ORGANICS

General Chemistry I, Lecture Series 11

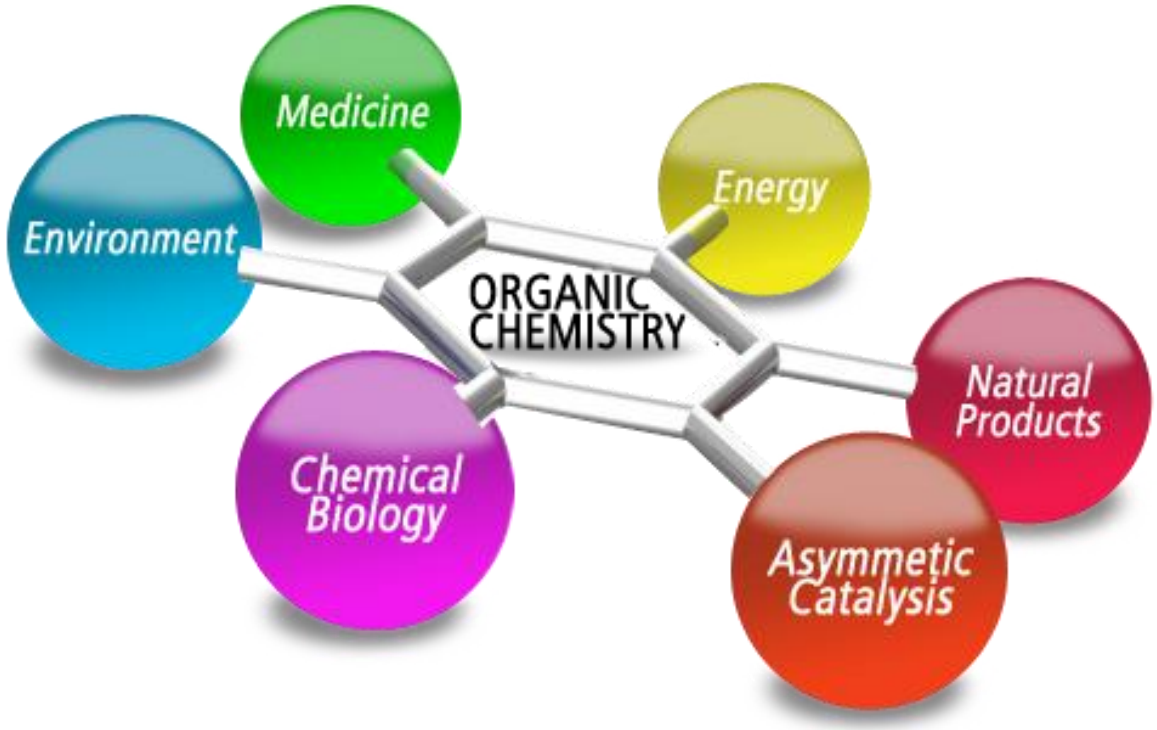
Pengxin Liu

Reading:

OGB8 §7

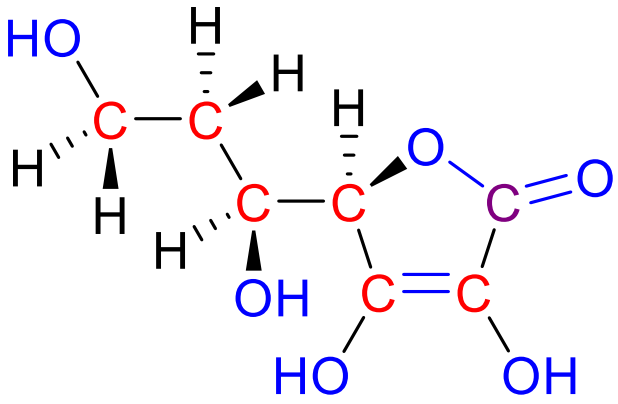
Outline

- Organic compounds (the nature of bonding)
- Interaction between functional groups (conjugation)
- Resonance structures (1930s)



The organic compounds

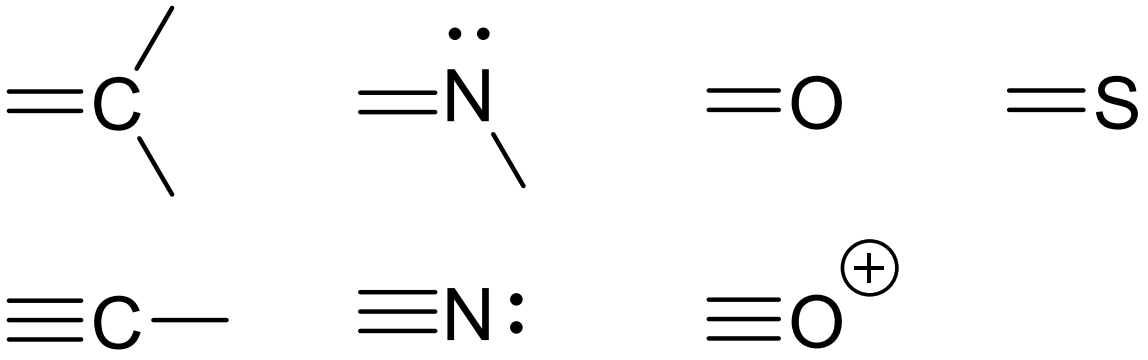
- The carbon chain
- The functional groups 官能团



Ascorbic Acid 抗坏血酸
(Vitamin C 维生素C)

Why Carbon?

Electrons	0	1	2	3	4	5	6	7	8
Valence	0	1	2	3	4	3	2	1	0
Examples	H^+			C^+	N^+	O^+			
		H		B	C	N	O	F	Ne
					B^-	C^-	N^-	O^-	F^-

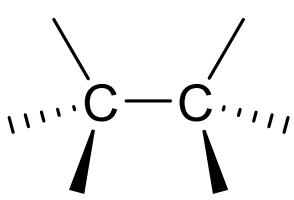


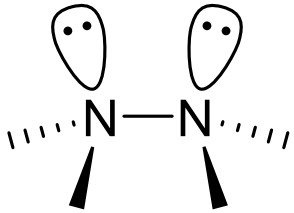
Why Carbon?

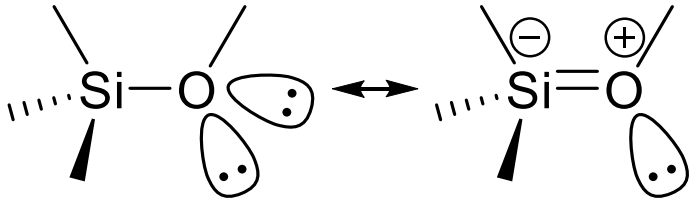
Organic Chemistry:
The study of the compounds of carbon.

Average Bond Dissociation Energies ($kJ \cdot mol^{-1}$)

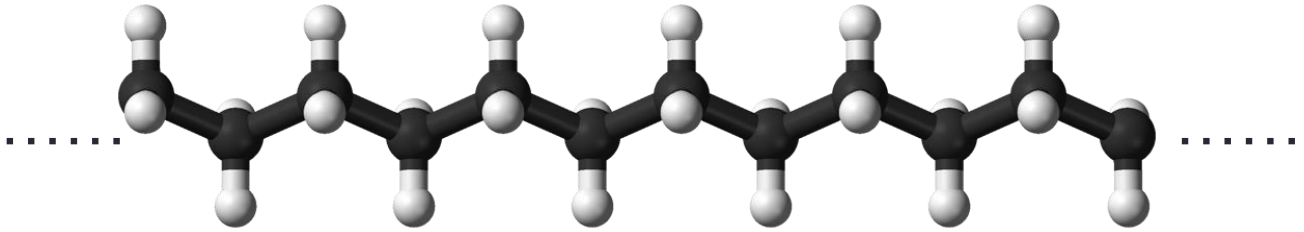
H—H	C—H	C—C	N—N	O—O	F—F	Si—O	P—O
436	414	347	161	146	153	460	377



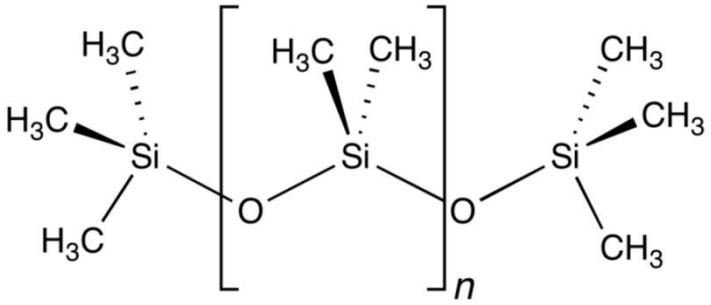




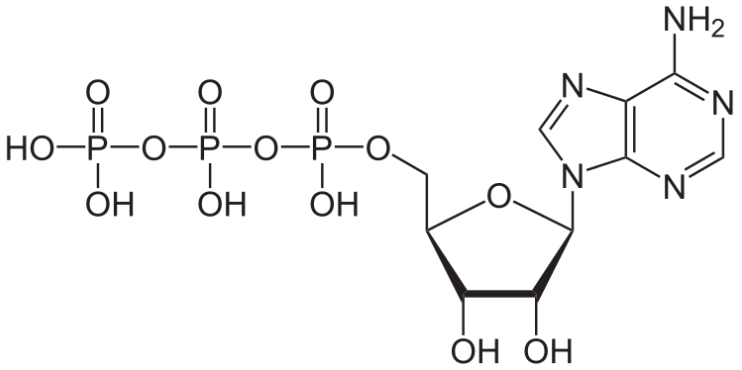
Long, Long Chains



Polyethylene 聚乙烯



Silicone 硅油，硅橡胶



Adenosine triphosphate
三磷酸腺苷 (ATP)

Long, Long Chains

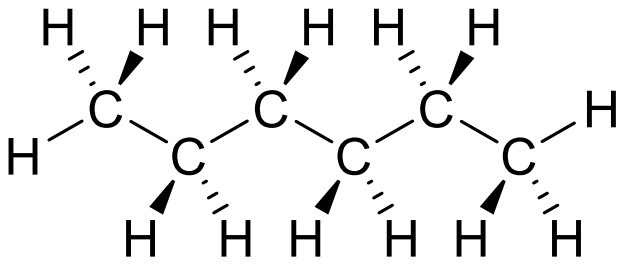
烃 tīng = 碳 + 氢 hydrocarbon （not carbohydrate)

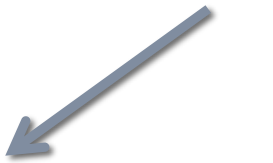
烷 alkane C_nH_{2n+2}
烯 alkene C_nH_{2n}
炔 alkyne C_nH_{2n-2}

取代烃 Substituted hydrocarbons
卤代烃 Haloalkanes or Halogen substituted hydrocarbons

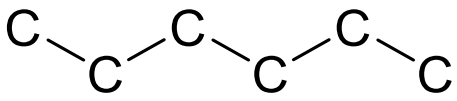
Alkane

烷 alkane C_nH_{2n+2}

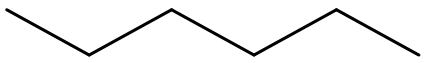




$CH_3CH_2CH_2CH_2CH_2CH_3$



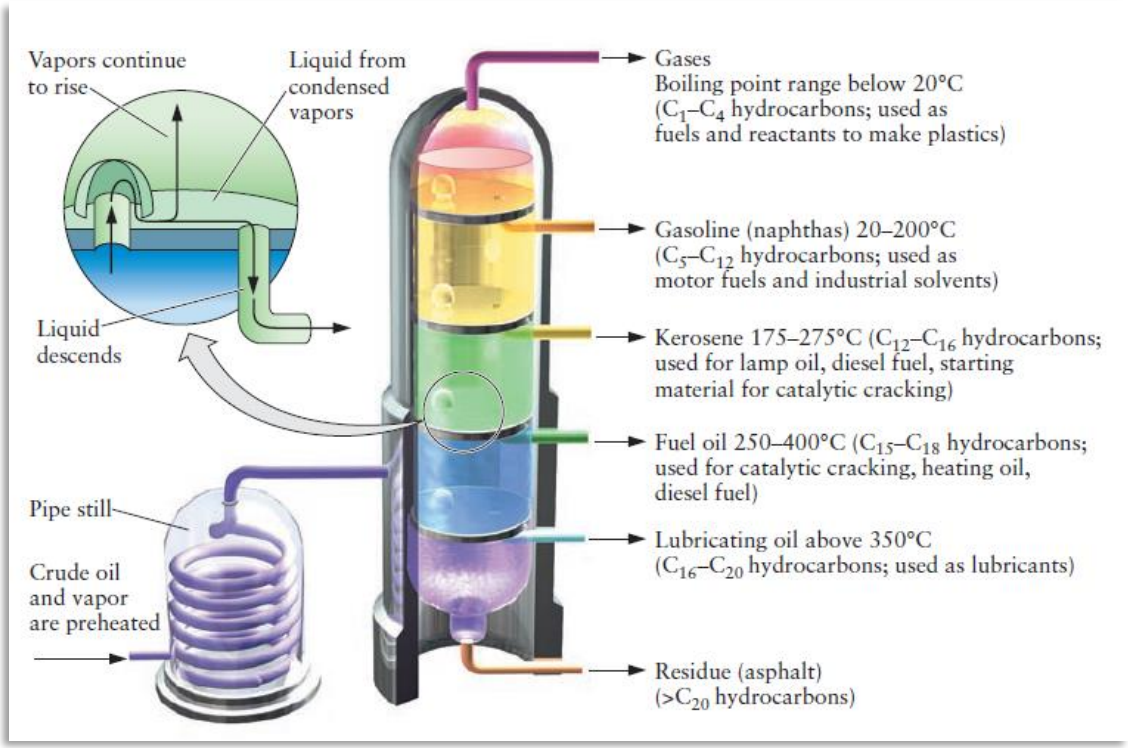
$CH_3(CH_2)_4CH_3$, C_6H_{14}



n	Name
1	Methane 甲烷
2	Ethane 乙烷
3	Propane 丙烷
4	Butane 丁烷
5	Pentane 戊烷
6	Hexane 己烷
7	Heptane 庚烷
8	Octane 辛烷
9	Nonane 壬烷
10	Decane 癸烷
11	Undecane 十一烷
12	Dodecane 十二烷
13	Tridecane 十三烷
14	Tetradecane 十四烷
15	Pentadecane 十五烷

Alkane

Distillation of petroleum



Butane C_4
B.p.沸点 ~0°C

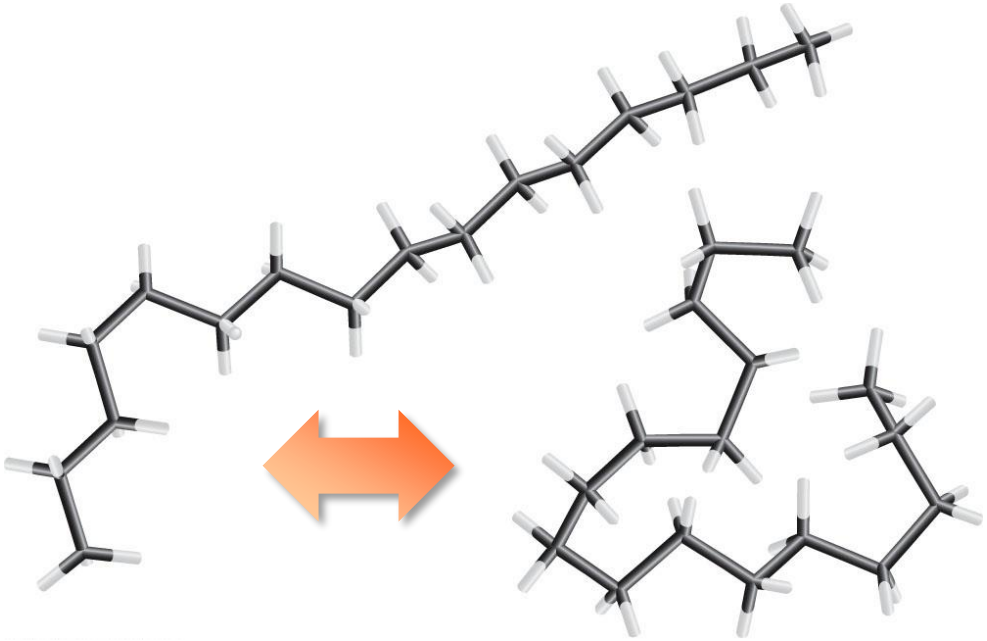
Diesel C_{10}–C_{22}
B.p. 180–370°C

Vaseline C_{20}–C_{30}
M.p. ~37°C

HDPE $C_{\sim100000}$
M.p. ~130°C

Alkane (2)

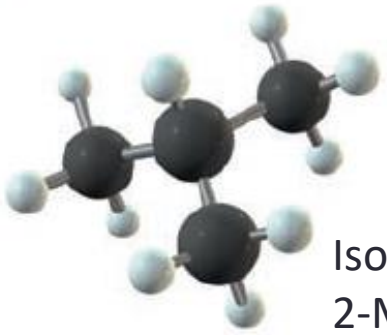
Chain alkanes (normal alkanes, or n-alkanes)
Branched-Chain Alkanes



Different conformations 构象

n-Butane

(a)

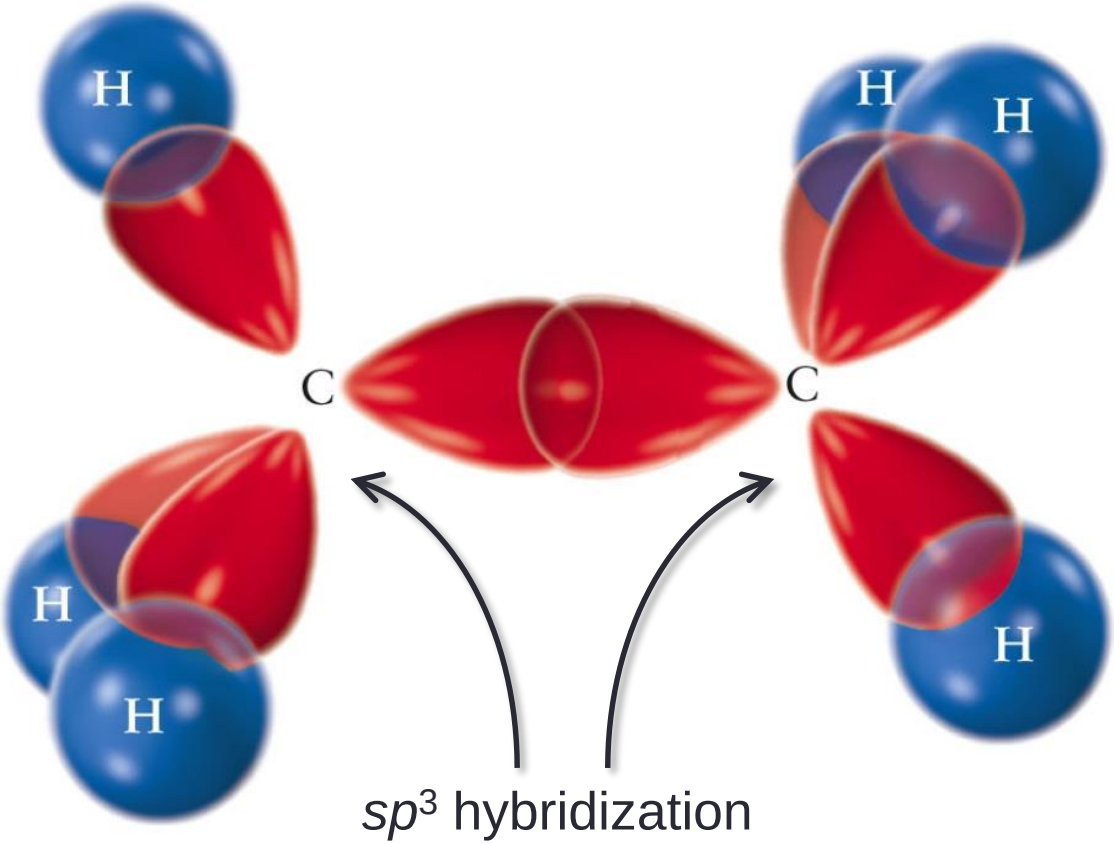


Isobutane or
2-Methylpropane

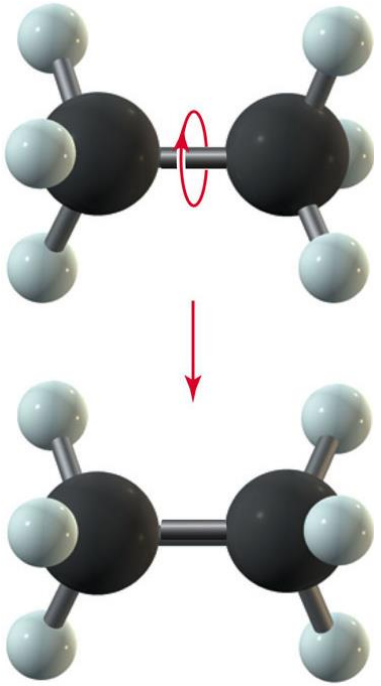
(b)

geometrical isomers

Alkane (3)

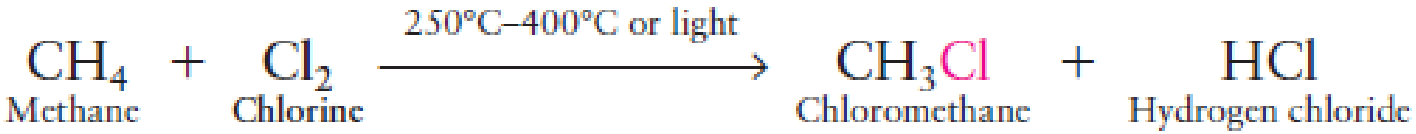


sp^3 hybridization



Haloalkanes or halides 卤代烷烃

Halogen 卤素



$$Cl\cdot + CH_4 \longrightarrow HCl + \cdot CH_3 \qquad \text{(propagation)}$$

$$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \qquad \text{(propagation)}$$

Dichloromethane (CH_2Cl_2, also called methylene chloride)
Trichloromethane ($CHCl_3$, chloroform)
Tetrachloromethane (CCl_4, carbon tetrachloride).

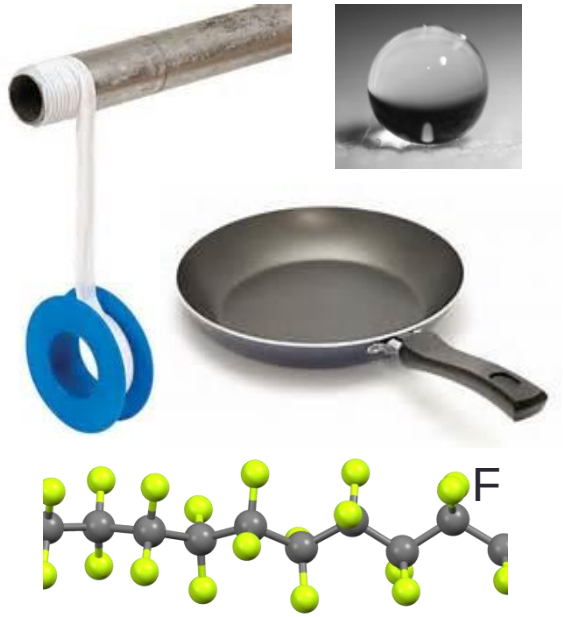
$$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl$$

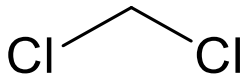
Haloalkane (2)

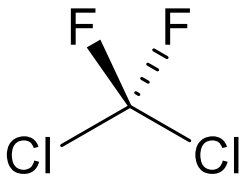
Average Bond Dissociation Energies (kJ·mol^{-1})

C—H	C—F	C—Cl	C—Br	C—I
414	485	339	285	213

C - sp^3, X - p







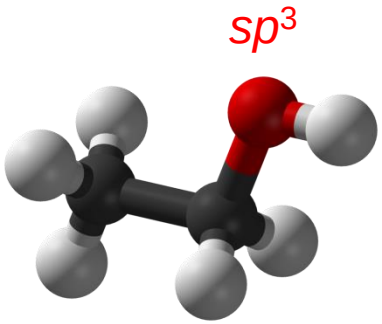
Dichloromethane
二氯甲烷

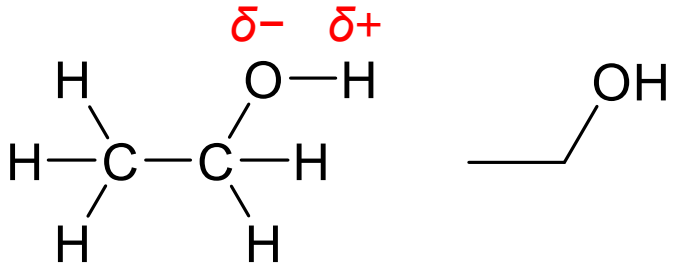
Dichlorodifluoromethane
二氟二氯甲烷
(Freon 氟利昂)

Polytetrafluoroethylene
聚四氟乙烯
(Teflon 特氟龙)

Alcohol 醇

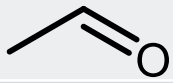
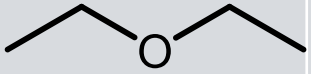
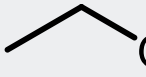
C - sp^3, O – sp^3





Ethanol; ethyl alcohol;
EtOH 乙醇

Polar solvent
极性溶剂

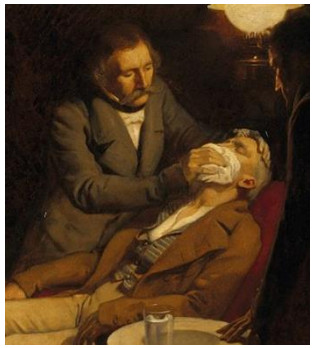
	B.p. (°C)
	11
	20
	35
	78

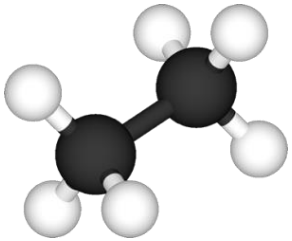
High b.p. due to
hydrogen bond

Ether 醚

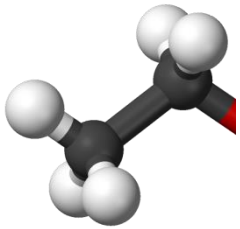
Average Bond Dissociation Energies (kJ·mol^{-1})

C—H	C—N	C—O
414	305	358

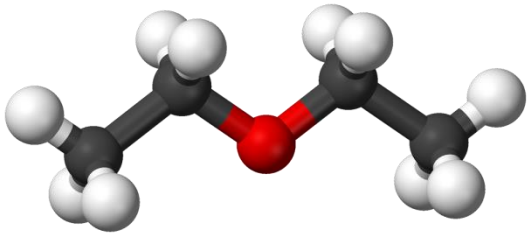




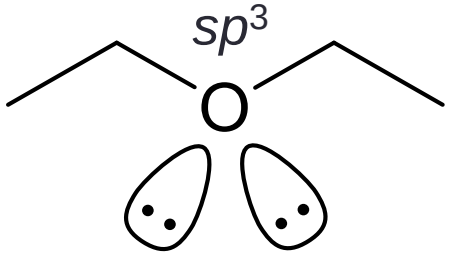
Ethane 乙烷



Ethyl 乙基



(Di)ethyl ether
(二)乙(基)醚



(Halo)alkane & Ether: Summary

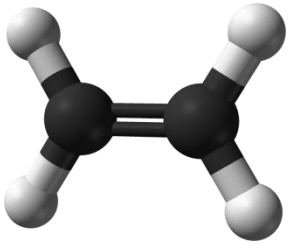
sp^3 hybridization

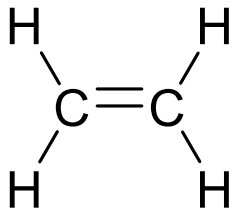
- No lone pairs or empty orbitals on C
- Stable at room temperature
- Reactive at high temperatures

Low polarity 极性

- Lipophilic 亲油性
- Low solubility 溶解度 in H_2O
- Anesthetic

Alkene 烯烃





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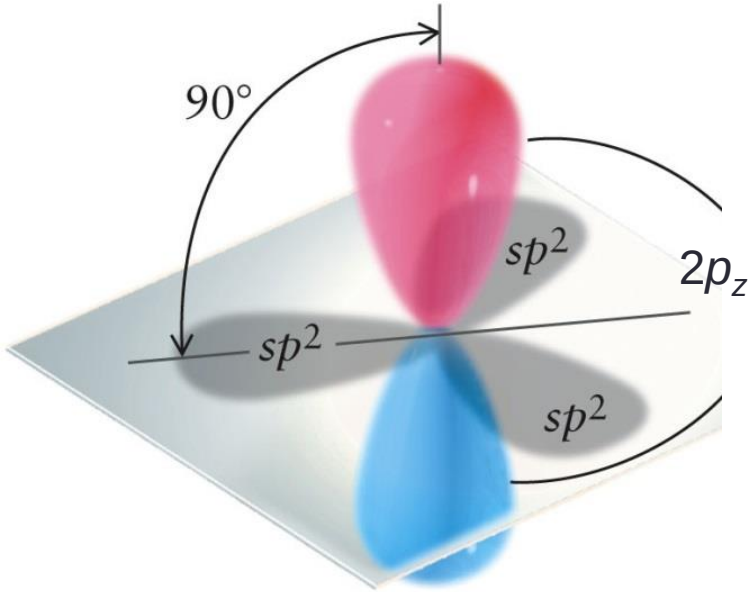
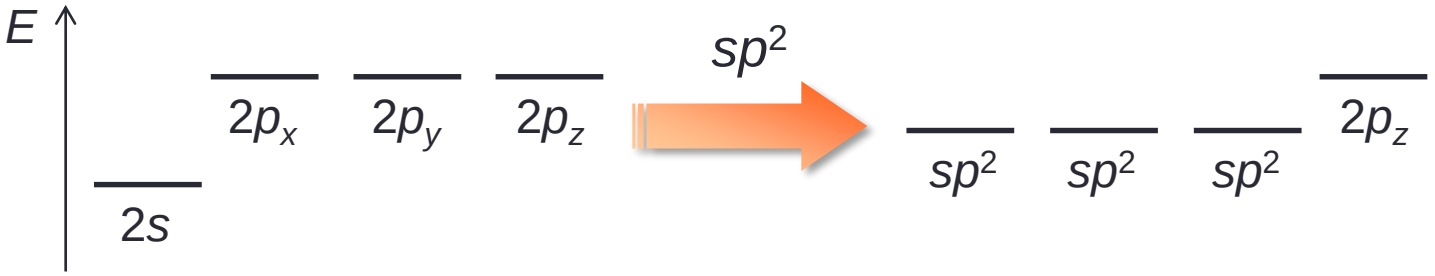
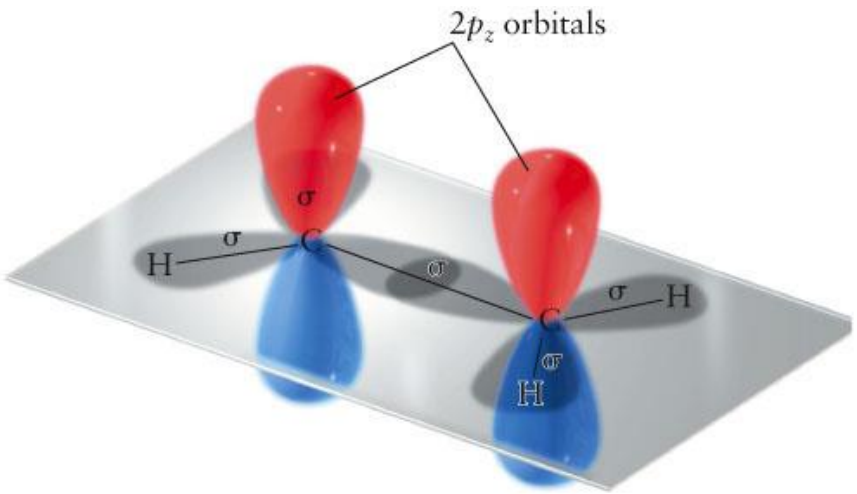
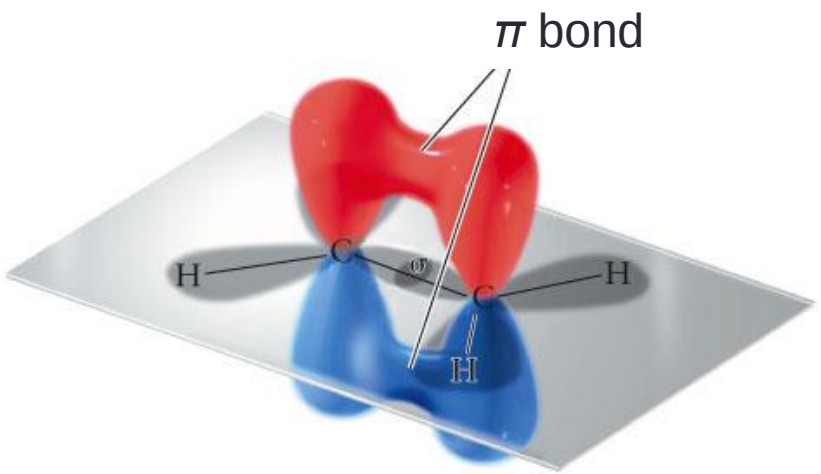


Ethene; ethylene
乙烯



Alkene (2)



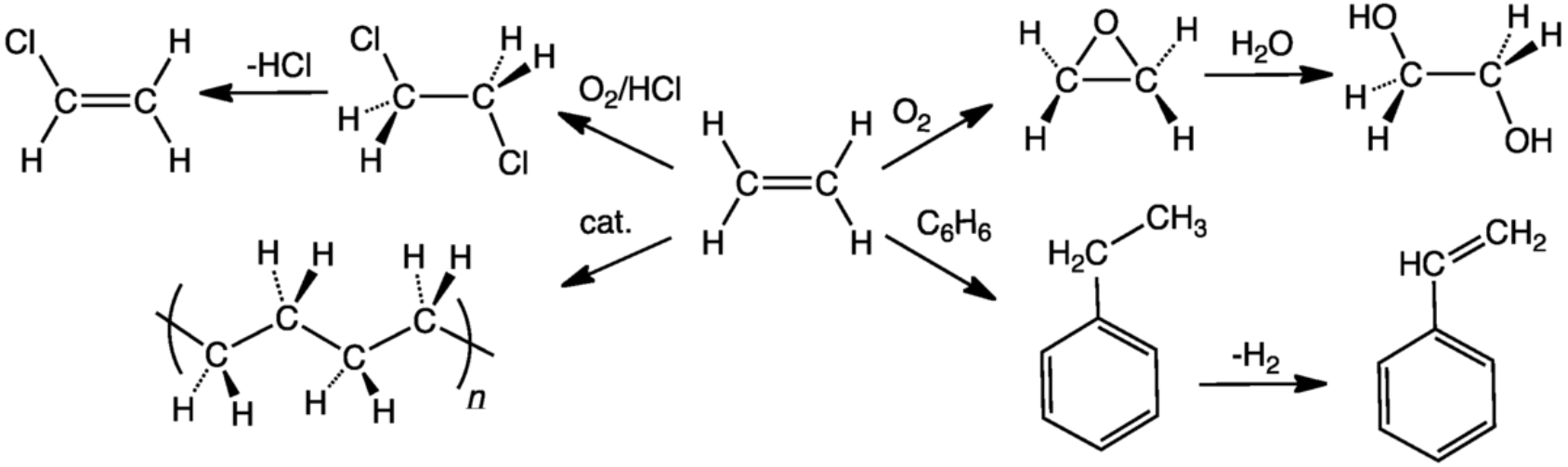


Alkene (3)

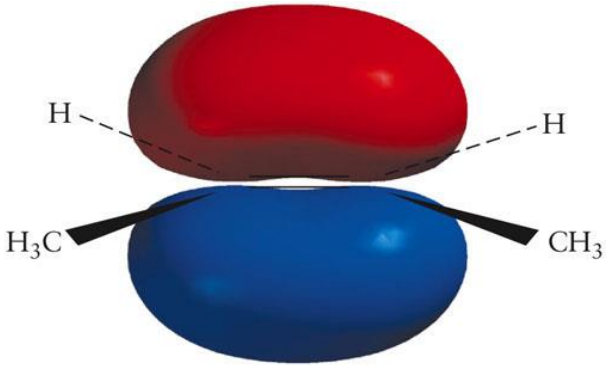
Average Bond Dissociation Energies ($kJ \cdot mol^{-1}$)

C—H	C—C	C=C
414	347	611

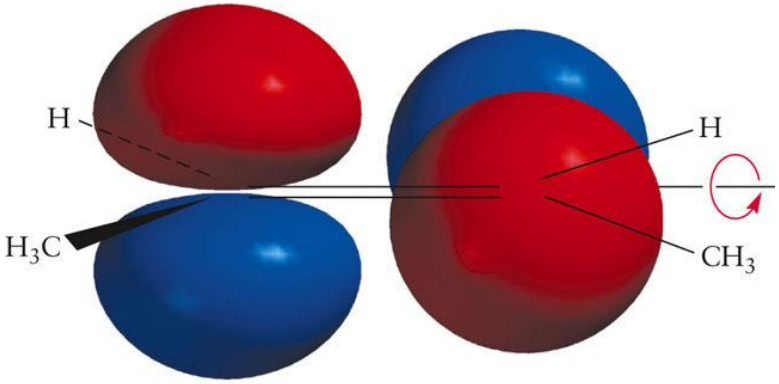
加成反应 Addition reaction:



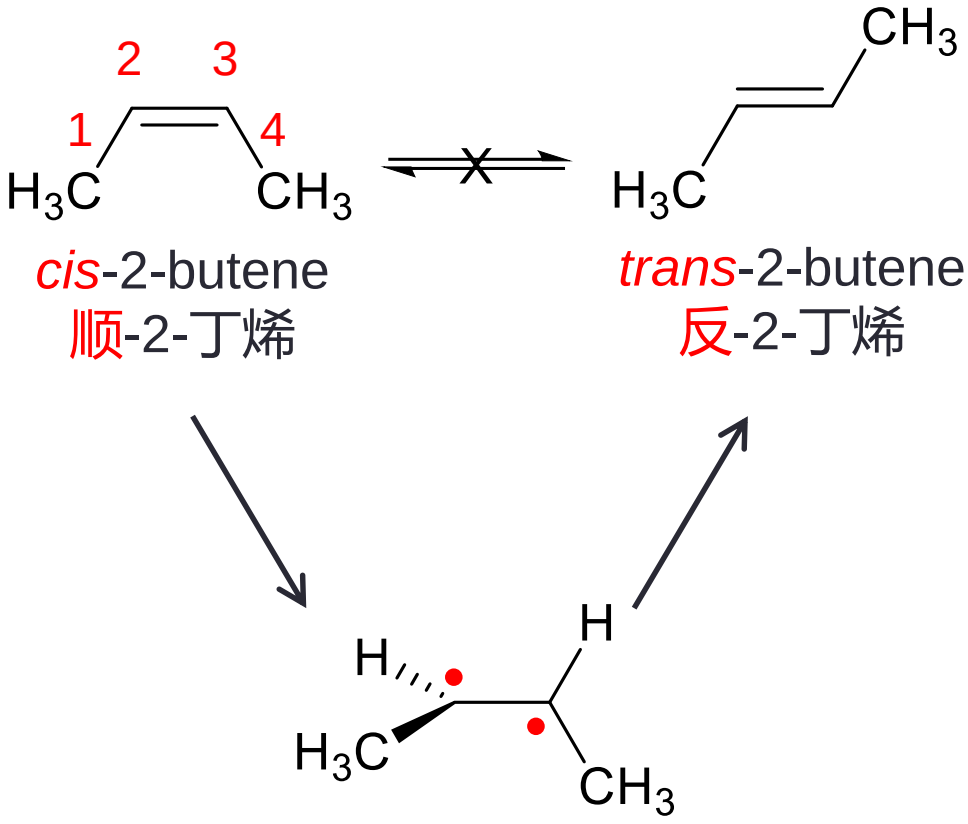
Alkene (4)



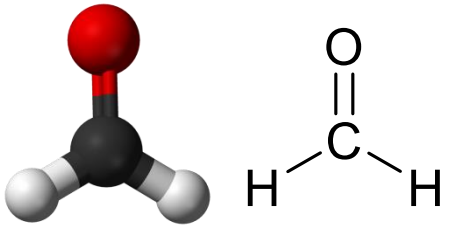
Low-energy structure



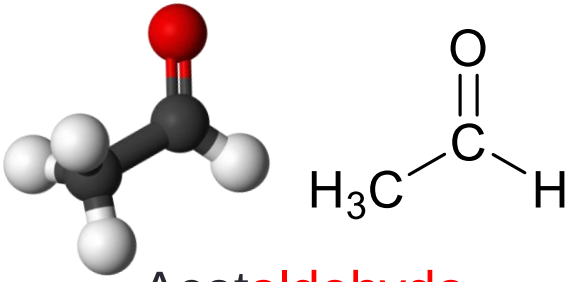
High-energy structure



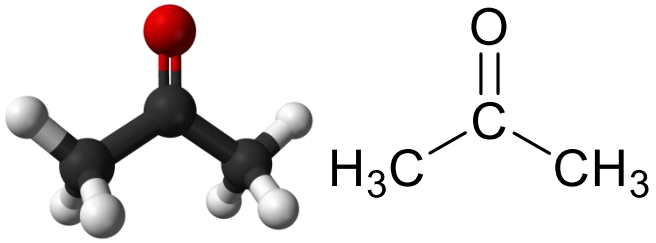
Aldehyde 醛 and Ketone 酮 (1)



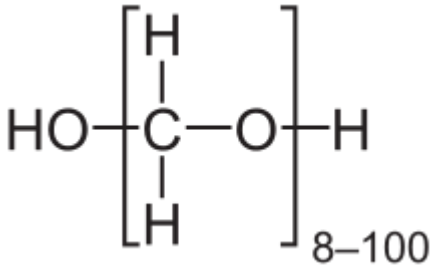
Formaldehyde
Methanal
甲醛



Acetaldehyde
Ethanal
乙醛

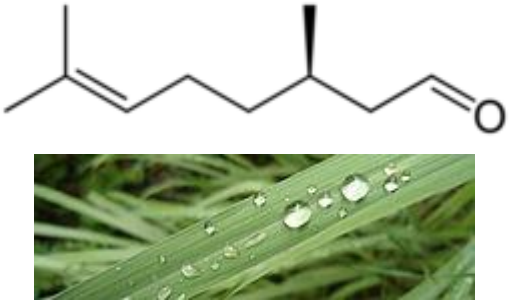


Acetone
Propanone
丙酮



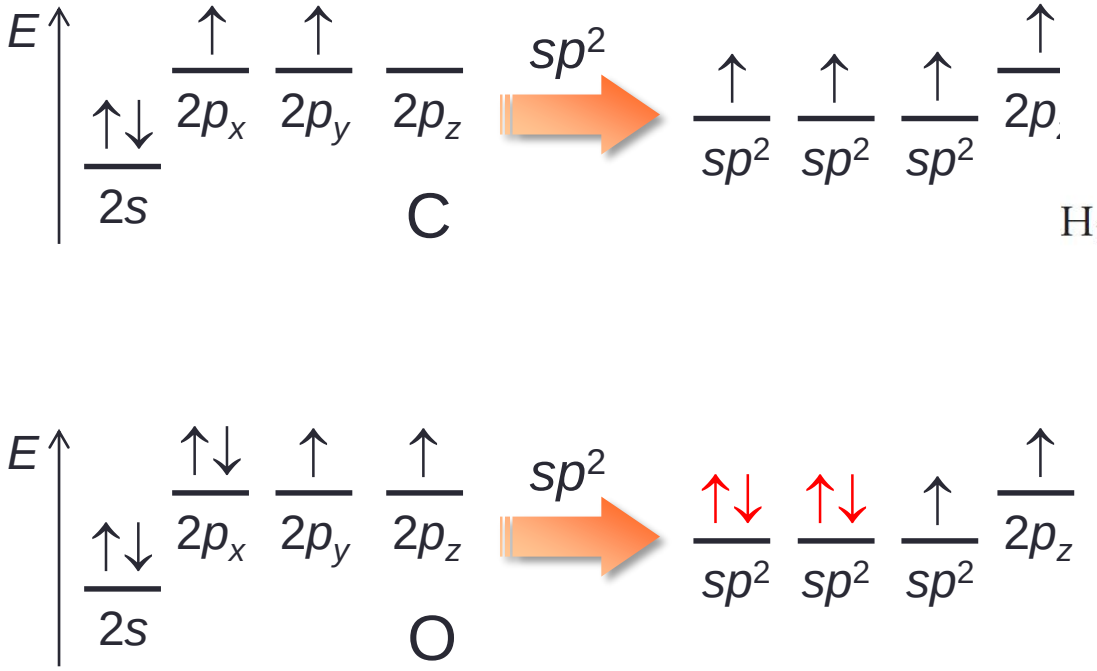
Paraformaldehyde
多聚甲醛

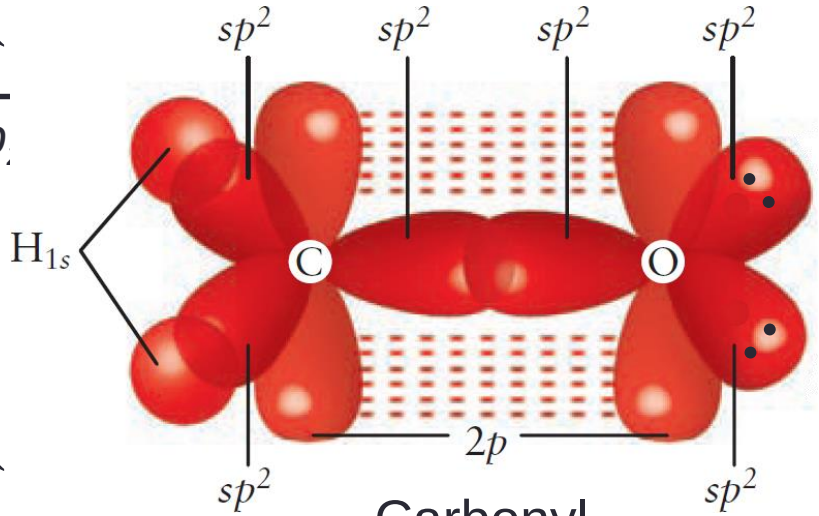
Cinnamaldehyde
肉桂醛



Citronellal
香茅醛

Aldehyde and ketone (2)

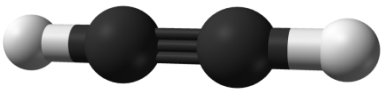




Carbonyl
羰基

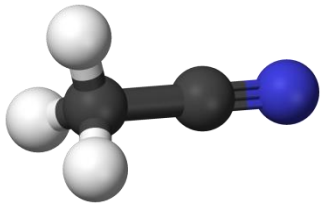
羰 tāng = 碳 + 氧

Alkyne 炔 and Nitrile 腈 jīng



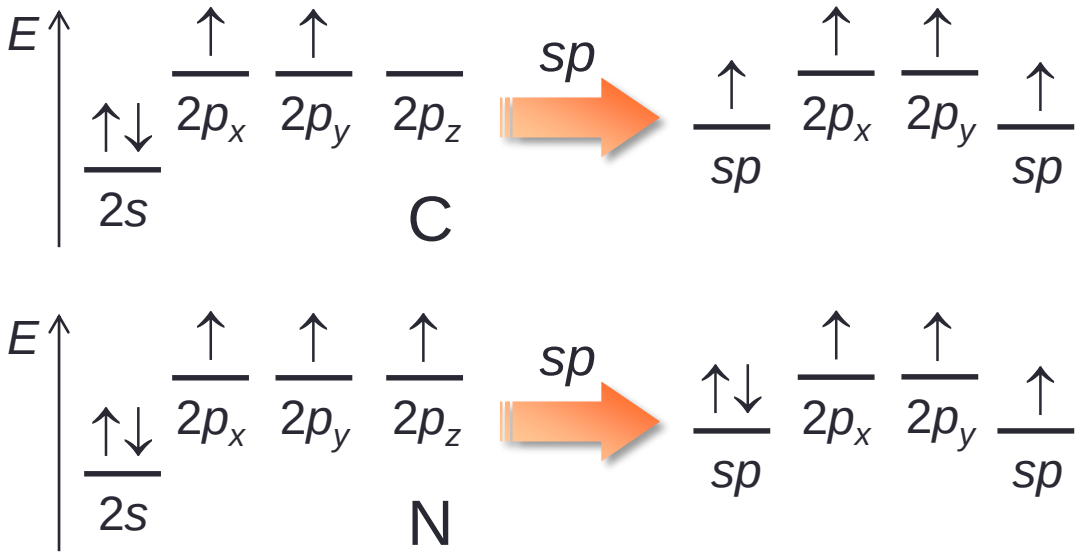
H—C≡C—H

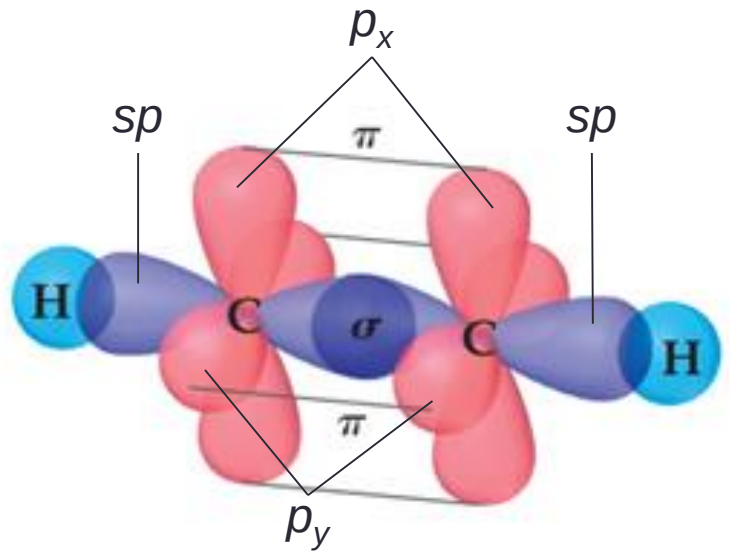
Acetylene
Ethyne
乙炔



$H_3C—C≡N$

Acetonitrile
Ethanenitrile
乙腈





Double and Triple Bonds: Summary

sp^2 hybridization

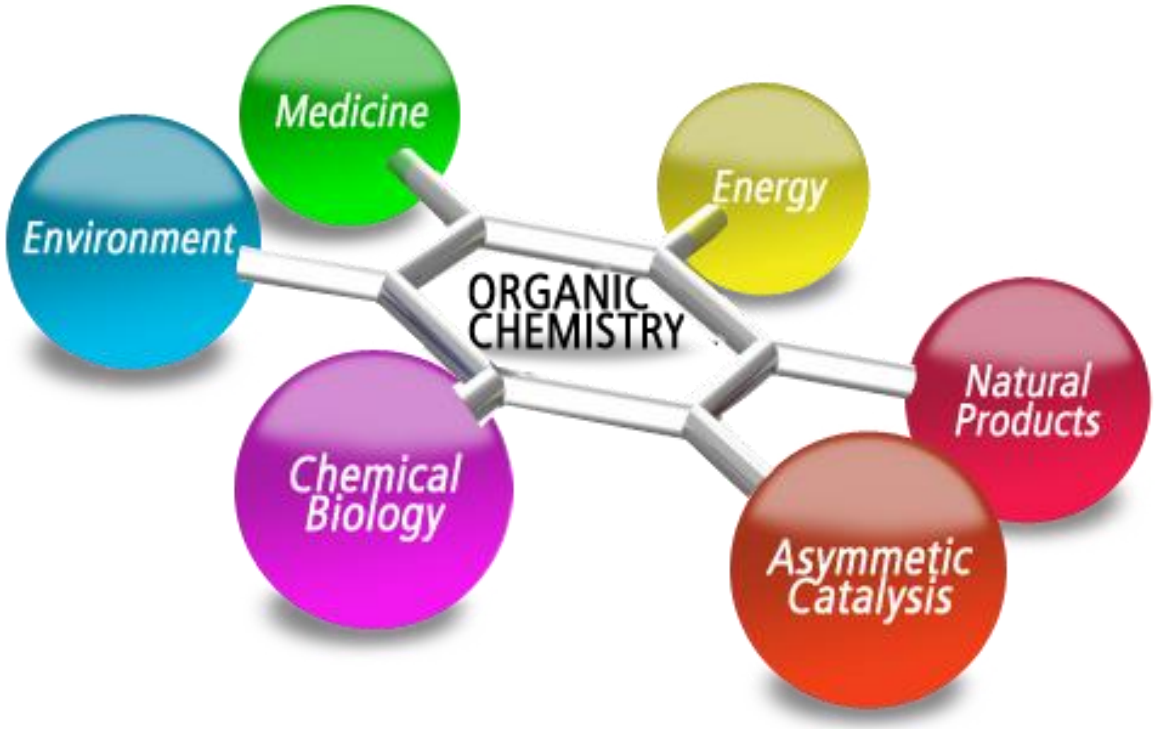
- 1 σ bond, 1 π bond;
  π bond has higher energy
- π bond cannot rotate
- Addition reaction
- C=C is nonpolar;
  C=O is polar.

sp hybridization

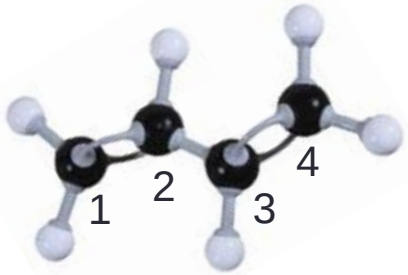
- 1 σ bond, 2 π bond;
  π bonds have higher energy
- Addition reaction
- C≡C is nonpolar;
  C≡N is polar.

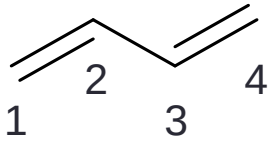
Outline

- Organic compounds (the nature of bonding)
- Interaction between functional groups (conjugation)
- Resonance structures (1930s)



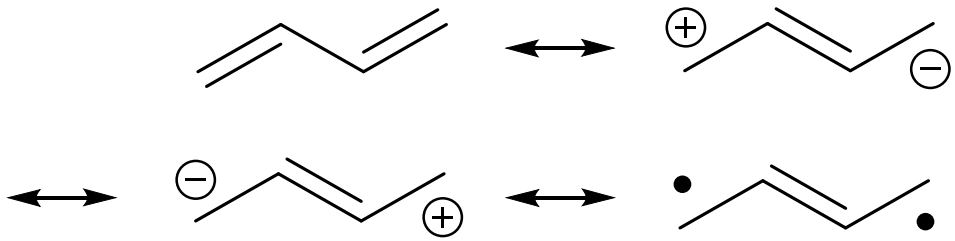
Interaction between π bonds



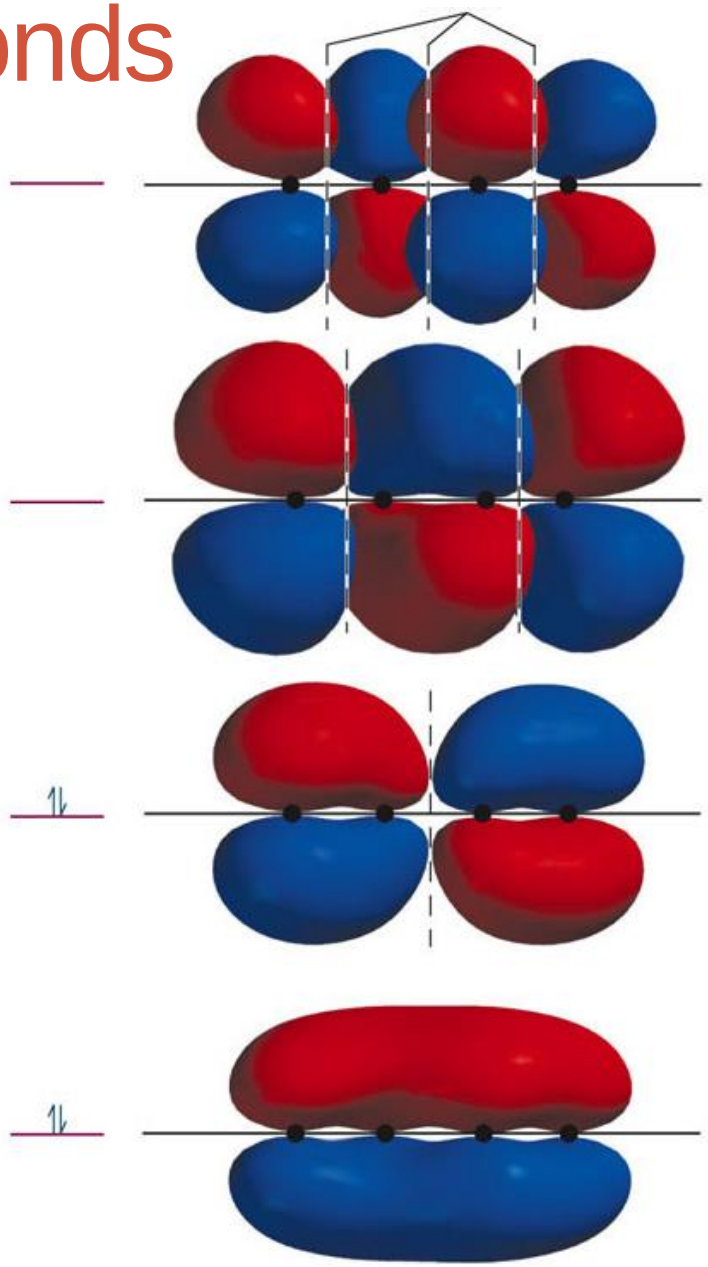


1,3-Butadiene
1,3-丁二烯

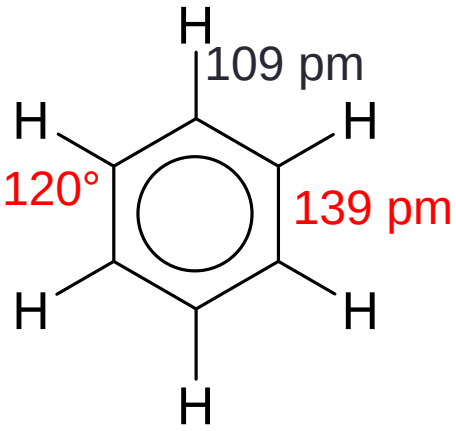
Conjugated
double bonds
共轭双键



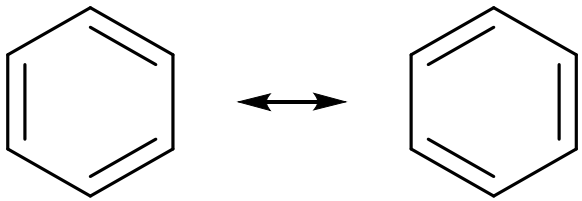
Nodal planes

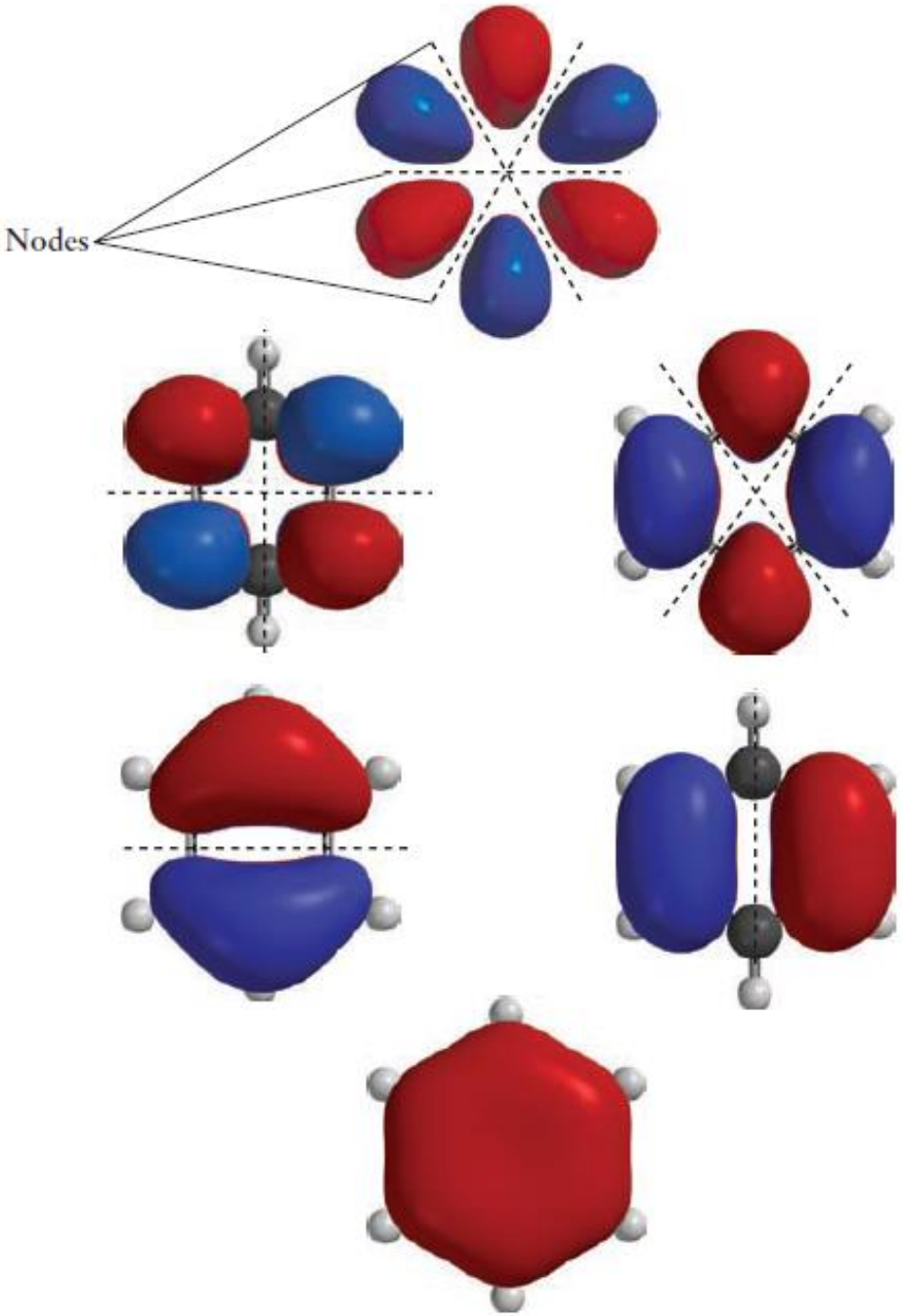


Benzene

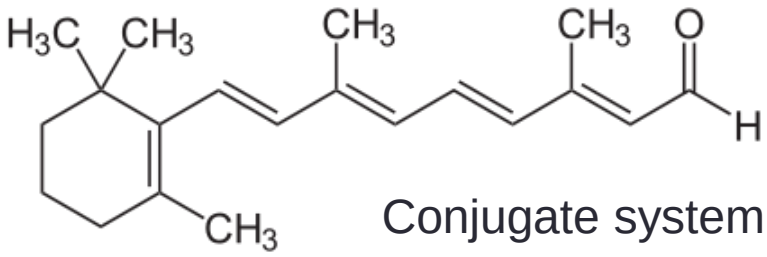


C–H 109 pm
C–C 154 pm
C=C 134 pm





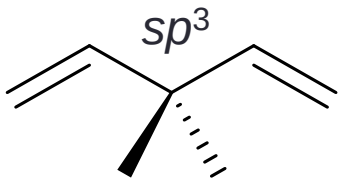
Conjugate *vs*. Non-conjugate

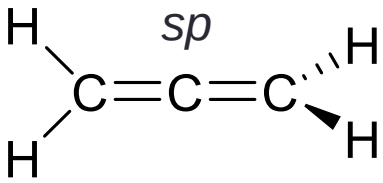


Conjugate system

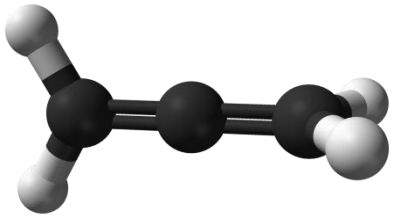
Retinal
视黄醛

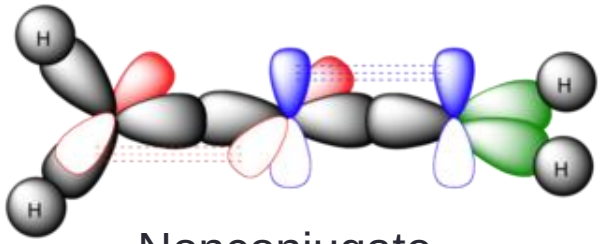
Nonconjugate





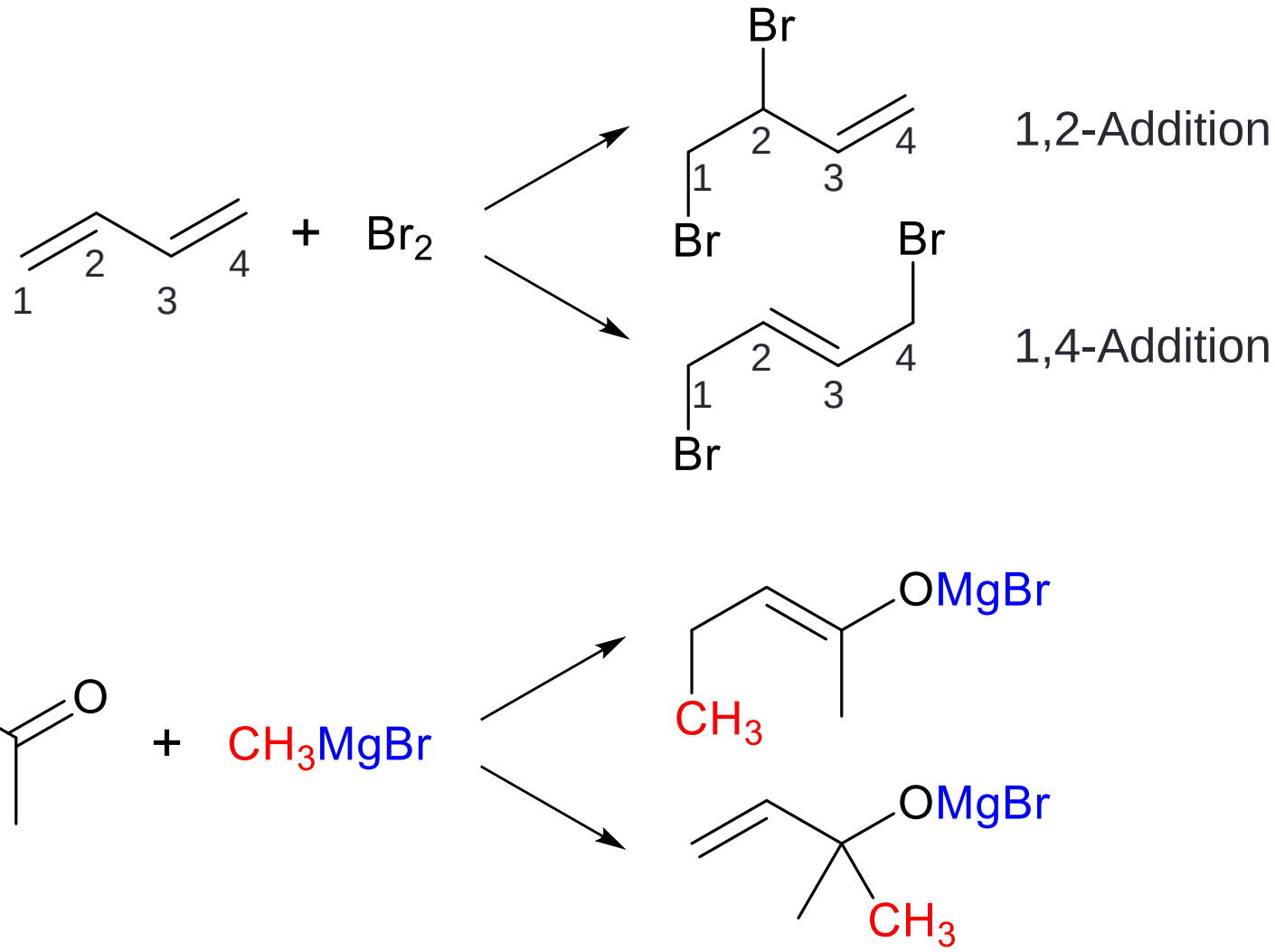
Allene 丙二烯





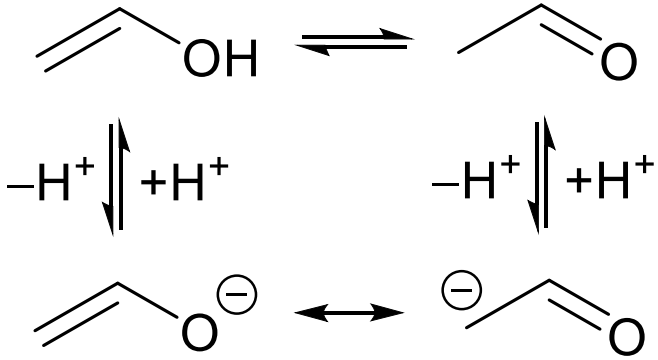
Nonconjugate

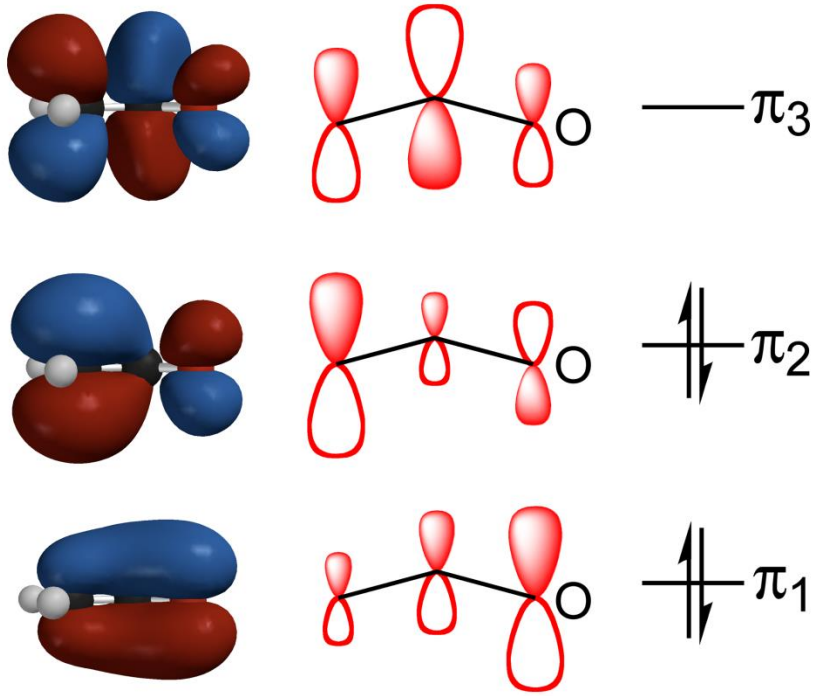
Conjugate Addition

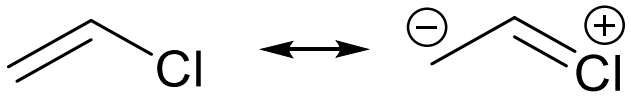


Conjugation between π and Lone Pair

Enol 烯醇 Aldehyde 醛

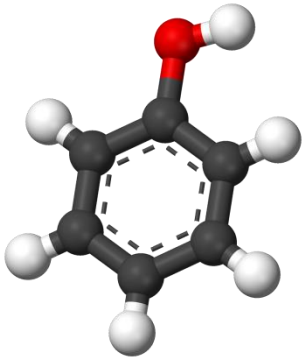




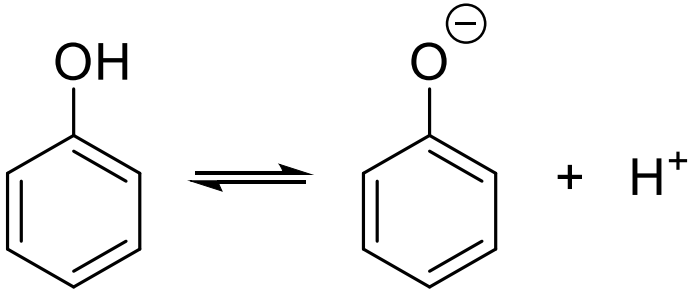


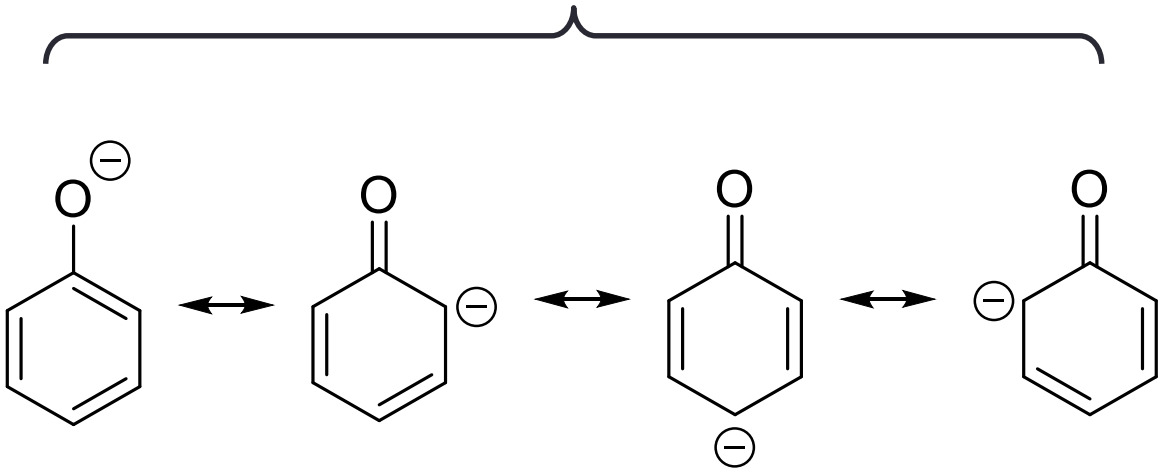
Vinyl chloride
Chloroethylene
氯乙烯

Phenol 酚 (1)

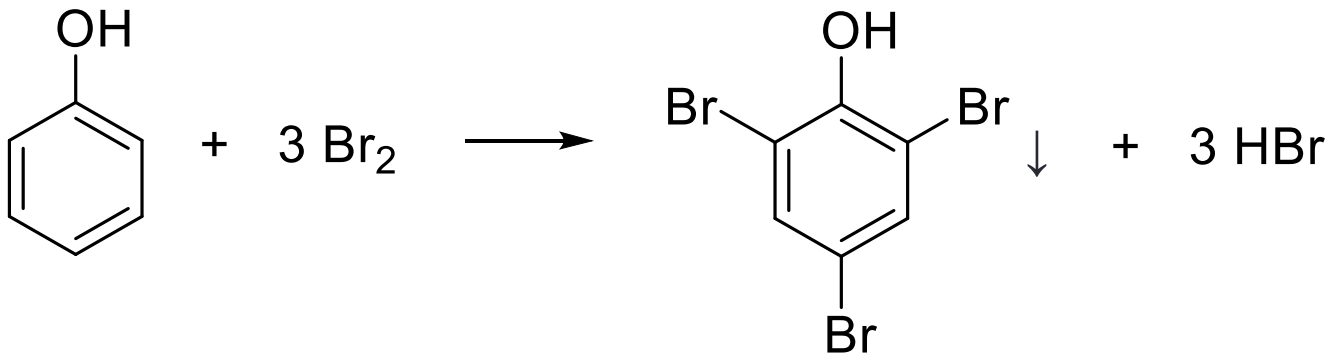


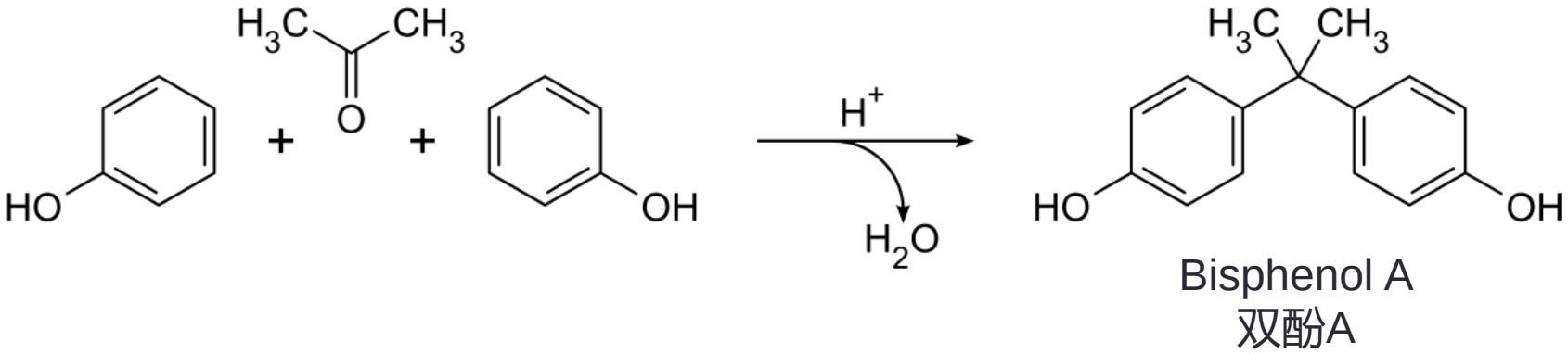
Phenol 苯酚





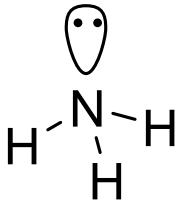
Phenol 酚 (2)



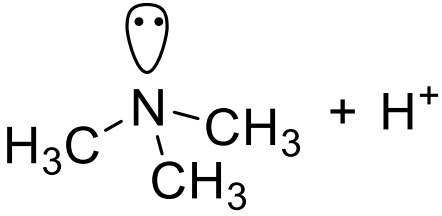


Bisphenol A
双酚A

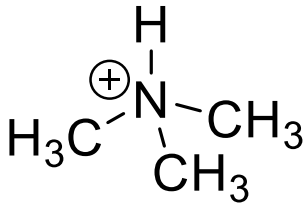
Amine, Aniline, and Amide



Ammonia
氨

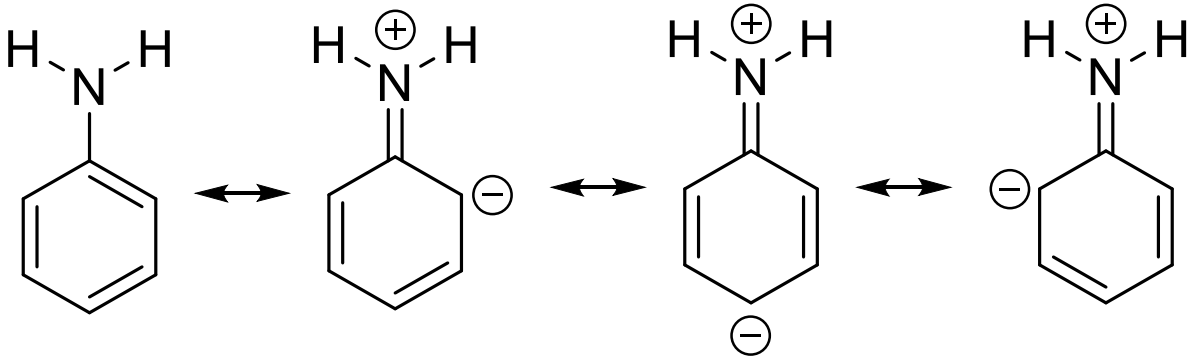


Trimethylamine
三甲基胺

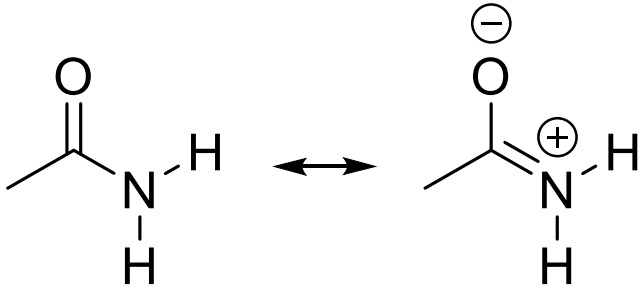


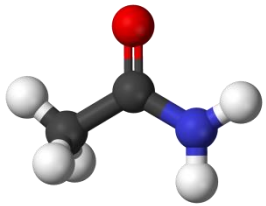
Trimethylammonium
三甲基铵

Aniline
Phenylamine
苯胺



Acetamide
乙酰胺



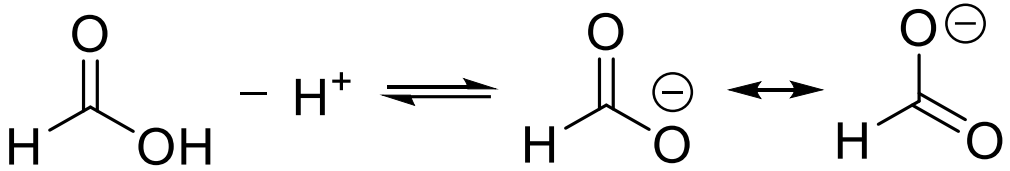


Basic
碱性

Weakly
basic

Neutral
中性

Carboxylic Acid 羧酸



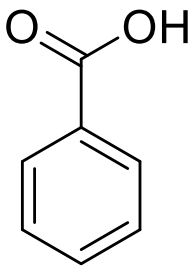
Formic acid 甲酸
Methanoic acid

Formate 甲酸根

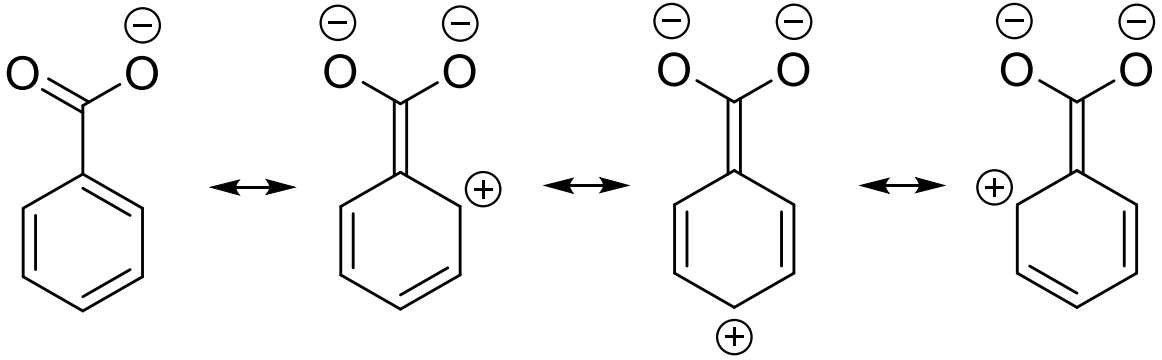
Acidic
酸性

Weakly
Acidic

Benzoic acid
苯甲酸

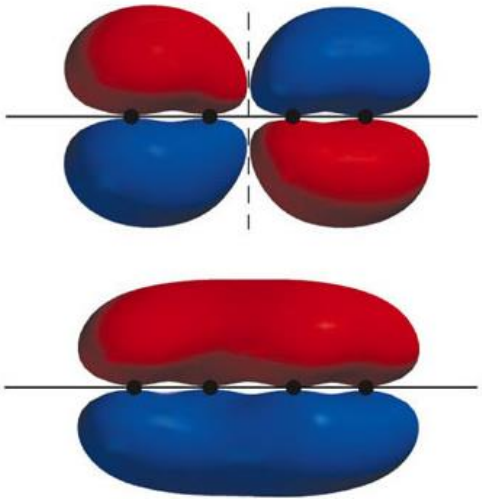


Benzoate
苯甲酸根

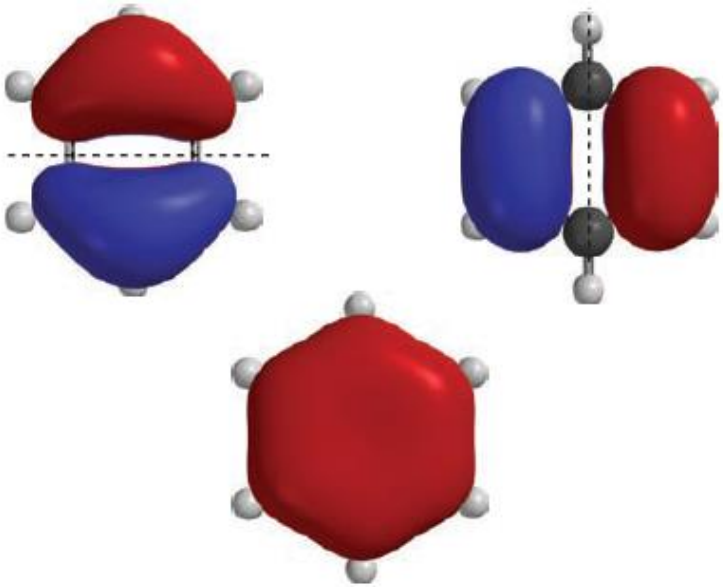


Summary: π-conjugation Systems

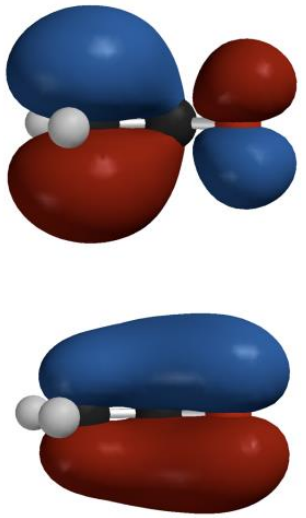
1. Compatible orbital symmetries
2. Maximum orbital overlap
3. Approximate atomic orbital energies



4 orbital, 4 electrons



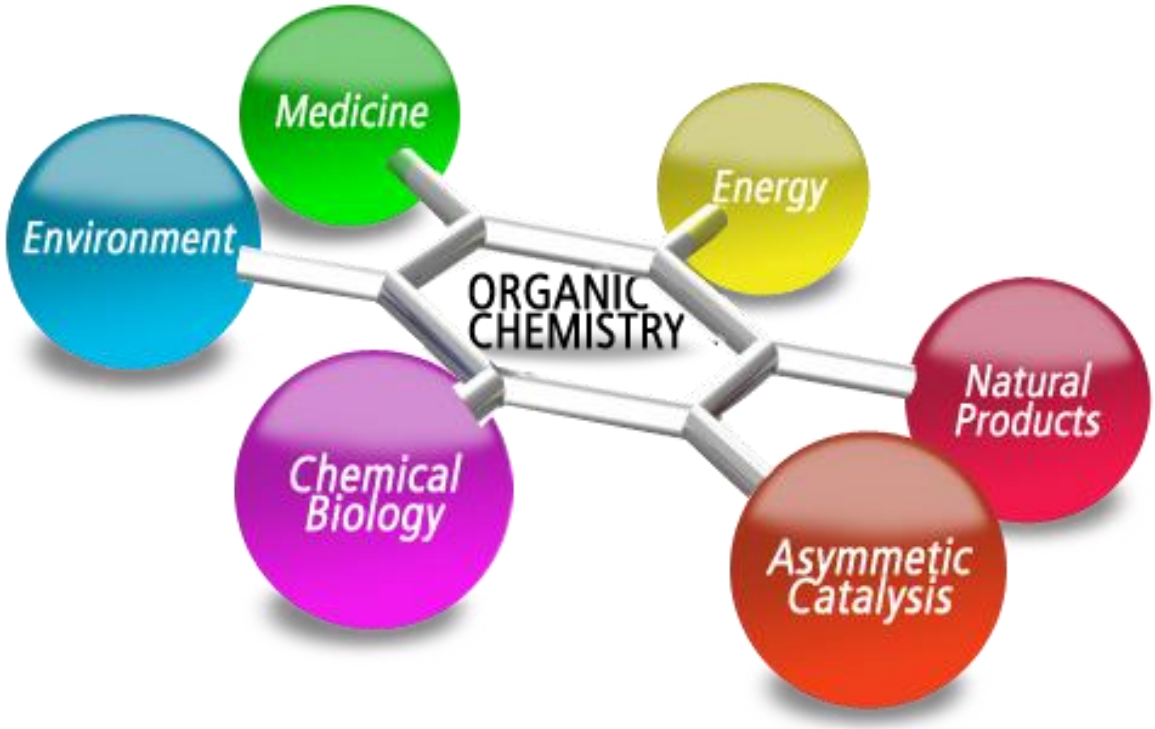
6 orbital, 6 electrons



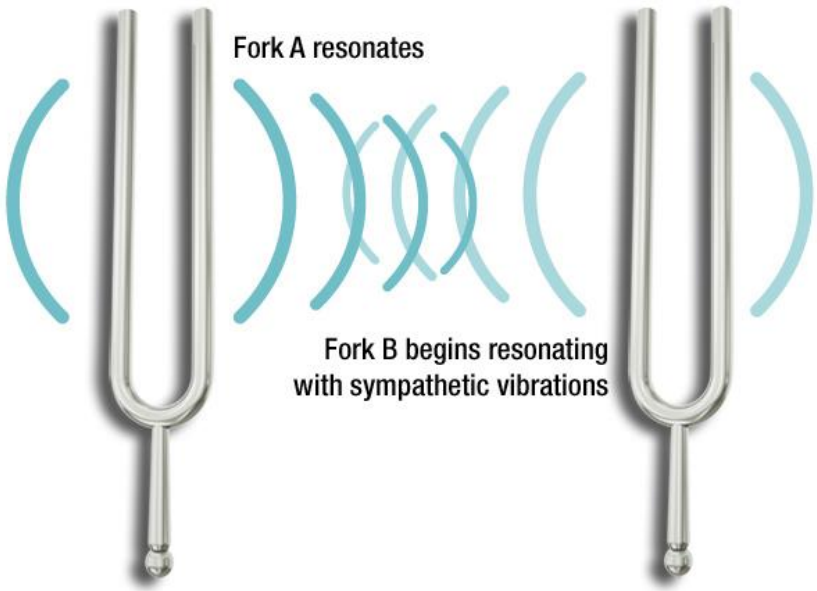
3 orbital,
4 electrons

Outline

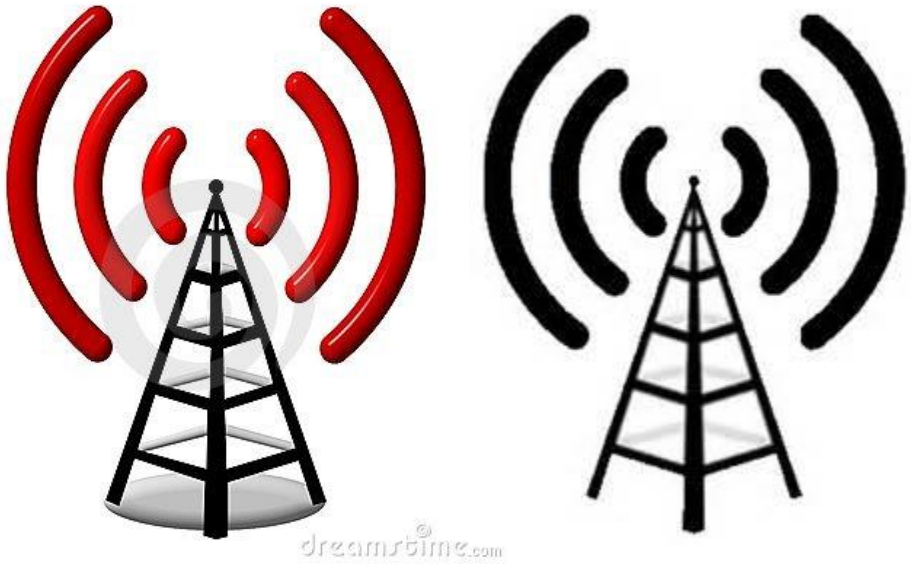
- Organic compounds (the nature of bonding)
- Interaction between functional groups (conjugation)
- Resonance structures (1930s)



What is Resonance?



Acoustic resonance

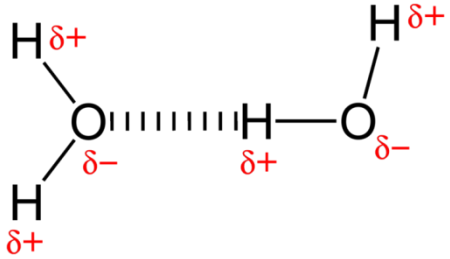


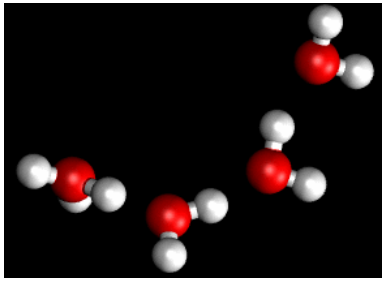
Electromagnetic resonance

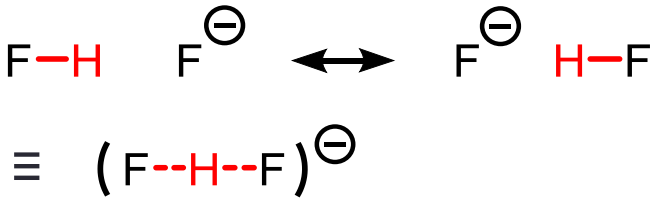
1. Two separate units
2. Identical or very close *E* or *v*
3. Moderate coupling 耦合

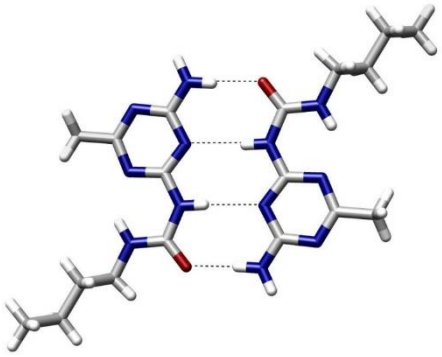
Resonance in Chemistry

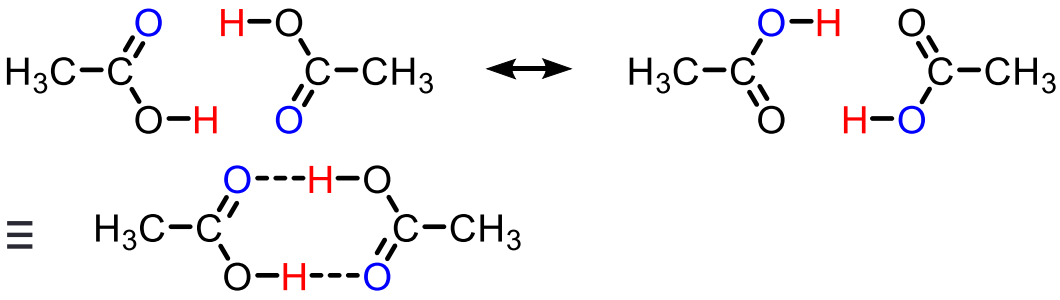
- The Hydrogen Bond
- Attractive force between X−H and Y (X, Y = F, O, N)
- H is unique being light and mobile



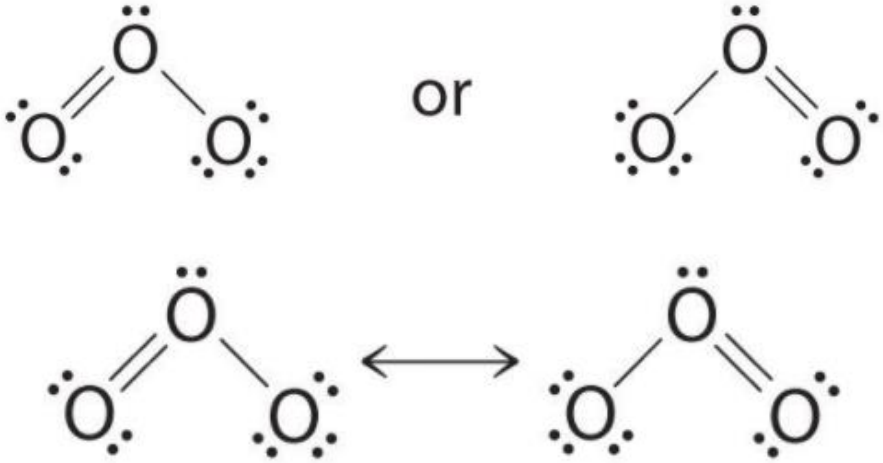


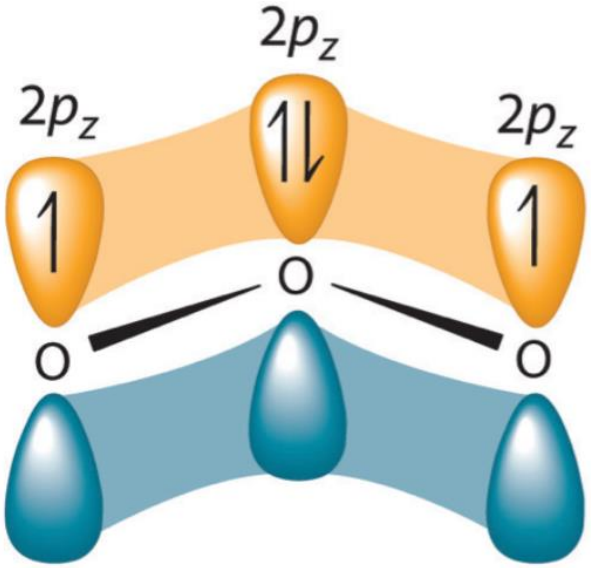




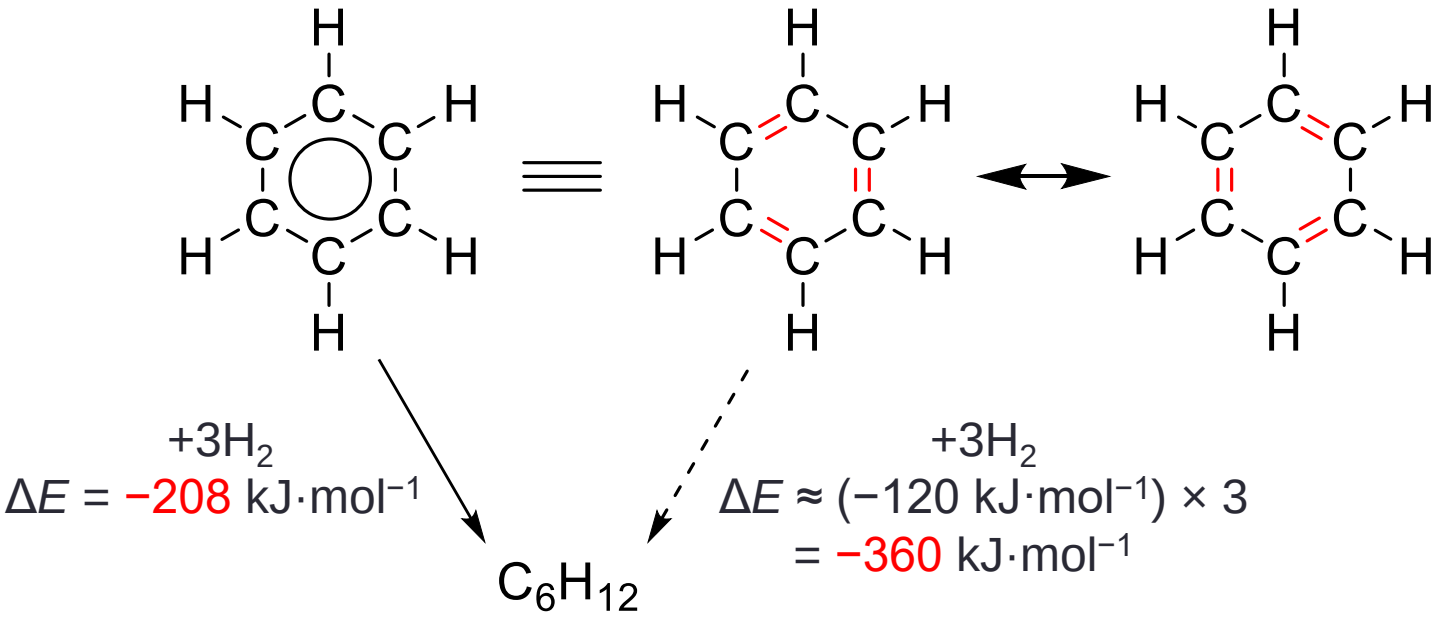


Resonance Structures of O_3



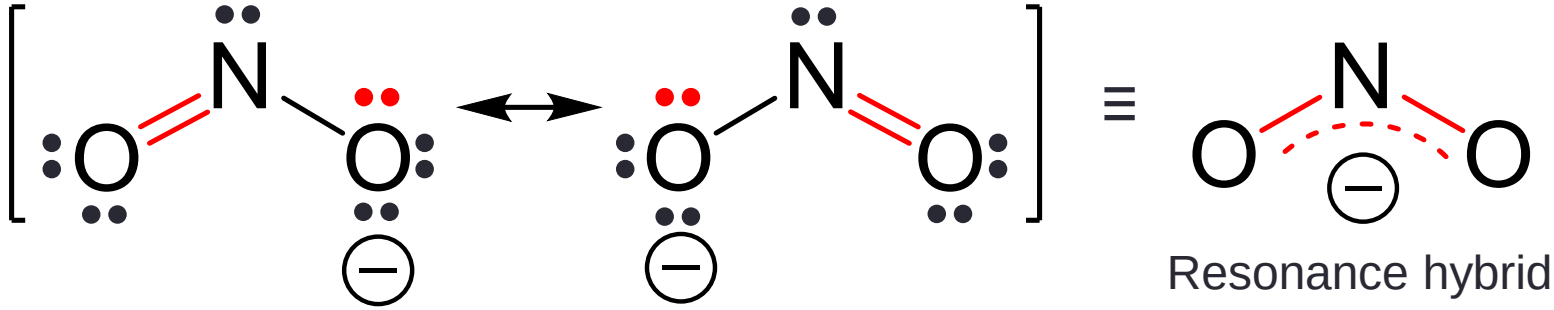


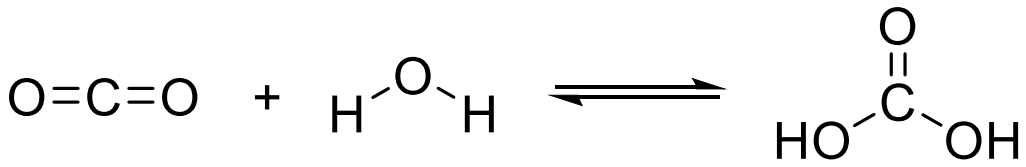
Resonance in Chemistry



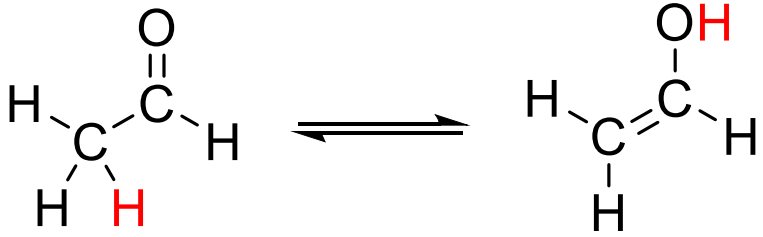
Resonance energy for benzene = 152 kJ·mol^{-1}

Resonance in Chemistry





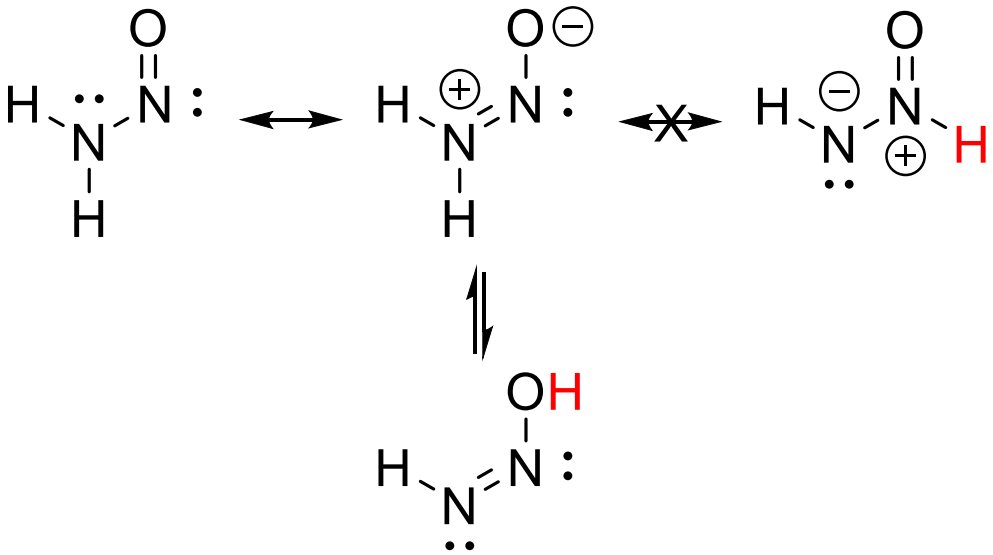
Chemical equilibrium
化学平衡

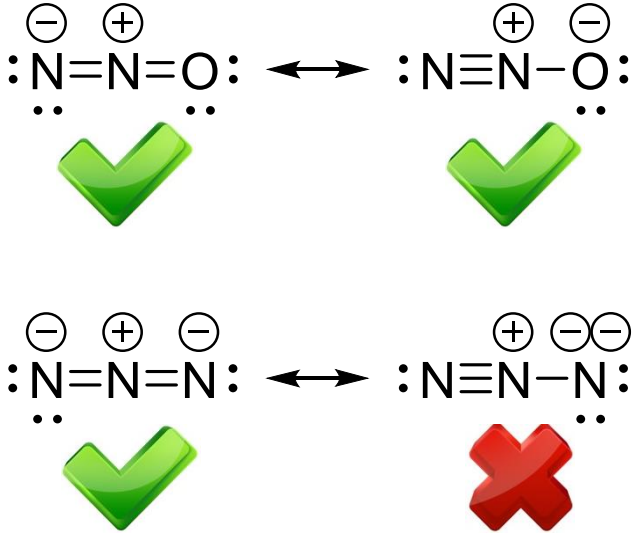


Tautomerism
互变异构

Rules of Resonance Structures

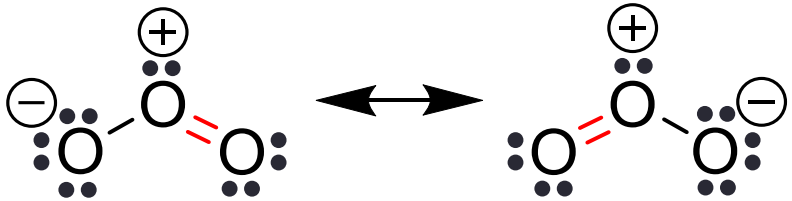
- Valid Lewis dot structure
- Fixed atomic positions
- Lowest energy
  - Follow the trend of electronegativity
  - The more bonds, the more stable
  - More resonance structures → Better delocalization



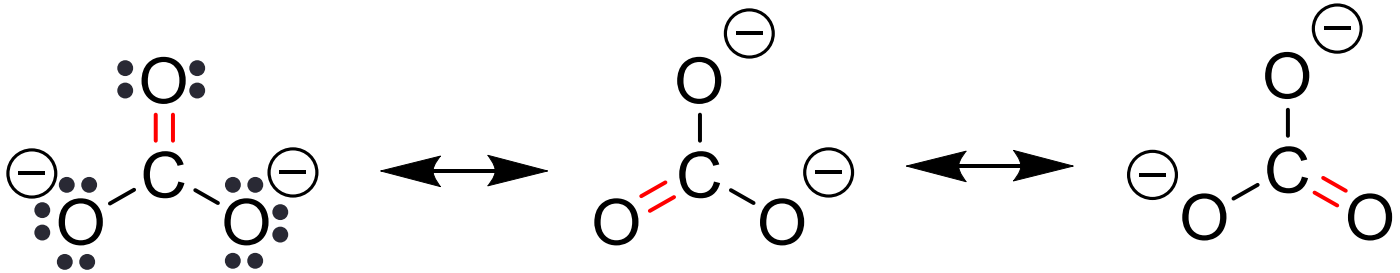


Resonance Structure and Bond Order

B.O.(Resonance hybrid) ≈ $\overline{\text{B.O.(Canonical forms)}}$

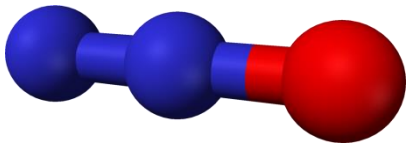


O–O bond order = 1.5

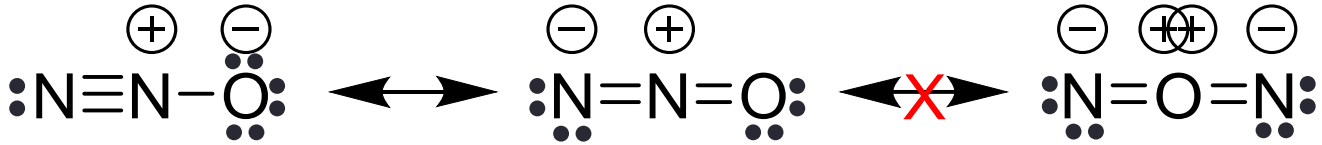


C–O bond order ≈ 1.3

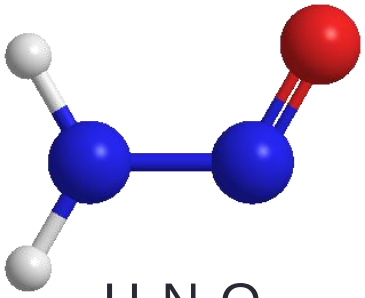
Asymmetric Resonance Structures



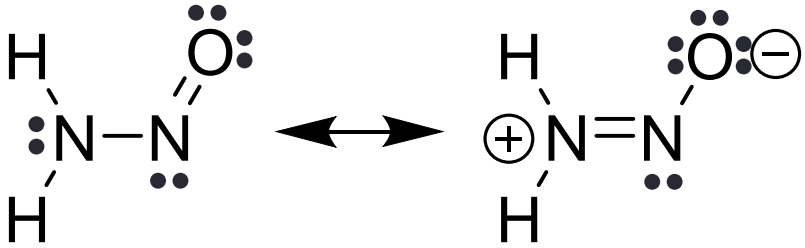
N_2O



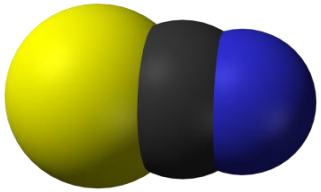
N–N bond order ≈ 2.5



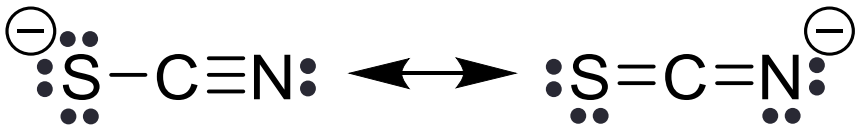
H_2N_2O



N–N bond order ≈ 1.5

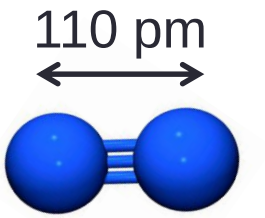


SCN^-
thiocyanate
硫氰酸根

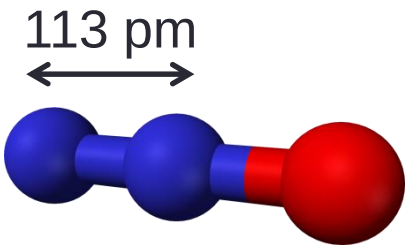


C–N bond order ≈ 2.5

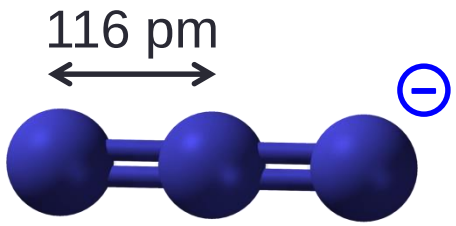
Polyatomic Molecules: Bond Lengths



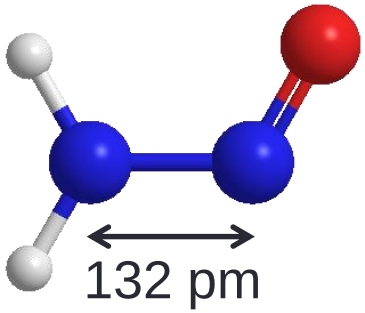
N_2



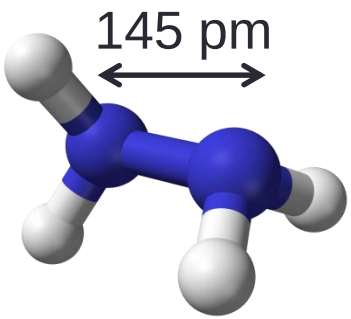
N_2O



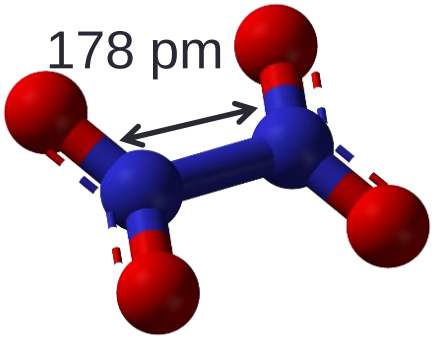
N_3^-
Azide 叠氮



H_2NNO
Nitrosamine 亚硝胺

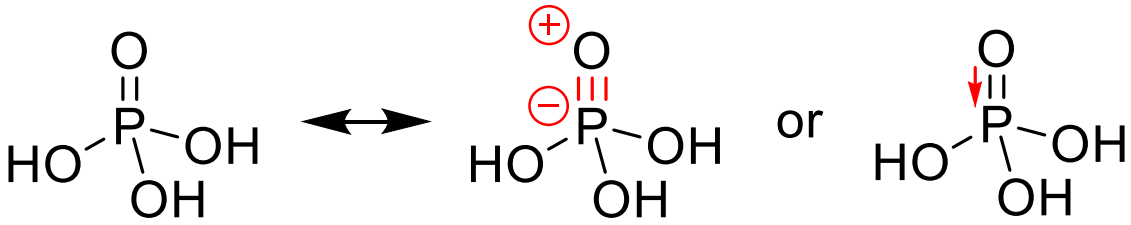


N_2H_4
Hydrazine 肼



N_2O_4

Back coordinate bond



2 < BO(P=O) < 3

Next lecture Series: Transition Metals

Reading: OGB8 §8, YY §18