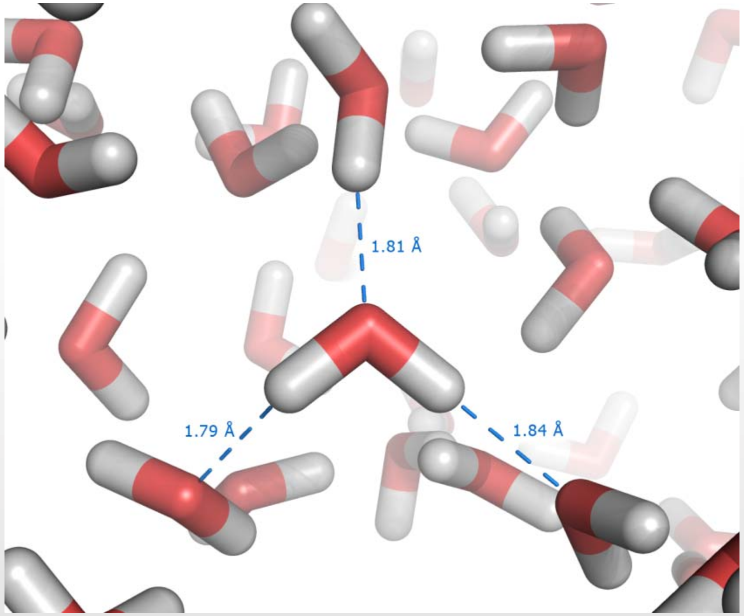


1.3 Bonding weaker than covalent bond

Noncovalent bonding

- In general, noncovalent bonding refers to a variety of interactions that are not covalent in nature between molecules or parts of molecules that provide force to hold the molecules or parts of molecules together, usually in a specific orientation or conformation. Noncovalent bonding is the dominant type of bonding in supramolecular chemistry. These noncovalent interactions include:
  - hydrogen bonds
  - ionic bonds
  - hydrophobic interactions
  - Van der Waals forces (i.e. "London dispersion forces“)
  - Dipole-dipole bonds

1.3.1 Hydrogen Bonding



Snapshot from a simulation of liquid water. The dashed blue lines from the molecule in the center of the picture represent hydrogen bonds.

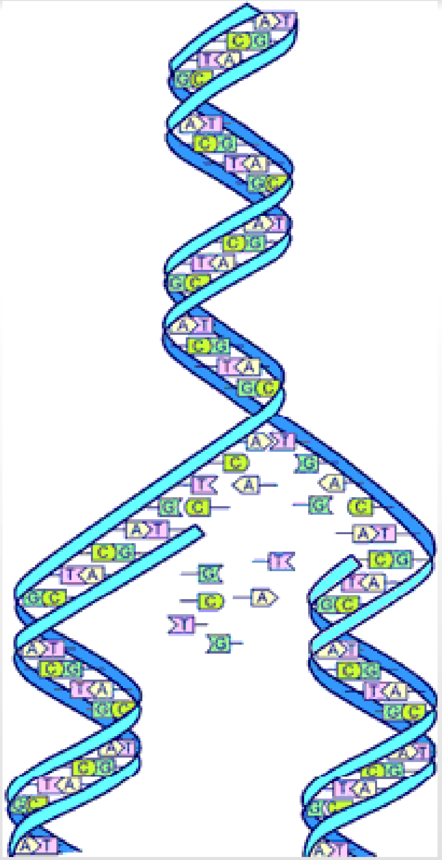
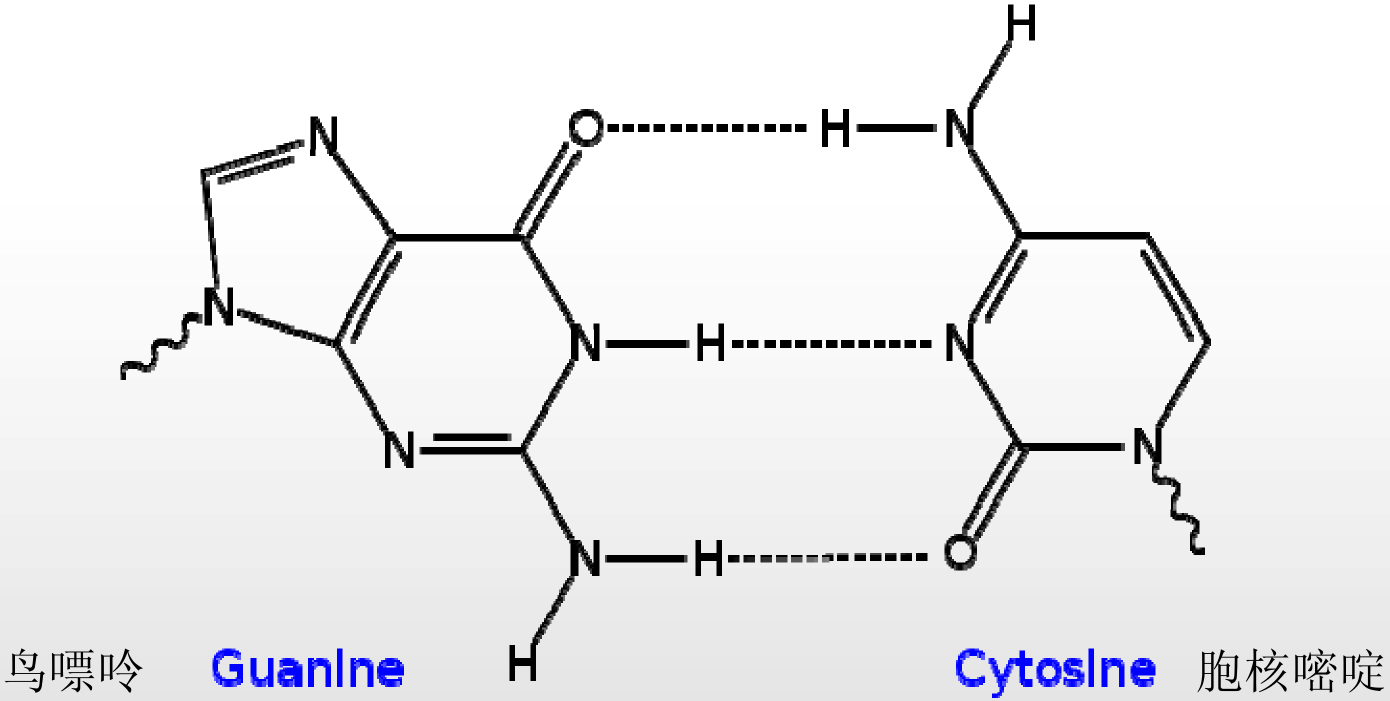


Image of a DNA chain which shows the double helix replicating itself.

PresentationPoint

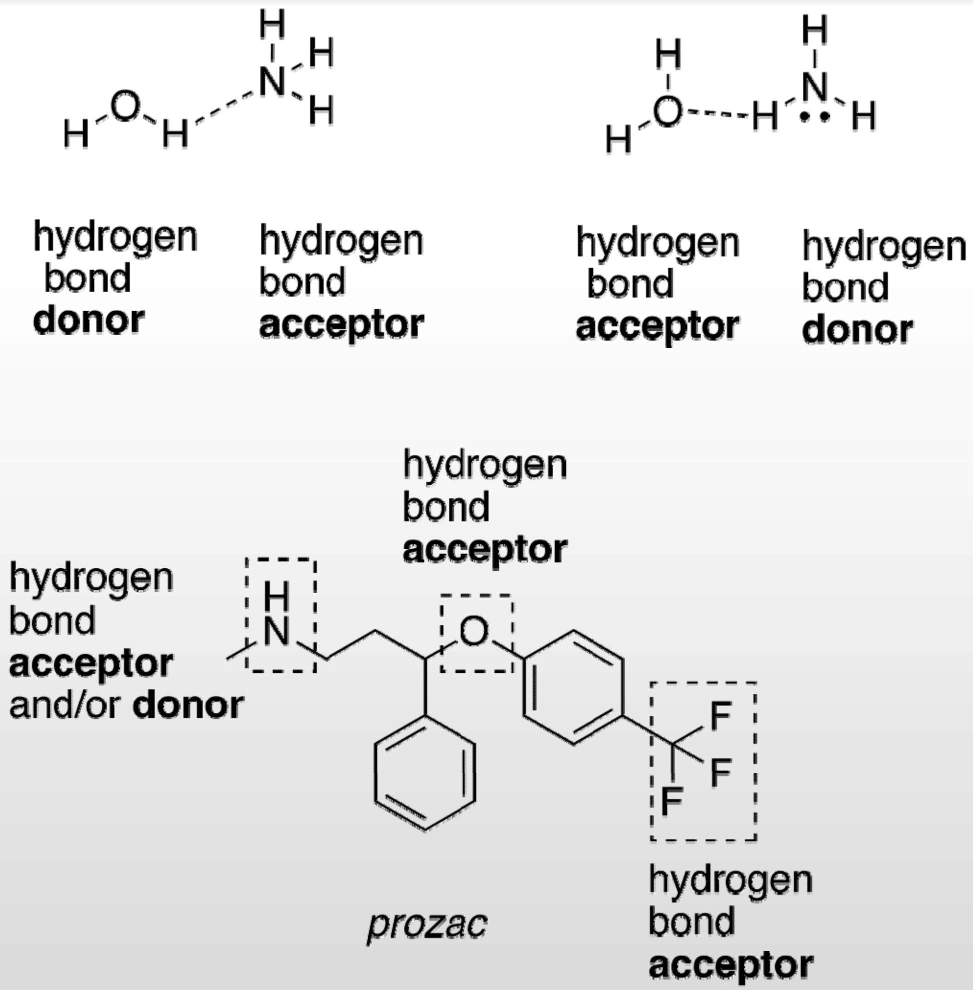


Hydrogen bonding between guanine and cytosine, one of two types of base pairs in DNA.

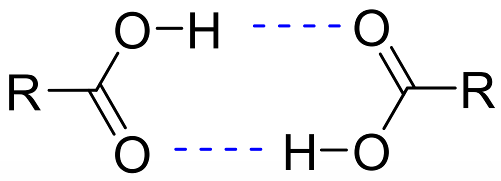
- A hydrogen bond is the attractive interaction of a hydrogen atom with an electronegative atom, like nitrogen, oxygen or fluorine.

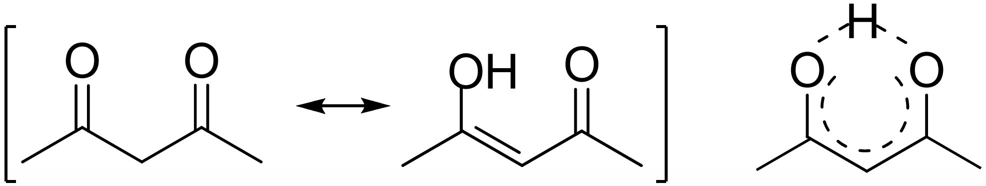
- A hydrogen bond strength: 25-30 kJ/mol (covalent bond 200-400 kJ/mol)

- Hydrogen bonds can exist in the solid and liquid phases and in solution.



Examples of hydrogen bond donating (donors) and hydrogen bond accepting groups (acceptors)





Intermolecular H-bonding:
Carboxylic acids often
form dimers in vapor phase.

Intramolecular H-bonding
in acetylacetone helps to stabilize
the enol tautomer.

♦ Hydrogen bonds can vary in strength from very weak (1-2 kJ mol^{-1}) to extremely strong (>155 kJ mol^{-1}):

F—H···:F	(155 kJ/mol)
O—H···:N	(29 kJ/mol)
O—H···:O	(21 kJ/mol)
N—H···:N	(13 kJ/mol)
N—H···:O	(8 kJ/mol)
HO—H···:OH_3^+	(18 kJ/mol)

The hydrogen bond strength is dependent on temperature, pressure, bond angle, and environment (usually characterized by local dielectric constant).

Effect of hydrogen bonding

1. Intermolecular hydrogen bonding raises boiling points and frequently melting points. NH_3, H_2O, HF (PH_3, H_2S, and HCl)
2. Hydrogen bonding → solubility: ammonia in water
3. Hydrogen bonding causes lack of ideality in gas and solution law. Dimer formation in carboxylic acids and hexamer formation in hydrogen fluoride.
4. Hydrogen bonding changes spectral absorption positions.
5. Hydrogen bonding, especially the intramolecular variety, changes many chemical properties.

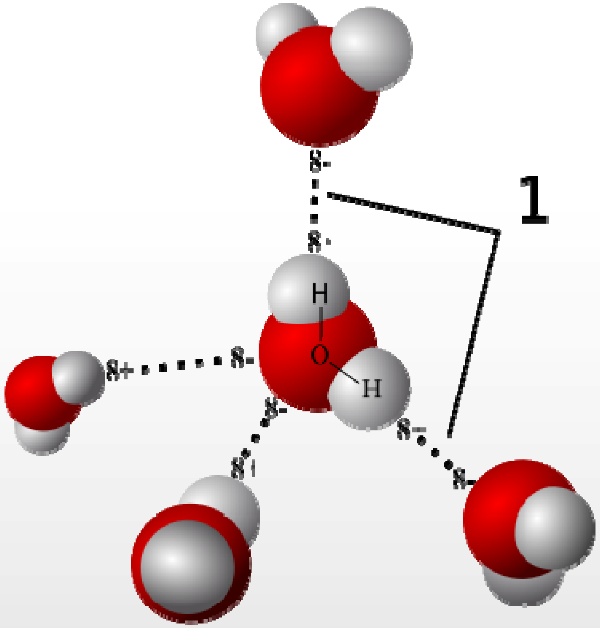
For example:

1) the large amount of enol present in the certain tautomeric equilibria;

2) the conformation of molecules

Detection of hydrogen bonding

- Measurements of dipole moments
- Solubility behavior
- Freezing-point lowering
- Heats of mixing
- Infrared spectroscopy
- Raman
- NMR



Example: alcohol, phenol:

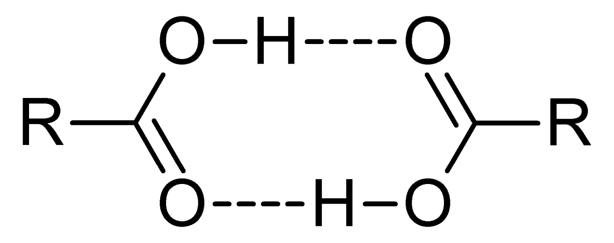
free O—H 3590~3650 cm^{-1}

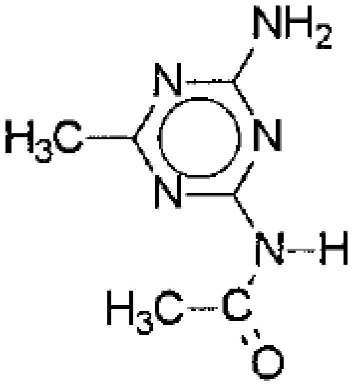
H-bonded O—H ~50-100 cm^{-1} lower

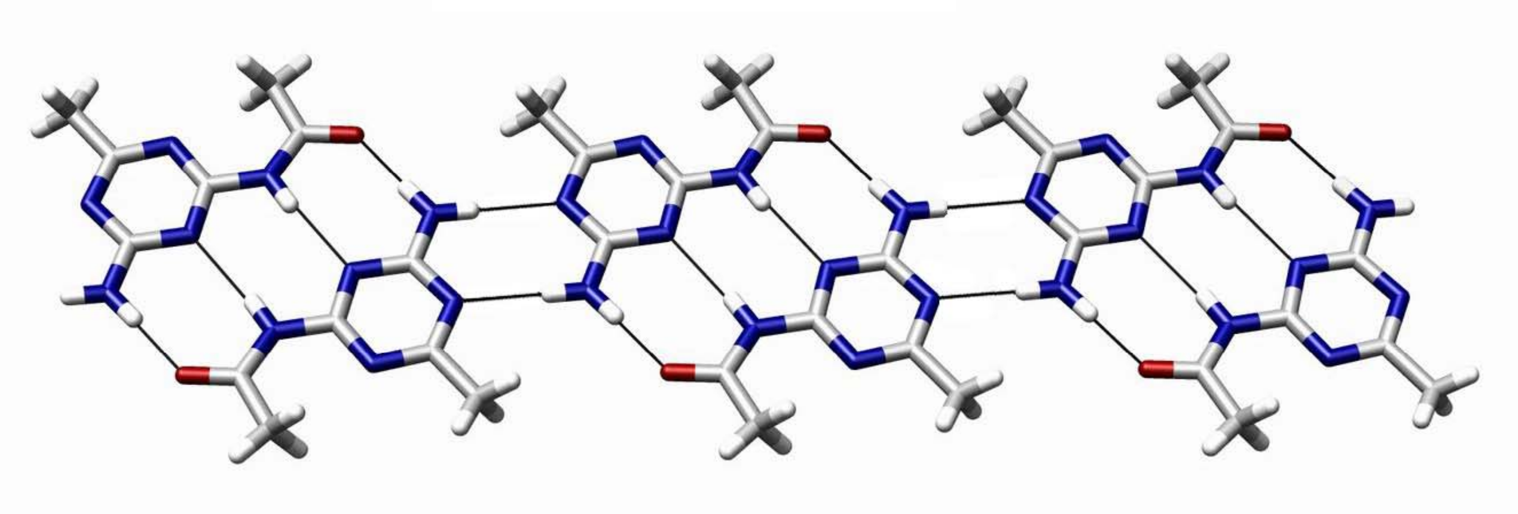
➢ Partial hydrogen bonding: two peaks

➢ Intra- and intermolecular hydrogen bonding:

[concentration] ~ peak strength

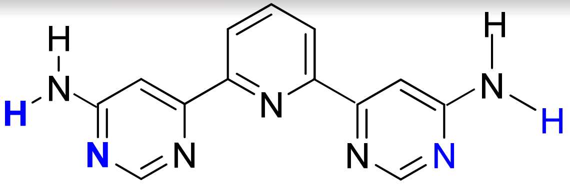






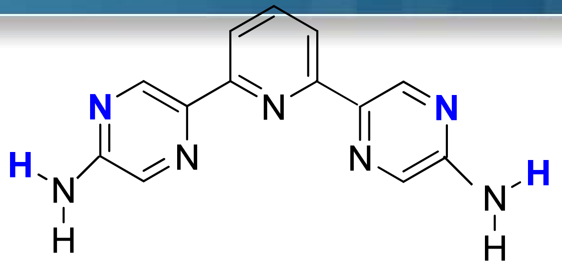
An example of a molecular self-assembly through hydrogen bonds reported by Meijer and coworkers.

Angew. Chem. Int. Ed. 1998, **37** (1-2): 75–78.



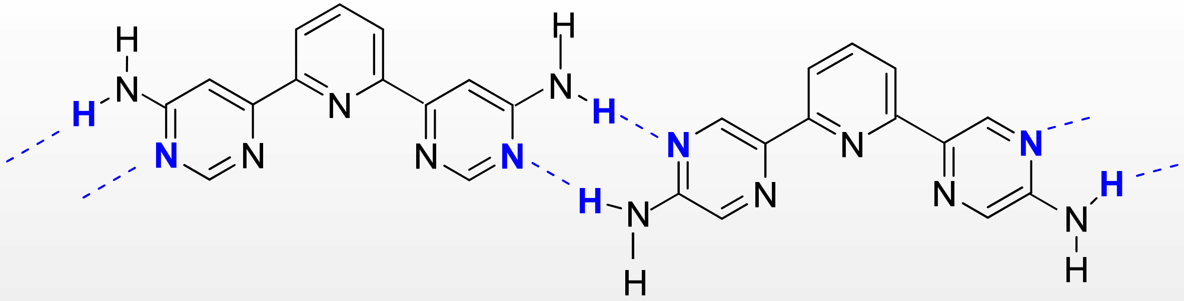
amino¨Cpyrimidine

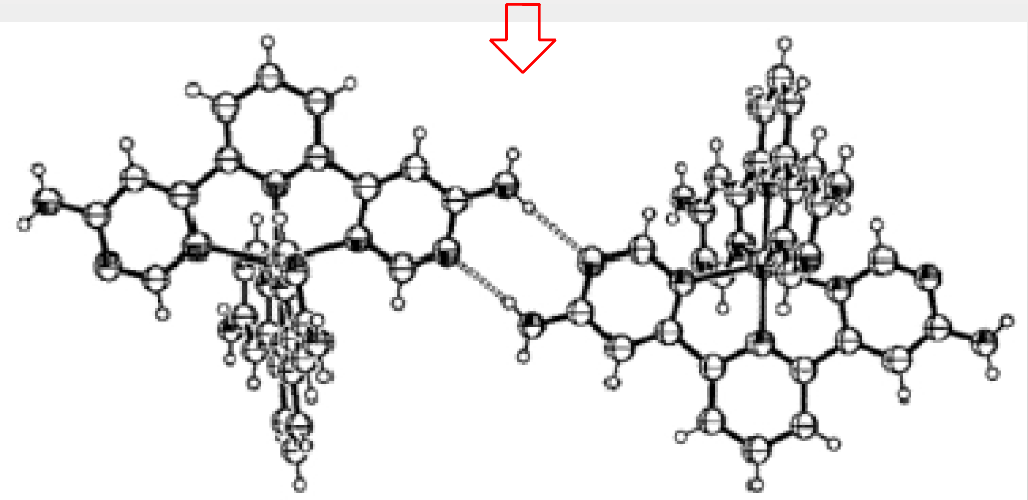
嘧啶



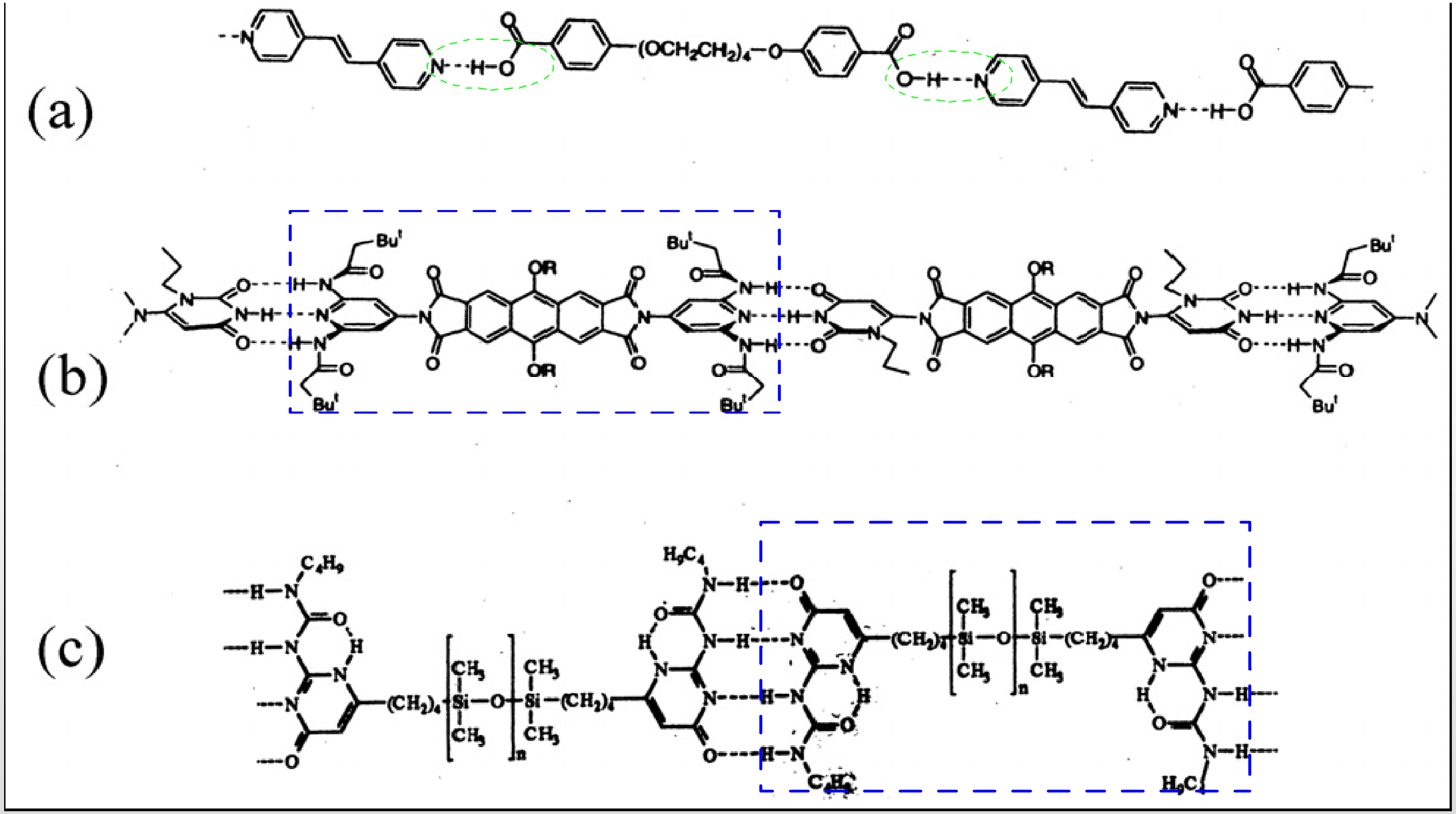
amino¨Cpyrazine

吡嗪





U. Ziener et al *Chem.–Eur. J.* 2000, **6**,4132–4139.



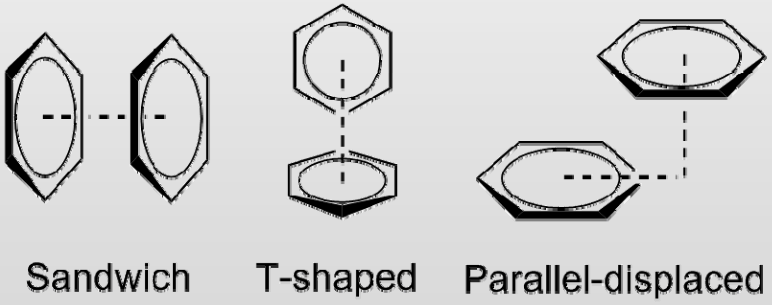
Supramolecular polymers stabilized by main-chain links based on (a) one, (b) three, and (c) four H-bonds.

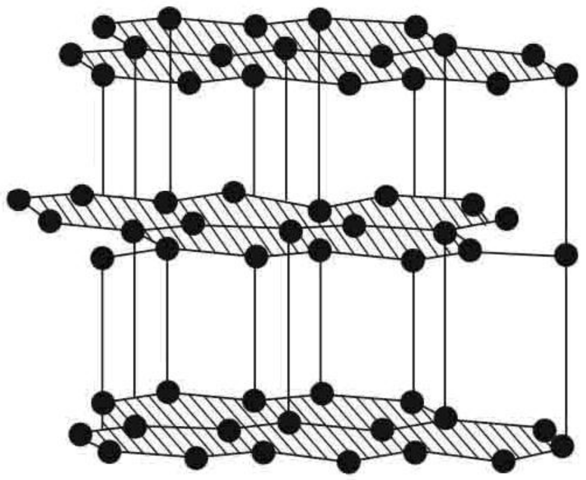
PresentationPoint

1.3.2 π-π stacking

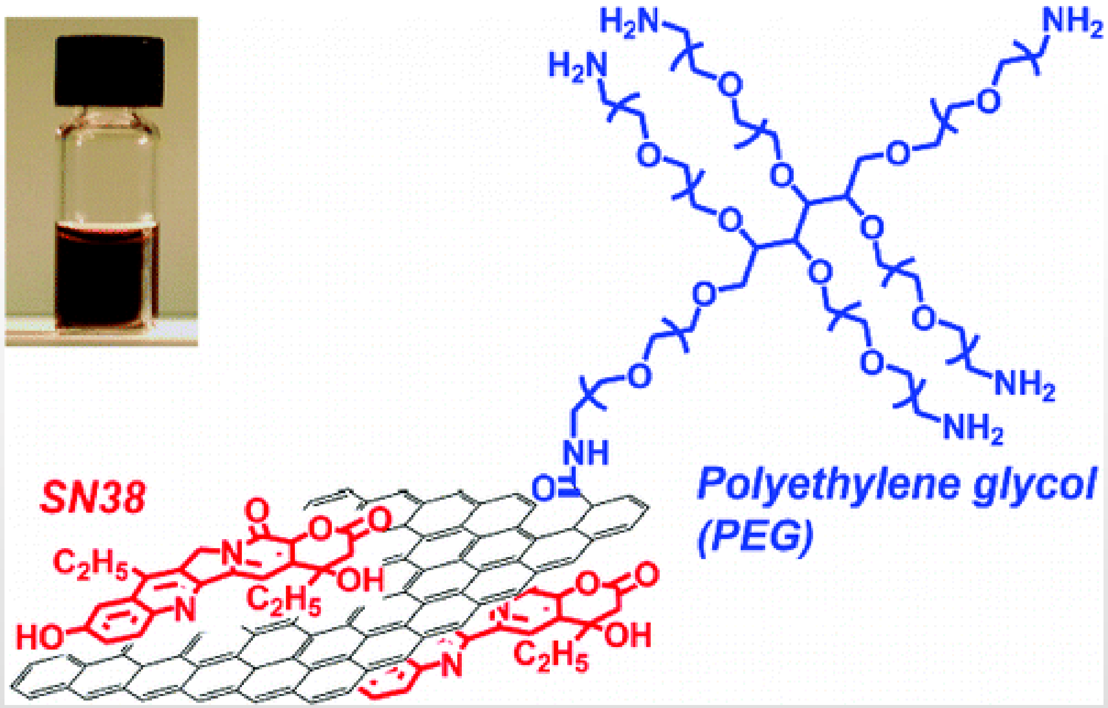
π–π stacking, also called **pi stacking** refers to attractive, noncovalent interactions between aromatic rings.

Benzene dimer is the prototypical system for the study of pi stacking, and is experimentally bound by 8–12 kJ/mol





石墨原子排列图



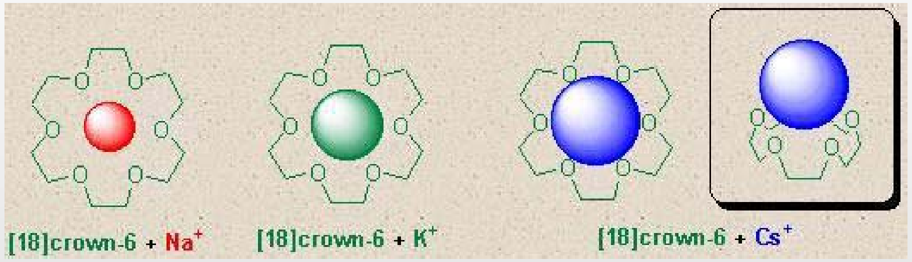
NGO−PEG conjugate is stable in various biological solutions, and used for attaching hydrophobic aromatic drugs via π-π stacking

JACS, 2008, *130* (33), 10876–10877

1.3.3 Addition compound

- **Electron donor-acceptor complexes (配位化合物)**

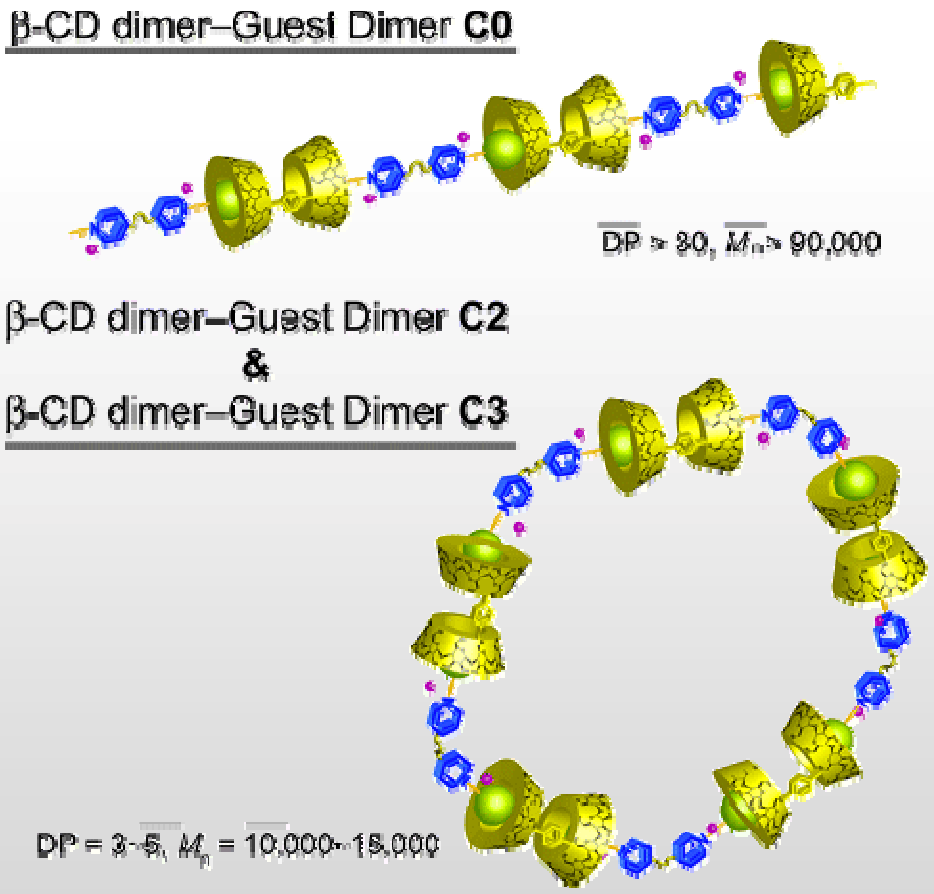
- **Crown ether (冠醚) complexes**



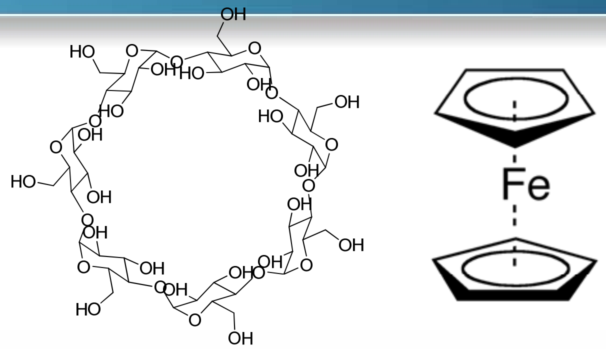
- **Inclusion compounds**

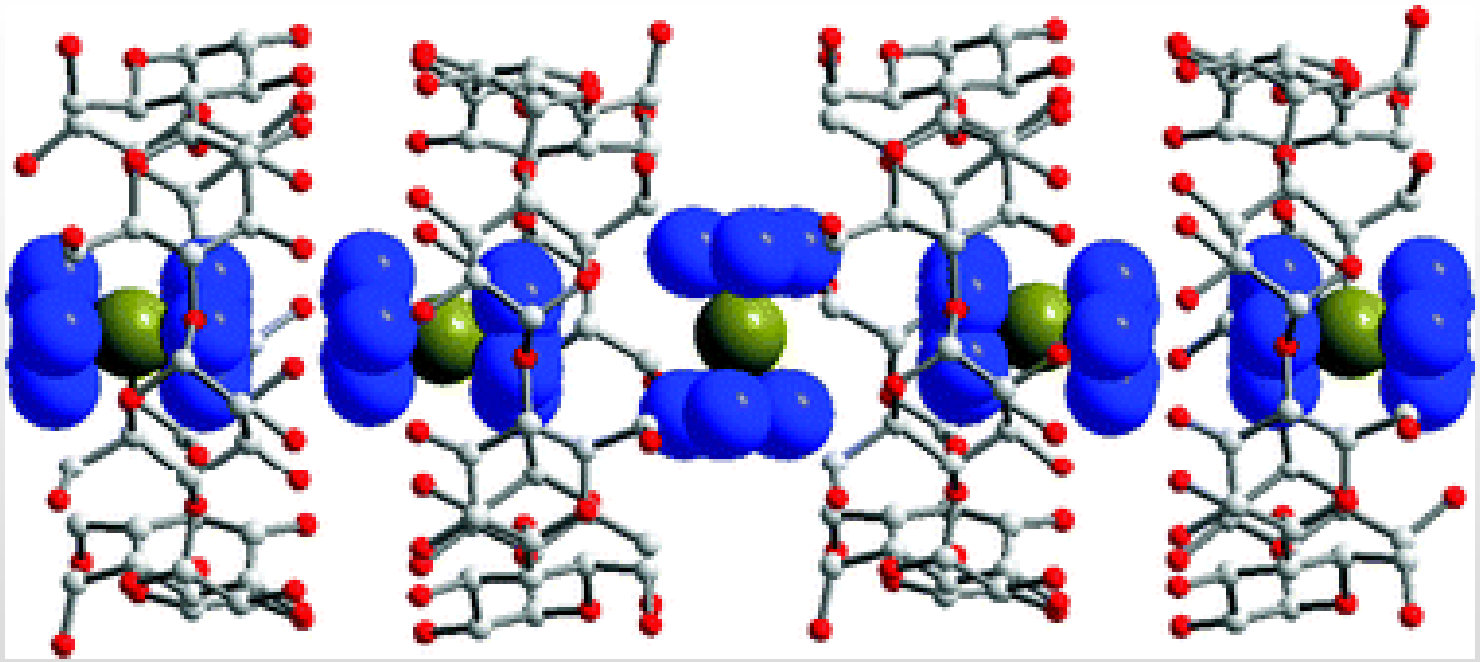
- **Catenanes and rotaxanes**

Inclusion compounds



Macromolecules, **2005**, *38* (14), 5897–5904

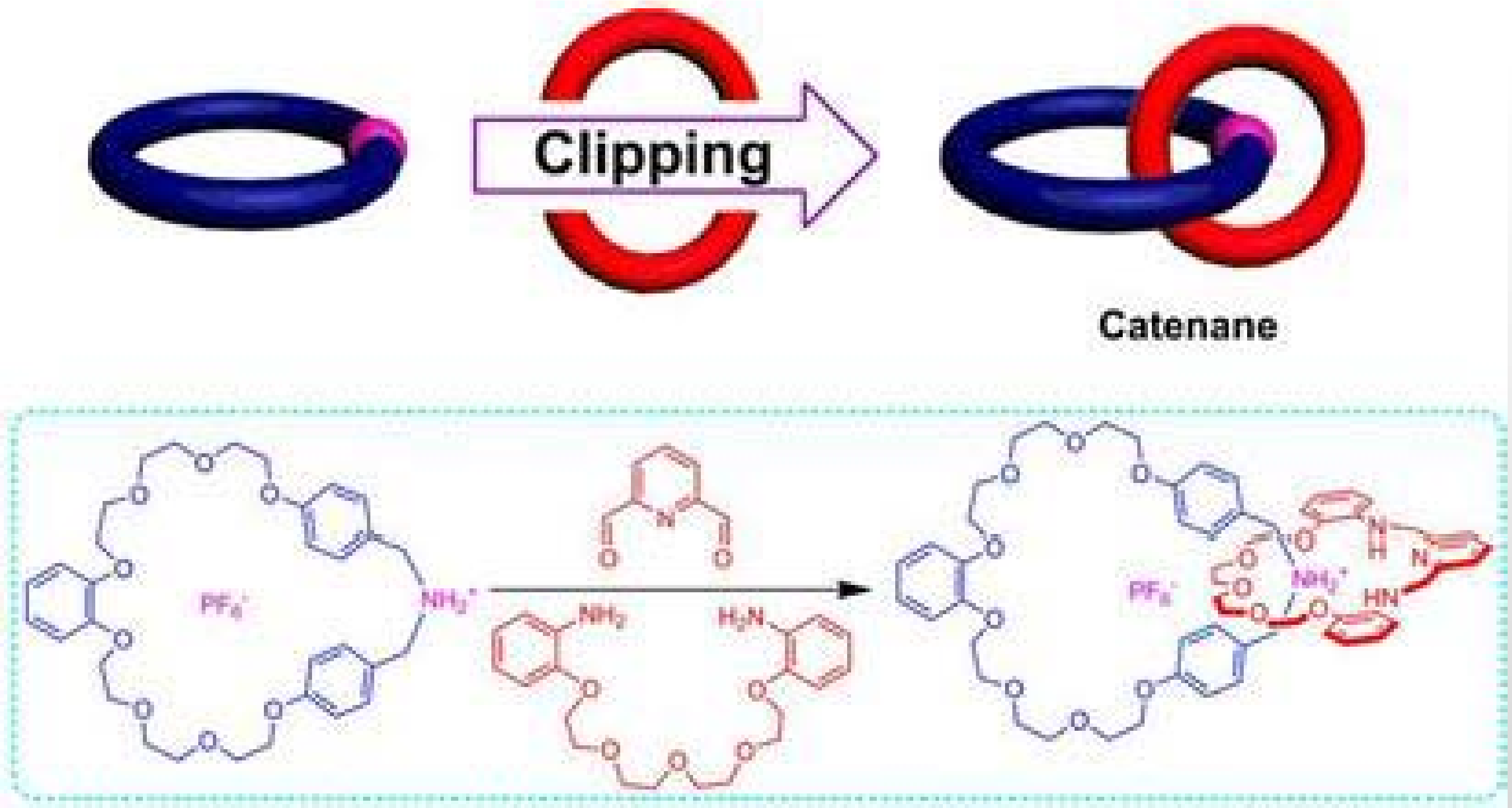




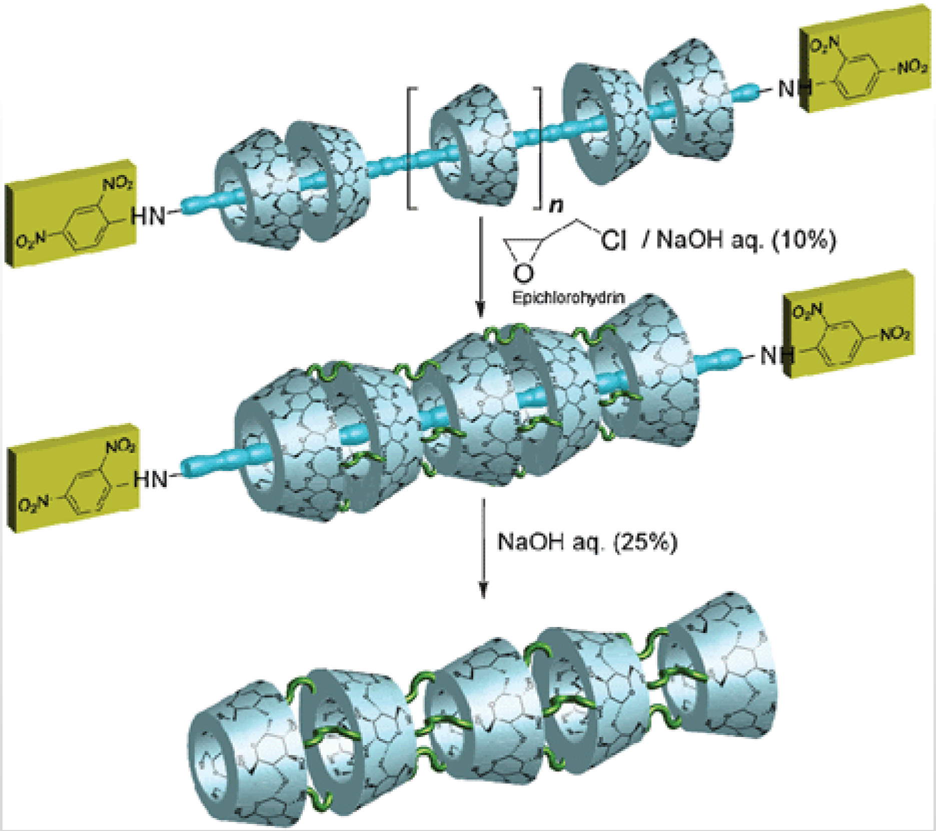
A unique tetramer of 4:5 β-cyclodextrin–ferrocene in the solid state

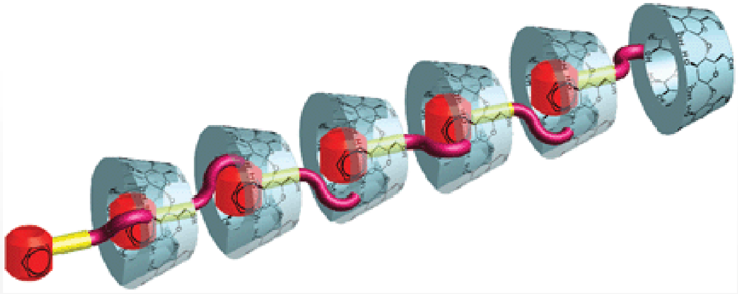
Chem. Commun., 2005, (17), 2211-2213

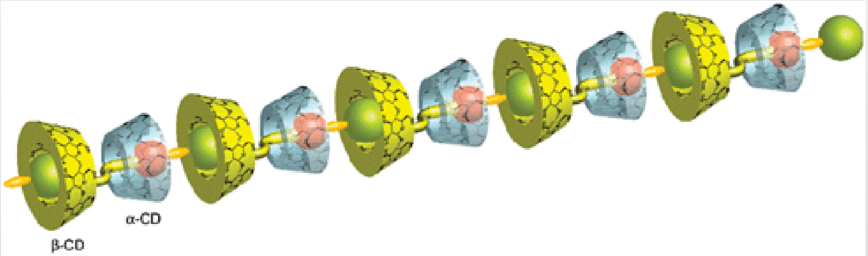
Catenanes



Rotaxanes





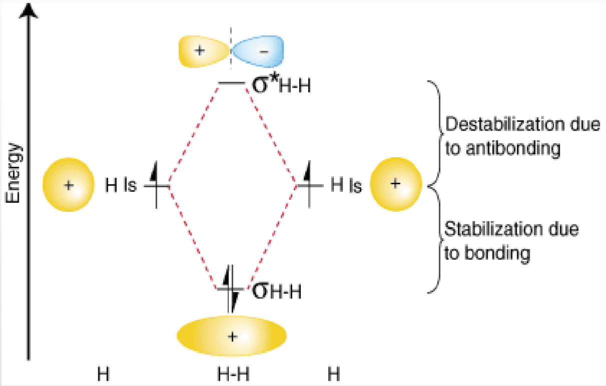


Chem. Soc. Rev., 2009, **38**, 875-882 by Harada A et al.

Overview of Chapter 1

- 何为共价化学键？原子核对电子的共享
- **2**个理论：价键理论（**8**电子规则）与分子轨道理论（*前线*、*休克尔理论*，一般了解，记住几个要点）

bonding orbitals, **anti-bonding orbitals**, and **non-bonding orbitals**



能画出H_2、 N_2、 O_2、 F_2、**1,3-**丁二烯、苯的分子轨道

分子轨道理论能够解释一些价键理论不能解释的问题，如：氧气的顺磁性、甲烷的光电子能谱、**4n+2**规则等

任何理论都有局限性，要活学活用！

Overview of Chapter 1

重要概念：

- 电负性→偶极距→场效应
- 轨道的杂化， N，O也能sp^3杂化，NH_3，H_2O；P的sp^3d、S的sp^3d^2杂化
- 键长（大致什么范围？）、键能（大致什么范围？）、键角（杂化对其的影响）
- 非定域化学键：多个原子共享电子
- 共振式（又称极限式、正则式等）：用定域化学键来表示非定域化学键
- 共振能：实际分子与最稳定共振式之间的能量差异，能量更低，共轭效应
- 共振式的书写规则
- 超共轭效应，一般书写共振式不考虑
- **Ylide** 试剂与**Ylide** （**Wittig**）反应
- 芳香性的判定
- 芳香族化合物共振式的书写，判断取代反应的位点
- 氢键：一般**N**、**O**、**F**与极化的**H**原子，键能？应用**?**