西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

Chapter 3

Alkanes and Cycloalkanes

3.1 What Are Alkanes?

3.2 What Is Constitutional Isomerism in Alkanes?

3.3 How Do We Name Alkanes?

3.4 What Are Cycloalkanes?

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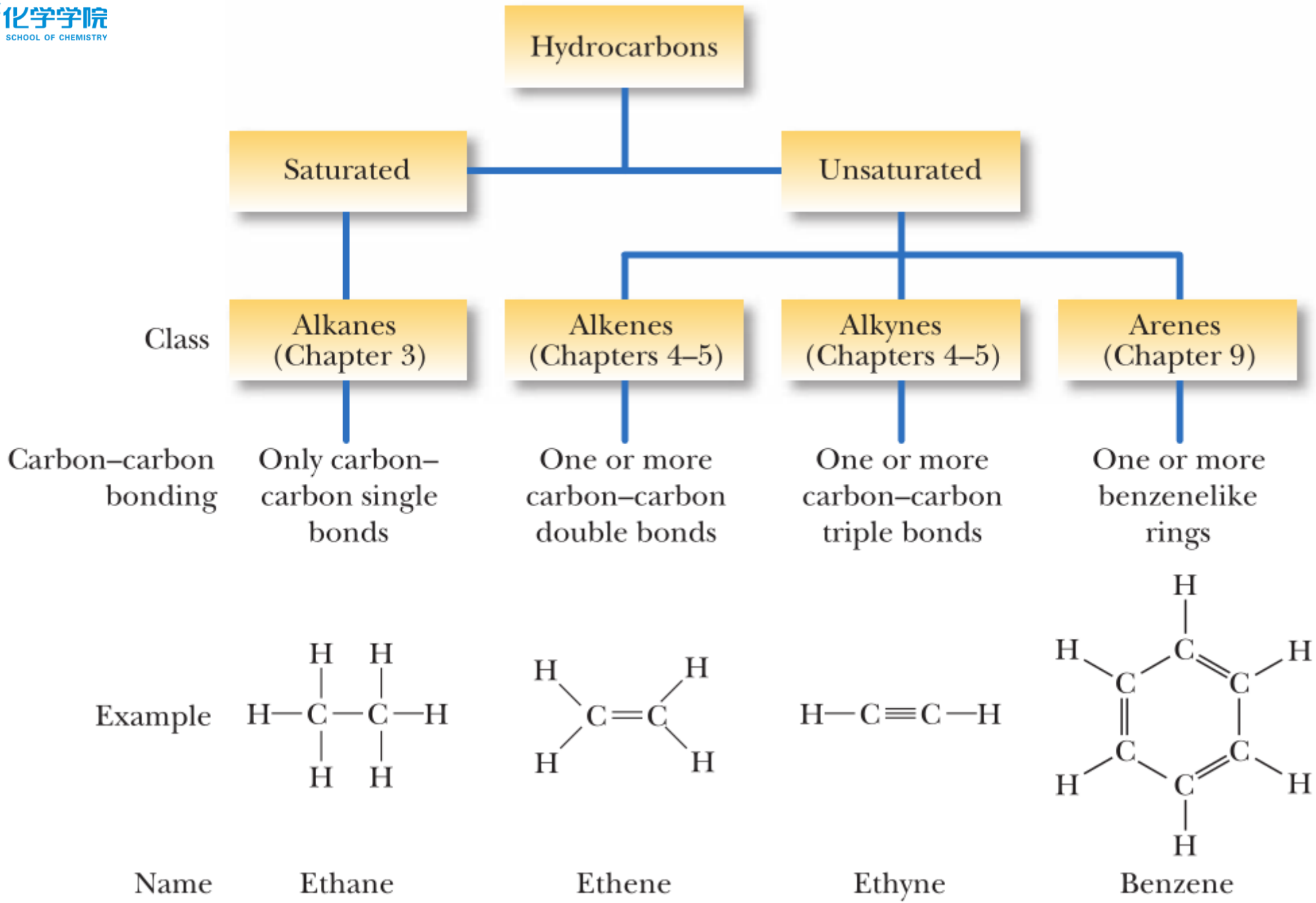
3.9 What Are the Characteristic Reactions of Alkanes?

3.10 What Are the Sources of Alkanes?

The four classes of hydrocarbons



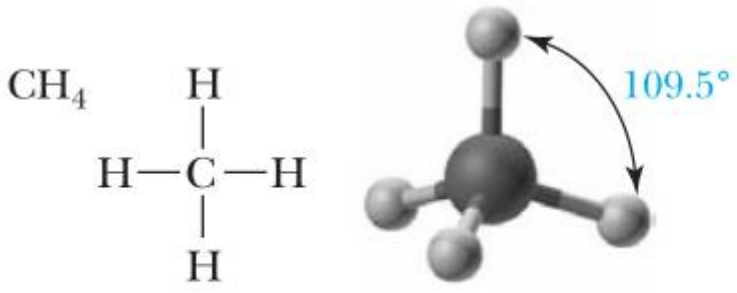
3.1 What Are Alkanes?

Alkane A saturated hydrocarbon whose carbon atoms are arranged in an open chain (烷烃)

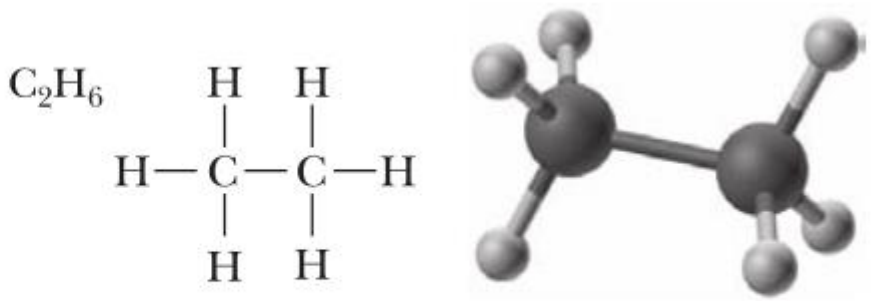
Saturated hydrocarbon A hydrocarbon containingonly carbon–carbon single bonds. (饱和烃)

Aliphatic hydrocarbon An alternative term to describe an alkane. (脂肪族烃)

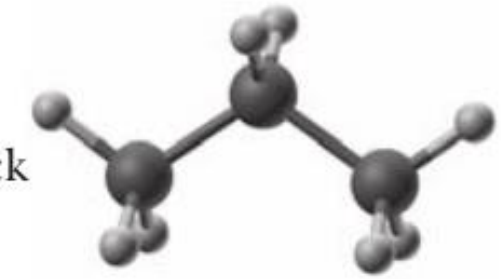
Alkanes have the general molecular formula C_nH_{2n+2}



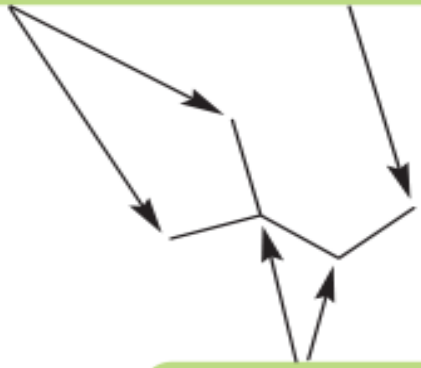
Methane



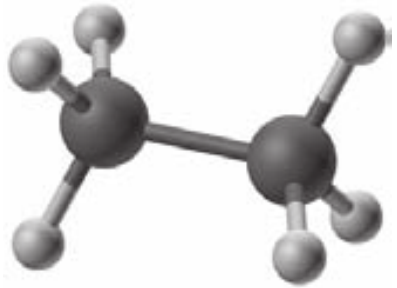
Ethane

Ball-and-stick model			
Line-angle formula			
Condensed structural formula	$CH_3CH_2CH_3$	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$
	Propane	Butane	Pentane

a carbon is located at every end



a carbon is located at every bend



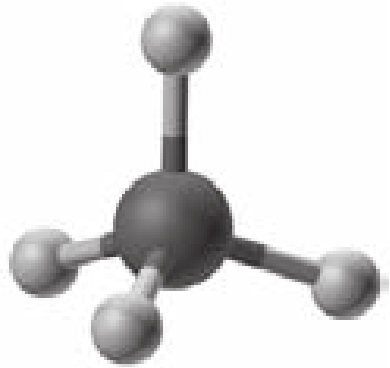
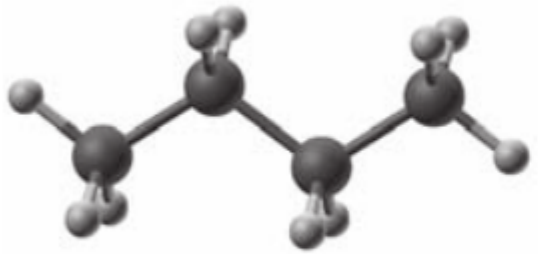


TABLE 3.1 Names, Molecular Formulas, and Condensed Structural Formulas for the First 20 Alkanes with Unbranched Chains

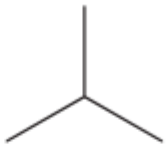
Name	Molecular Formula	Condensed Structural Formula	Name	Molecular Formula	Condensed Structural Formula
methane	CH_4	CH_4	undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
ethane	C_2H_6	CH_3CH_3	dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
propane	C_3H_8	$CH_3CH_2CH_3$	tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

3.2 What Is Constitutional Isomerism(构造异构) in Alkanes?



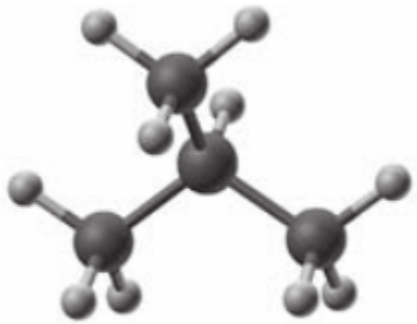
$CH_3CH_2CH_2CH_3$

Butane
(boiling point
= –0.5 °C)



CH_3CHCH_3
|
CH_3

2-Methylpropane
(boiling point
= –11.6 °C)



Carbon Atoms	Constitutional Isomers
1	0
5	3
10	75
15	4,347
25	36,797,588

3.3 How Do We Name Alkanes?

A. The IUPAC System

(1) a prefix that indicates the number of carbon atoms in the chain and

(2) the ending -ane to show that the compound is a saturated hydrocarbon.

Table 3.2 gives theprefixes used to show the presence of 1 to 20 carbon atoms.

(1) 表示直链烷烃中碳原子数的前缀;

(2) 结尾为“烷”，表示该化合物为饱和烃。表3.2给出了用于表示1到20个碳原子的前缀。

The IUPAC name of an alkane with a branched chain consists of a parent name that indicates the longest chain of carbon atoms in the compound and substituent names that indicate the groups bonded to the parent chain.

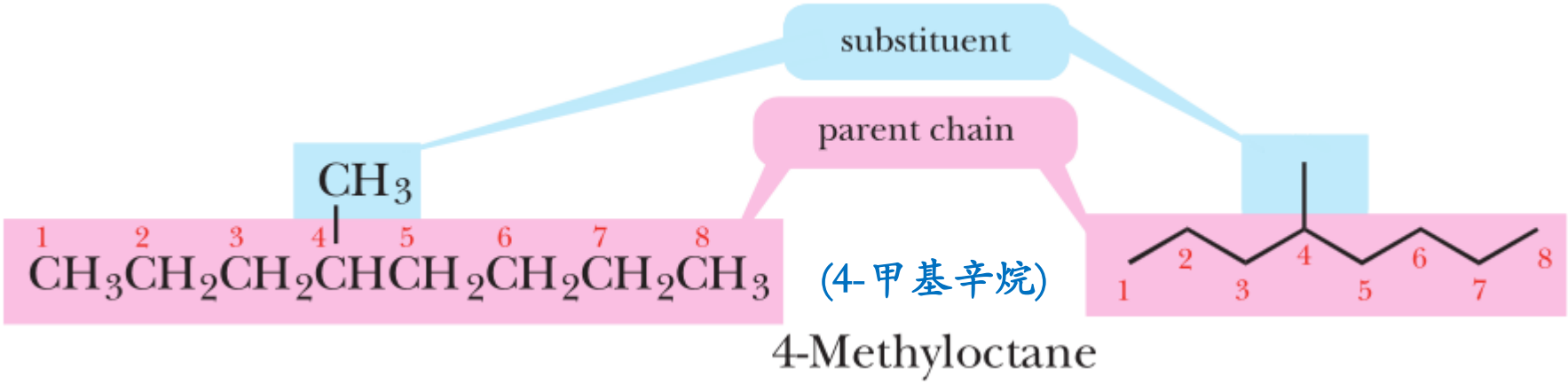


TABLE 3.2 Prefixes Used in the IUPAC System to Show the Presence of 1 to 20 Carbons in an Unbranched Chain

Prefix	Number of Carbon Atoms	Prefix	Number of Carbon Atoms
meth-	1	undec-	11
eth-	2	dodec-	12
prop-	3	tridec-	13
but-	4	tetradec-	14
pent-	5	pentadec-	15
hex-	6	hexadec-	16
hept-	7	heptadec-	17
oct-	8	octadec-	18
non-	9	nonadec-	19
dec-	10	eicos-	20

(常见的烷基名称)

TABLE 3.3 Names of the Most Common Alkyl Groups

Name	Condensed Structural Formula	Name	Condensed Structural Formula
methyl	$-CH_3$	isobutyl (异丁基)	$-CH_2CH(CH_3)_2$
ethyl	$-CH_2CH_3$	*sec*-butyl (仲丁基)	$-CH(CH_3)CH_2CH_3$
propyl (正丙基)	$-CH_2CH_2CH_3$	*tert*-butyl (叔丁基)	$-C(CH_3)_3$
isopropyl (异丙基)	$-CH(CH_3)_2$		
butyl (丁基)	$-CH_2CH_2CH_2CH_3$		

abbreviation for "secondary"

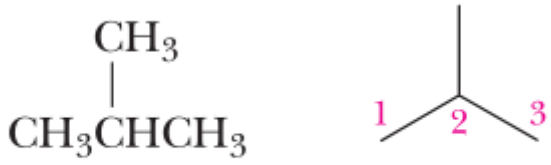
abbreviation for "tertiary"

The rules of the IUPAC system for naming alkanes are as follows:

1. The name for an alkane with an unbranched chain of carbon atoms consists of a prefix showing the number of carbon atoms in the chain and the ending -ane.

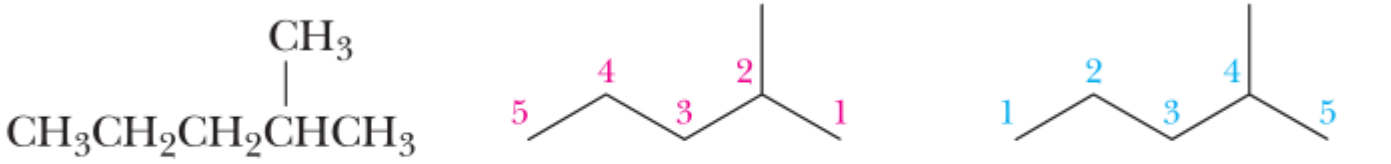
2. For branched-chain alkanes, take the longest chain of carbon atoms as the parent chain, and its name becomes the root name.

3. Give each substituent on the parent chain a name and a number. The number shows the carbon atom of the parent chain to which the substituent is bonded. Use a hyphen to connect the number to the name:



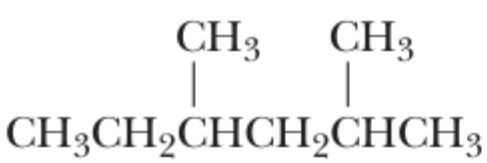
2-Methylpropane

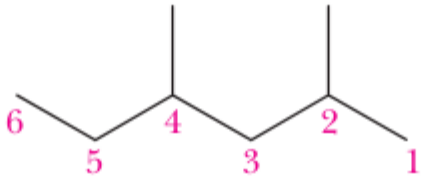
4. If there is one substituent, number the parent chain from the end that gives it the lower number:



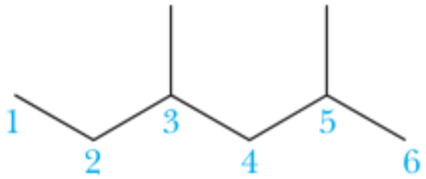
2-Methylpentane (not 4-methylpentane)

5. If there are two or more identical substituents, number the parent chain from the end that gives the lower number to the substituent encountered first. The number of times the substituent occurs is indicated by the prefix di-, tri-, tetra-, penta-, hexa-, and so on. A comma is used to separate position numbers:



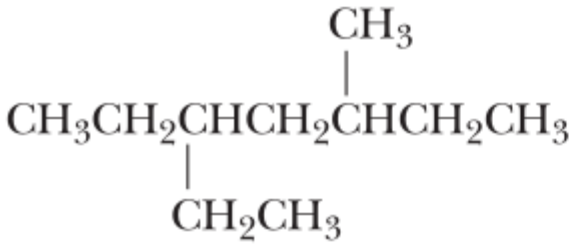


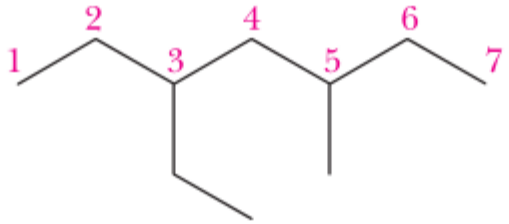
2,4-Dimethylhexane



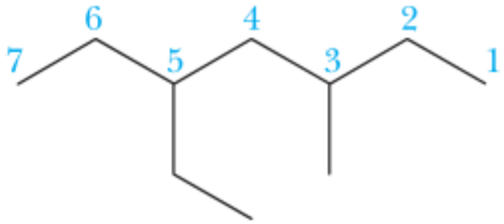
(not 3,5-dimethylhexane)

6. If there are two or more different substituents, list them in alphabetical order, and number the chain from the end that gives the lower number to the substituent encountered first. If there are different substituents in equivalent positions on opposite ends of the parent chain, the substituent of lower alphabetical order is given the lower number:



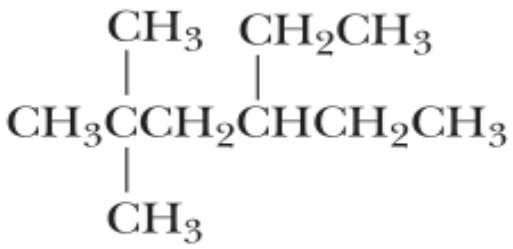


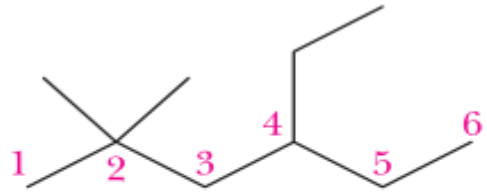
3-Ethyl-5-methylheptane



(not 3-methyl-5-ethylheptane)

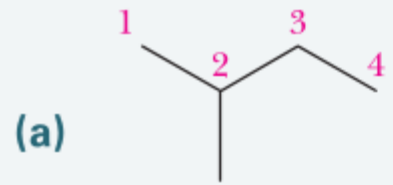
7. The prefixes di-, tri-, tetra-, and so on are not included in alphabetizing. Neither are the hyphenated prefixes sec- and tert-. "Iso," as in isopropyl, is included in alphabetizing. Alphabetize the names of the substituents first, and then insert the prefix. In the following example, the alphabetizing parts are ethyl and methyl, not ethyl and dimethyl:



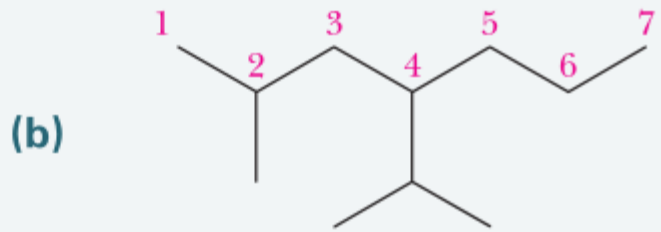


4-Ethyl-2,2-dimethylhexane
(not 2,2-dimethyl-4-ethylhexane)

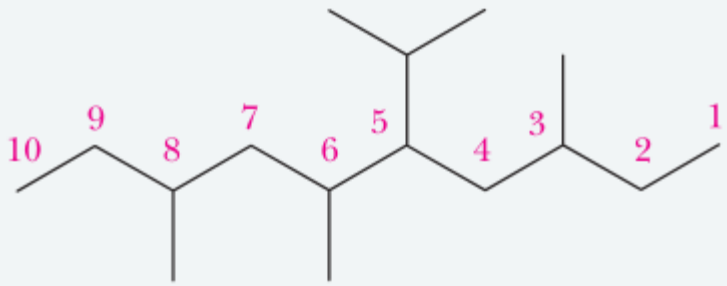
(前缀di-、tri-、tetra-等不包括在字母排序中。连字符前缀sec-和tert-也不是。"Iso"，如"异丙基"，包括在字母排序。先把取代基的名字按字母顺序排列，然后加上前缀。在下面的例子中，按字母顺序排列的部分是乙基和甲基，而不是乙基和二甲基:)



2-Methylbutane



4-Isopropyl-2-methylheptane

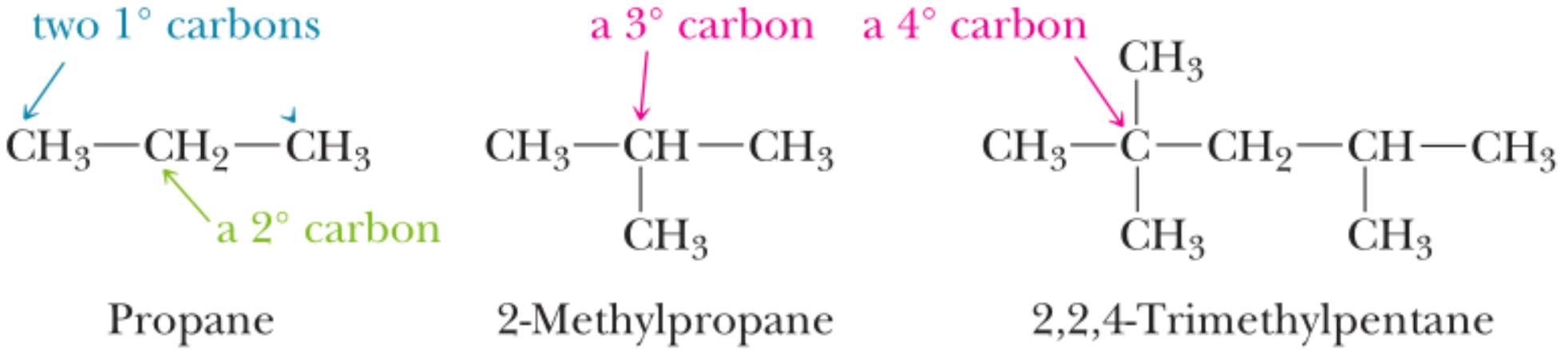


5-Isopropyl-3,6,8-trimethyldecane
(not 6-isopropyl-3,5,8-trimethyldecane)

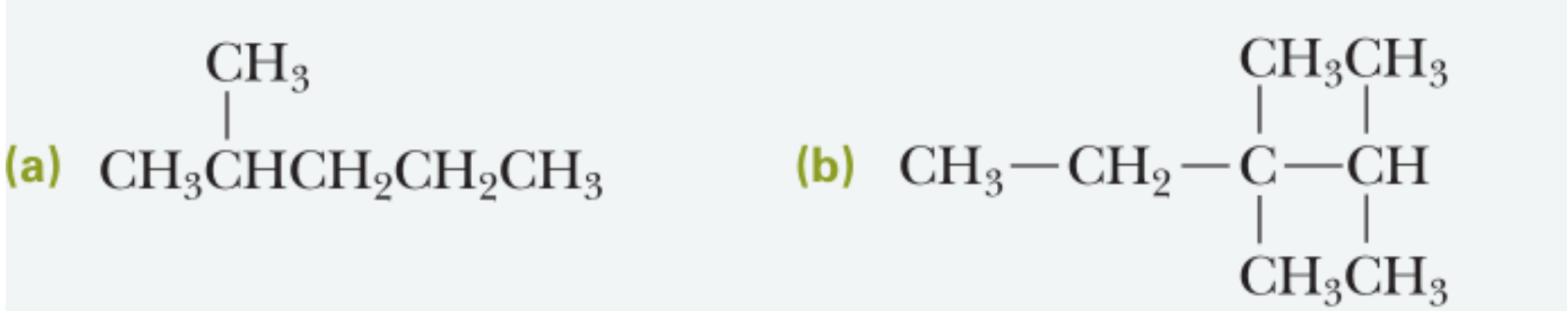
B. Common Names(普通命名法)

C. Classification of Carbon and Hydrogen Atoms

We classify a carbon atom as primary (1°), secondary (2°), tertiary (3°), or quaternary(4°), (伯、仲、叔、季) depending on the number of carbon atoms bonded to it.

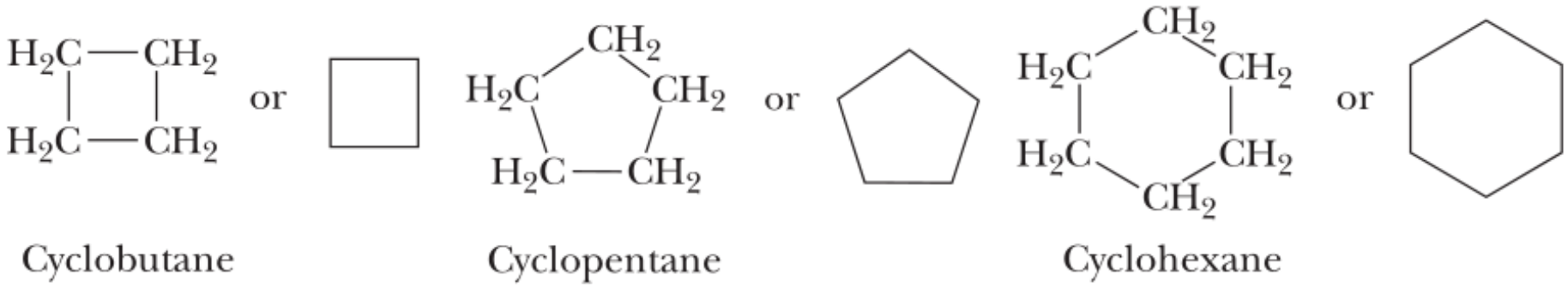


Hydrogens（H） are also classified as primary, secondary, or tertiary（伯、仲、叔）, depending on the type of carbon to which each is bonded. Those bonded to a primary carbon are classified as primary hydrogens, those on a secondary carbon are secondary hydrogens, and those on a tertiary carbon are tertiary hydrogens.



3.4 What Are Cycloalkanes?

Cycloalkane A saturated hydrocarbon that contains carbon atoms joined to form a ring. (C_nH_{2n})

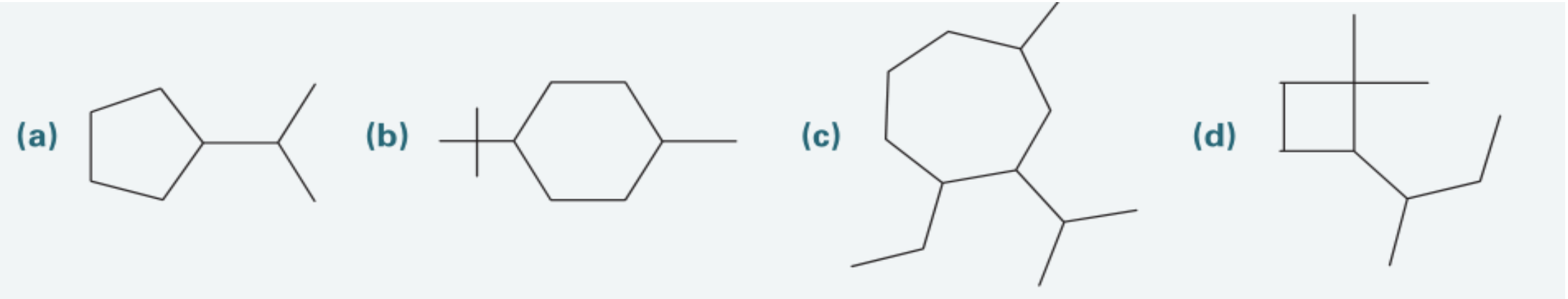


Cyclobutane Cyclopentane Cyclohexane

命名原则：

1. 首先确定环烷烃的母体名称。
2. 将取代基命名并按字母顺序排列
3. 给主链编号，采用最低次序原则，（使取代基位次最小）
4. 若取代基具有等价的位置，则按字母顺序使排在前的取代基位次较小。

例：



1-异丙基环戊烷
1-Isopropylcyclopentane

1-乙基-2-异丙基-4-甲基环庚烷
1-Ethyl-2-isopropyl-4-methylcycloheptane

1-叔丁基-4-甲基环己烷
1-Tert-butyl-4-methylcyclohexane

2-仲丁基-1,1-二甲基环丁烷
2-Sec-butylcy-1,1-dimethylclobutane

3.5 What Is the IUPAC System of Nomenclature?

a prefix + an infix + a suffix.
（前缀）+ （中缀）+ （后缀）

1. **The prefix shows the number of carbon atoms in the parent chain. Prefixes that show the presence of 1 to 20 carbon atoms in a chain were given in Table 3.2.**

2. **The infix shows the nature of the carbon–carbon bonds in the parent chain:**

Infix	Nature of Carbon–Carbon Bonds in the Parent Chain
-an-	all single bonds
-en-	one or more double bonds
-yn-	one or more triple bonds

keep in mind that the infix refers to the nature of the *C–C bonds in the parent chain*

3. The suffix shows the class of compound to which the substance belongs:

Suffix	Class of Compound
-e	hydrocarbon
-ol	alcohol
-al	aldehyde
-one	ketone
-oic acid	carboxylic acid

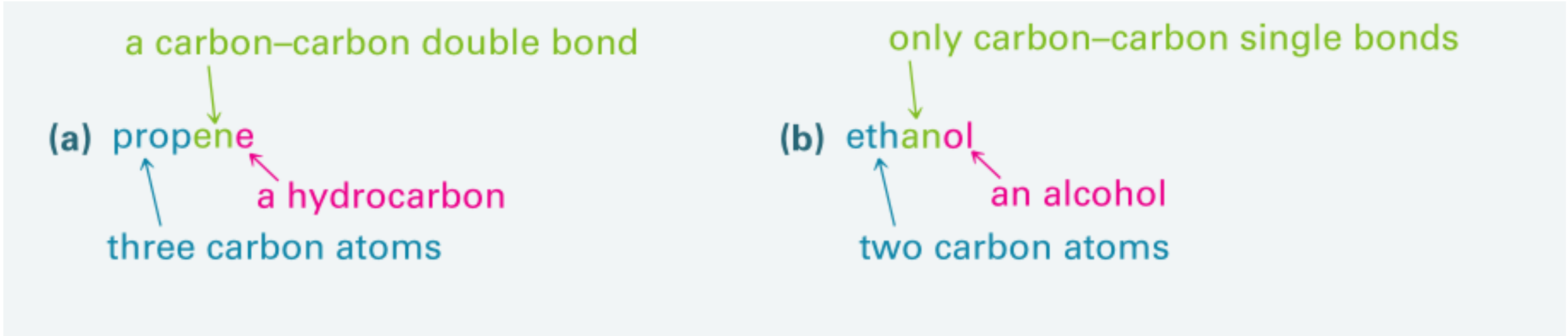
we will learn suffixes for other classes of compounds in later chapters

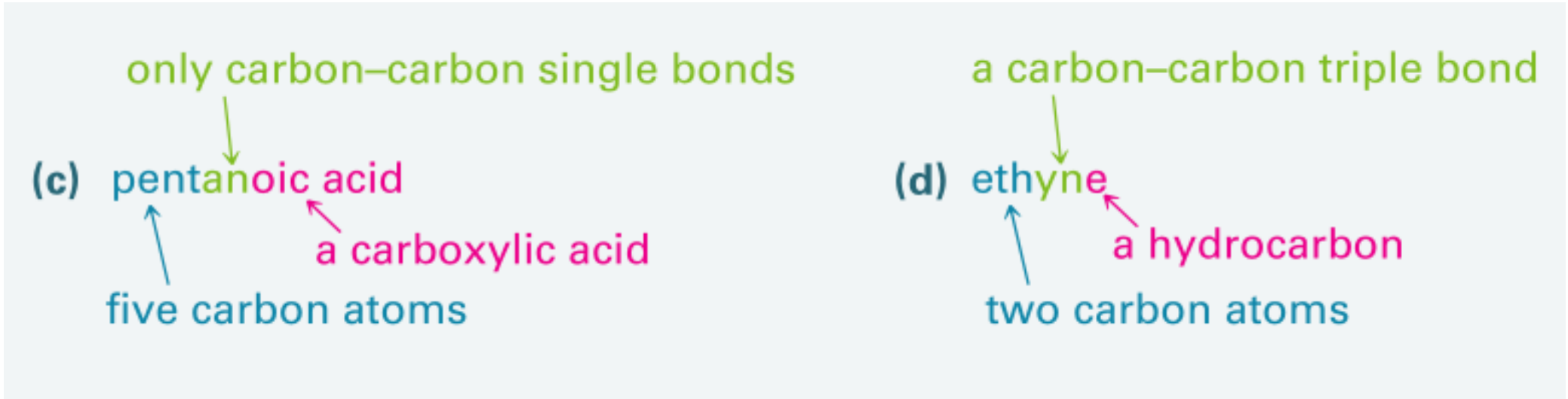
(a) $CH_2{=}CHCH_3$ Propene

(b) CH_3CH_2OH Ethanol

(c) $CH_3CH_2CH_2CH_2C(=O)OH$ Pentanoic acid

(d) $HC{\equiv}CH$ Ethyne


a carbon–carbon double bond
(a) propene
a hydrocarbon
three carbon atoms
only carbon–carbon single bonds
(b) ethanol
an alcohol
two carbon atoms

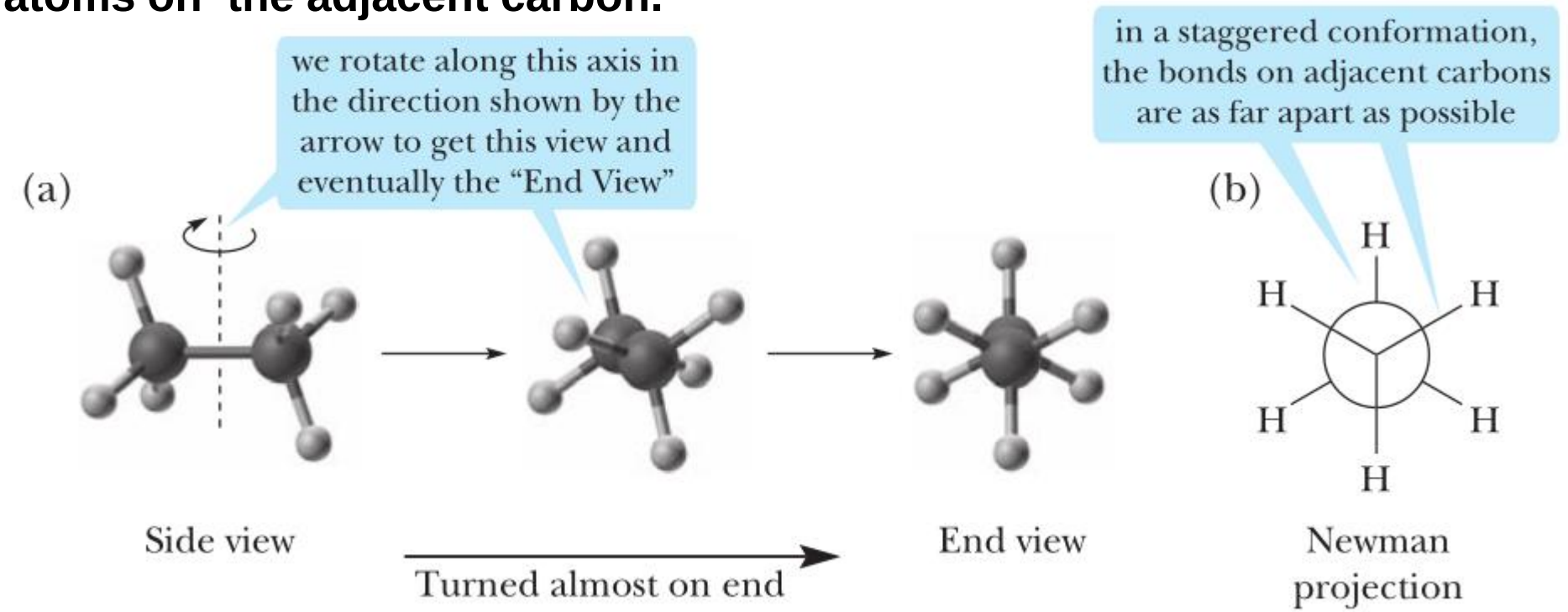

only carbon–carbon single bonds
(c) pentanoic acid
a carboxylic acid
five carbon atoms
a carbon–carbon triple bond
(d) ethyne
a hydrocarbon
two carbon atoms

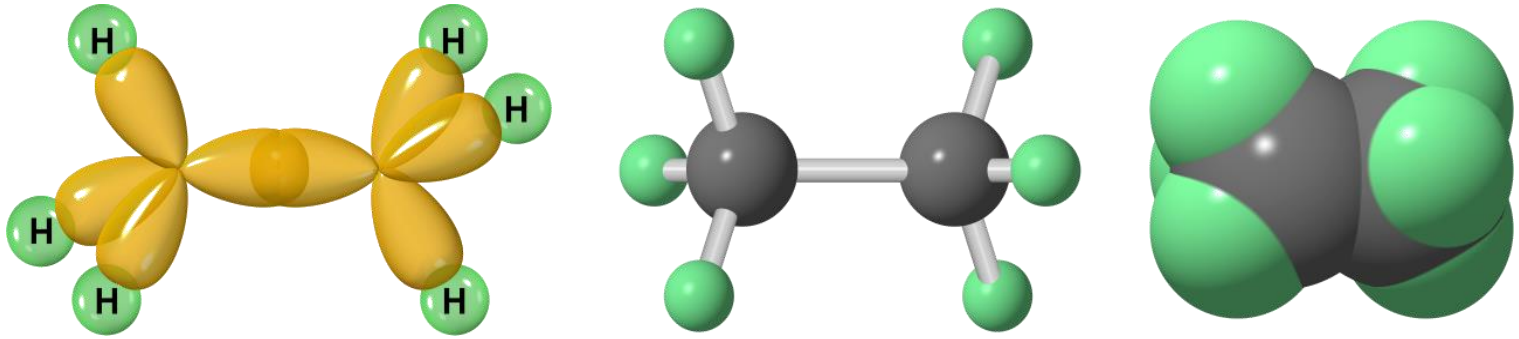
3.6 What Are the Conformations of Alkanes and Cycloalkanes?

Conformation **Any three-dimensional arrangement of atoms in a molecule that results by rotation about a single bond.**

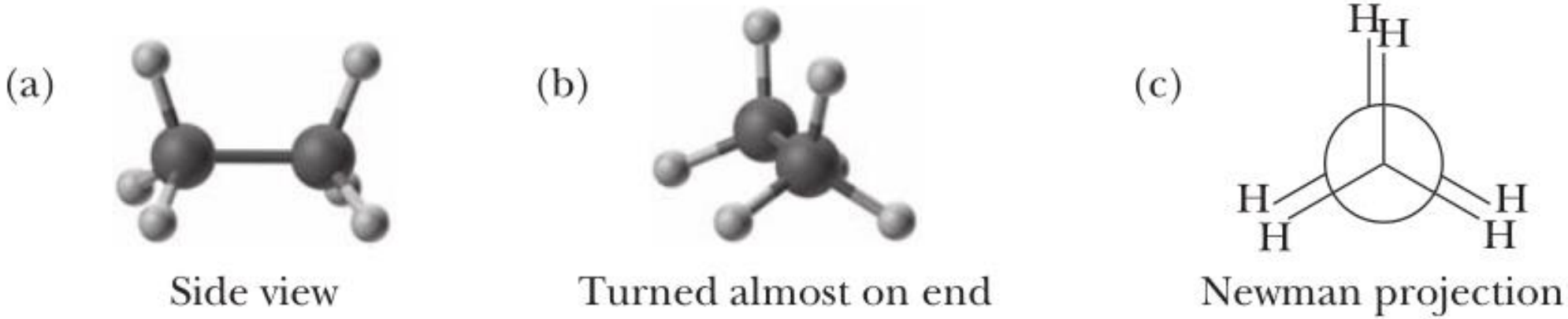
A. Alkanes

Staggered conformation （对位交叉构象）A conformation about a carbon–carbon single bond in which the atoms on one carbon are as far apart as possible from the atoms on the adjacent carbon.

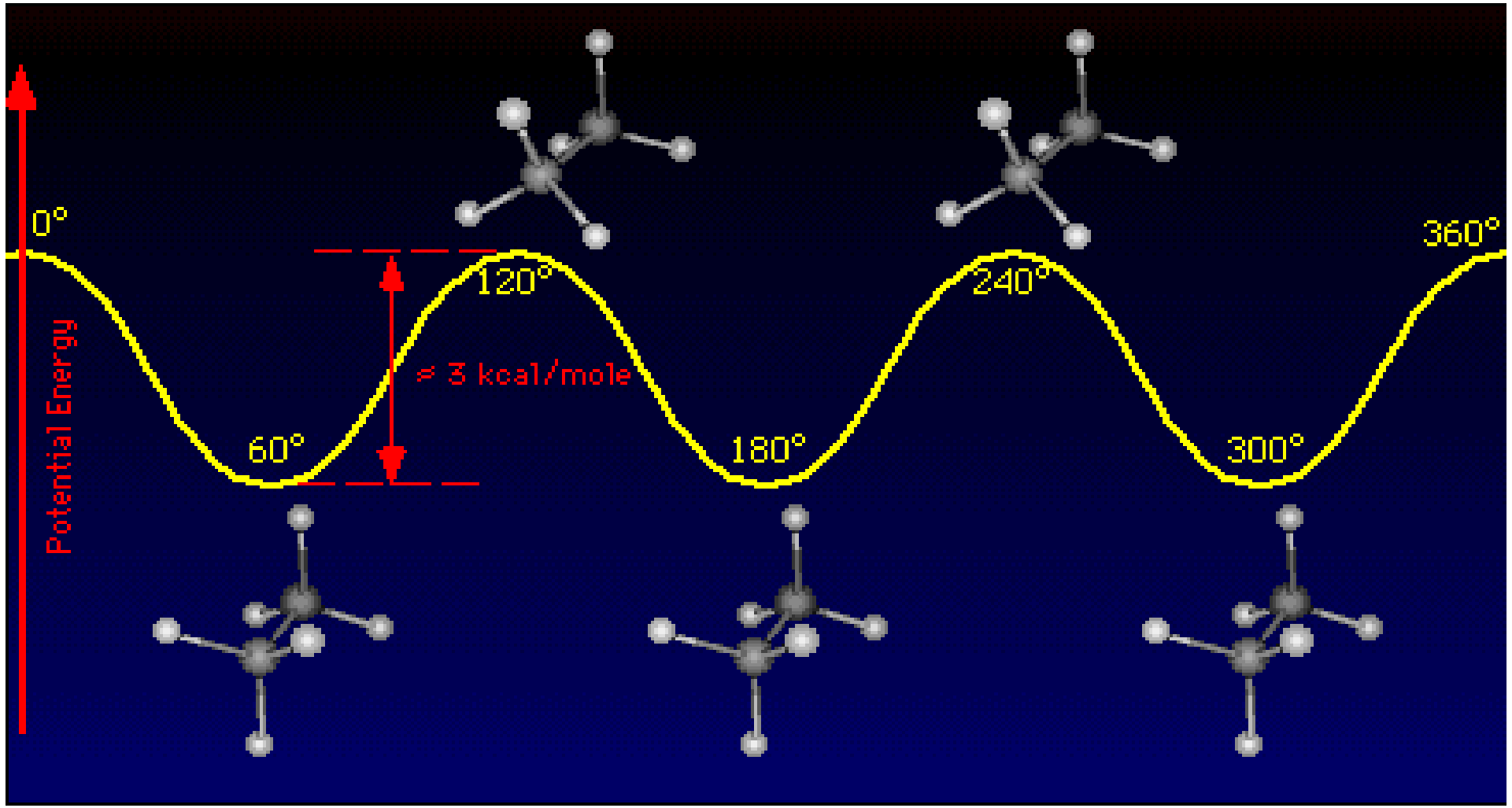




eclipsed conformation （重叠式构象） **A conformation about a carbon–carbon single bond in which the atoms on one carbon are as close as possible to the atoms on the adjacent carbon.**

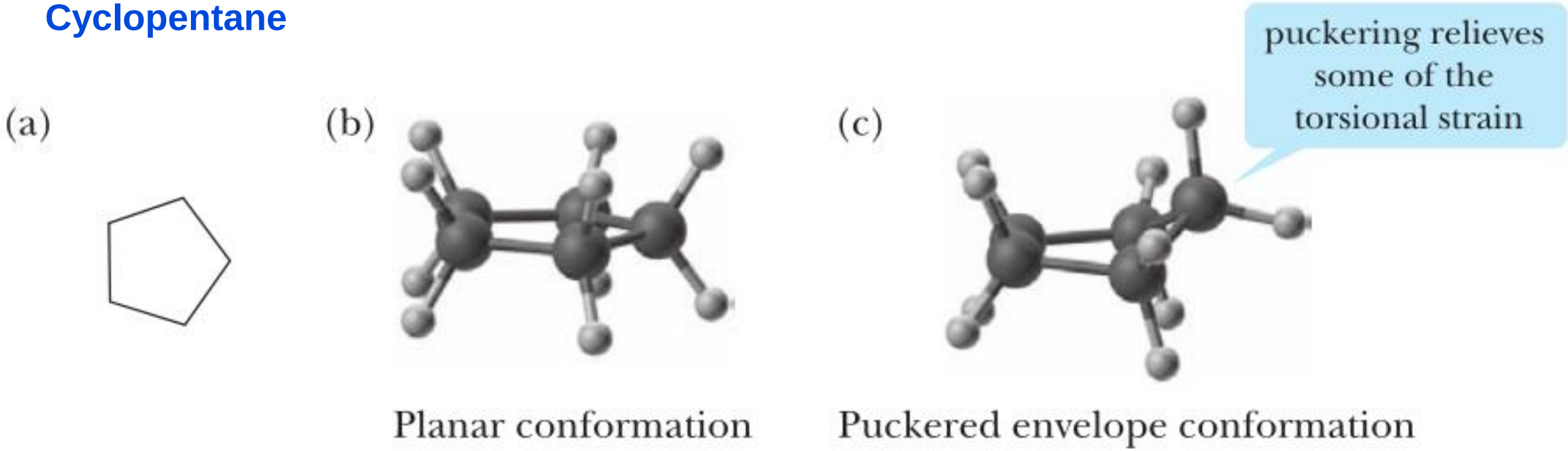


乙烷有无数个构象，最稳定（能量最低）的构象是交叉式。



B. Cycloalkanes

Cyclopentane

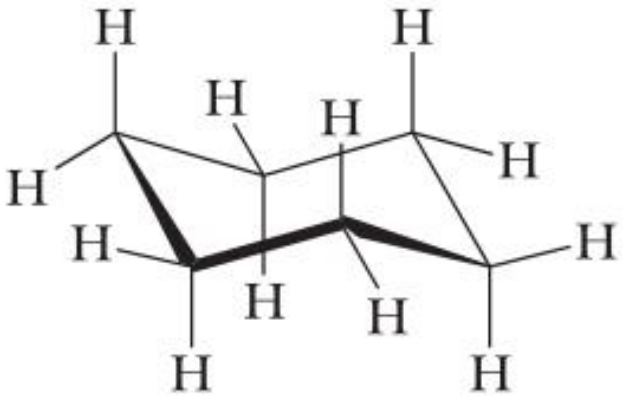


信封式

Angle strain（角张力） **The strain that arises when a bond angle is either compressed or expanded compared with its optimal value.**

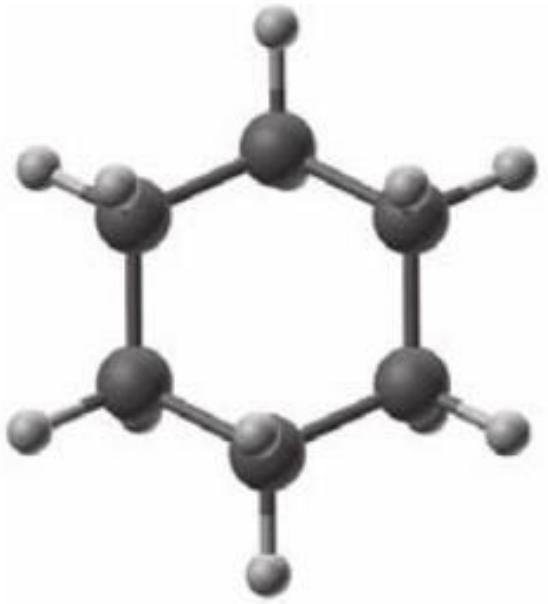
Cyclohexane

Chair conformation（椅式）



Skeletal model

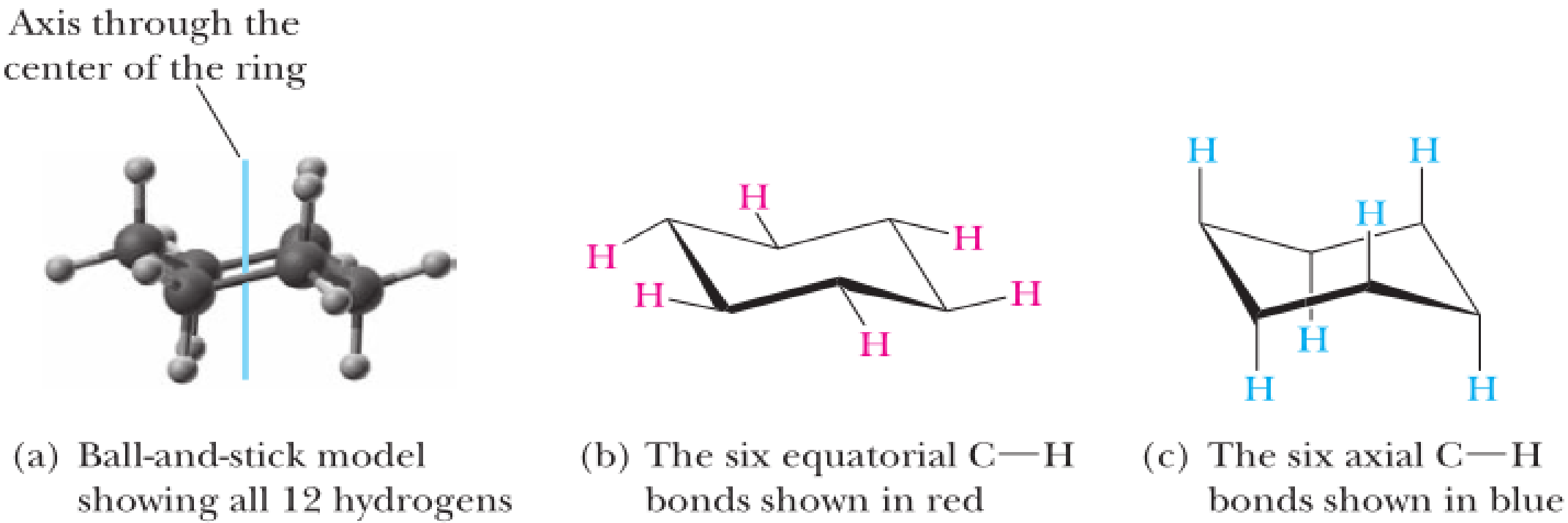
Ball-and-stick model
viewed from the side



Ball-and-stick model
viewed from above

Axial bond（直立键）

Equatorial bond（平伏键）

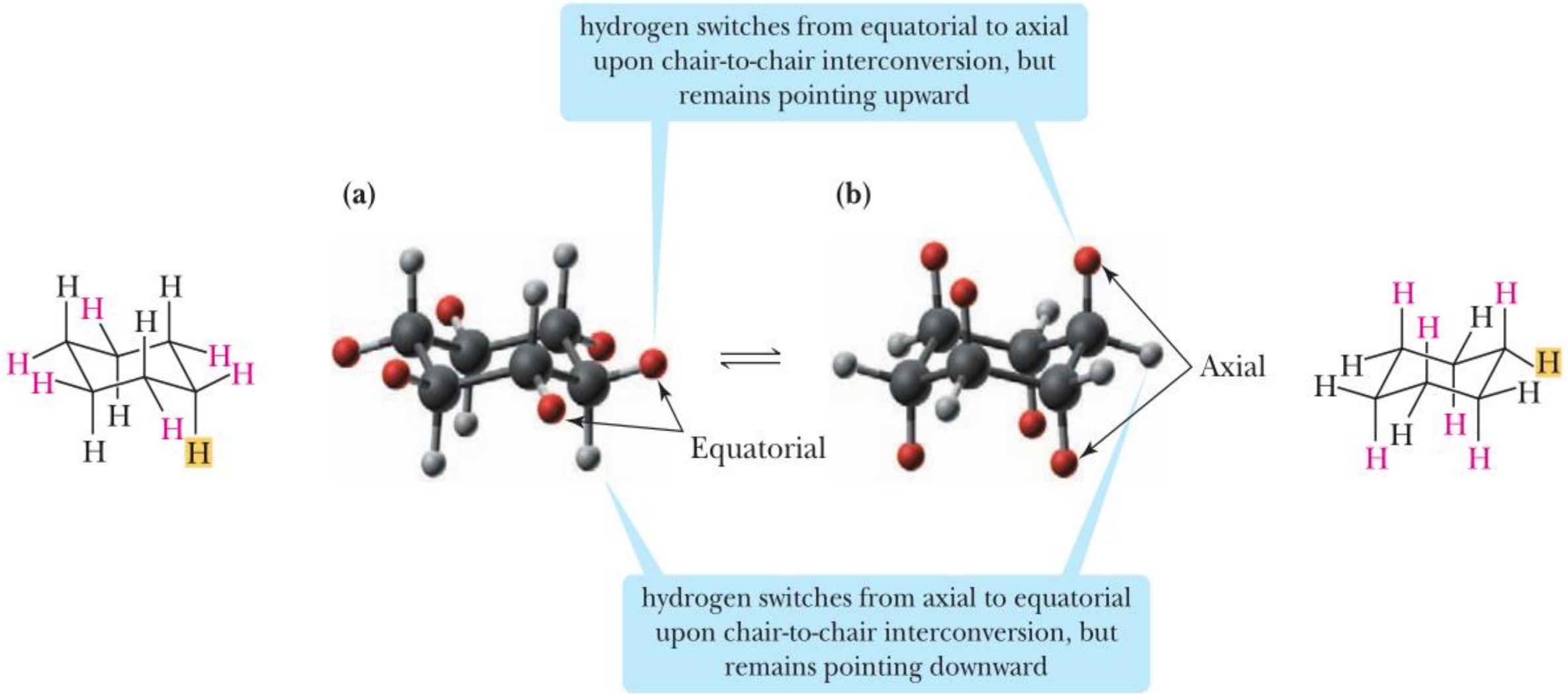


(a) Ball-and-stick model showing all 12 hydrogens

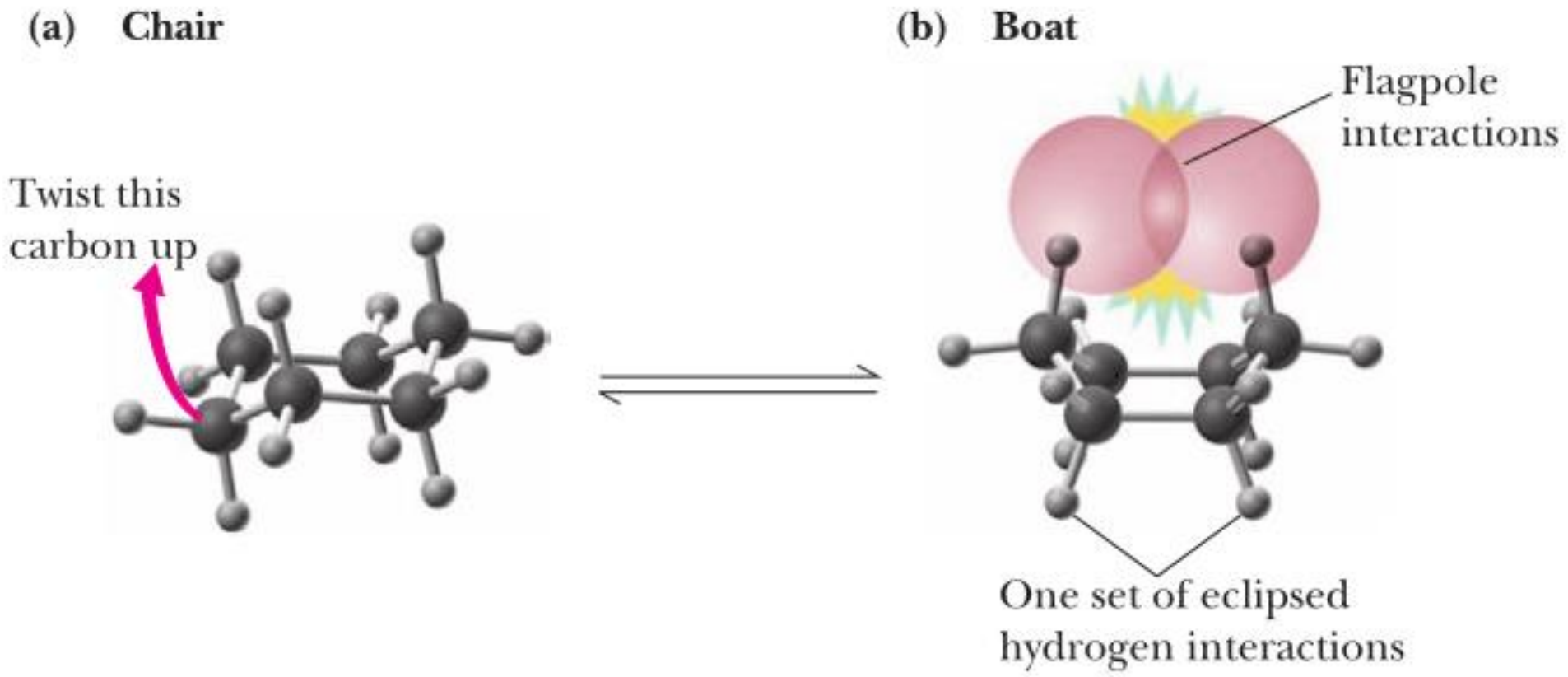
(b) The six equatorial C—H bonds shown in red

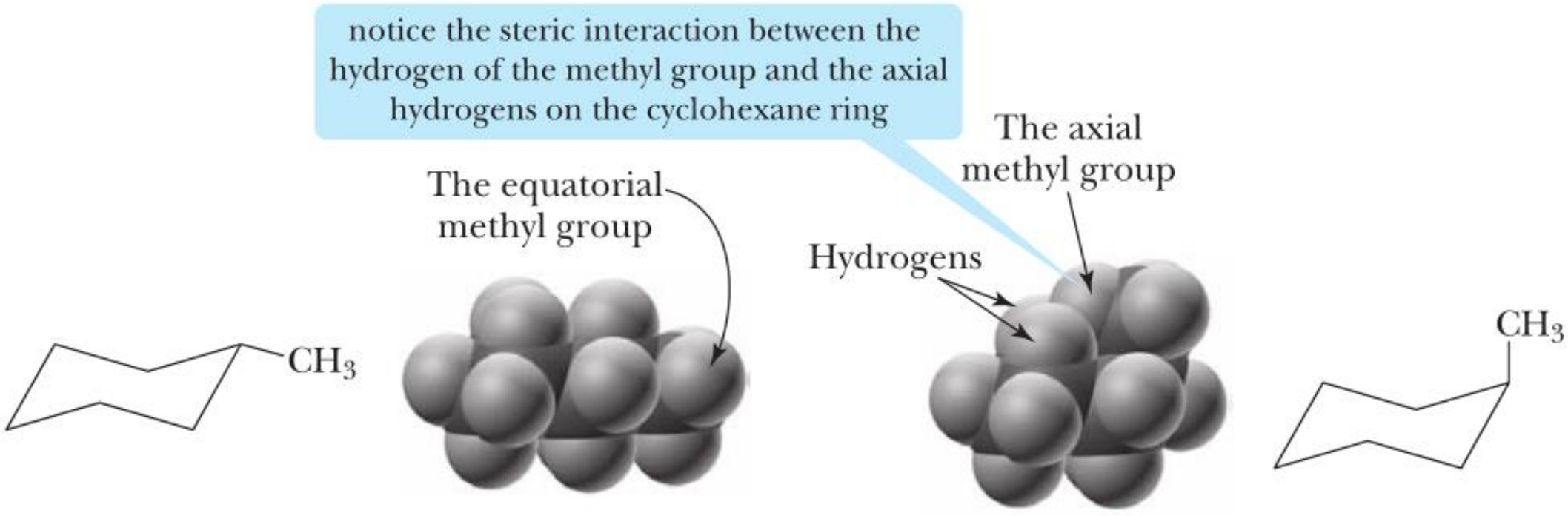
(c) The six axial C—H bonds shown in blue

FIGURE 3.8
Chair conformation of cyclohexane, showing axial and equatorial C—H bonds.


hydrogen switches from equatorial to axial upon chair-to-chair interconversion, but remains pointing upward
(a)
(b)
Equatorial
Axial
hydrogen switches from axial to equatorial upon chair-to-chair interconversion, but remains pointing downward

Boat conformation（船式构象）





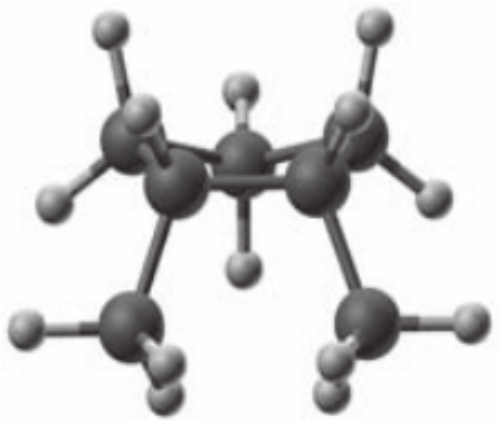
(a) Equatorial methylcyclohexane

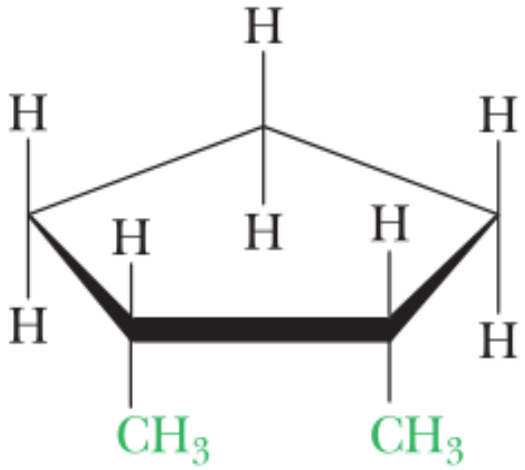
(b) Axial methylcyclohexane

3.7 What Is Cis–Trans Isomerism（顺反异构） in Cycloalkanes?

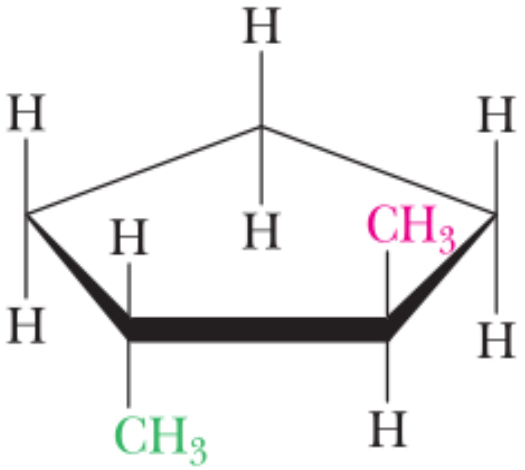
Cis–trans isomers **Isomers that have the same order of attachment of their atoms,but a different arrangement of their atoms in space, due to the presence of either a ring or a carbon–carbon double bond.**

Cis （顺） **A prefix meaning “on the same side.”**
Trans （反） **A prefix meaning“across from.”**

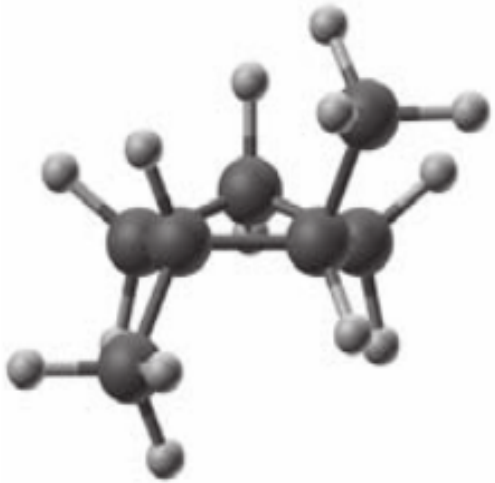


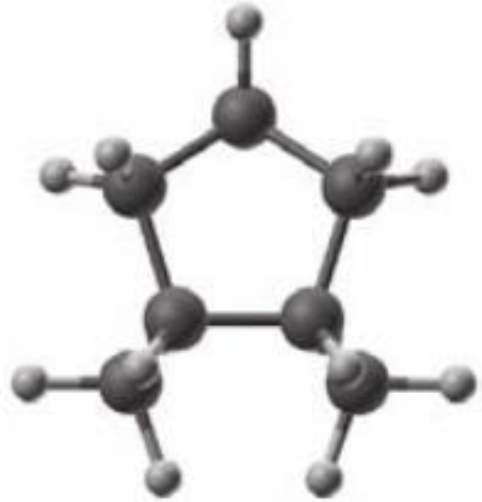


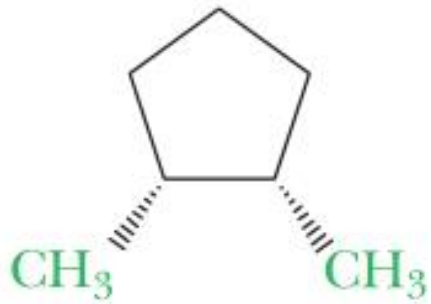
cis-1,2-Dimethyl-cyclopentane



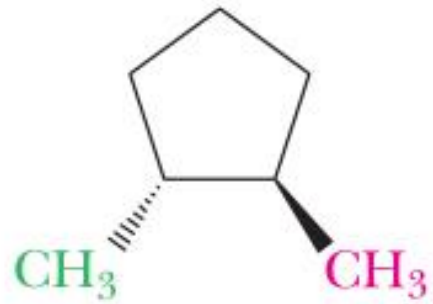
trans-1,2-Dimethyl-cyclopentane



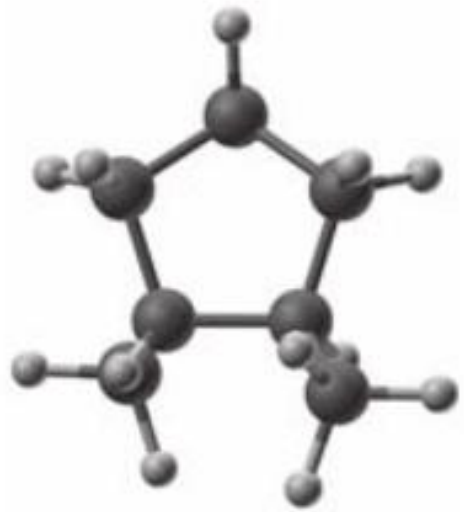




cis-1,2-Dimethyl-cyclopentane



trans-1,2-Dimethyl-cyclopentane



3.8 What Are the Physical Properties of Alkanes and Cycloalkanes?

TABLE 3.4 Physical Properties of Some Unbranched Alkanes

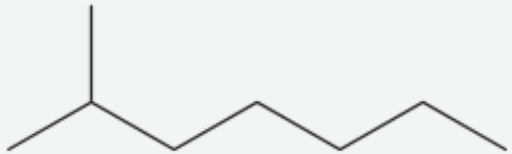
Name	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)	*Density of Liquid (g/mL at 0 °C)
methane	CH_4	−182	−164	(a gas)
ethane	CH_3CH_3	−183	−88	(a gas)
propane	$CH_3CH_2CH_3$	−190	−42	(a gas)
butane	$CH_3(CH_2)_2CH_3$	−138	0	(a gas)
pentane	$CH_3(CH_2)_3CH_3$	−130	36	0.626
hexane	$CH_3(CH_2)_4CH_3$	−95	69	0.659
heptane	$CH_3(CH_2)_5CH_3$	−90	98	0.684
octane	$CH_3(CH_2)_6CH_3$	−57	126	0.703
nonane	$CH_3(CH_2)_7CH_3$	−51	151	0.718
decane	$CH_3(CH_2)_8CH_3$	−30	174	0.730

*For comparison, the density of H_2O is 1 g/mL at 4 °C.

the greater the branching, the lower is the surface area, causing a decrease in the dispersion forces and a decrease in boiling point

Dispersion forces 色散力

2,2,4-Trimethylpentane
(bp 99 °C)



2-Methylheptane
(bp 118 °C)

Octane
(bp 125 °C)

3.9 What Are the Characteristic Reactions of Alkanes?

when balancing equations for combustion reactions of hydrocarbons, first balance the number of carbons, next balance the number of hydrogens, then balance the number of oxygens. If the equation is still not balanced, consider doubling all coefficients on each side of the equation arrow

1.

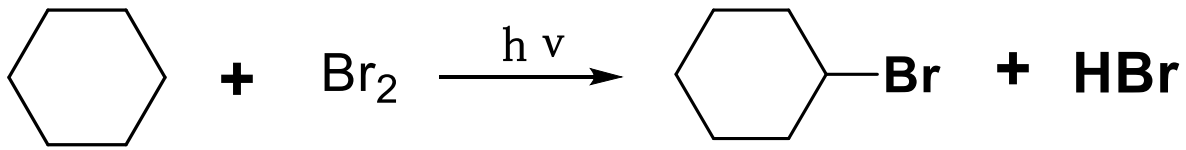
$$\underset{\text{Methane}}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H^\circ = -886\ \text{kJ/mol}(-212\ \text{kcal/mol})$$

$$\underset{\text{Propane}}{CH_3CH_2CH_3} + 5O_2 \longrightarrow 3CO_2 + 4H_2O \quad \Delta H^\circ = -2{,}220\ \text{kJ/mol}(-530\ \text{kcal/mol})$$

2.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

自由基取代反应



烷烃的卤代反应历程-自由基取代

链引发

$$X_2 \xrightarrow{\text{光或热}} 2X\bullet$$

链增长

$$RH + X\bullet \longrightarrow R\bullet + HX$$

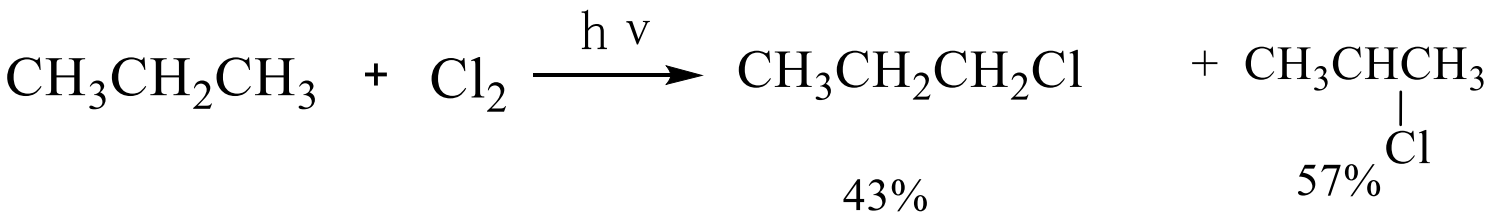
$$R\bullet + X_2 \longrightarrow RX + X\bullet$$

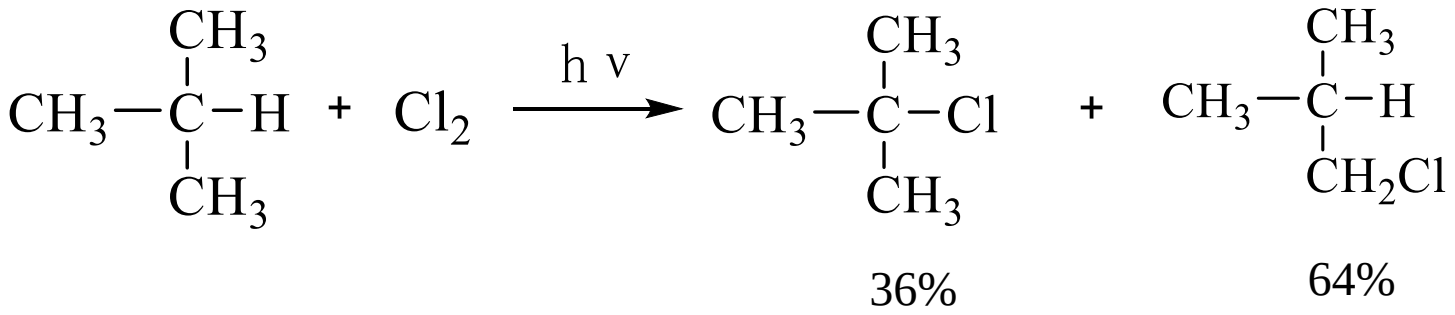
链终止

$$X\bullet + X\bullet \longrightarrow X_2$$

$$X\bullet + R\bullet \longrightarrow RX$$

$$R\bullet + R\bullet \longrightarrow R\text{-}R$$


CH3CH2CH3 + Cl2
h v
CH3CH2CH2Cl
43%
+ CH3CHCH3
Cl
57%


CH3
CH3—C—H
CH3
+ Cl2
h v
CH3
CH3—C—Cl
CH3
36%
+
CH3
CH3—C—H
CH2Cl
64%

作 业

3.24、3.25 （c、e、g、h）、

3.36、47（a、c）、56

Put it together

2、4、5、6