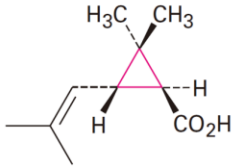
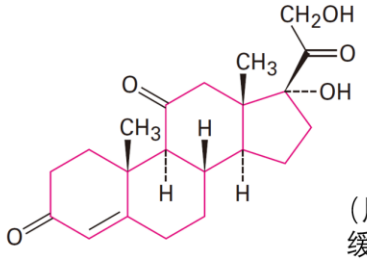


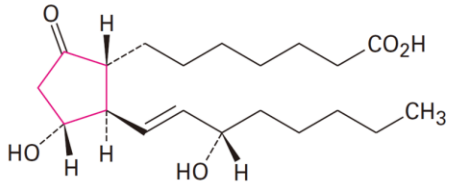
Chrysanthemic acid

除虫菊酯



Cortisone

可的松
（用于治疗关节炎等
缓解肿胀的激素）



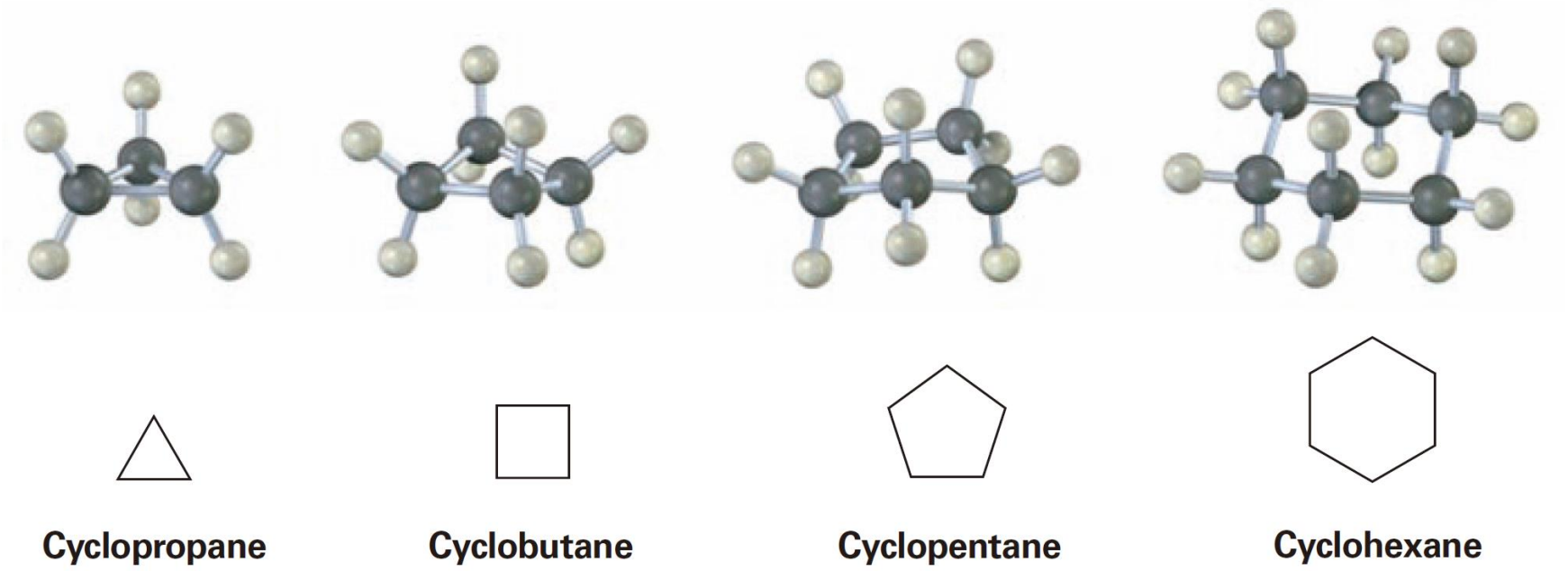
Prostaglandin E_1

前列腺素

4 环烷烃

4.1 环烷烃的命名

- 3, 4, 5, 6元环



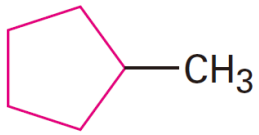
4.1 环烷烃的命名

- 第一步：找到母环

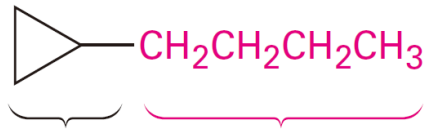
STEP 1

Find the parent.

Count the number of carbon atoms in the ring and the number in the largest substituent. If the number of carbon atoms in the ring is equal to or greater than the number in the substituent, the compound is named as an alkyl-substituted cycloalkane. If the number of carbon atoms in the largest substituent is greater than the number in the ring, the compound is named as a cycloalkyl-substituted alkane. For example:



Methylcyclopentane



3 carbons 4 carbons

1-Cyclopropylbutane

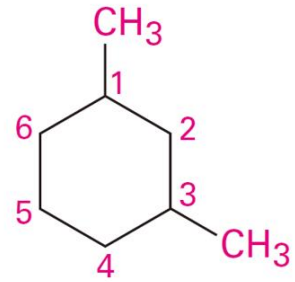
4.1 环烷烃的命名

- 第二步：编号。尽可能使取代基的编号最小。

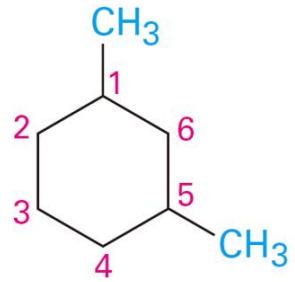
STEP 2

Number the substituents, and write the name.

For an alkyl- or halo-substituted cycloalkane, choose a point of attachment as carbon 1 and number the substituents on the ring so that the *second*



NOT



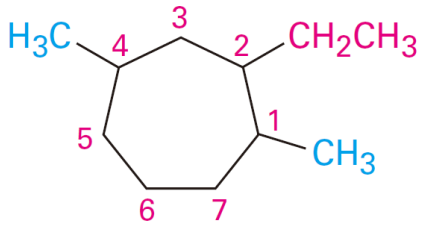
1,3-Dimethylcyclohexane

Lower

1,5-Dimethylcyclohexane

Higher

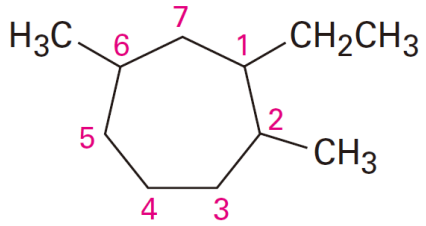
4.1 环烷烃的命名



2-Ethyl-1,4-dimethylcycloheptane

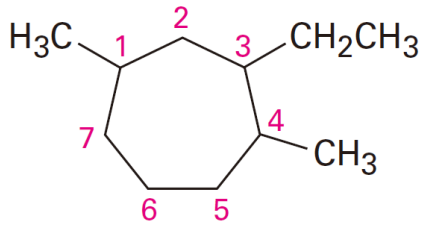
Lower Lower

NOT



1-Ethyl-2,6-dimethylcycloheptane

Higher

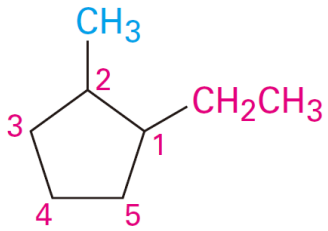


3-Ethyl-1,4-dimethylcycloheptane

Higher

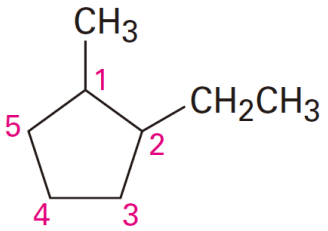
4.1 环烷烃的命名

(a) When two or more different alkyl groups that could potentially receive the same numbers are present, number them by alphabetical priority, ignoring numerical prefixes such as di- and tri-.



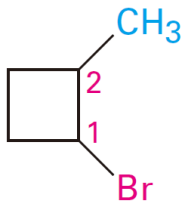
1-Ethyl-2-methylcyclopentane

NOT



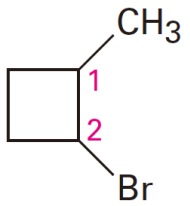
2-Ethyl-1-methylcyclopentane

(b) If halogens are present, treat them just like alkyl groups.



1-Bromo-2-methylcyclobutane

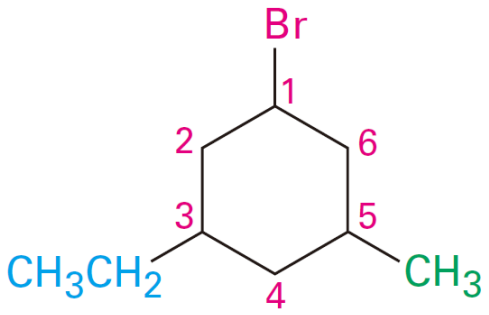
NOT



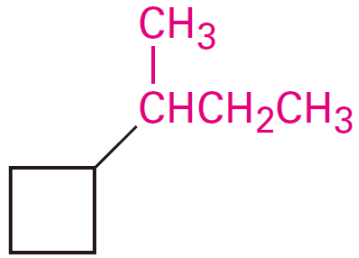
2-Bromo-1-methylcyclobutane

4.1 环烷烃的命名

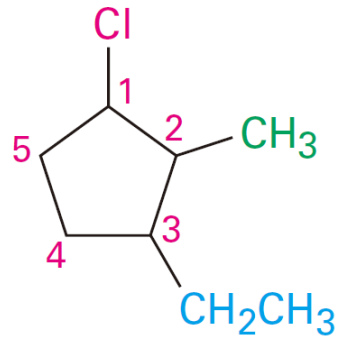
Some additional examples follow:



1-Bromo-3-ethyl-5-methyl-cyclohexane



(1-Methylpropyl)cyclobutane or *sec*-butylcyclobutane



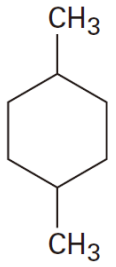
1-Chloro-3-ethyl-2-methyl-cyclopentane

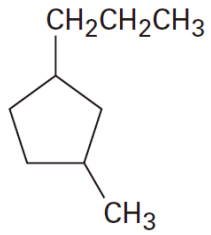
4.1 环烷烃的命名

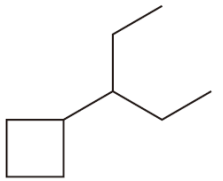
- 课堂练习

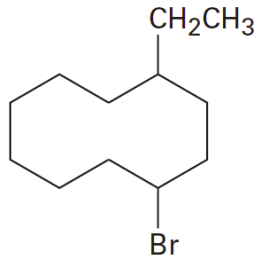
Problem 4.1

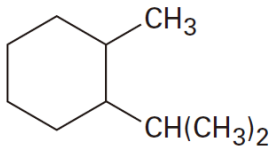
Give IUPAC names for the following cycloalkanes:

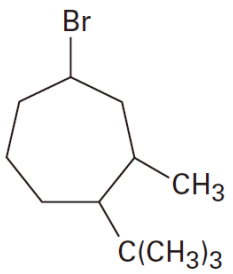
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

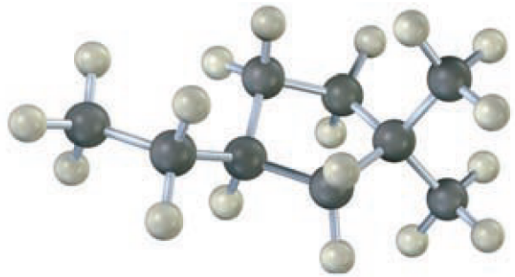
Problem 4.2

Draw structures corresponding to the following IUPAC names:

(a) 1,1-Dimethylcyclooctane **(b)** 3-Cyclobutylhexane
(c) 1,2-Dichlorocyclopentane **(d)** 1,3-Dibromo-5-methylcyclohexane

Problem 4.3

Name the following cycloalkane:



4.2 顺式和反式

- 由于环的存在，σ键不能自由旋转，产生顺反异构

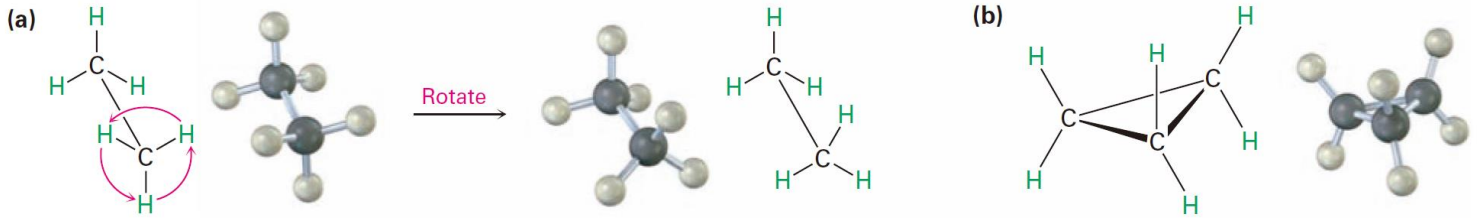
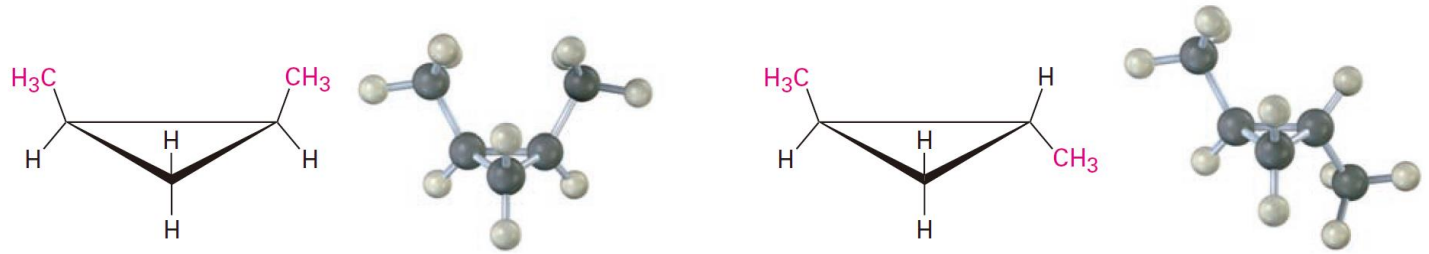


Figure 4.1 **(a)** Rotation occurs around the carbon–carbon bond in ethane, but **(b)** no rotation is possible around the carbon–carbon bonds in cyclopropane without breaking open the ring.



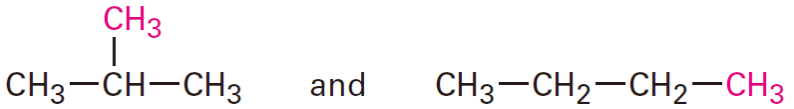
***cis*-1,2-Dimethylcyclopropane** ***trans*-1,2-Dimethylcyclopropane**

Figure 4.2 There are two different 1,2-dimethylcyclopropane isomers, one with the methyl groups on the same face of the ring (cis) and the other with the methyl groups on opposite faces of the ring (trans). The two isomers do not interconvert.

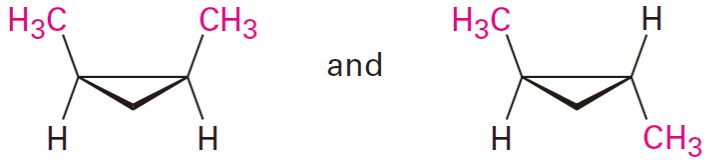
4.2 顺式和反式

- 构造异构与顺反异构

Constitutional isomers
(different connections between atoms)



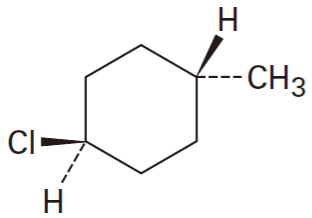
Stereoisomers
(same connections but different three-dimensional geometry)



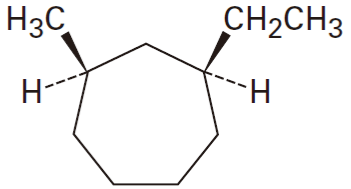
Problem 4.4

Name the following substances, including the *cis*- or *trans*- prefix:

(a)

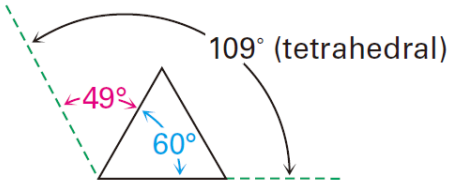


(b)

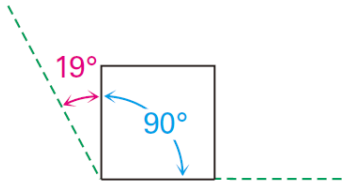


4.3 环烷烃的稳定性

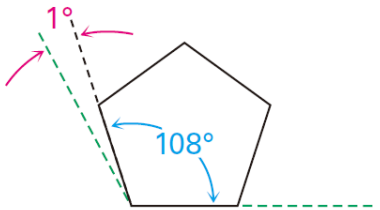
- 拜耳张力学说：假定碳环在同一平面上，这样碳的键角势必与正常键角产生偏差，若有偏差就存在着张力，偏差越大，张力越大，碳环就越不稳定。
- 拜耳张力学说有一定道理，但并不完善，因为除了环丙烷，其他环系并不在同一个平面上。



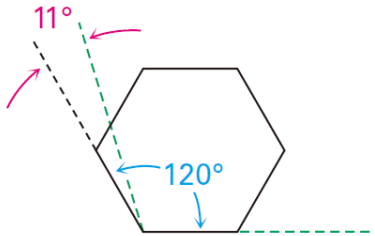
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

4.3 环烷烃的稳定性

- 通过与非环烷烃燃烧热的比较得出各环的环张力能量。

$$(CH_2)_n + 3n/2\ O_2 \longrightarrow n\ CO_2 + n\ H_2O + \textbf{Heat}$$

Because the heat of combustion of a cycloalkane depends on size, we need to look at heats of combustion per CH_2 unit. Subtracting a reference value derived from a strain-free acyclic alkane and then multiplying by the number of CH_2 units in the ring gives the overall strain energy. **Figure 4.3** shows the results.

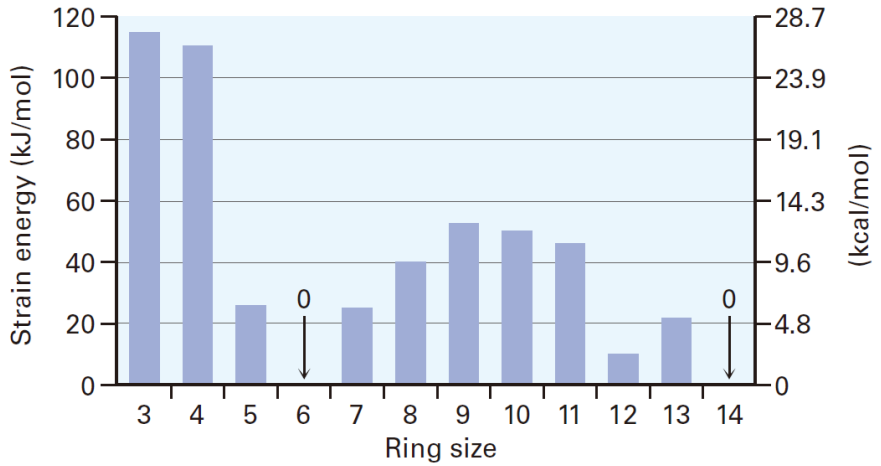


Figure 4.3 Cycloalkane strain energies, calculated by taking the difference between cycloalkane heat of combustion per CH_2 and acyclic alkane heat of combustion per CH_2, and multiplying by the number of CH_2 units in a ring. Small and medium rings are strained, but cyclohexane rings and very large rings are strain-free.

4.3 环烷烃的稳定性

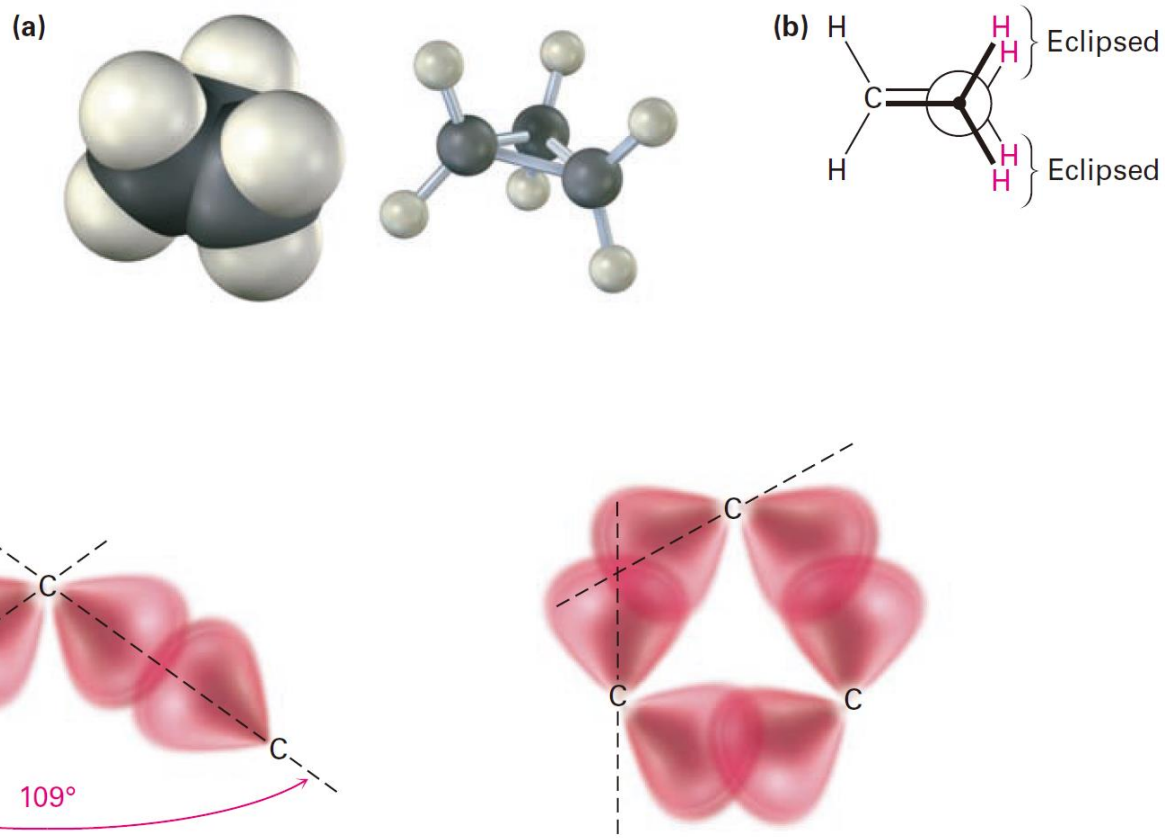
- 环烷烃的稳定性：角张力，扭转张力和空间张力。

- **Angle strain**—the strain due to expansion or compression of bond angles
- **Torsional strain**—the strain due to eclipsing of bonds on neighboring atoms
- **Steric strain**—the strain due to repulsive interactions when atoms approach each other too closely

4.4 环烷烃的构象

- 环丙烷

Figure 4.4 The structure of cyclopropane, showing the eclipsing of neighboring C—H bonds that gives rise to torsional strain. Part **(b)** is a Newman projection along a C—C bond.



4.4 环烷烃的构象

- 环丁烷

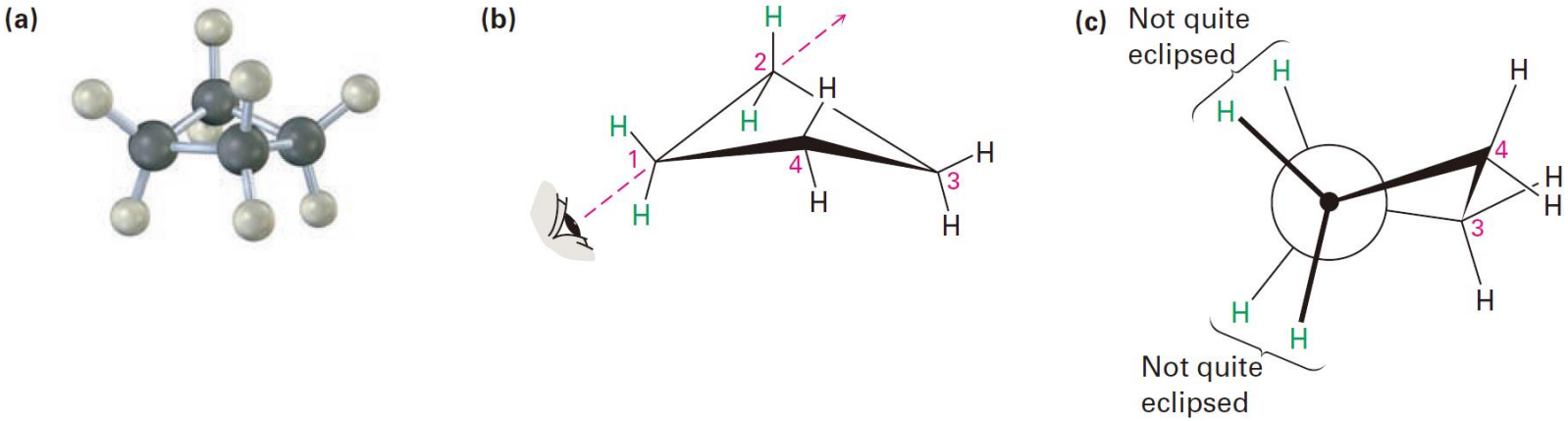


Figure 4.5 The conformation of cyclobutane. Part **(c)** is a Newman projection along a C—C bond, showing that neighboring C—H bonds are not quite eclipsed.

4.4 环烷烃的构象

- 环戊烷

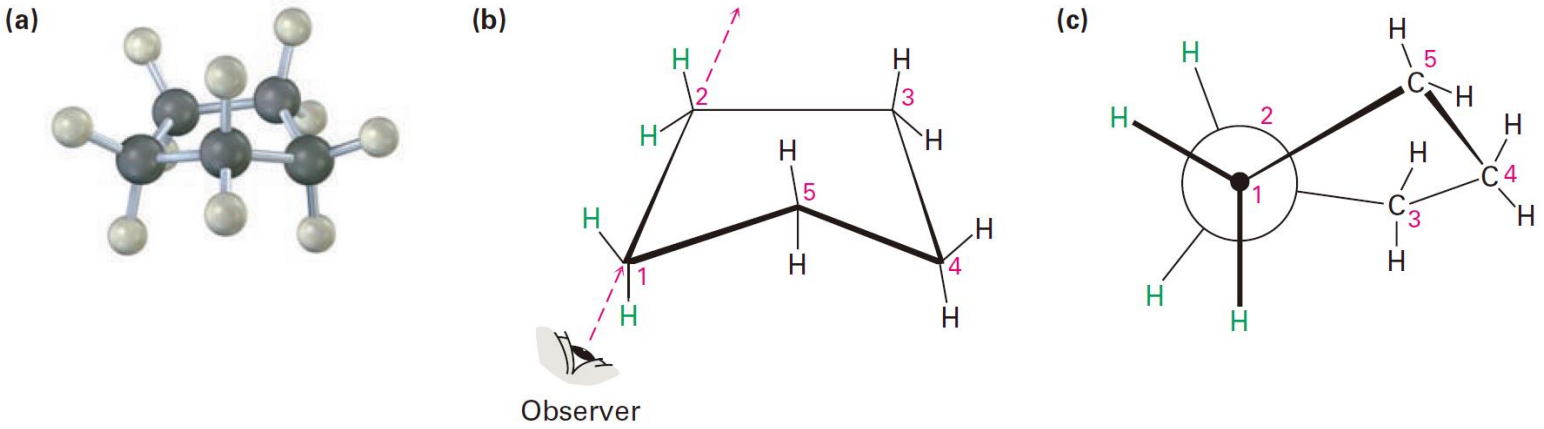
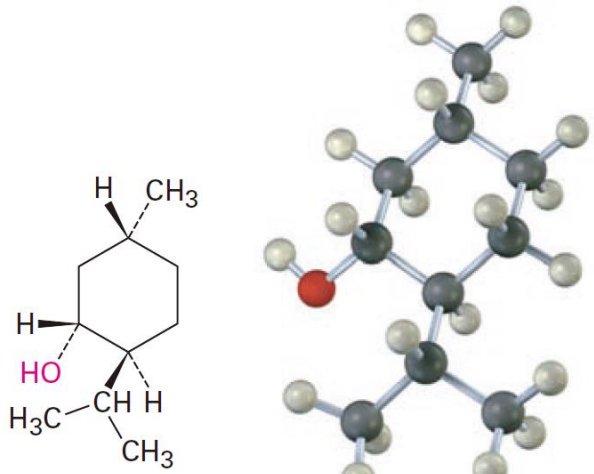


Figure 4.6 The conformation of cyclopentane. Carbons 1, 2, 3, and 4 are nearly planar, but carbon 5 is out of the plane. Part **(c)** is a Newman projection along the C1–C2 bond, showing that neighboring C—H bonds are nearly staggered.

4.5 环己烷的构象

- 薄荷醇是一种重要香料。左旋薄荷醇由于其清凉效果，大量用于香烟、化妆品、牙膏、口香糖、甜食和药物、涂擦剂。。。

Substituted cyclohexanes are the most common cycloalkanes and occur widely in nature. A large number of compounds, including steroids and many pharmaceutical agents, have cyclohexane rings. The flavoring agent menthol, for instance, has three substituents on a six-membered ring.



Menthol

4.5 环己烷的构象

- 两种稳定的环己烷构象：椅式和扭船式

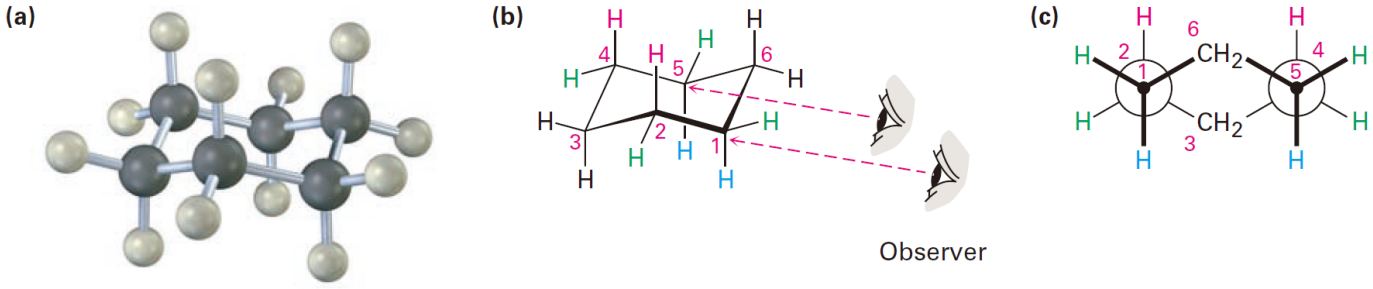
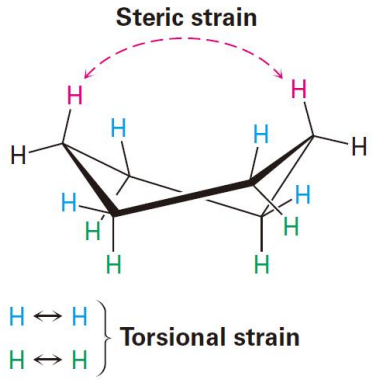
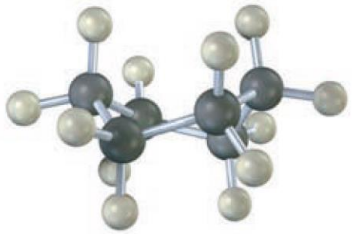
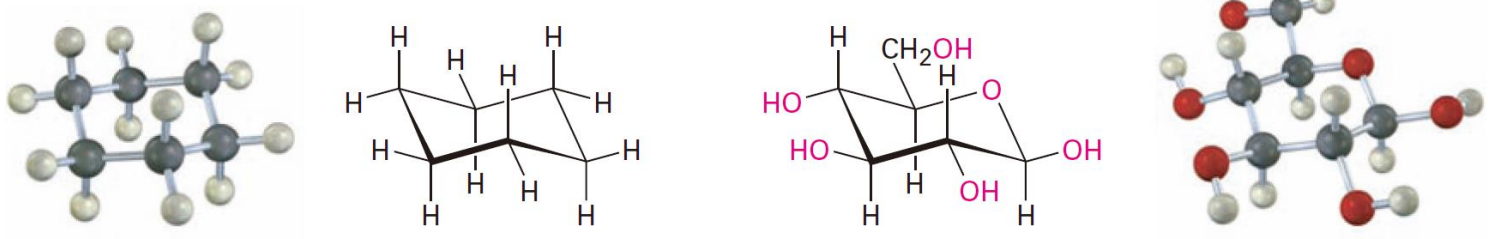


Figure 4.7 The strain-free chair conformation of cyclohexane. All C—C—C bond angles are 111.5°, close to the ideal 109.5° tetrahedral angle, and all neighboring C—H bonds are staggered.





Twist-boat cyclohexane (23 kJ/mol strain)

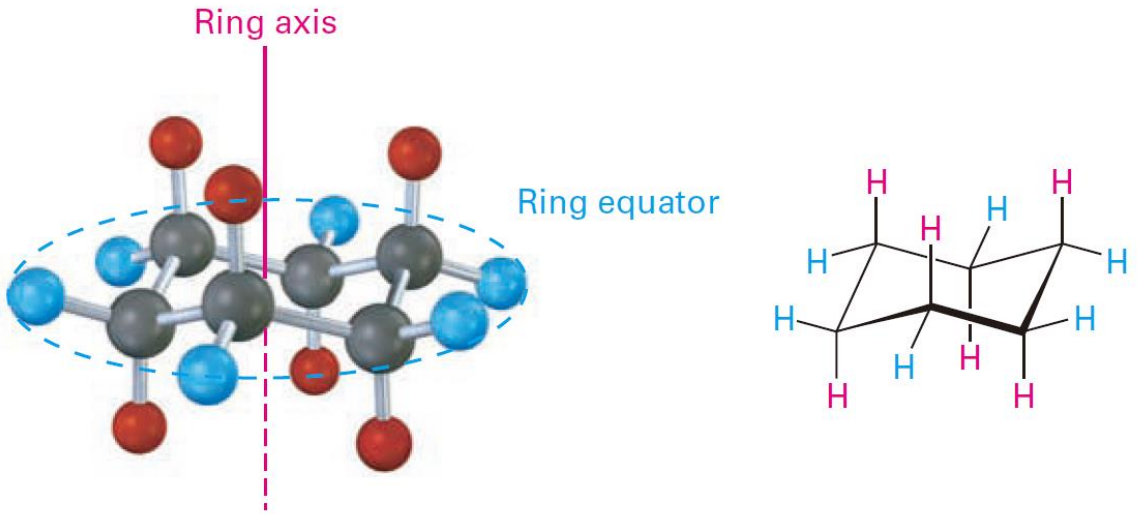


Cyclohexane (chair conformation)

Glucose (chair conformation)

4.6 直立键和平伏键

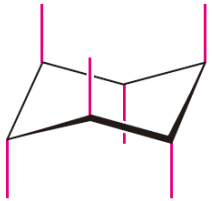
Figure 4.8 **Axial** and **equatorial** positions in chair cyclohexane. The six axial hydrogens are parallel to the ring axis, and the six equatorial hydrogens are in a band around the ring equator.



4.6 直立键和平伏键

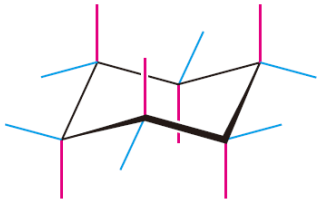
- 直立键和平伏键的画法

Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up–down.



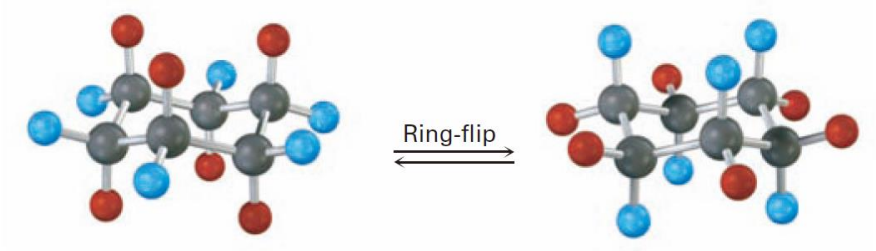
Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

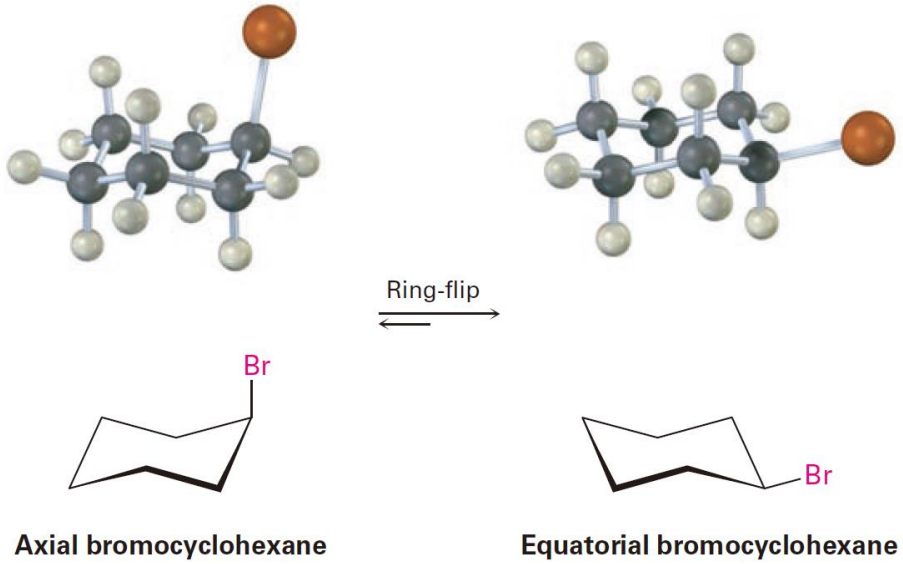
Completed cyclohexane



4.6 直立键和平伏键

- 直立键和平伏键的转化





4.7 单取代环己烷的构象

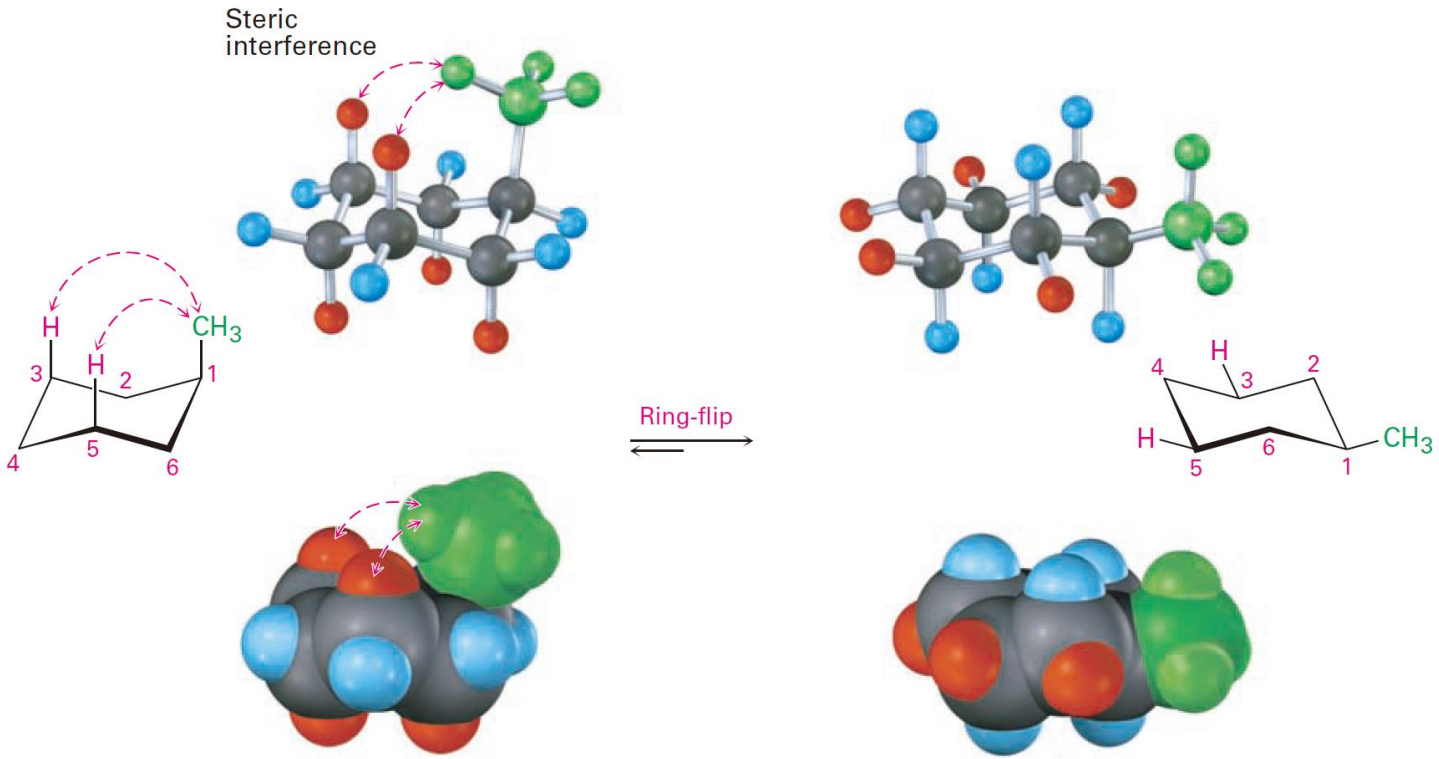
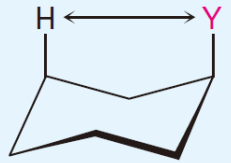


Figure 4.13 Interconversion of axial and equatorial methylcyclohexane, as represented in several formats. The equatorial conformation is more stable than the axial conformation by 7.6 kJ/mol.

4.7 单取代环己烷的构象

Table 4.1 Steric Strain in Monosubstituted Cyclohexanes



Y	1,3-Diaxial strain (kJ/mol)	1,3-Diaxial strain (kcal/mol)
F	0.5	0.12
Cl, Br	1.0	0.25
OH	2.1	0.5
CH_3	3.8	0.9
CH_2CH_3	4.0	0.95
$CH(CH_3)_2$	4.6	1.1
$C(CH_3)_3$	11.4	2.7
C_6H_5	6.3	1.5
CO_2H	2.9	0.7
CN	0.4	0.1

4.8 双取代环己烷的构象

- *cis*-1,2双取代

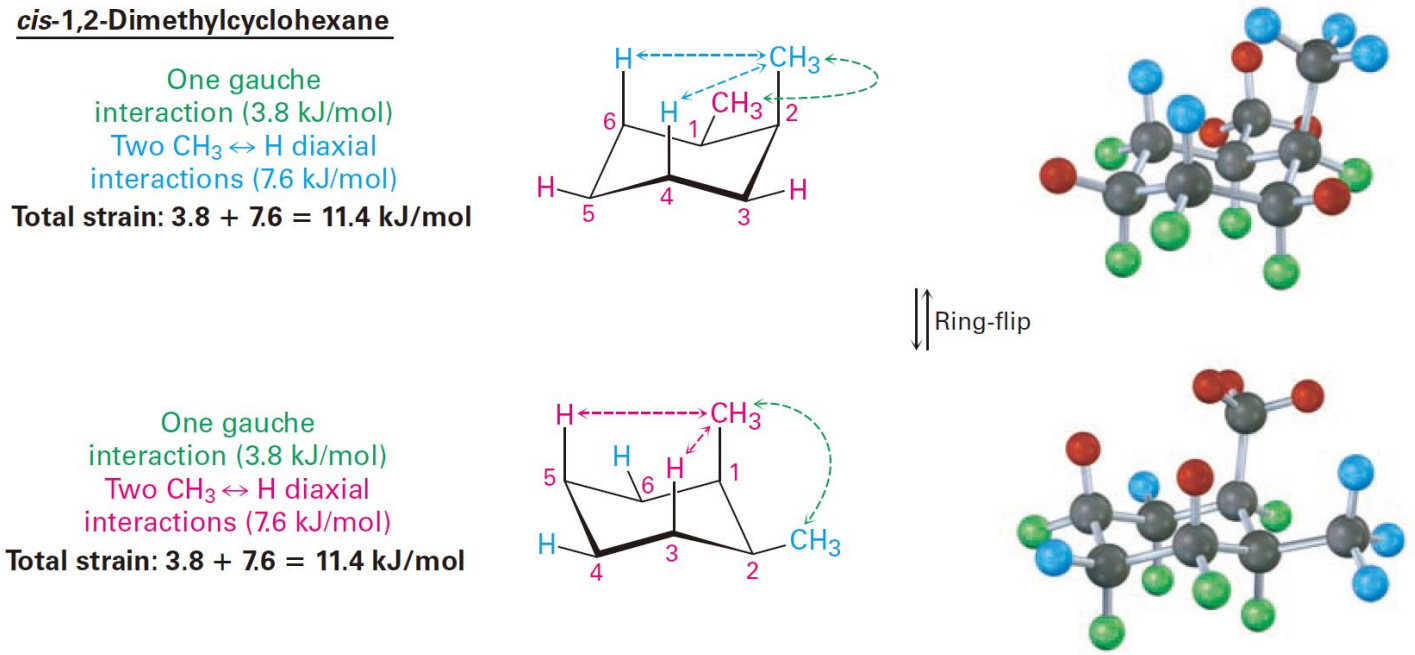


Figure 4.15 Conformations of *cis*-1,2-dimethylcyclohexane. The two chair conformations are equal in energy because each has one axial methyl group and one equatorial methyl group.

4.8 双取代环己烷的构象

- trans-1,2双取代

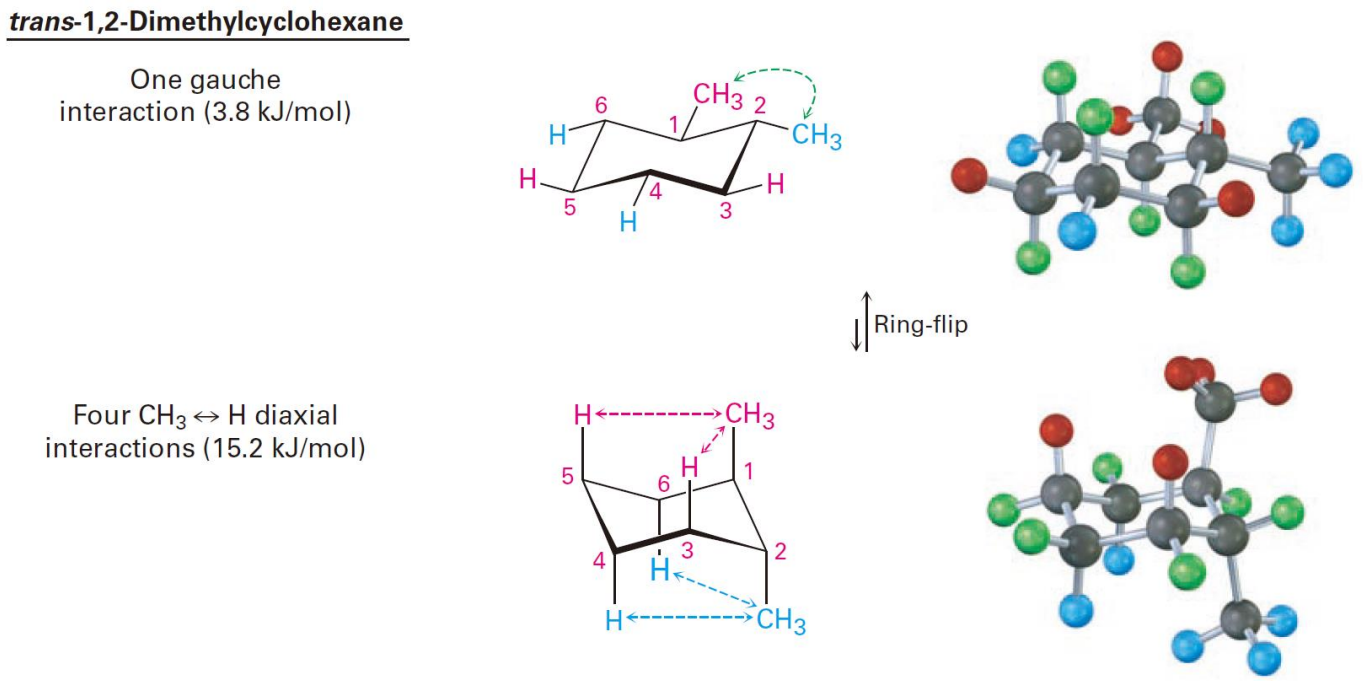
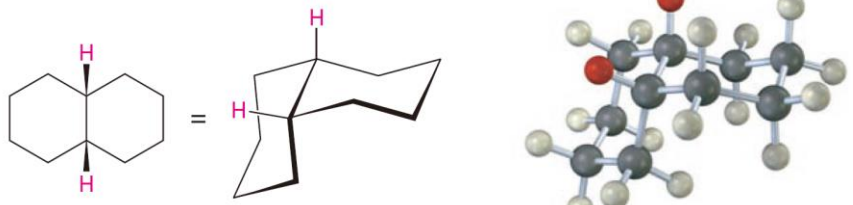


Figure 4.16 Conformations of *trans*-1,2-dimethylcyclohexane. The conformation with both methyl groups equatorial (top) is favored by 11.4 kJ/mol (2.7 kcal/mol) over the conformation with both methyl groups axial (bottom).

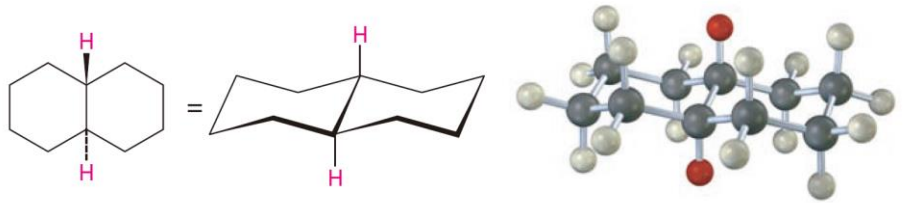
4.9 多环烷烃的构象

- 顺反十氢化萘及性激素

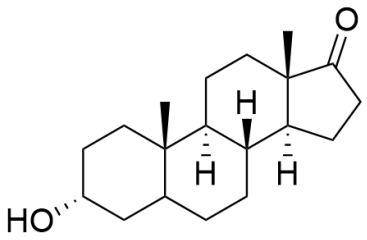
Figure 4.17 Representations of *cis*- and *trans*-decalin. The **hydrogen atoms** at the bridgehead carbons are on the same face of the rings in the cis isomer but on opposite faces in the trans isomer.



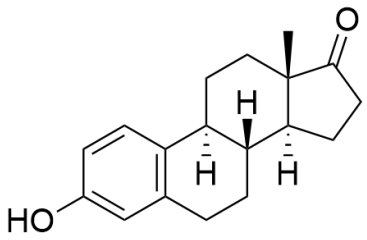
***cis*-Decalin**



***trans*-Decalin**



Androsterone
雄酮



Estrone
雌酮

作业

- 4.51-4.62