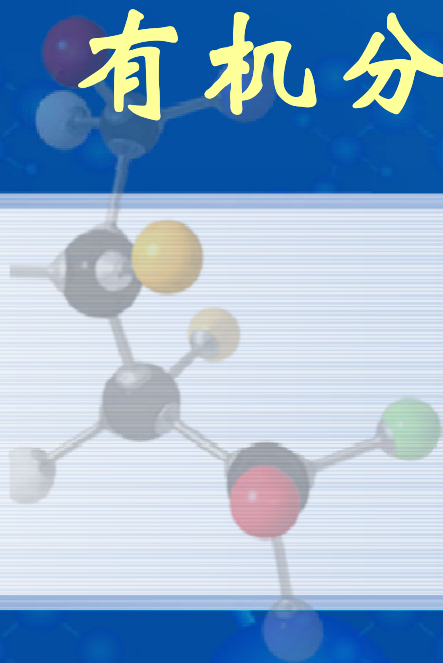


中科院研究生物理有机化学课程，2014年9月

第一讲

有机分子的结构和热力学性质



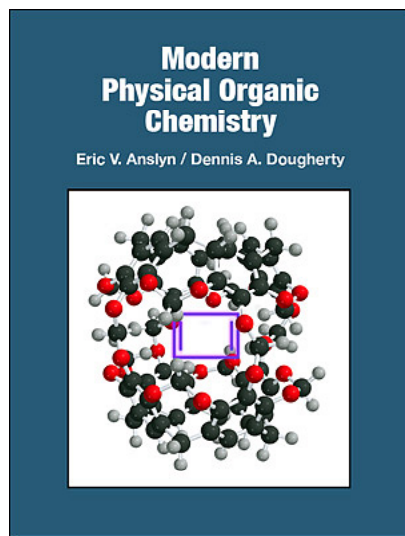
授课教师：王任小 研究员



中国科学院上海有机化学研究所
Shanghai Institute of Organic Chemistry

授课提纲

- 一、有机分子结构的基本理论 (chapter 1.1)
- 二、有机分子的热力学性质 (chapter 2.1)
- 三、反应中间体的结构和热力学性质 (chapter 1.4 & 2.2)



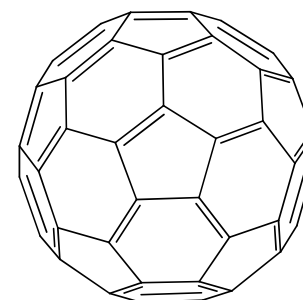
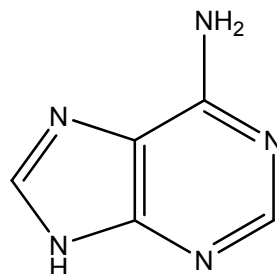
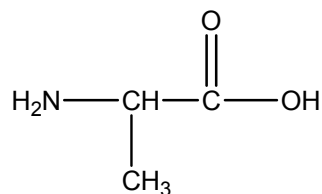
参考教材：

Eric V. Anslyn, Dennis A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, California, 2006.

I. Basic Bonding Concepts

■ 价键理论 (Valence Bond Theory, VBT)

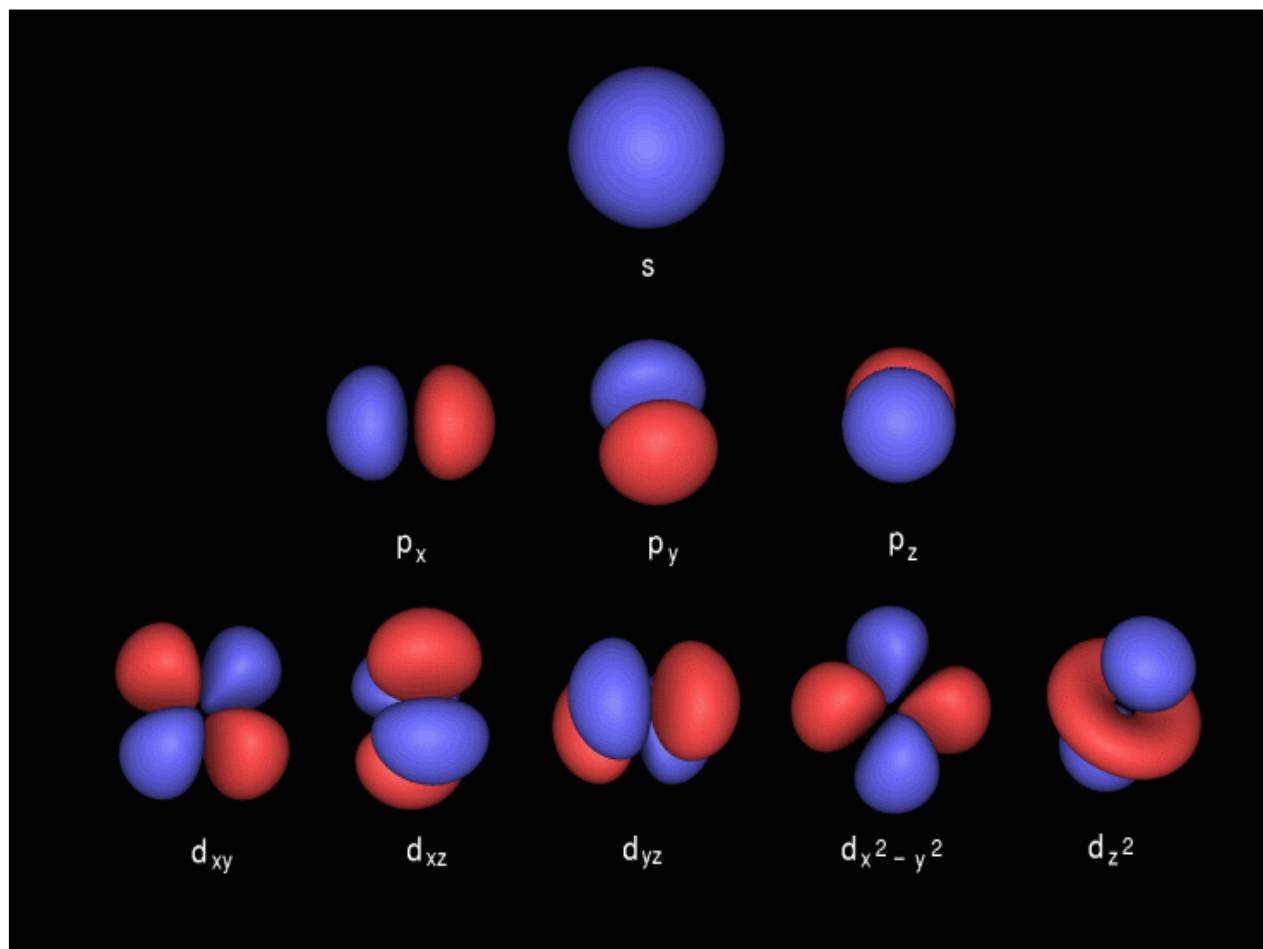
- 两个原子之间共享价层电子而形成化学键。
- 共享的价层电子对定域在两个原子之间。



■ 分子轨道理论 (Molecular Orbital Theory, MOT)

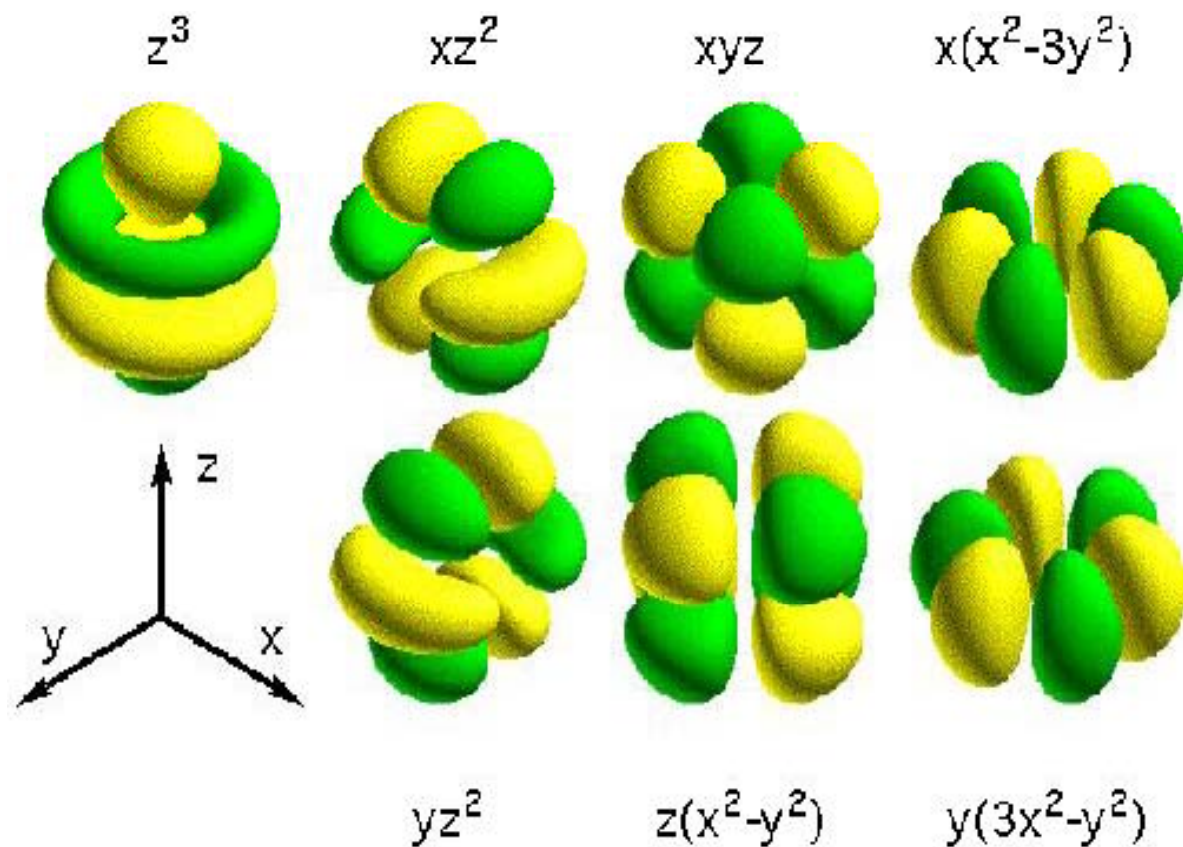
- 原子轨道组合成为离域的分⊂子轨道，所有电子填充在分子轨道中，不存在定域的化学键。

Atomic Orbitals



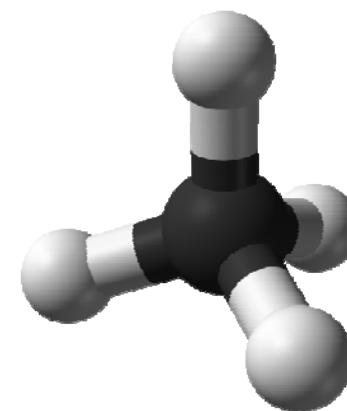
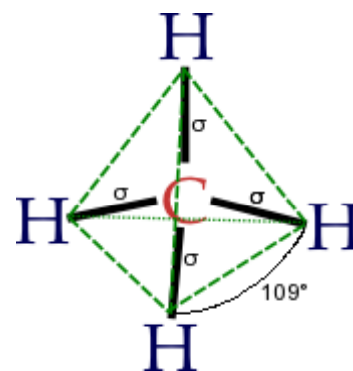
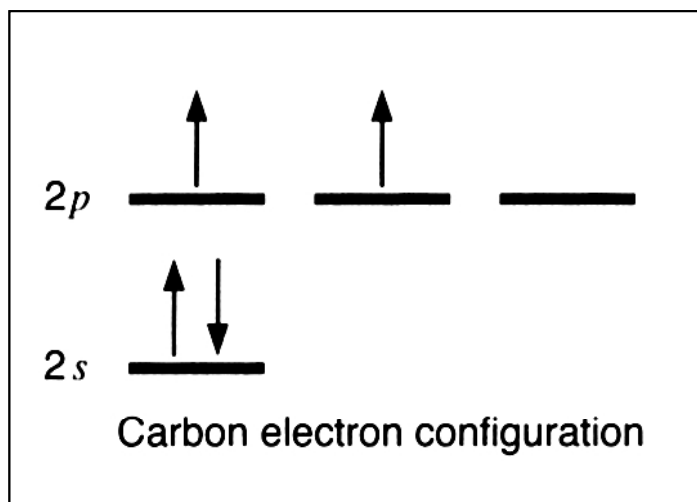
量子力学计算给出的氢原子 $1s$ 、 $2p$ 和 $3d$ 原子轨道波函数的形状

Atomic Orbitals

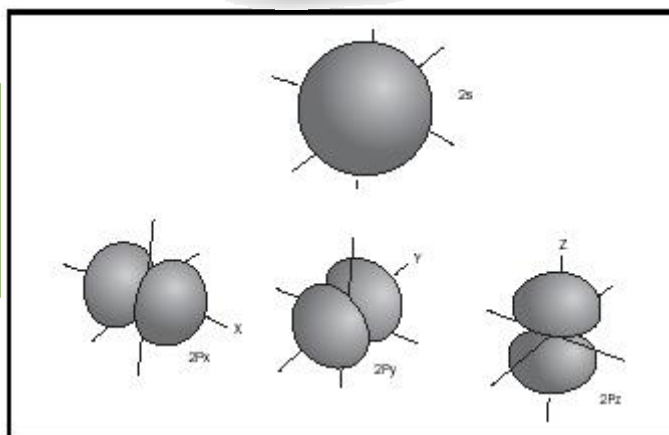


4f orbitals of a hydrogen atom

Hybridization Theory (杂化理论)

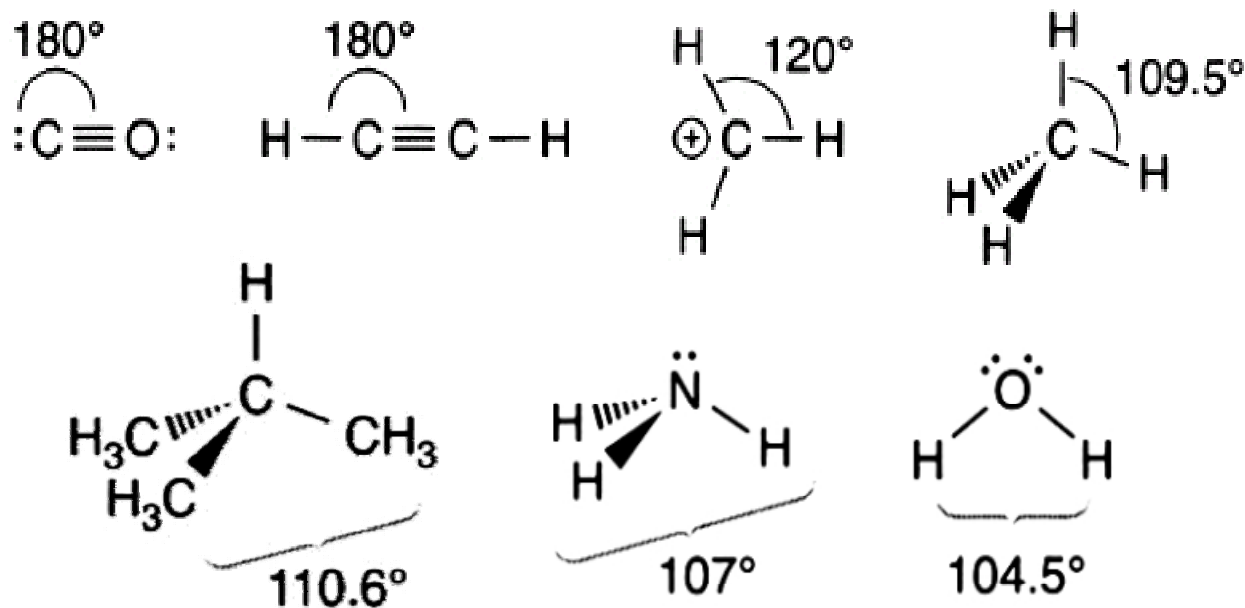


Structure of methane



价层电子对互斥规则 (VSEPR)

价层电子对互斥规则：所有成键价电子对和孤对电子在空间分布上倾向于相互之间距离最远。



Perturbation from the standard tetrahedral angle

过肘

提示：价层电子对互斥规则认为孤对电子比价电子对体积更大。

Hybridization Theory (杂化理论)

Pauling假设化学键的形成是由于原子轨道的重叠；原子轨道的有效重叠越大，形成的化学键就越强。

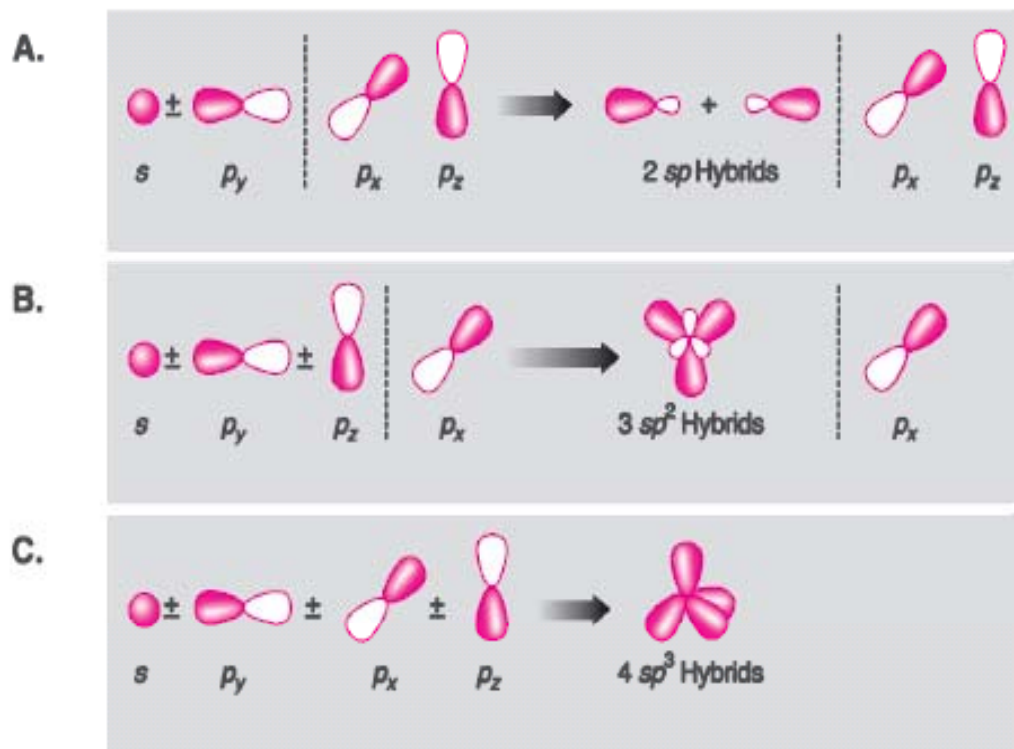
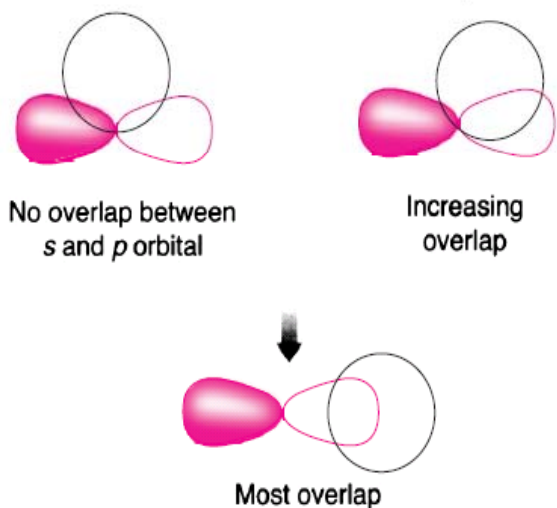
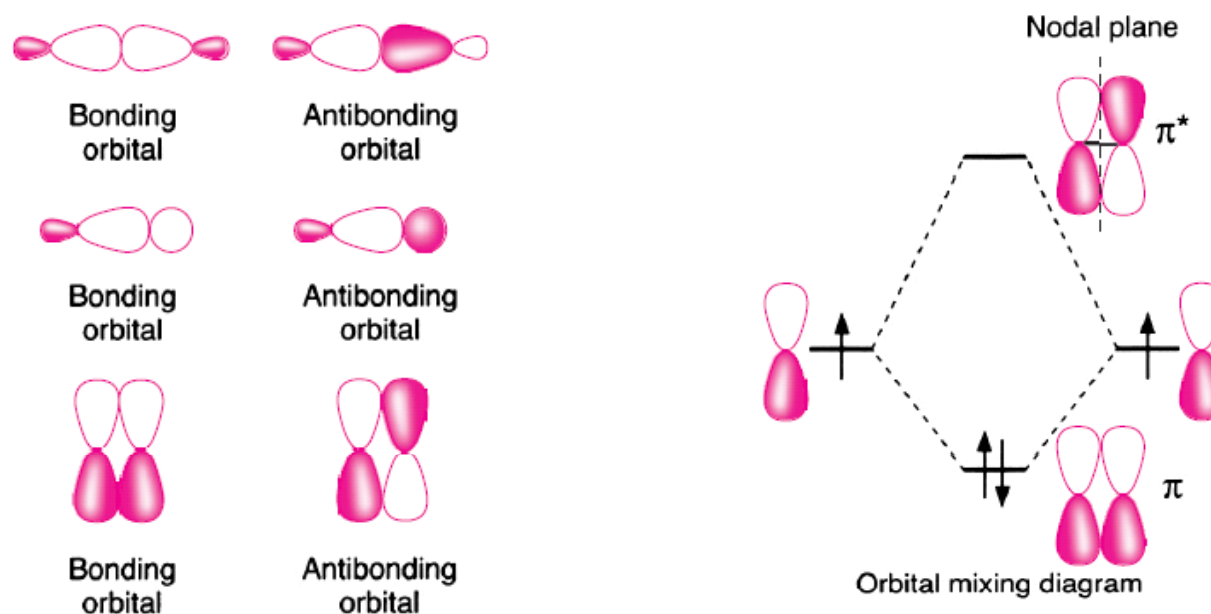


Figure 1.2
Forming hybrid orbitals. Combining an s orbital with one, two, or three p orbitals produces the familiar A. sp , B. sp^2 , and C. sp^3 hybrid orbitals.

Sigma Bonds and Pi Bonds

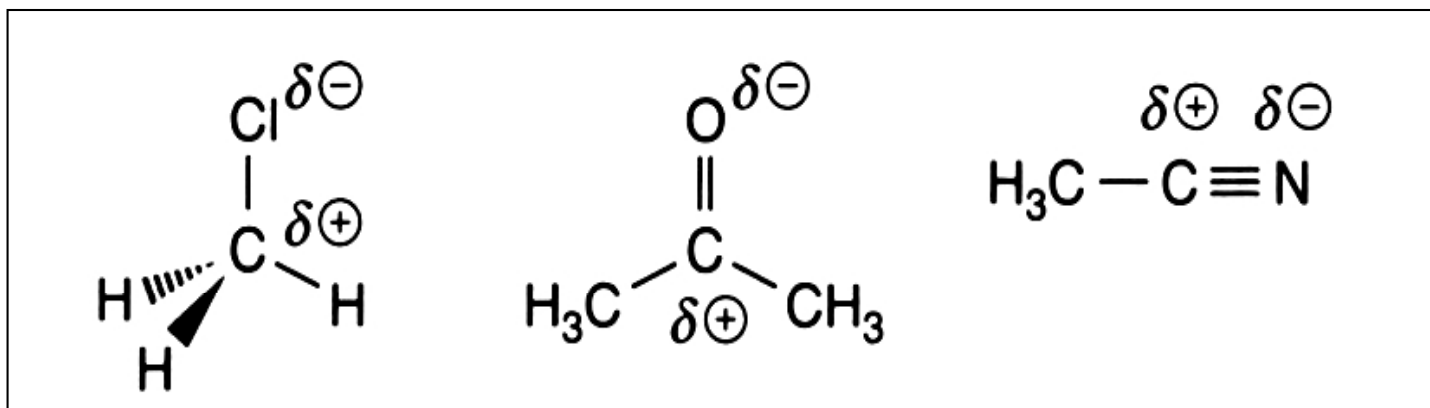
σ 键的电子密度沿成键方向呈轴向对称分布； π 键的电子密度则对称分布在成键方向的上下两侧。轨道相位相同为成键轨道，相位相反则为反键轨道。



右图表示两个原子p轨道形成 π 键的过程，这实际是吸收了分子轨道思想的价键理论模型。有机分子的基态里只有成键轨道(bonding orbitals)和非键轨道(nonbonding orbitals)才有电子填充。

Polar Covalent Bonding

A covalent bond that has an unequal sharing of the bonding pair of electrons is called a **polar covalent bond**.



Examples of polar covalent bonds

Electronegativity (电负性)

Table 1.1
Electronegativities of Atoms According to
the Scales of Pauling and Mulliken*

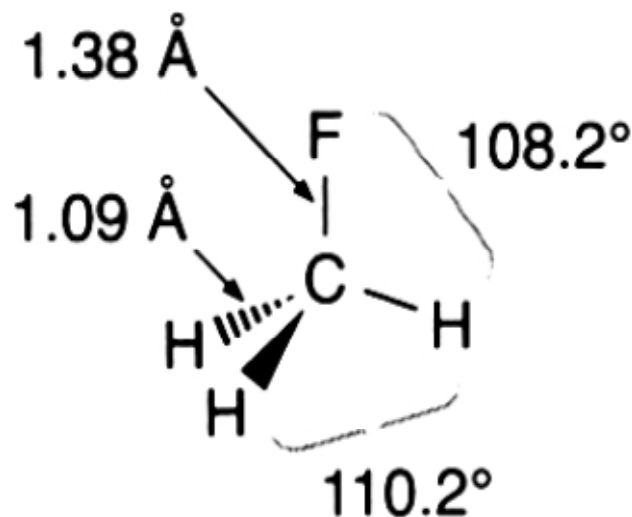
Atom	Pauling	Mulliken
H	2.1	3.01
B	2.0	1.83
C	2.5	2.67
N	3.0	3.08
O	3.5	3.22
F	4.0	4.44
Cl	3.0	3.54
Br	2.8	3.24
I	2.5	2.88
Li	1.0	1.28
Na	0.9	1.21
K	0.8	1.03
Mg	1.2	1.63
Ca	1.0	1.30
Al	1.5	1.37
Si	1.8	2.03
P	2.1	2.39
S	2.5	2.65

Pauling将电负性的概念描述为：“*the power of an atom in a molecule to attract electrons to itself...*”. Pauling电负性数值主要是通过通过分析各种原子间形成的化学键的离解能 (bond dissociation energies) 而得出的，因此反映的是原子在分子中的性质。

Mulliken电负性数值主要是通过通过分析各种原子的离子化势 (ionization potentials) 和电子亲和性 (electron affinities) 而得出的，因此反映的是原子本身的性质。

A Tricky Example

价层电子对互斥规则不能圆满地解释这个分子的结构。



杂化轨道理论认为： F-C键与C-H键均为 sp^3 杂化。由于氟原子的高电负性，可以更多地从碳原子外层的p轨道拿电子，造成F-C键与C-H键相比具有更多的p轨道性质。所以，与F-C键相关的键角更接近纯粹p轨道所形成的夹角(90°)，造成F-C-H键角比标准值(109°)略小。

Group Electronegativity

基团电负性：把化学基团看作一个整体，赋予其相应的电负性数值，衡量其吸电子能力。



Table 1.2
Group Electronegativities, Scaled to be
Compatible with the Pauling Scale*

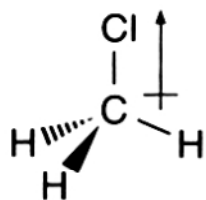
Group	Electronegativity
CH ₃	2.3
CH ₂ Cl	2.8
CHCl ₂	3.0
CCl ₃	3.0
CF ₃	3.4
Ph	3.0
CH=CH ₂	3.0
C≡CH	3.3
C≡N	3.3
NH ₂	3.4
NH ₃ ⁺	3.8
NO ₂	3.4
OH	3.7

Understanding Bond Lengths

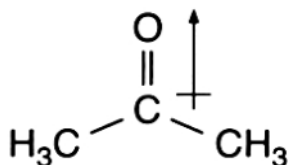
Table 1.4
Typical Bond Lengths of Some Covalent Bonds*

Bond	Length (Å)	Bond	Length (Å)
Single bonds		Double bonds	
C(sp ³)-C(sp ³)	1.53-1.55	C(sp ²)-C(sp ²)	alkenes 1.31-1.34
C(sp ³)-C(sp ²)	1.49-1.52	C(sp ²)-C(sp ²)	arenes 1.38-1.40
C(sp ²)-C(sp ²)	conjugated 1.45-1.46	C(sp ²)-O(sp ²)	aldehydes and ketones 1.19-1.22
	nonconjugated 1.47-1.48	C(sp ²)-O(sp ²)	esters 1.19-1.20
C(sp)-C(sp)	1.37-1.38	C(sp ²)-O(sp ²)	amides 1.225-1.24
C(sp ³)-O(sp ³)	ethers 1.42-1.44	C(sp ²)-N(sp ²)	imines 1.35
C(sp ³)-N(sp ³)	amines 1.46-1.48	Triple bonds	
C-F	1.39-1.43	C(sp)-C(sp)	alkynes 1.17-1.20
C-Cl	1.78-1.85		
C-Br	1.95-1.98		
C-I	2.15-2.18		
C(sp ³)-H	1.09-1.10		
C(sp ²)-H	1.075-1.085		
C(sp)-H	1.06		
N-H	1.00-1.02		
O-H	0.96-0.97		

Bond Dipole (键偶极)

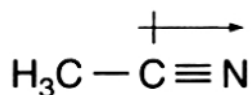


如果知道参与成键的原子上的电荷分布，则该化学键的偶极矩可以采用下式计算：



$$\mu = q \times r$$

charge distance



Bond dipole moments

偶极矩的单位通常用Debye (D)来表示：

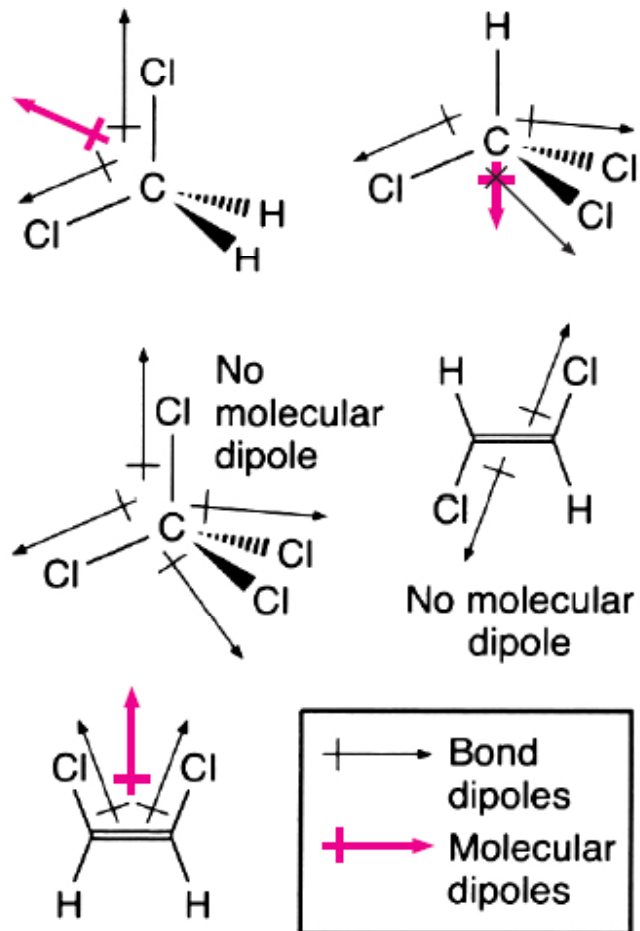
$$1\text{D} = 10^{-18} \text{esu} \cdot \text{cm}.$$

Helpful
Tips

Typical dipole moments for simple diatomic molecules are in the range of **0~11D**. a symmetrical molecule such as chlorine (Cl_2), has zero dipole moment, while gas phase potassium bromide (KBr) has a dipole moment of 10.5D.

Molecular Dipole (分子偶极)

分子偶极在概念上可以认为是分子中所有键偶极的矢量加合：



$$p = \sum_{i=1}^N q_i \times \vec{r}_i$$



如果已知分子内各个原子上的部分电荷，请问如何计算分子的偶极矩？

Molecular Dipole

Compound	Molecular dipole (D)	Compound	Molecular dipole (D)
CCl ₄	0.0	CH ₃ COCH ₃	2.9
CHCl ₃	1.0	CH ₃ COOH	1.7
CH ₂ Cl ₂	1.6	CH ₃ COCl	2.7
CH ₃ Cl	1.9	CH ₃ COOCH ₃	1.7
CH ₃ F	1.8	C ₆ H ₅ Cl	1.8
CH ₃ Br	1.8	C ₆ H ₅ NO ₂	4.0
CH ₃ I	1.6	1-Butene	0.34
CH ₃ OH	1.7	1-Propyne	0.80
CH ₃ OCH ₃	1.3	<i>cis</i> -2-Butene	0.25
CH ₃ CN	4.0	<i>cis</i> -1,2-Dichloroethene	1.9
CH ₃ NO ₂	3.4	Tetrahydrofuran	1.6
CH ₃ NH ₂	1.3	Water	1.8

Atomic Polarizability (极化率)

原子的极化率衡量该原子的电子云当存在外部电场影响时的变形程度。

Atomic polarizabilities										
H	0.6668								He	0.205
		C	1.76	N	1.10	O	0.802	F	0.557	
				P	3.13	S	2.90	Cl	2.18	
								Br	3.05	
								I	4.7 (or 5.35)	



Helpful
Tips

电负性是决定原子极化率的关键因素：电负性大的原子不容易被极化。

Molecular Polarizability

分子极化率可以定义为：单位电场梯度所诱导出的分子偶极矩的大小。分子极化率通常采用的单位为($\text{cm}^3/10^{-24}$)，具有与体积相同的量纲。

$$\alpha = p / E$$

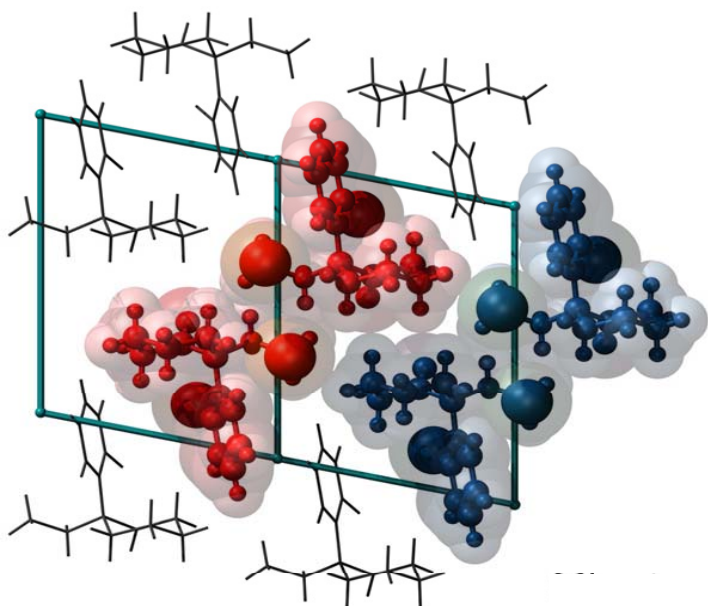
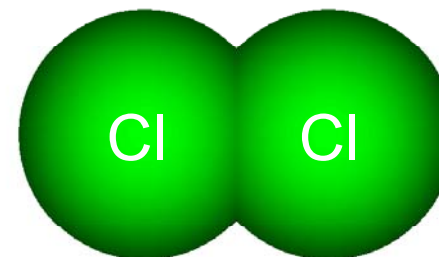
极化率 诱导偶极 电场梯度

CH ₄	2.6	NH ₃	2.21	H ₂ O	1.45	H ₂ S	3.8
CO ₂	2.91	CS ₂	8.8	CF ₄	3.84	CCl ₄	11.2
C ₂ H ₂	3.6	C ₂ H ₄	4.25	C ₂ H ₆	4.45	CH ₃ OH	3.23
Benzene	10.32	Cyclohexene	10.7	Cyclohexane	11.0		

*CRC Handbook of Chemistry and Physics, D. R. Lide (ed.), CRC Press, Inc., Boca Raton, FL (1990-1), pp. 10-193-10-209.

Atomic Radii

共价半径 (covalent radius): 两个同种类型原子之间所成的共价键键长的一半。



范德华半径 (van der Waals radius): 该数值是对原子体积大小的一种量度,可以认为是两个同种类型原子之间最小非键距离的一半。

$$V_{vdw} = \frac{4}{3} \times \pi \times R_{vdw}^3$$

Atomic Radii

Table 1.5
Covalent, Ionic, and van der Waals Radii of Select Atoms (Å)*

Atom	Covalent	VDW	Ion	Ionic
C	0.77	1.68		
H	0.30	1.11	H ⁻	2.08
N	0.70	1.53		
O	0.66	1.50		
F	0.64	1.51	F ⁻	1.36
Cl	0.99	1.84	Cl ⁻	1.81
Br	1.14	1.96	Br ⁻	1.95
I	1.33	2.13	I ⁻	2.16

*Pauling, L. (1960). *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; an Introduction to Modern Structural Chemistry*, 3d ed., Cornell University Press, Ithaca, NY.

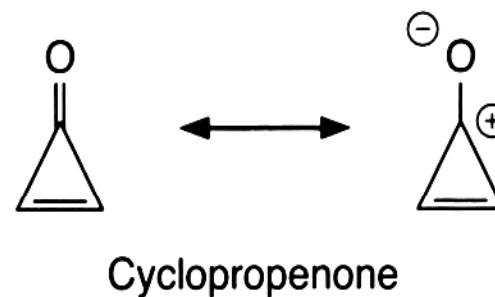
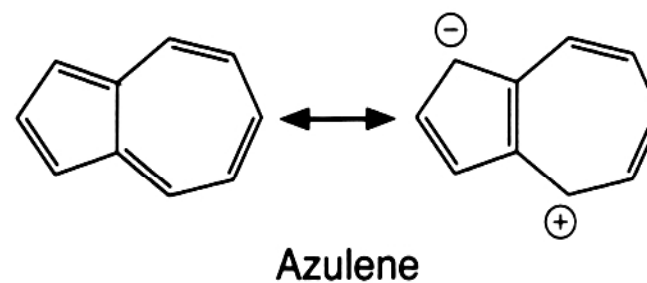
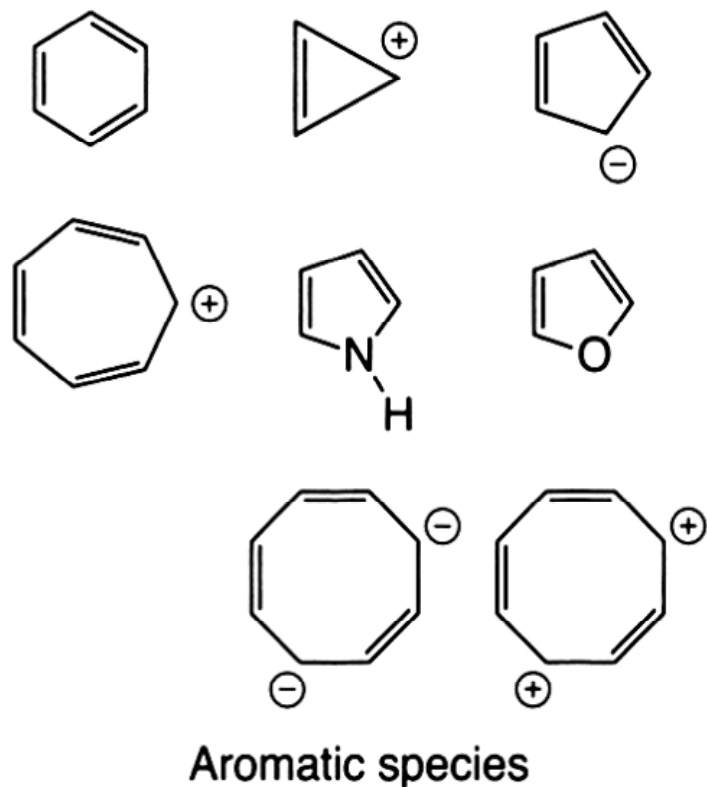
Aromaticity

芳香体系的特征:

- 分子中存在离域共轭的 π 体系，整个体系为平面结构，所有原子均处于该平面中。
- 结构式通常可以表示为单键-双键交替排列的方式，但是体系中各化学键的键长发生平均化。
- 体系具有特殊的稳定性，反应性质不同于通常的烯烃，例如：芳香环上易发生亲电取代反应，而不是加成反应。
- 在核磁谱中体现出环流效应 (ring current effects) 以及一些其他特殊的磁性性质。

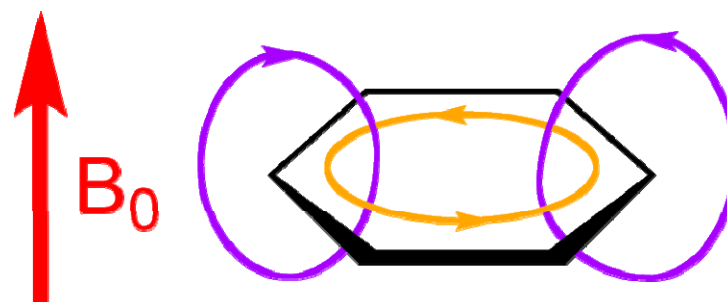
The Hückel Rule

Any hydrocarbon or heterocycle with $4n+2$ electrons in a fully conjugated cyclic π system is considered aromatic.



Aromatic Ring Current in NMR Spectroscopy

如果在垂直芳环的方向存在外在磁场，将在芳环离域的 π 电子中诱导出环流 (ring current)，而诱导出的环流将产生次生磁场。该次生磁场的方向在环流内与外部磁场方向相反，在环流之外与外部磁场方向相同。



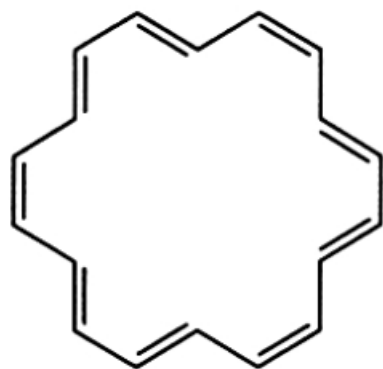
因此，芳环之外的氢原子将位于增强的磁场之中，其化学位移向低场移动，称为**反磁位移 (diamagnetic shift)**；而芳环之内的氢原子将位于被部分屏蔽的磁场之中，其化学位移向高场移动，称为**顺磁位移 (paramagnetic shift)**。

Helpful
Tips

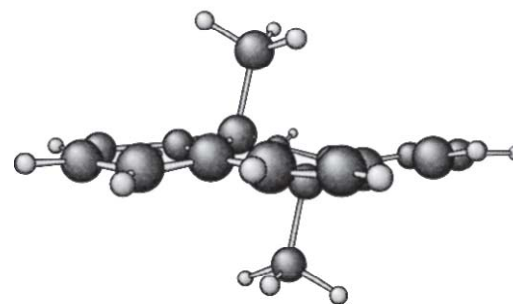
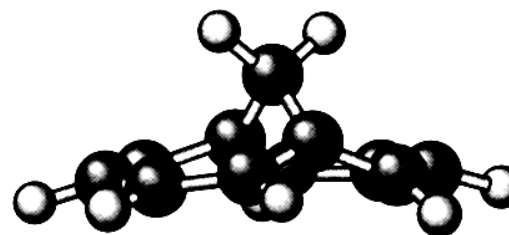
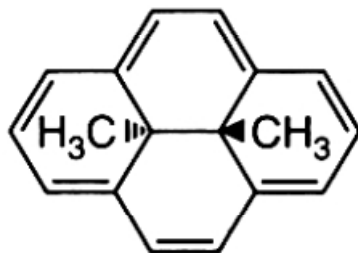
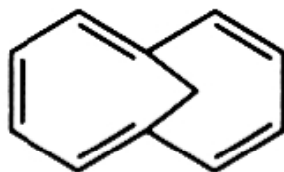
芳环上氢原子的典型化学位移值为7.3 ppm；而环己烯双键上的氢原子化学位移值为5.6 ppm。

The Hückel Rule: Large Annulenes (轮烯)

通常认为芳香体系的上限为22个 π 电子，更大的环系不具有芳香性所带来的额外稳定性。



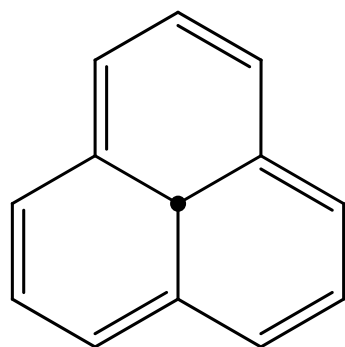
[18]-Annulene



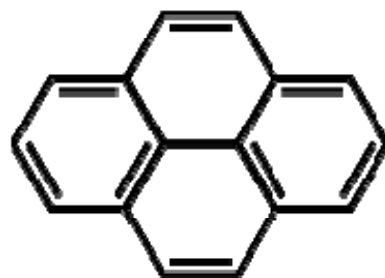
Examples of aromatic large annulenes

Polycyclic Aromatic Hydrocarbons

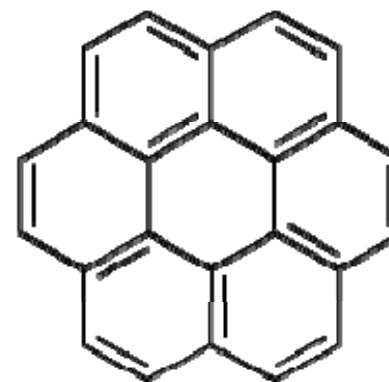
事实上Hückel规则只严格适用于单环的芳香体系。许多含有三个或更多芳香环的分子体系不符合Hückel规则，但是也具有芳香性。



3a¹H-phenalene



pyrene

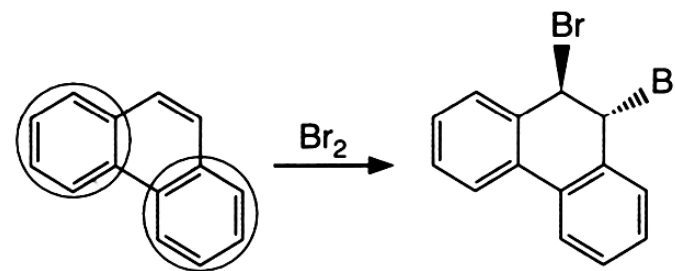
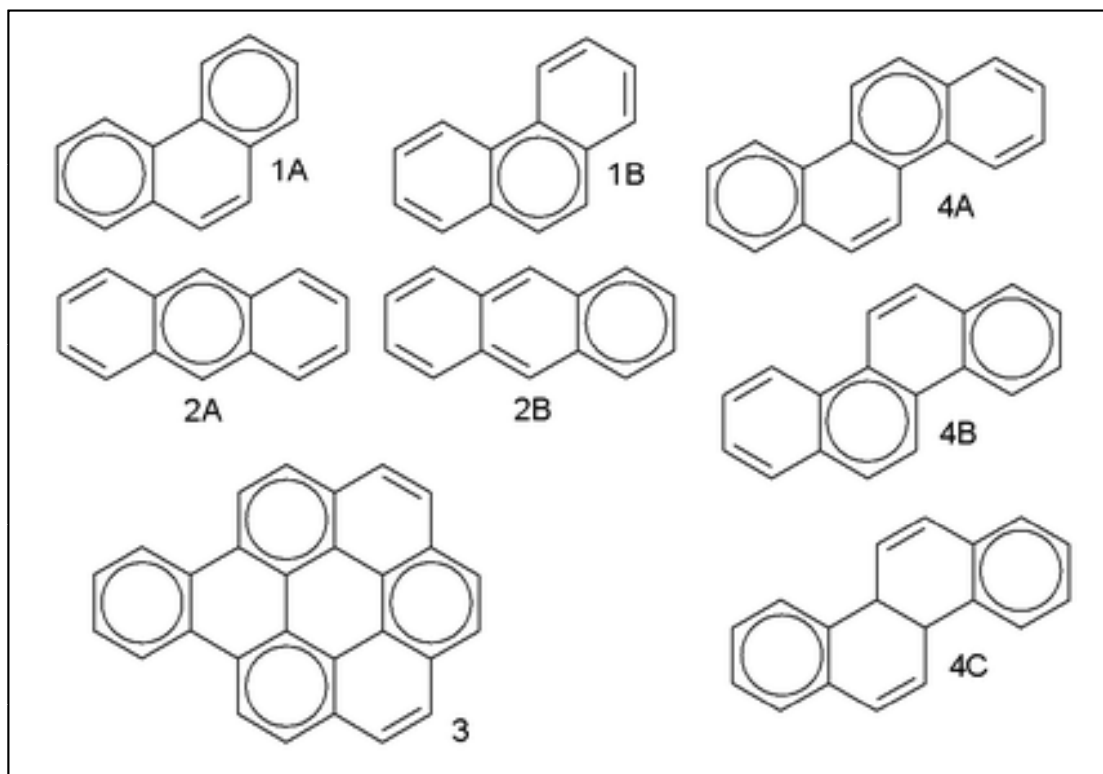


coronene

These polycyclic molecules are aromatic even though they fail the $4n+2$ rule.

Polycyclic Aromatic Hydrocarbons

Clar Rule (由Eric Clar在1964提出): 在一个稠环芳香体系所有可能的共振式中, 具有最大数目的孤立的六员芳香核 (aromatic π sextets) 者最能代表整个体系的性质。

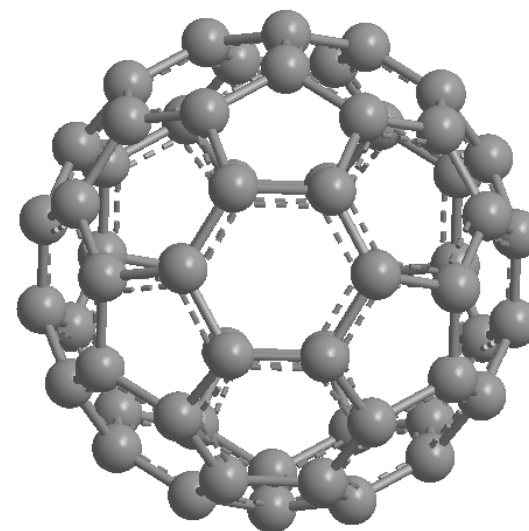


Fullerenes & Super-aromaticity

A spherical fullerene of n carbon atoms has n pi-bonding electrons. The quantum mechanics of such an arrangement should be like one stable filled shell for $n = 2, 8, 18, 32, 50, 72, 98, 128$, etc.; i.e. **twice a perfect square number**. This series does not include 60.

Fullerene does not exhibit “**super-aromaticity**”, that is, the electrons in the hexagonal rings do not delocalize over the whole molecule.

As a result, C_{60} in water tends to pick up two more electrons and become an anion. Researchers have been able to increase the reactivity of fullerenes by attaching active groups to their surfaces.



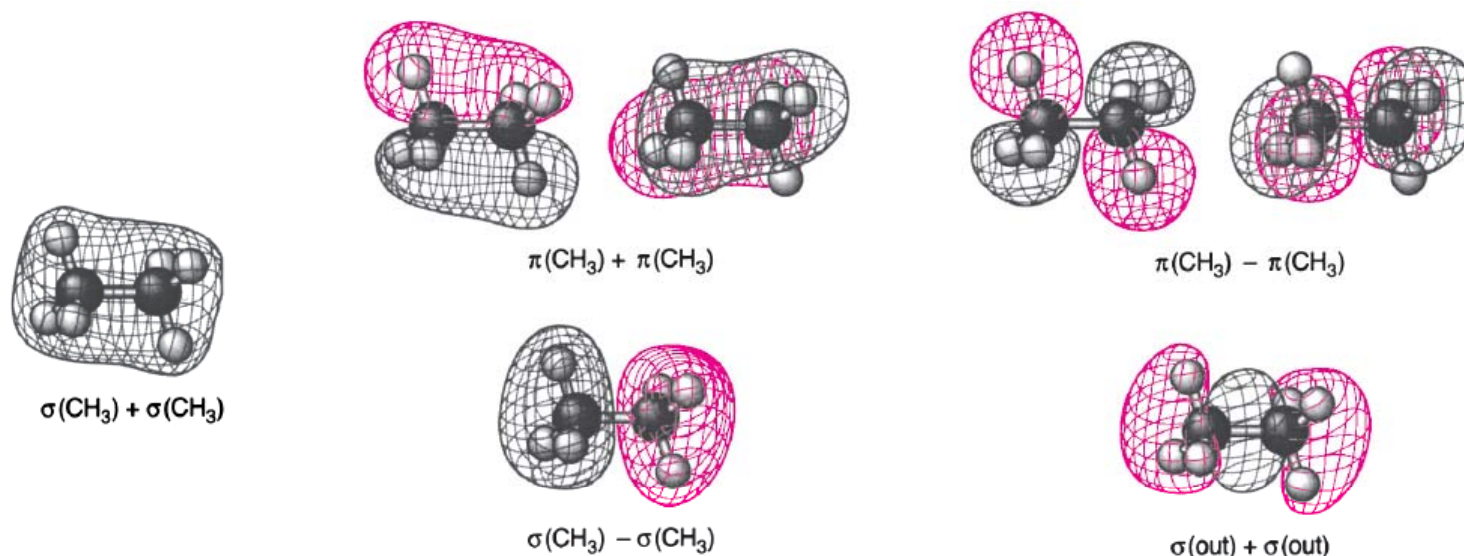
Hirsch, Andreas; Chen, Zhongfang; Jiao, Haijun, “Spherical Aromaticity in Symmetrical Fullerenes: The $2(N+1)^2$ Rule”, *Angew. Chem., Int. Ed. Engl.* **2000**, 39 (21): 3915–17.

Summary: Useful Concepts in VBT

- Hybridization theory, σ and π bonds
- Electronegativity
- Dipole and polarizability
- Aromaticity

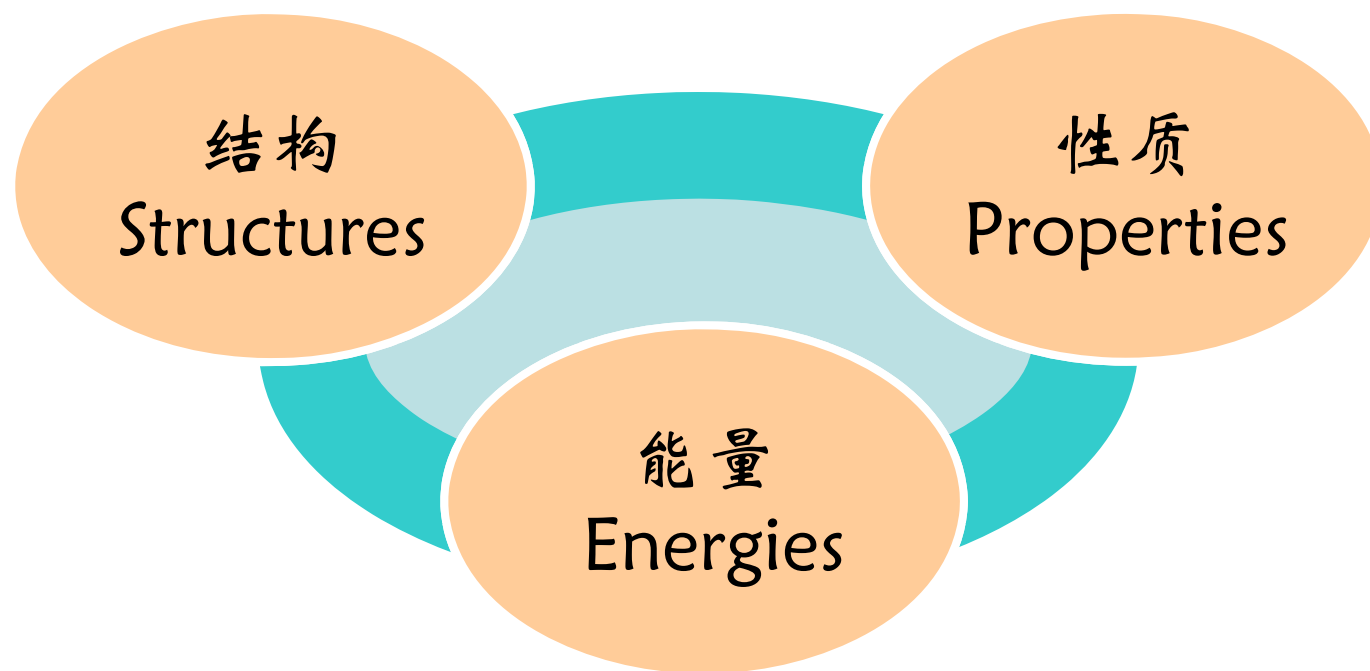
Further Reading

Qualitative Molecular Orbital Theory (QMOT, 定性分子轨道理论): 通过混合原子轨道来获得化学基团甚至整个分子的离域分子轨道的一套经验规则。



Computed molecular orbitals of ethane

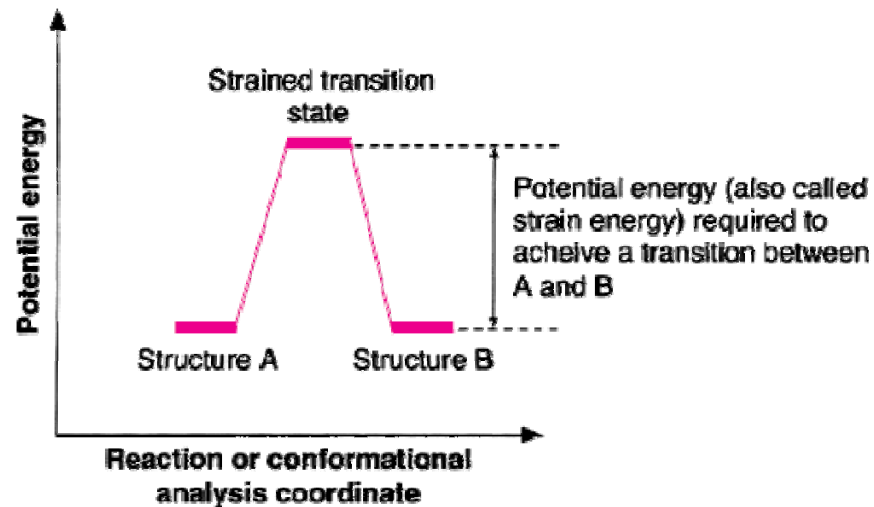
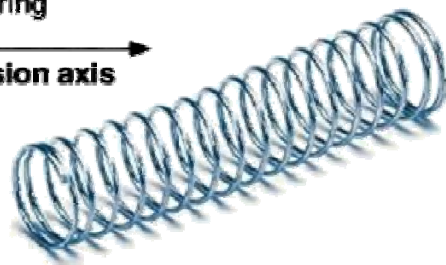
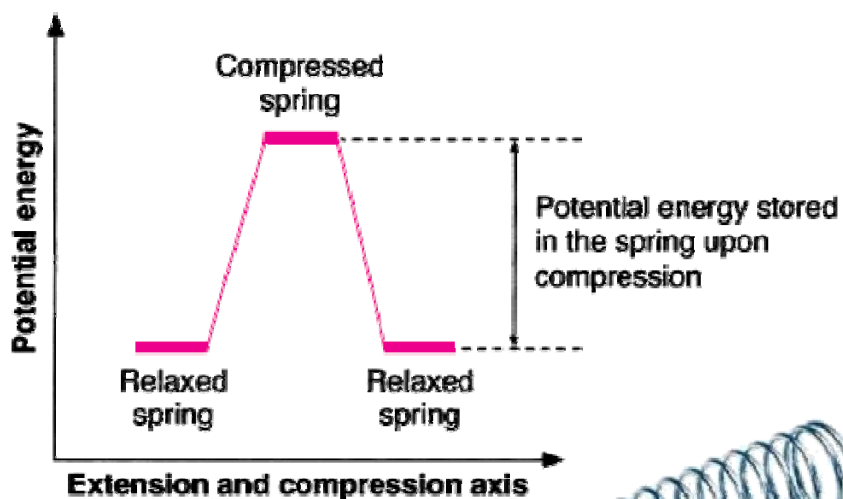
II. Thermochemistry of Stable Molecules



Structures and energies are so intimately connected.

Concepts of Energy: Internal Energy (内能)

分子的内能 (internal energy, U or E) 包含由于分子的各种运动形式 (平动、转动、振动) 而具有的动能 (kinetic energy) 以及与分子振动和电子结构相关的势能 (potential energy)。



Concepts of Energy: Enthalpy (焓)

热力学第一定律 (the first law of thermodynamics) 的一种表述方式为：物体内能的增加等于物体吸收的热量和物体所作的功的总和。

$$dU = \delta Q - \delta W$$

↑ ↑
Heat Work

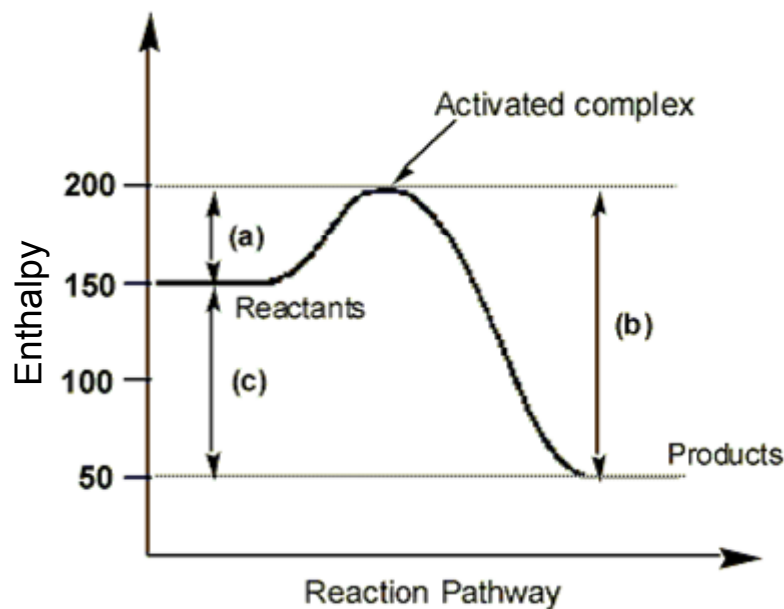
在恒定压力下，体系在两种状态间焓的变化(ΔH)为体系吸收或放出的热量。

$$H = U + pV \quad \Rightarrow \quad \begin{aligned} dH &= dU + (pdV + V dp) \\ &= (\delta Q - p dV) + (p dV + V dp) \\ &= \delta Q + V dp \end{aligned}$$

Concepts of Energy: Enthalpy (焓)

反应热 (Heat of reaction, $\Delta H_{\text{rxn}}^\circ$ or ΔH°):

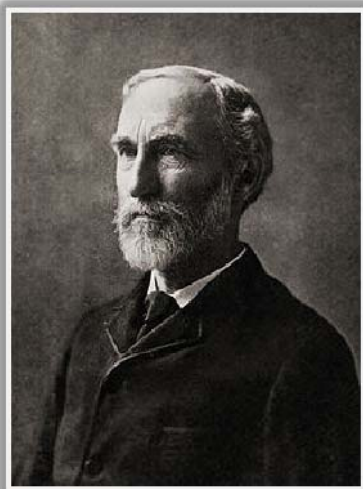
- When $\Delta H^\circ < 0$: the reaction is **exothermic** (放热反应).
- When $\Delta H^\circ > 0$: the reaction is **endothermic** (吸热反应).



Concepts of Energy: Gibbs Free Energy

Gibbs-Helmholtz equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$



Josiah W. Gibbs
(1839 - 1903)



Hermann von Helmholtz
(1821 - 1894)

Gibbs free energy (G): The energy that can be converted into work at a constant temperature and pressure.

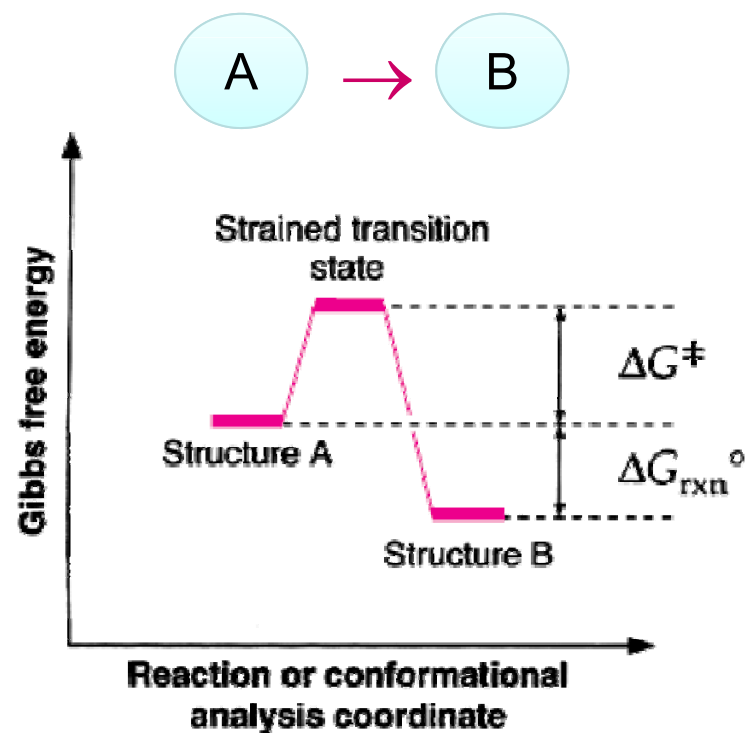
Helmholtz free energy (F): The energy that can be converted into work at a constant temperature and volume.

Concepts of Energy: Gibbs Free Energy

Gibbs free energy (ΔG°) determines the equilibrium between two chemical states under standard states and constant pressure.

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} \quad K_{\text{eq}} = \frac{[\text{B}]}{[\text{A}]}$$

- When $\Delta G^\circ < 0$: the transformation of A to B is **exergonic** (放能的).
- When $\Delta G^\circ > 0$: the transformation of A to B is **endergonic** (吸能的).



Concepts of Energy: Gibbs Free Energy

Table 2.1
Composition of an A/B Mixture as a Function of
Gibbs Free Energy Difference and Temperature

ΔG°	K	% B	% A
At 298 K			
0	1	50	50
-1.36	10	90.9	9.1
-2.72	100	99	1
-4.08	1000	99.9	0.1
-0.5	2.33	70	30
-1.0	5.44	85	15
At 195.15 K (-78 °C)			
-1.0	13.2	93	7

$$\ln K_{eq} = \frac{-\Delta G^\circ}{RT}$$

在室温298K下，一个反应的标准自由能每变化 **1.36 kcal/mol**，该反应的平衡常数就变化 **10倍**。

← Compare this!

Concepts of Energy: Entropy (熵)

在分子体系中，熵是与原子以及分子的各种运动形式联系在一起的，这些运动形式又称为自由度 (degrees of freedom)。

- **平动自由度** (translational)
- **转动自由度** (rotational)
- **振动自由度** (vibrational, 包括分子内部的各种运动形式，如键伸缩、键的旋转、键角的振动等等)。



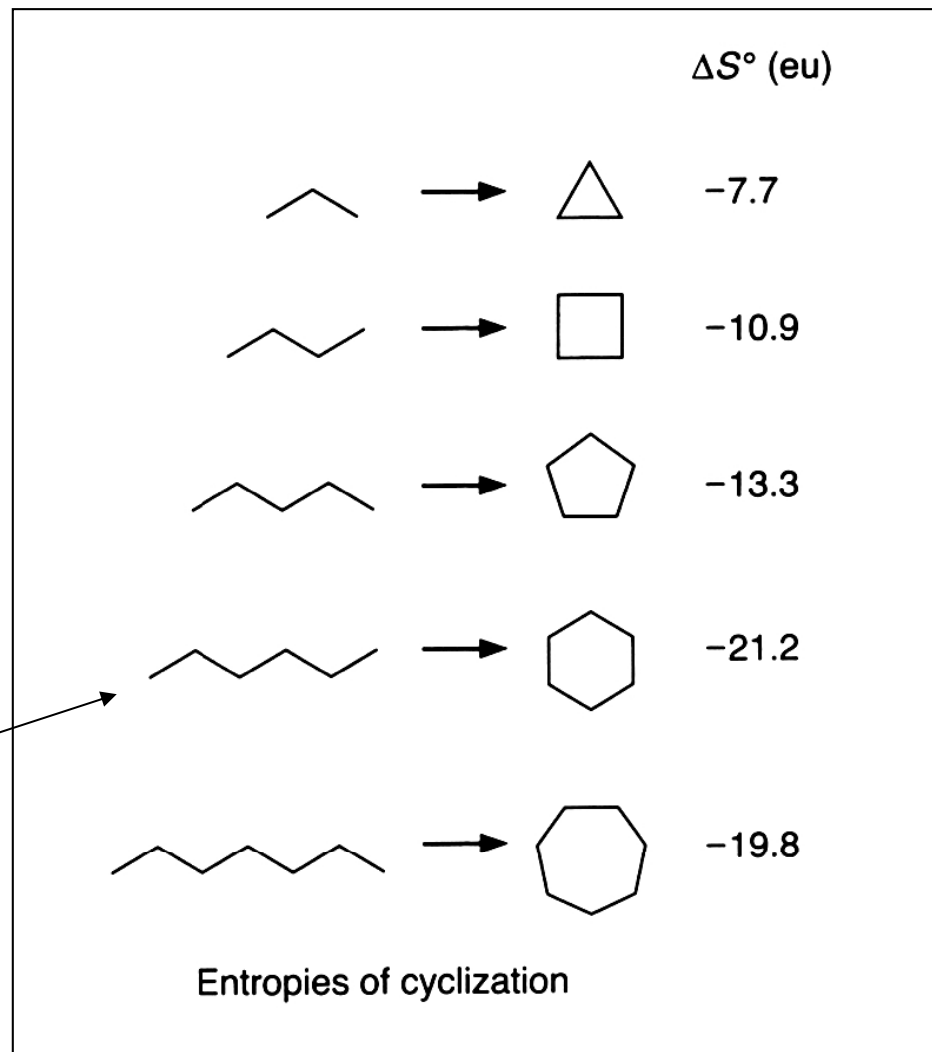
Entropy is a measure of disorder.

Concepts of Energy: Entropy (熵)

熵值的变化对某些化学结构的变化过程具有明显的影响。

例如，在烷烃的环化中每多固定一个可旋转单键，体系的熵大约会损失3~4 eu。

Cyclohexane is an exception!



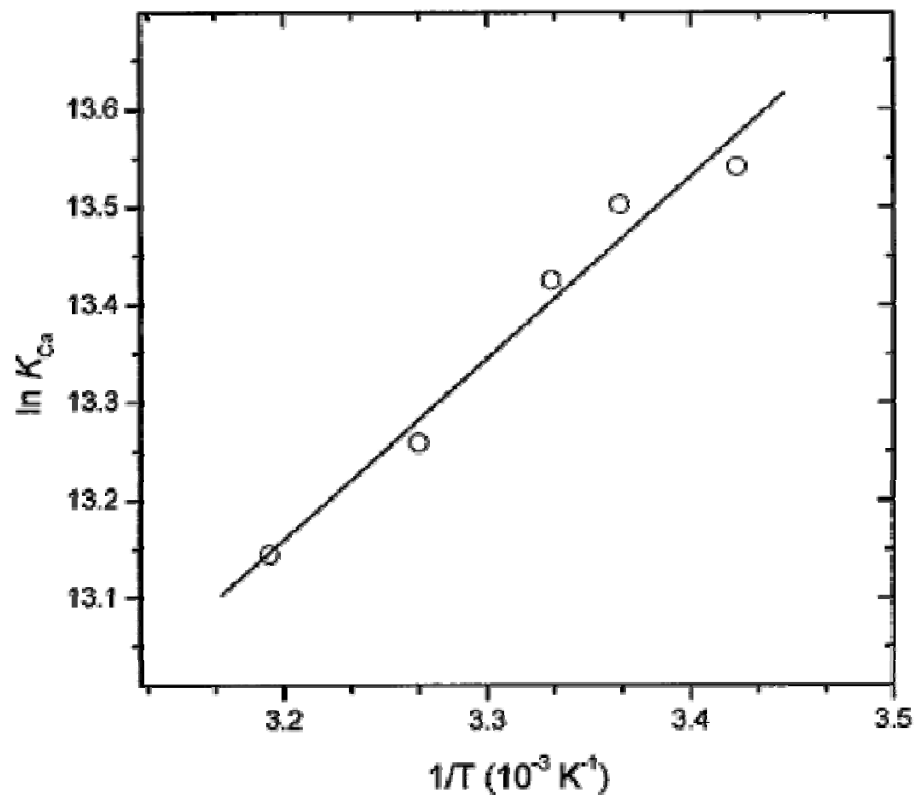
The van't Hoff Plot

以化学反应的 $\ln K_{\text{eq}}$ 对 $1/T$ 作图可得直线，直线的截距和斜率分别与反应的标准焓变和标准熵变相关。

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT}$$

$$\ln K_{\text{eq}} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$



注意：此处假设反应体系的热容 C_p 在测量温度范围内不发生改变。

The van't Hoff Plot

Consider a conversion reaction: $A \rightarrow B$ $\ln K_{eq} = \frac{-\Delta G_{rxn}^0}{RT}$

$$\left. \begin{aligned} \frac{\partial H_A}{\partial T} &= C_{P(A)}^0 & H_A^0 &= H_{A,ref}^0 + (T - T_{ref}) \cdot C_{P(A)}^0 \\ \frac{\partial H_B}{\partial T} &= C_{P(B)}^0 & H_B^0 &= H_{B,ref}^0 + (T - T_{ref}) \cdot C_{P(B)}^0 \end{aligned} \right\} \begin{aligned} \Delta H_{rxn}^0 &= \Delta H_{rxn,ref}^0 + (T - T_{ref}) \cdot (C_{P(B)}^0 - C_{P(A)}^0) \\ &= \Delta H_{rxn,ref}^0 + (T - T_{ref}) \cdot \Delta C_P^0 \\ &= \Delta H_{rxn,ref}^{0'} + T \cdot \Delta C_P^0 \end{aligned}$$

$$\left. \begin{aligned} S_A^0 &= S_{A,ref}^0 + (\ln T - \ln T_{ref}) \cdot C_{P(A)}^0 \\ S_B^0 &= S_{B,ref}^0 + (\ln T - \ln T_{ref}) \cdot C_{P(B)}^0 \end{aligned} \right\} \begin{aligned} \Delta S_{rxn}^0 &= \Delta S_{rxn,ref}^0 + (\ln T - \ln T_{ref}) \cdot \Delta C_P^0 \\ &= \Delta S_{rxn,ref}^{0'} + \ln T \cdot \Delta C_P^0 \end{aligned}$$

The van't Hoff plot with heat capacity corrections (see Chapter 4.1):

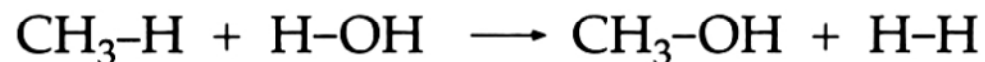
$$\ln K_{eq} = -\frac{\Delta H_{rxn,ref}^{0'}}{R} \cdot \left(\frac{1}{T}\right) + \Delta S_{rxn,ref}^{0'} \cdot \left(\frac{1}{R}\right) + \Delta C_P^0 (\ln T - 1) \cdot \left(\frac{1}{R}\right)$$

Bond Strength

键解离能 (bond dissociation energy, BDE) 可以用来衡量化学键的强度。



利用键解离能数据可以计算反应热 (heats of reaction, $\Delta H_{\text{rxn}}^\circ$ or ΔH°):

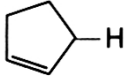
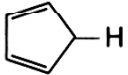
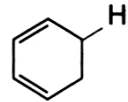
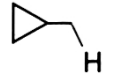
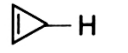


$$105.1 \quad + \quad 119 \qquad \qquad 92.3 \quad + \quad 104.2$$

$$\Delta H^\circ = (105.1 + 119) - (92.3 + 104.2) = 27.6 \text{ kcal/mol}$$

Bond Dissociation Energy

Table 2.2
Some Specific Bond Dissociation Energies (in kcal/mol)*

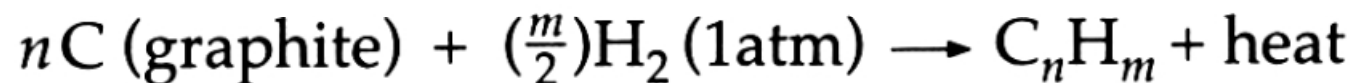
Bond	BDE	Bond	BDE	Bond	BDE
H-H	104.2 (104.2)	CH ₂ =CH-H	110 (110.7)	CH ₃ -CH ₃	90.4 (90.1)
CH ₃ -H	105.1 (105.0)	C ₆ H ₅ -H	110.9 (112.9)	CH ₃ -F	109.9 (115)
CH ₃ CH ₂ -H	98.2 (101.1)	HC≡C-H	132 (131.9)	CH ₃ -Cl	84.6 (83.7)
(CH ₃) ₂ CH-H	95.1 (98.6)	C ₆ H ₅ CH ₂ -H	88 (89.7)	CH ₃ -Br	70.9 (72.1)
(CH ₃) ₃ C-H	93.2 (96.5)	CH ₂ =CHCH ₂ -H	86.3 (88.8)	CH ₃ -I	57.2 (57.6)
c(CH ₂) ₃ -H	106.3	CH ₃ C(O)-H	86 (88.1)	CH ₃ -OH	92.3 (92.1)
c(CH ₂) ₄ -H	96.5	HO-H	119 (118.8)	CH ₃ -NH ₂	84.9 (85.2)
c(CH ₂) ₅ -H	94.5	CH ₃ O-H	104.4 (104.6)	CH ₃ -SH	74
c(CH ₂) ₆ -H	95.5	NH ₂ -H	107.4 (107.6)	CH ₃ -SiH ₃	88.2
 -H	82.3	CH ₃ S-H	90.7 (87.4)	CH ₃ -SiMe ₃	89.4
 -H	71.1	HO-OH	51	CH ₃ -GeMe ₃	83
 -H	73	CH ₃ O-OCH ₃	37.6 (38)	CH ₃ -SnMe ₃	71
 -H	97.4	HOCH ₂ -H	94 (96.1)	CH ₃ -PbMe ₃	57
 -H	90.6	H ₂ C=CH ₂	(174.1)	CH ₃ -OCH ₃	(83.2)
CH ₃ -CH=CH ₂	(101.4)	HC≡CH	(230.7)	CH ₃ -C ₂ H ₅	(89.0)
C ₆ H ₅ -C ₆ H ₅	(118)	H ₂ C=O	(178.8)	CH ₃ -CH(CH ₃) ₂	(88.6)
		CH ₃ -C ₆ H ₅	(103.5)	CH ₃ -C(CH ₃) ₃	(87.5)
		CH ₃ -CH ₂ C ₆ H ₅	(77.6)	CH ₃ -CH ₂ CH=CH ₂	(76.5)

重点关注电负性以及
原子的杂化状态对键
解离能的影响。



Thermodynamic Stability of a Molecule

化合物的标准生成焓(Standard heat of formation, ΔH_f°) 是在标准状态下由合适的单质生成一摩尔该化合物所伴随的焓变。



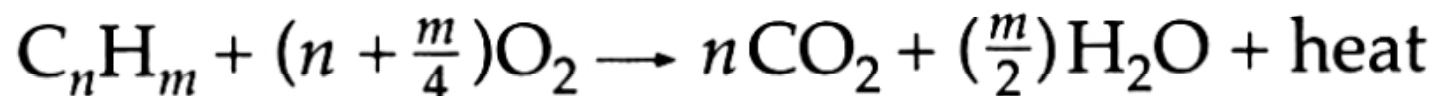
* The most stable form of the element at 1 bar of pressure and the specified temperature, usually 298.15 K.



Unfortunately, heat of formation is normally not easy to measure directly. Then how?

Deduction of Heat of Formation

化合物的**标准燃烧热** (heat of combustion, ΔH_c^0) 是指在标准状态下在氧气中燃烧1摩尔该化合物所释放的热量。



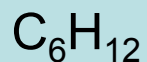
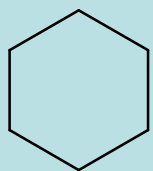
在以上反应中， CO_2 和 H_2O 的标准生成焓已知分别为 -94.05 和 -57.08 kcal/mol。因此就可以从该反应的标准燃烧热 (ΔH_c^0) 推导出 C_nH_m 的标准生成热 (ΔH_f^0)。



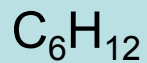
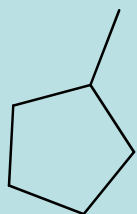
Thermodynamics vs. Kinetics

标准生成焓可以用来比较相关化合物(例如同分异构体)的热力学稳定性。

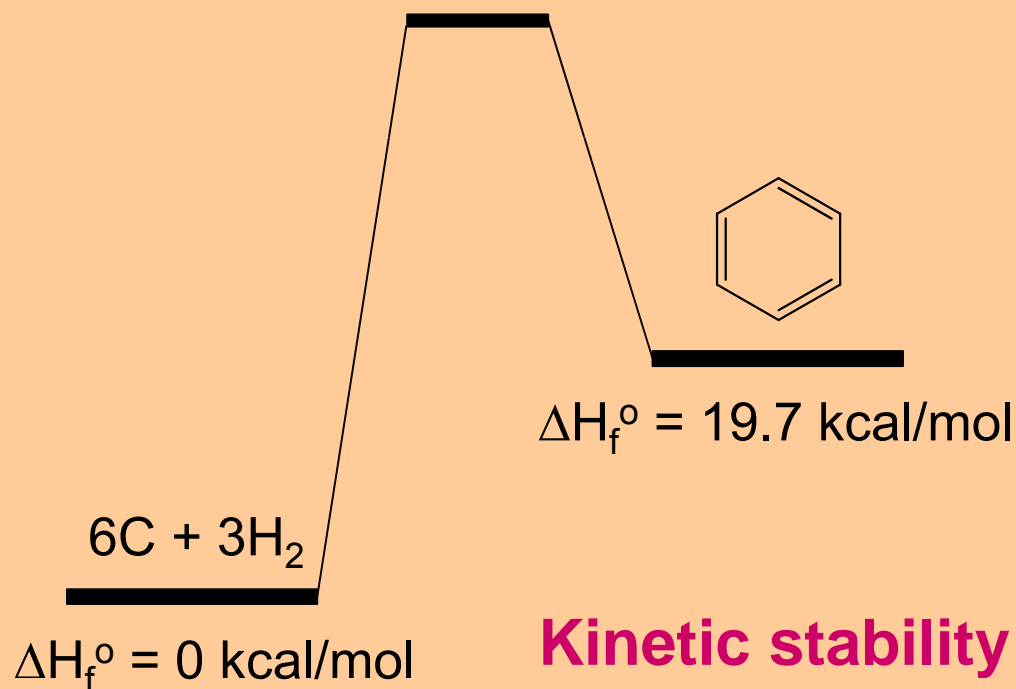
Thermodynamic stability



$$\Delta H_f^\circ = -29.4 \text{ kcal/mol}$$



$$\Delta H_f^\circ = -25.5 \text{ kcal/mol}$$



The Group Increment Method

基团加合法 (Group Increment Method) 认为化合物的标准生成焓可以看作是相关基团贡献值的加合。

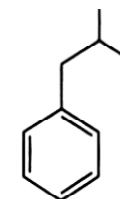
Table 2.3
Values for the Heats of Formation of
Simple Linear Alkanes (in kcal/mol)

Structure	ΔH_f°	$\Delta\Delta H_f^\circ$
CH ₃ -CH ₃	-20.24	—
CH ₃ -CH ₂ -CH ₃	-24.84	4.60
CH ₃ -CH ₂ -CH ₂ -CH ₃	-30.15	5.31
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃	-35.00	4.85
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	-39.96	4.96
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	-44.89	4.93
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	-49.81	4.92

The Group Increment Method

Table 2.4
Group Increments (in kcal/mol) for Fundamental Groupings*

Group	ΔH_f°	Group	ΔH_f°	Group	ΔH_f°
C-(H) ₃ (C)	-10.20	C-(O)(C _d)(H) ₂	-6.5	C-(O) ₂ (C) ₂	-18.6
C-(H) ₂ (C) ₂	-4.93	C _B -(O)	-0.9	C-(O) ₂ (C)(H)	-16.3
C-(H)(C) ₃	-1.90	O-(C) ₂	-23.2	C-(O) ₂ (H) ₂	-16.1
C-(C) ₄	0.50	O-(C)(H)	-37.9	C-(N)(H) ₃	-10.08
C _d -(H) ₂	6.26	O-(C _d) ₂	-33.0	C-(N)(C)(H) ₂	-6.6
C _d -(H)(C)	8.59	O-(C _d)(C)	-30.5	C-(N)(C) ₂ (H)	-5.2
C _d -(C) ₂	10.34	O-(C _B) ₂	-21.1	C-(N)(C) ₃	-3.2
C _d -(C _d)(H)	6.78	O-(C _B)(C)	-23.0	C _B -(N)	-0.5
C _d -(C _d)(C)	8.88	O-(C _B)(H)	-37.9	N-(C)(H) ₂	4.8
C _d -(C _B)(H)	6.78	C-(CO)(C) ₃	1.58	N-(C) ₂ (H)	15.4
C _d -(C _B)(C)	8.64	C-(CO)(C) ₂ (H)	-1.83	N-(C) ₃	24.4
C _d -(C _d) ₂	4.6	C-(CO)(C)(H) ₂	-5.0	N-(C _B)(H) ₂	4.8
C _B -(H)	3.30	C-(CO)(H) ₃	-10.08	N-(C _B)(C)(H)	14.9
C _B -(C)	5.51	C _B -(CO)	9.7	N-(C _B)(C) ₂	26.2
C _B -(C _d)	5.68	CO-(C) ₂	-31.4	N-(C _B) ₂ (H)	16.3
C _B -(C _B)	4.96	CO-(C)(H)	-29.1	N _f -(H)	16.3
C-(C _d)(C)(H) ₂	-4.76	CO-(H) ₂	-26.0	N _f -(C)	21.3
C-(C _d) ₂ (H) ₂	-4.29	CO-(C _B) ₂	-25.8	N _f -(C _B)	16.7
C-(C _d)(C _B)(H) ₂	-4.29	CO-(C _B)(C)	-30.9	CO-(N)(H)	-29.6
C-(C _B)(C)(H) ₂	-4.86	CO-(C _B)(H)	-29.1	CO-(N)(C)	-32.8
C-(C _d)(C) ₂ (H)	-1.48	CO-(O)(C)	-35.1	N-(CO)(H) ₂	-14.9
C-(C _B)(C) ₂ (H)	-0.98	CO-(O)(H)	-32.1	N-(CO)(C)(H)	-4.4
C-(C _d)(C) ₃	1.68	CO-(O)(C _d)	-32.0	N-(CO)(C) ₂	-
C-(C _B)(C) ₃	2.81	CO-(O)(C _B)	-36.6	N-(CO)(C _B)(H)	-
C-(O)(C) ₃	-6.6	CO-(C _d)(H)	-29.1	N-(CO) ₂ (H)	-18.5
C-(O)(C) ₂ (H)	-7.2	O-(CO)(C)	-43.1	N-(CO) ₂ (C)	-5.9
C-(O)(C)(H) ₂	-8.1	O-(CO)(H)	-58.1	N-(CO) ₂ (C _B)	-0.5
C-(O)(H) ₃	-10.08	C _d (CO)(C)	7.5		
C-(O)(C _B)(H) ₂	-8.1	C _d -(CO)(H)	5.0		



$$\begin{aligned}
 5 \text{ C}_B\text{-(H)} &= 5(3.30) = 16.50 \\
 1 \text{ C}_B\text{-(C)} &= 1(5.51) = 5.51 \\
 1 \text{ C-(C}_B\text{)(C)(H)}_2 &= 1(-4.86) = -4.86 \\
 1 \text{ C-(H)(C)}_3 &= 1(-1.90) = -1.90 \\
 2 \text{ C-(H)}_3\text{(C)} &= 2(-10.20) = -20.40 \\
 & \quad \quad \quad -5.15 \text{ kcal/mol}
 \end{aligned}$$

Experimental: -5.15 ± 0.34 kcal/mol

Example: Estimation of the heat of formation of i-Bu-benzene using group increments.



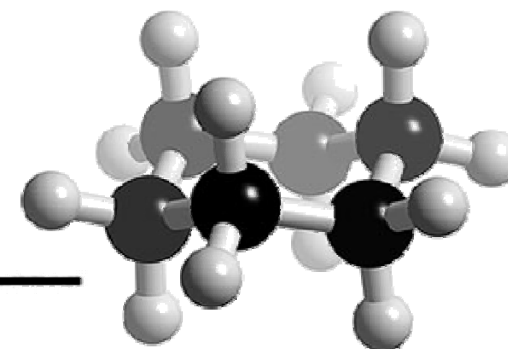
Strain Energy

张力能 (Strain energy) 是指标准生成焓的实验值 ($\Delta H_f^0_{exp}$) 与使用基团加合法获得的计算值 ($\Delta H_f^0_{calc}$) 之间的差别。

$$E_{strain} = \Delta H_{f,exp}^0 - \Delta H_{f,calc}^0$$

Table 2.5
Calculated vs. Observed ΔH_f° Values
(in kcal/mol) for Selected Molecules

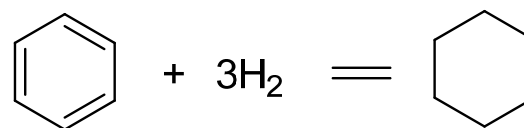
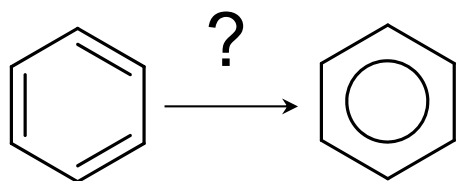
	ΔH_f° calculated by group increments	ΔH_f° experimental
Cyclohexane	-29.6	-29.9
Cyclopentane	-24.7	-18.3
Cyclobutane	-19.7	+6.7
Cyclopropane	-14.8	+12.7



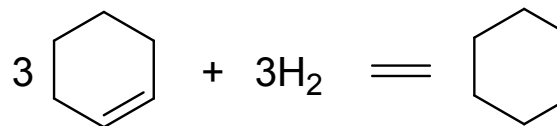
Stabilization by Aromaticity

苯分子具有的芳香性究竟对其热力学稳定性带来了多大的贡献？通常认为是 $\sim 32 \text{ kcal/mol}$.

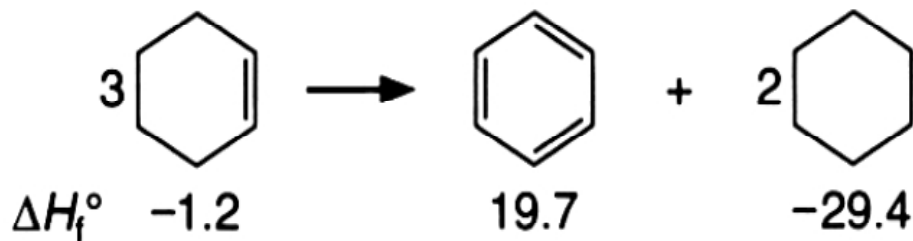
Method A



Method B



Method C (isodesmic reaction):



$$\begin{aligned}\Delta H^0 &= (-29.4) \times 2 + 19.7 + 1.2 \times 3 \\ &= -35.5 \text{ kcal/mol}\end{aligned}$$

环己烯的张力能
= 1.4 kcal/mol

$$E_{\text{aromatic}} = -35.5 - 3 \times (-1.4) = -31.3 \text{ kcal/mol}$$

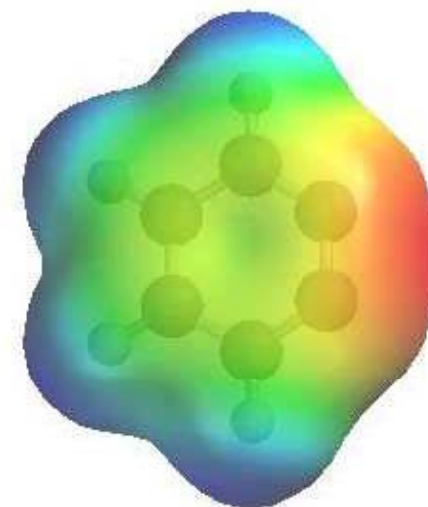
Summary

- 热力学中关于能量的各种基本概念: Internal energy, enthalpy, entropy, free energy
- 键解离能: 作为化学键强度的量度
- 标准生成焓: 作为化合物热力学稳定性的量度
- 能量没有绝对值! 我们总是在比较两个相关的化学状态: 化学反应的起点和终点、分子的两个构象、或者是分子的不同能级等等。

III. Reactive Intermediates

四种基本的反应中间体 (reactive intermediates)

- 碳正离子 (carbocations)
- 碳负离子 (carbanions)
- 自由基 (radicals)
- 碳烯 (carbenes)



Carbocations (碳正离子)

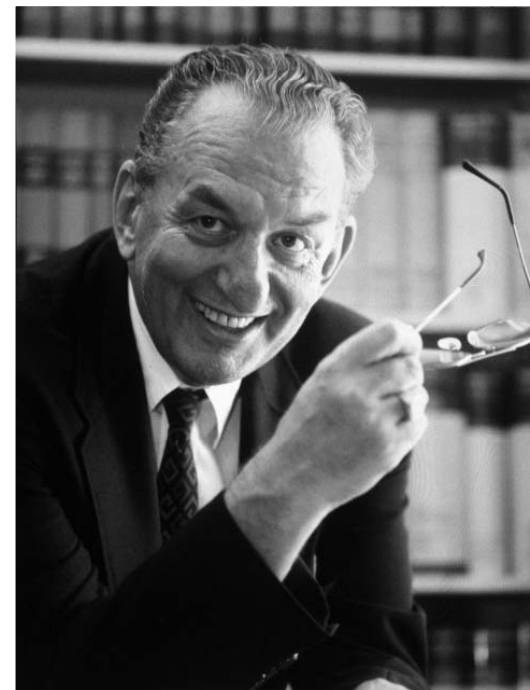
- Carbenium Ions (碳烯正离子)



- Carbonium Ions (碳正离子)



These definitions are introduced in analog to:

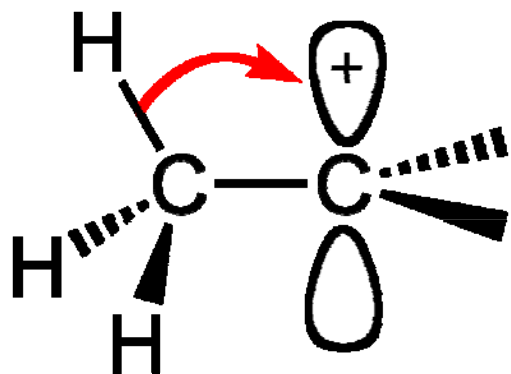


Prof. George A. Olah
Winner of the Nobel Prize
in chemistry in 1994

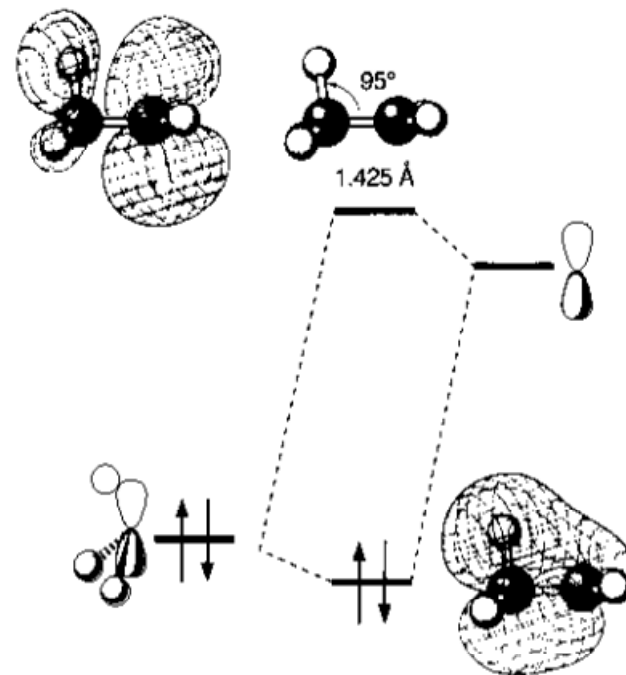
Carbenium Ions

价键理论认为碳烯正离子中的碳原子可以看作是 sp^2 杂化并拥有一个空的 p 轨道。

烷基取代可以稳定碳烯正离子，其稳定性顺序一般为：



价键理论的解释：超共轭效应

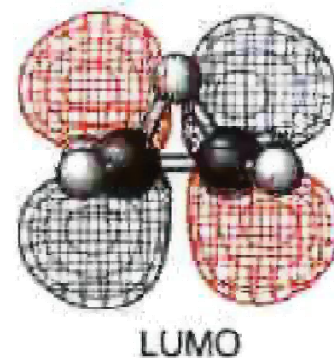
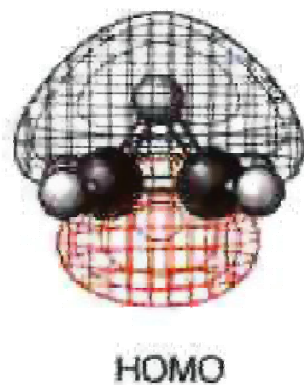
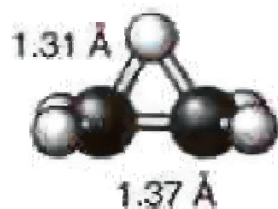
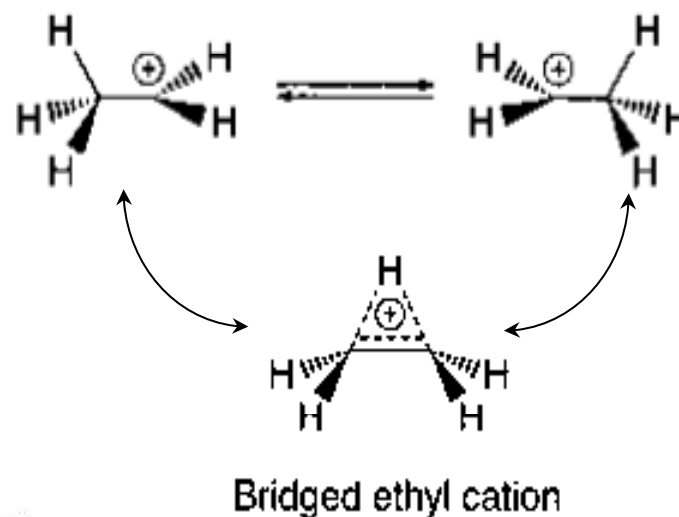


QMOT理论的解释

Orbital mixing diagram between an empty p orbital and a $\pi(\text{CH}_3)$ orbital

Bridged Ethyl Cation

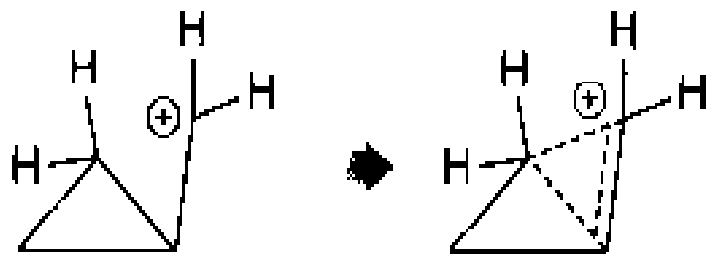
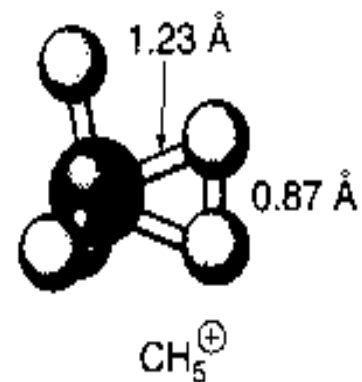
碳烯正离子特别容易发生异构化：乙基正离子实际上采取下图中所示的桥式构型。



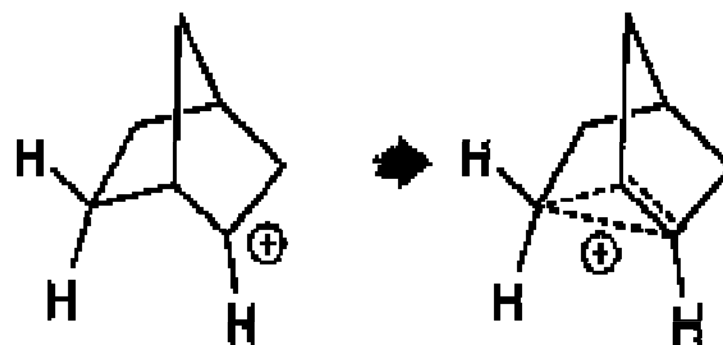
乙基正离子的构型以及分子轨道

Carbonium Ions

碳正离子 CH_5^+ 可以看作作为碳烯正离子 CH_3^+ 与一分子 H_2 成键：该分子中存在一个三中心两电子键 (three-center-two-electron bond)。



Cyclopropylcarbinyl cation



Norbornyl cation

碳烯正离子向碳正离子的异构化

Stability of Carbocations

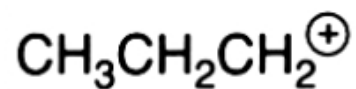
Hydride ion affinity (HIA, 氢负离子亲和性) is defined as the ΔH^0 of the reaction below.



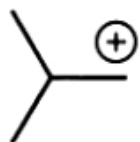
HIA provides a number that can be compared directly for cations of dissimilar structure. A larger positive HIA implies a less stable carbocation.

Stability of Carbocations

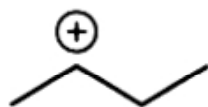
Table 2.8
Gas Phase Hydride Ion Affinities
(HIA, in kcal/mol) for Selected
Carbocations (in kcal/mol)*



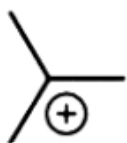
266



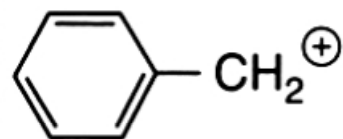
265



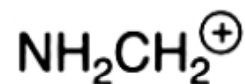
247



231



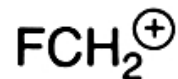
234



218



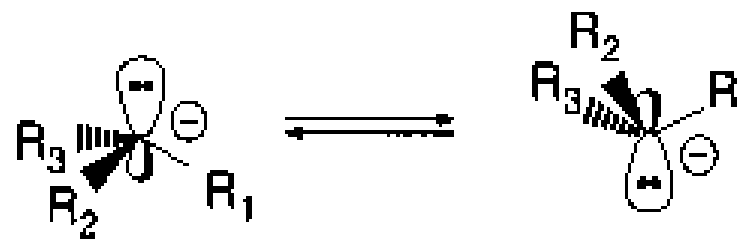
243



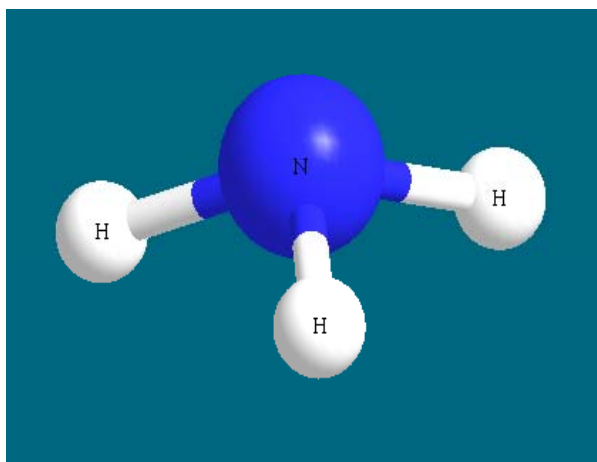
290

Carboanions (碳负离子)

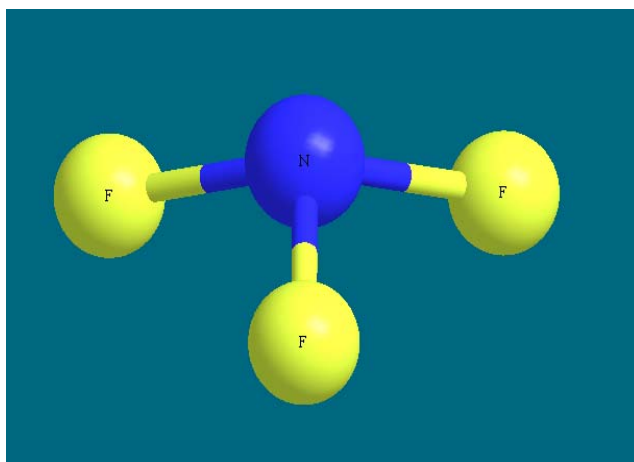
价键理论认为碳负离子中的碳原子采取 sp^3 杂化，其上存在一个孤电子对。碳负离子的构型可以发生翻转。



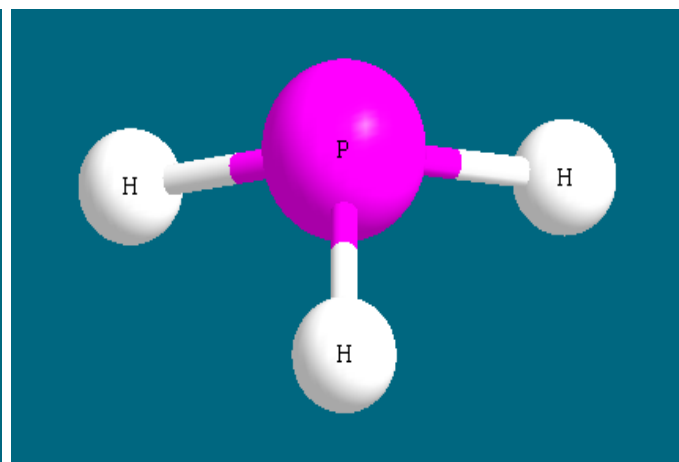
Comparison of inversion barriers



NH_3 : ~5 kcal/mol



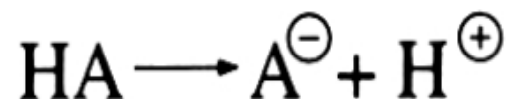
NF_3 : ~50 kcal/mol



PH_3 : ~35 kcal/mol

Stabilities of Carbanions

Stabilities of carbanions can be measured by the ΔH^0 for the reaction below:



A more commonly used indicator is the pK_a ($-\log K_a$) value of the carbon acid.

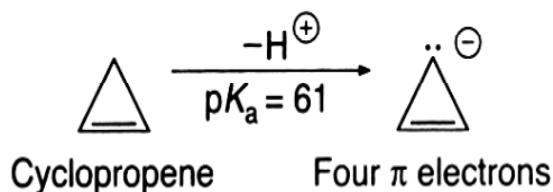
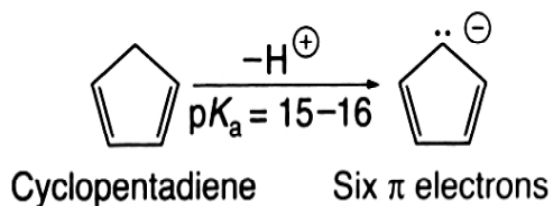
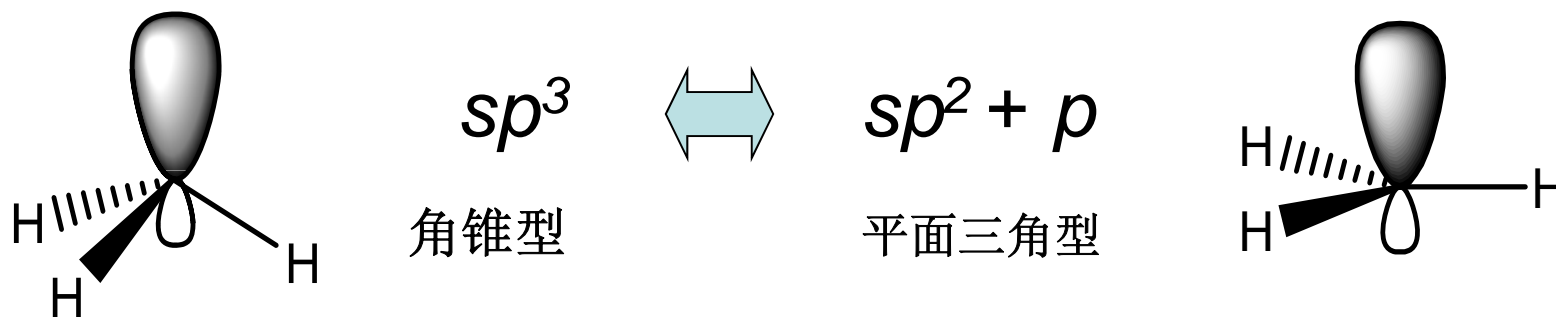


Table 2.10
 pK_a Values of Selected Carbon Acids

Ethane	50
Cyclohexane	45
$(\text{CH}_3)_3\text{CH}$	71
Ethylene	44
Benzene	43 or 37
Acetylene	24
Phenylacetylene	19.9
PhCH_3	41.2
$\text{CH}_2=\text{CHCH}_3$	43
Ph_2CH_2	33.0
Ph_3CH	31.5
Cyclopentadiene	16.0
Cyclopropene	61
CH_3COCH_3	20.0
$\text{CH}_3\text{COCH}_2\text{COCH}_3$	8.84
CH_3NO_2	10.2
CH_3CN	25.0
CH_3SOCH_3	28.5

Radicals

事实上所有定域的碳自由基都采取角锥构型，只有甲基自由基是完全的平面构型。



- 电负性强的取代基使碳自由基的构型更加趋于角锥化。
- 带有离域 π 体系的取代基使碳自由基的构型更加趋于平面化。

Stability of Radicals

键离解能 (BDE) 可以用来衡量自由基的稳定性:



烷基取代基同样可以稳定自由基, 其稳定性的顺序为:

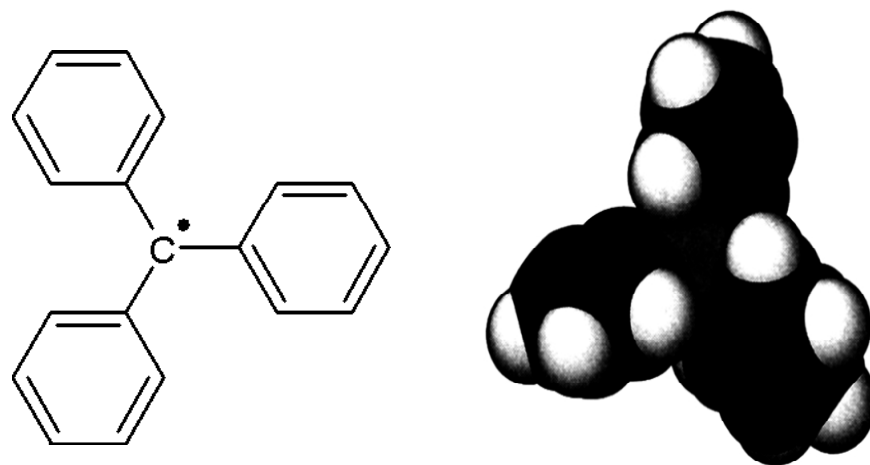


BDE values (kcal/mol)

CH ₃ -H	105.1
CH ₃ CH ₂ -H	98.2
(CH ₃) ₂ CH-H	95.1
(CH ₃) ₃ C-H	93.2

Persistence of Radicals

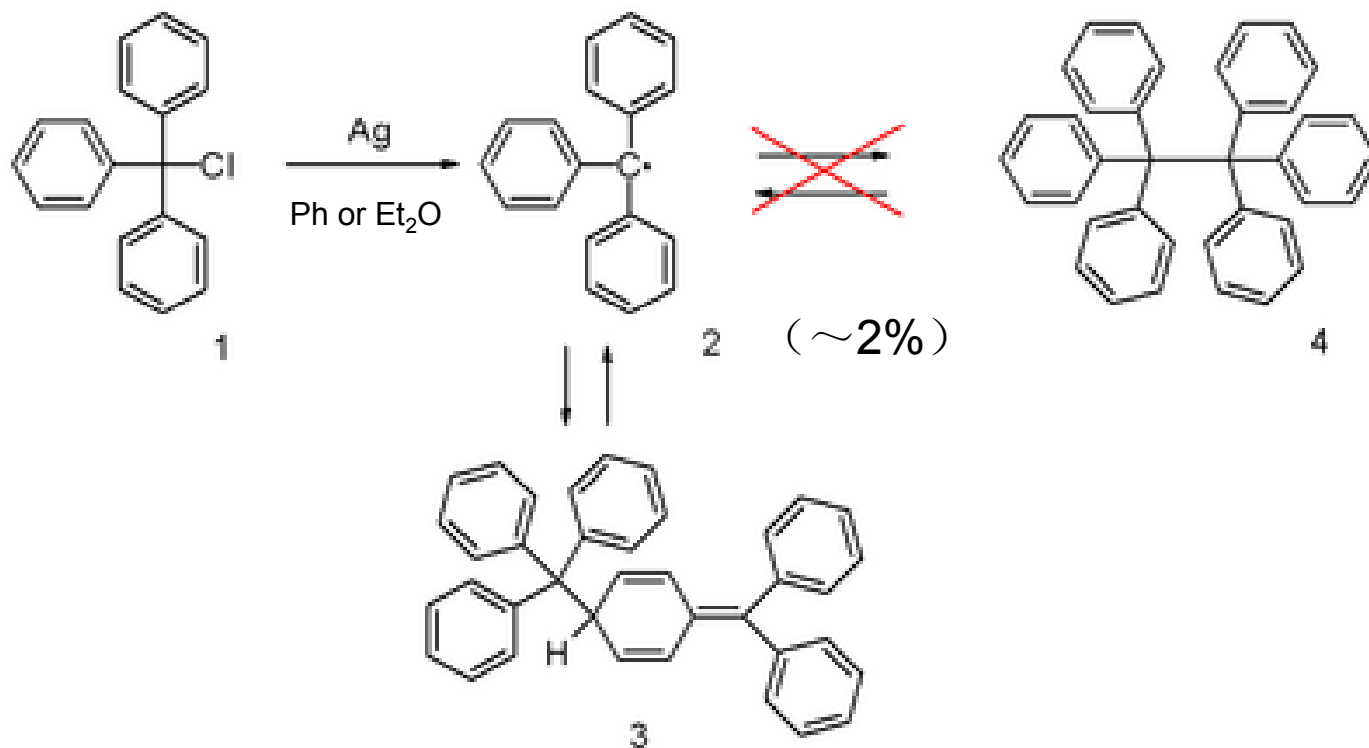
- 自由基分子的**稳定性 (stability)**是指与参考态相比的热力学稳定性。
- 自由基分子的**持久性 (persistence)**是指其寿命长短，衡量其动力学性质。



Trityl radical (Triphenylmethyl radical)

The Triphenylmethyl Radical

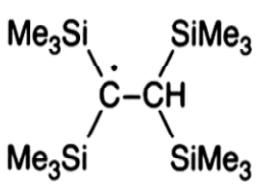
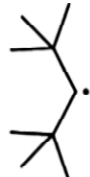
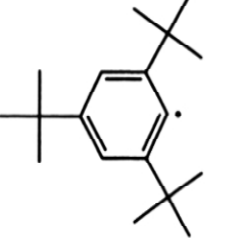
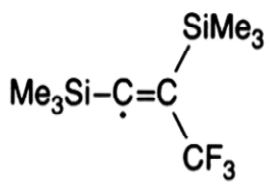
Preparation of the triphenylmethyl radical:



Moses Gomberg
(1866-1947)

Long-life Radicals

Table 2.6
The Persistence of Various Radicals*

R•	$t_{1/2}$, 25 °C, 10^{-5} M	R•	$t_{1/2}$, 25 °C, 10^{-5} M
CH ₃ •	20 μs		> 110 days
	1 min		6 ms
(t-Bu) ₃ C•	8.4 min		1 min
(Me ₃ Si) ₃ C•	2.3 days		

TMS = trimethylsilyl.

*Ingold, K. U. "Free Radical Clocks." *Acc. Chem. Res.*, **13**, 317 (1980).

长寿命的自由基往往带有立体位阻大的取代基。

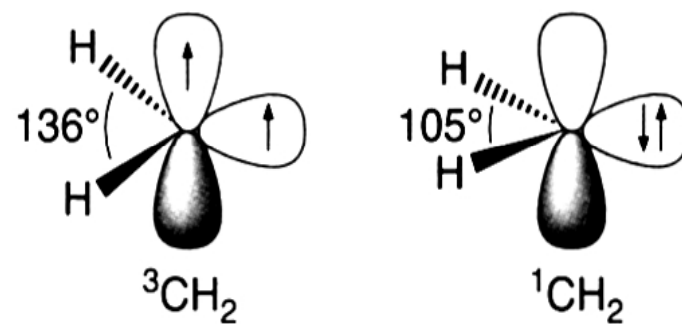


Carbenes

单线态 (singlet state): $S = (\frac{1}{2}) + (-\frac{1}{2}) = 0$; $m_s = 2S + 1 = 1$

三线态 (triplet state): $S = (\frac{1}{2}) + (\frac{1}{2}) = 1$; $m_s = 2S + 1 = 3$

由于存在两个自旋相同的单电子，洪特规则 (Hund's rule) 预测三线态更加稳定。事实上所有简单结构的碳烯分子的基态都是三线态。



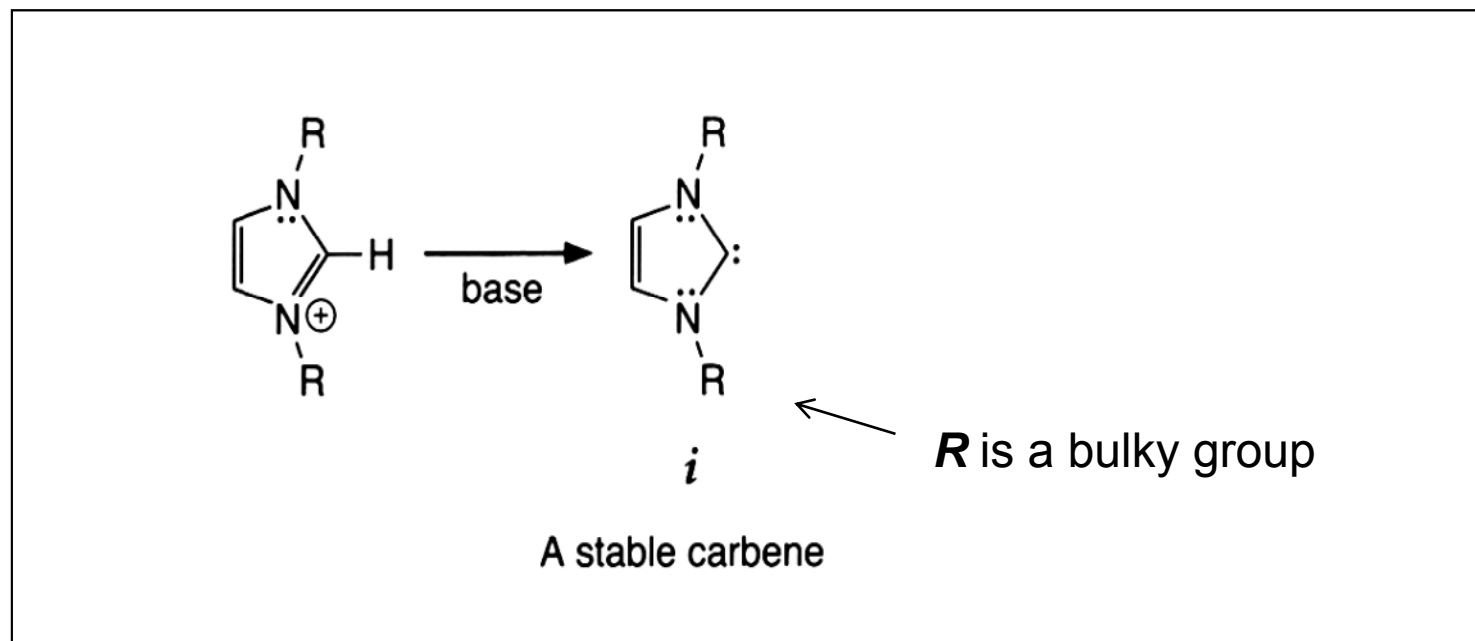
Carbene electron configurations



注意：价键理论不适用于解释碳烯分子的三线态或单线态构型。

A stable carbene in the singlet state!

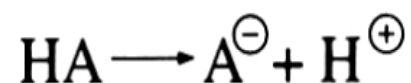
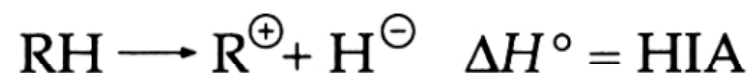
Carbenes with **lone-pair donating substituents** such as N, O, and halogens can have singlet ground states.



Arduengo, A. J. III. "Looking for stable carbenes.", *Acc. Chem. Res.* **32**, 913-921 (1999).

Summary

- 价键理论也可以用来解释反应中间体的相关性质，但并不总是适用。要小心！
- 可以用相关化学过程的能量变化来比较反应中间体的热力学稳定性：



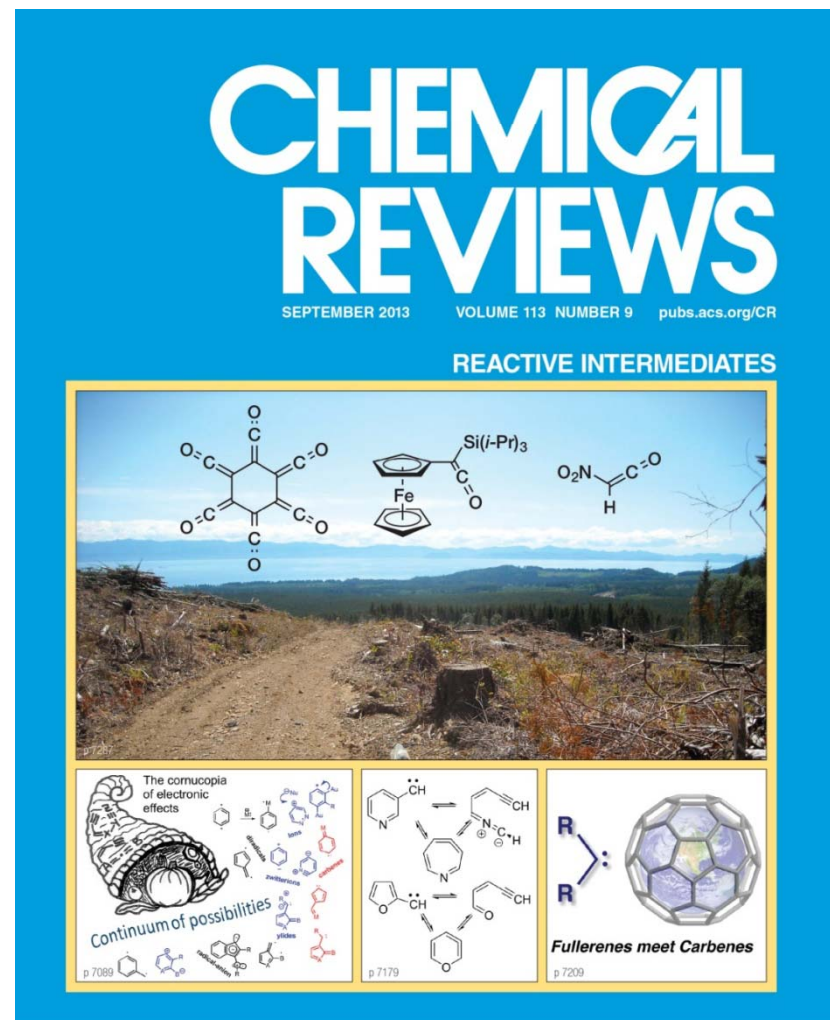
- 取代基效应：alkyl, electronegative, conjugated substituents

An awesome reference!

CHEMICAL REVIEWS

Introduction to Reactive Intermediates

Volume 113, number 9, 2013



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