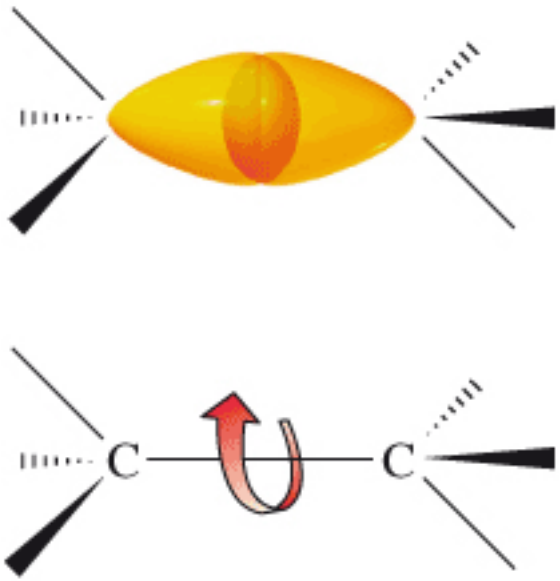
Analisi conformazionale

Proiezioni di Newman

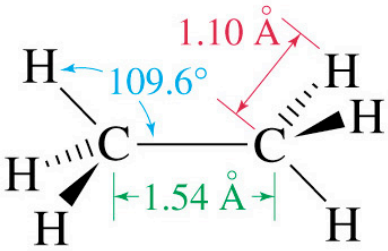
Tensione d'anello

Conformazioni del cicloesano

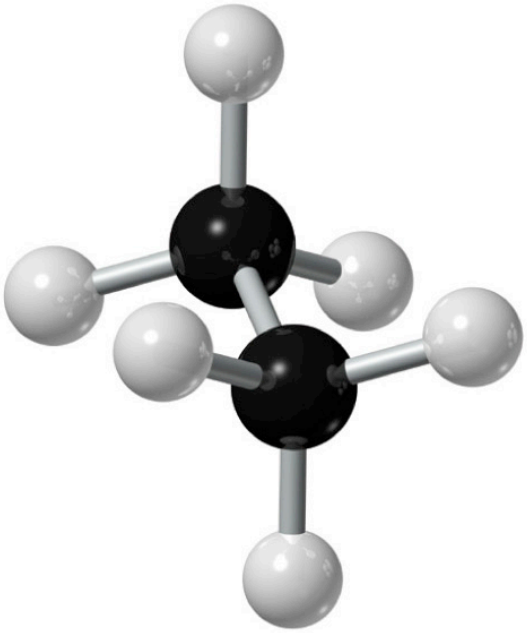


▲ Figura 2.3
Il legame carbonio–carbonio è formato dalla sovrapposizione di orbitali sp^3 a simmetria cilindrica. Per questo, si può avere rotazione intorno al legame senza che l'entità della sovrapposizione cambi.

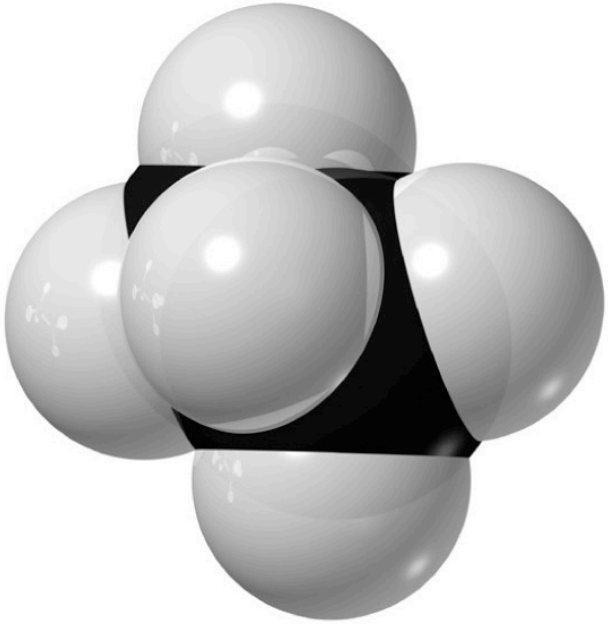
Views of Ethane



ethane

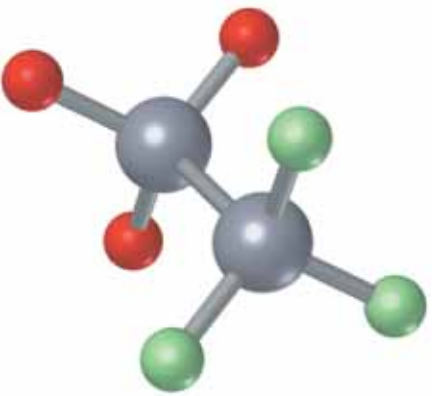


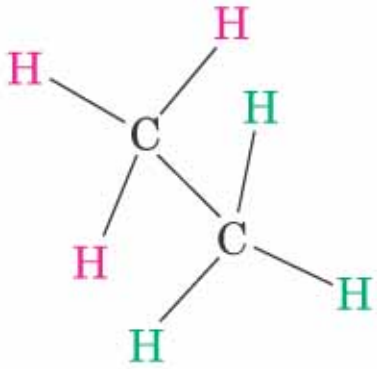
ethane



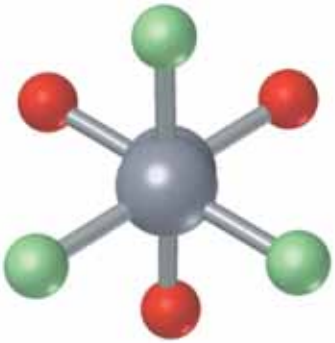
ethane

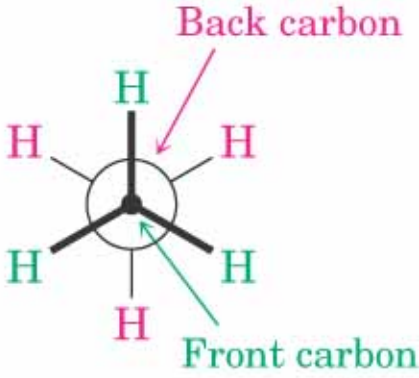
The Newman Projection





Sawhorse representation

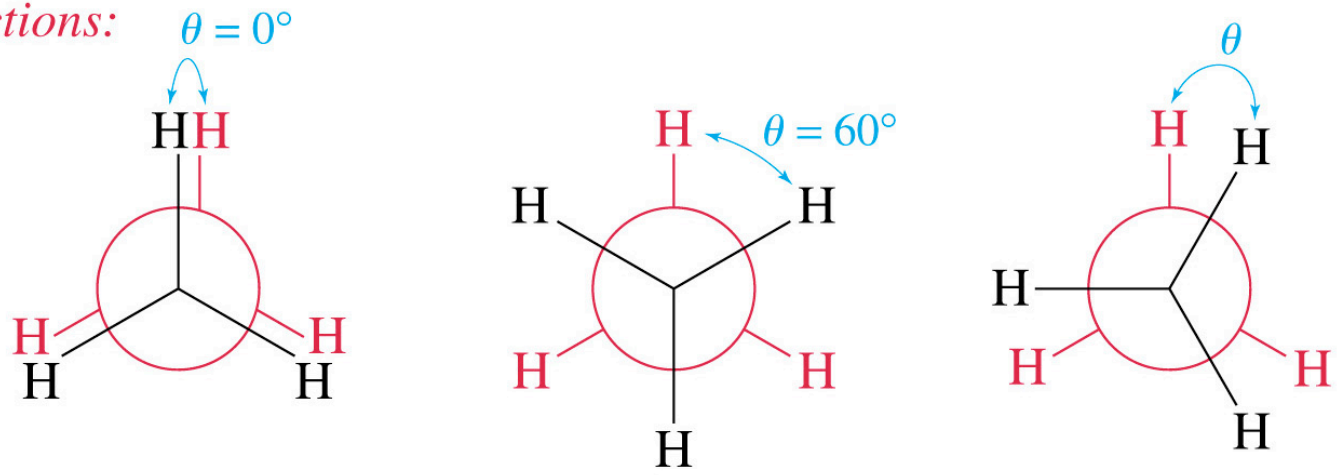




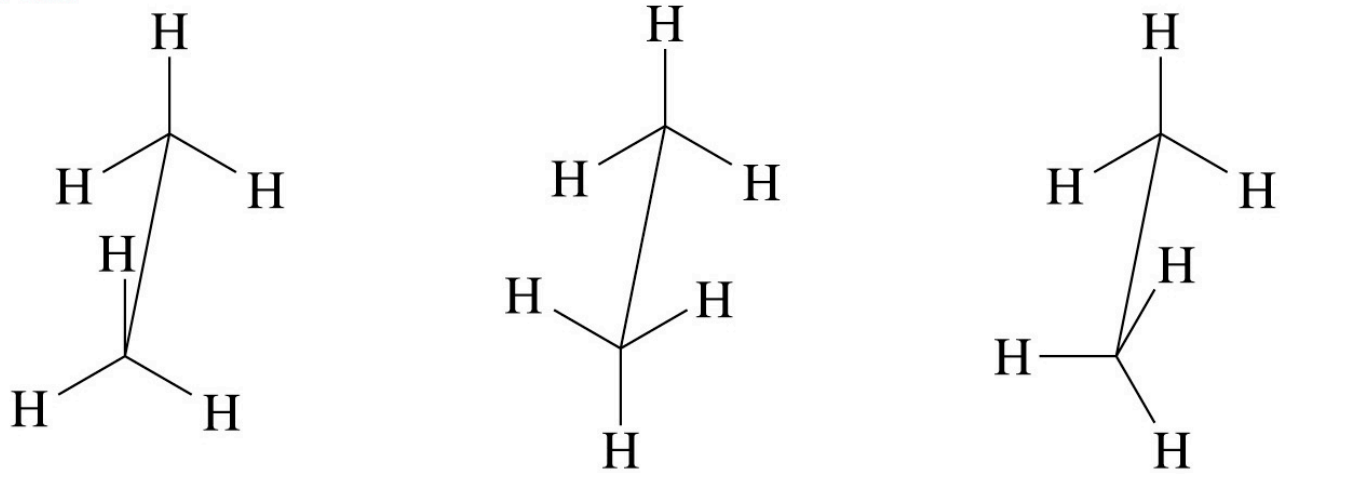
Newman projection

Rotational Conformations of Ethane

Newman projections:



Sawhorse structures:

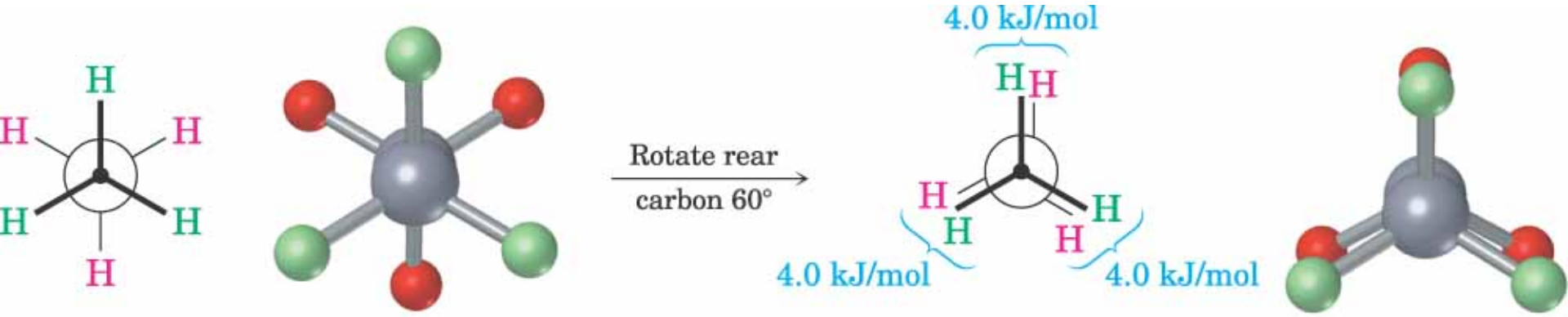


eclipsed, $\theta = 0°$ staggered, $\theta = 60°$ skew, $\theta =$ anything else

Definitions

- Conformations - Different spatial arrangments that a molecule can adopt due to rotation about sigma bonds.
- Staggered - A low energy conformation where the bonds on adjacent atoms bisect each other (60^{o} dihedral angle), maximizing the separation.
- Eclipsed - A high energy conformation where the bonds on adjacent atoms are aligned with each other (0^{o} dihedral angle).

60° Rotation Causes Torsional or Eclipsing Strain



Ethane—staggered conformation

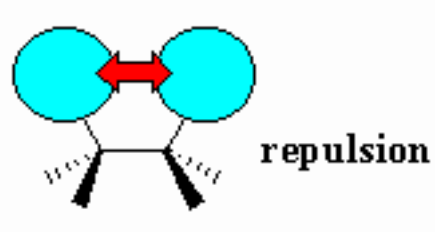
Ethane—eclipsed conformation

Types of Strain

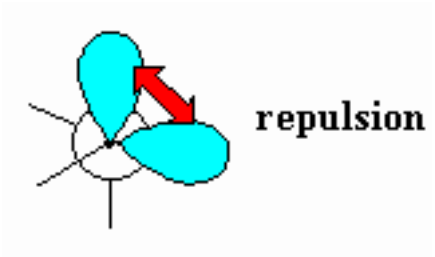
- Steric - Destabilization due to the repulsion between the electron clouds of atoms or groups. Groups try to occupy some common space.
- Angle - Destabilisation due to distortion of a bond angle from its optimum value (i.e. 109.5°) caused by the electrostatic repulsion of the electrons in the bonds. e.g. cyclopropane
- Torsional - Destabilization due to the repulsion between pairs of bonds caused by the electrostatic repulsion of the electrons in the bonds. Groups are eclipsed.

strain (tensione)

steric strain
van der Waals repulsion)



angle strain



torsional strain

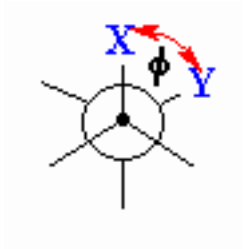


diagramma dell'energia potenziale

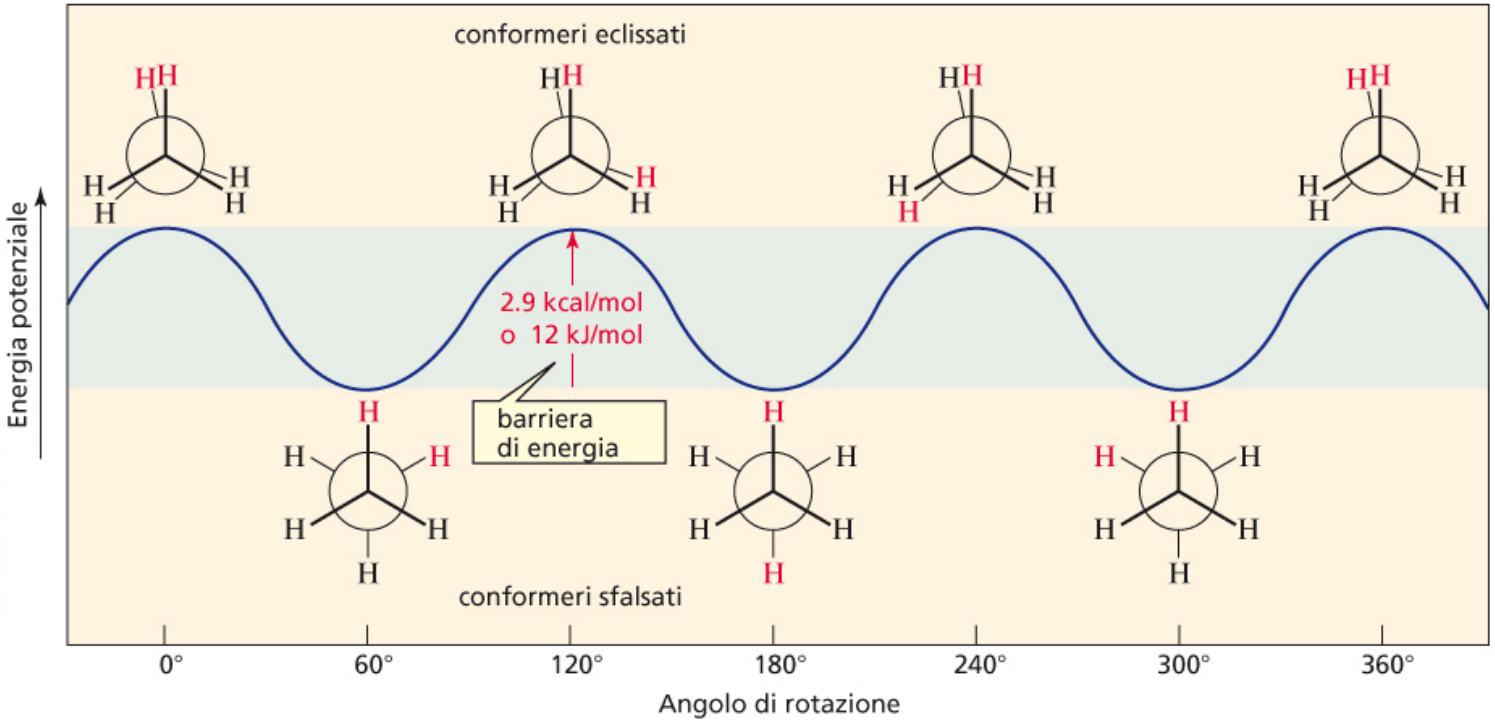
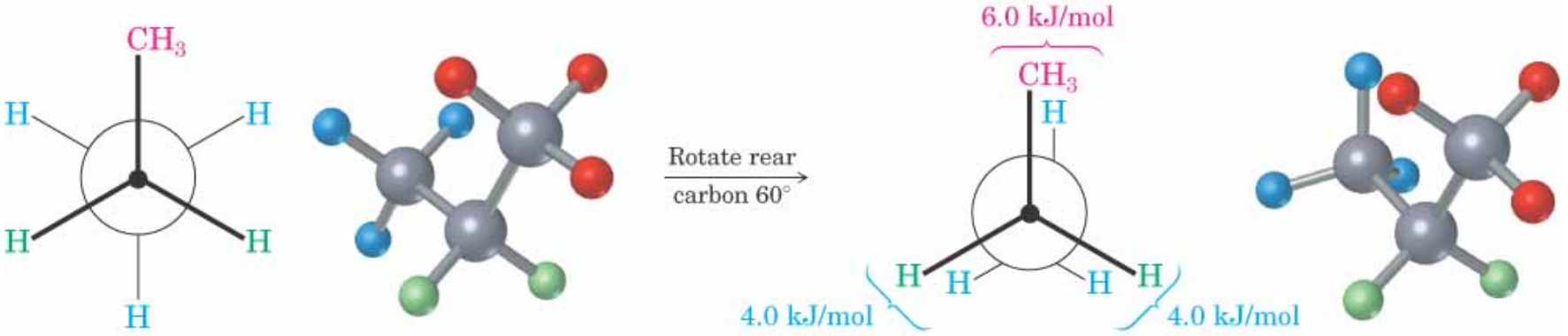
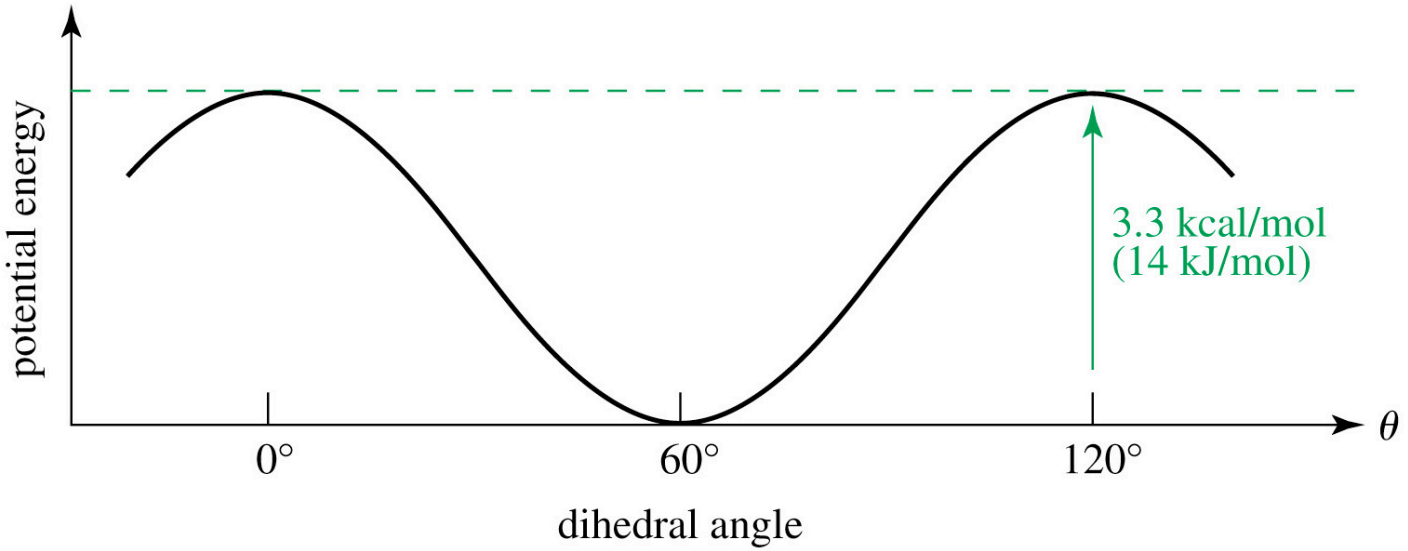


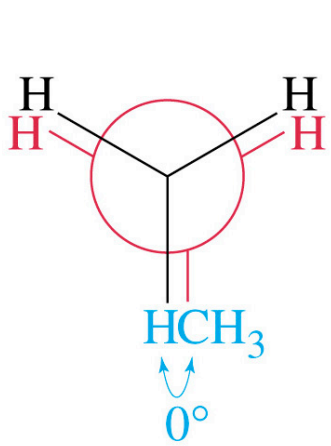
Figura 2.4 Energia potenziale dell'etano in funzione dell'angolo di rotazione intorno al legame carbonio–carbonio.

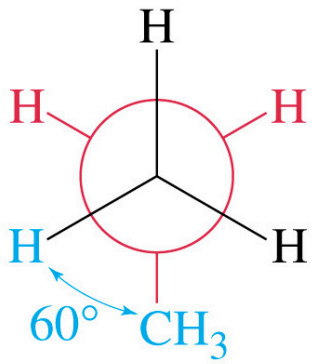


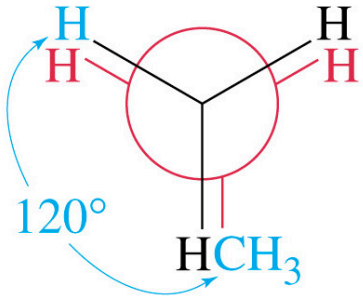
Staggered propane **Eclipsed propane**

Propane Conformations: Larger Barrier to Rotation





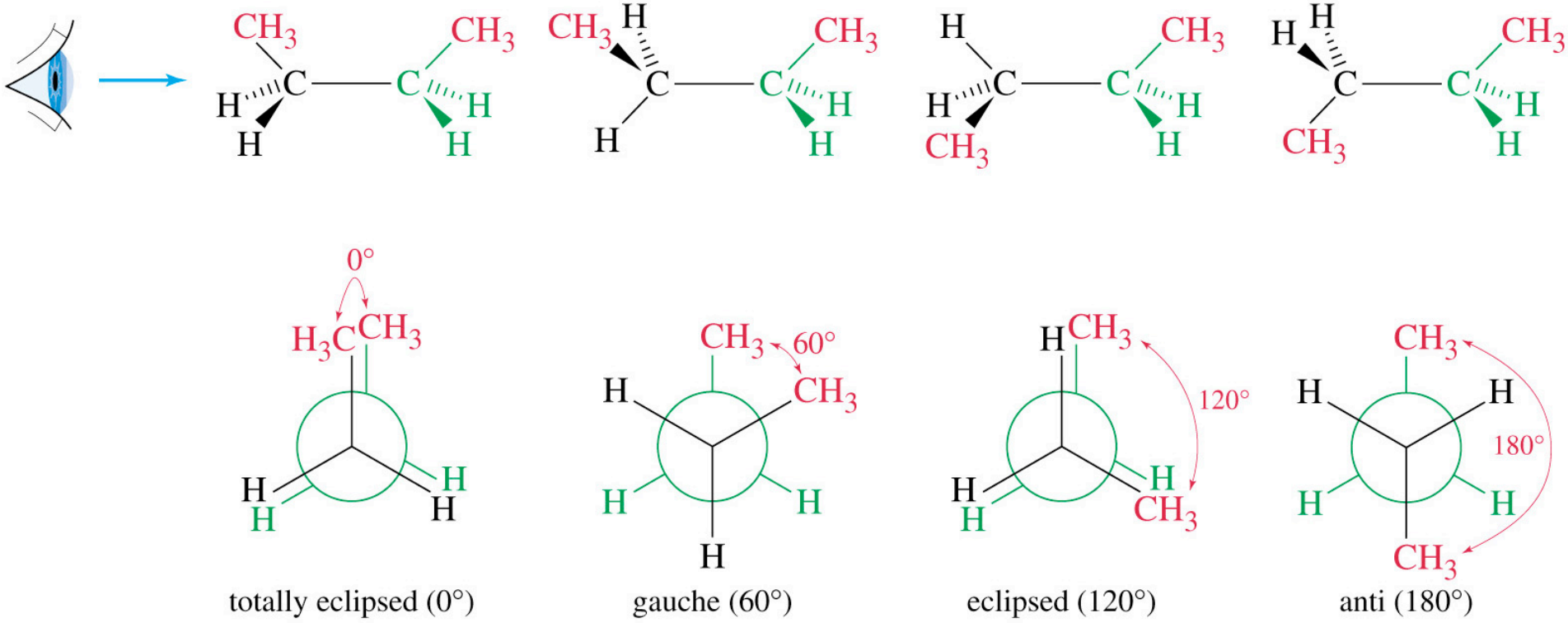




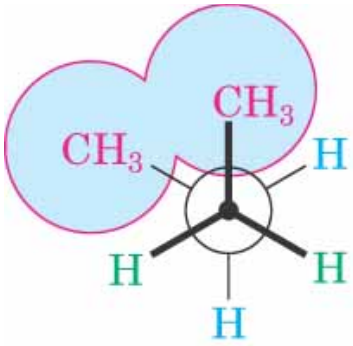
Definitions

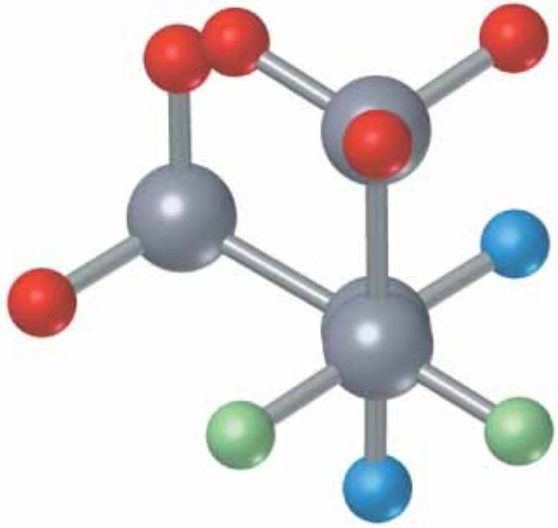
- Anti - Description given to two substitutents attached to adjacent atoms when their bonds are at 180^{o} with respect to each other.
- Syn - Description given to two substitutents attached to adjacent atoms when their bonds are at 0^{o} with respect to each other.
- Gauche - Description given to two substitutents attached to adjacent atoms when their bonds are at 60^{o} with respect to each other.

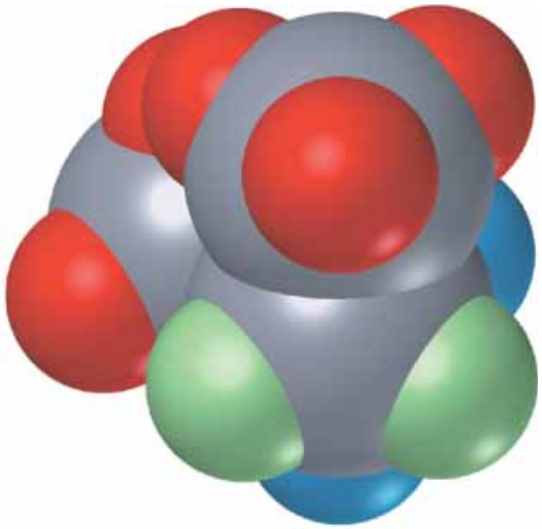
Butane Conformations (C_2-C_3)



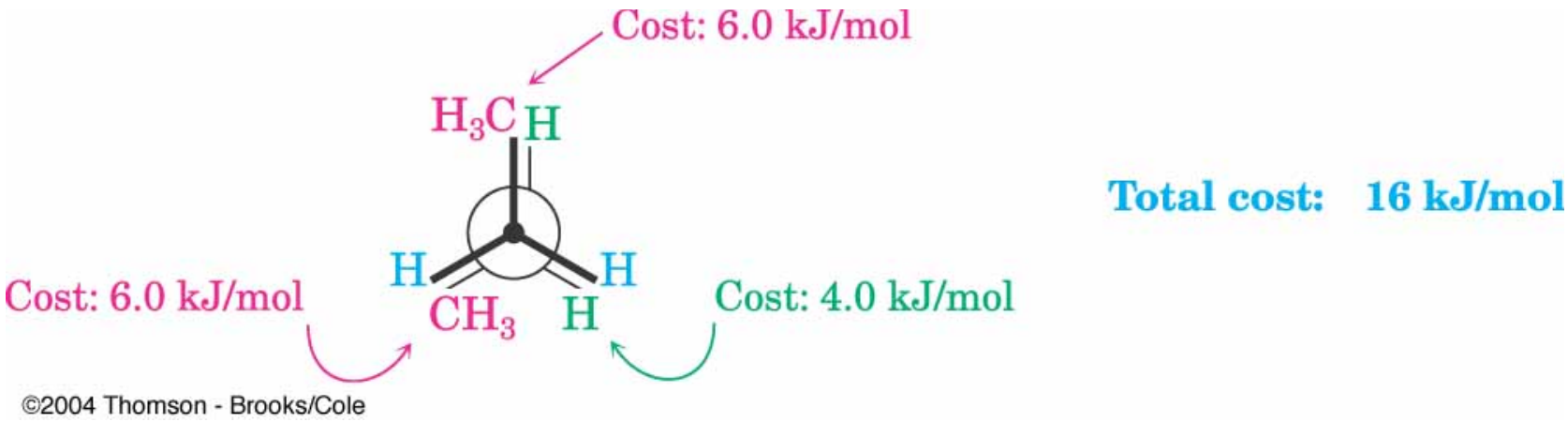
Gauche Interaction in Butane

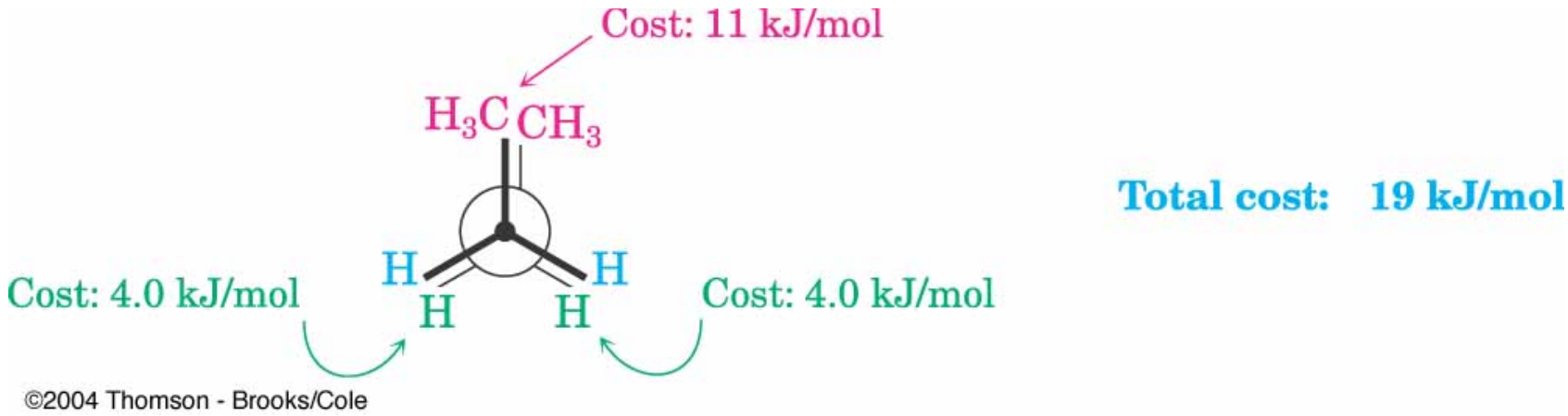






2 different eclipsed conformations



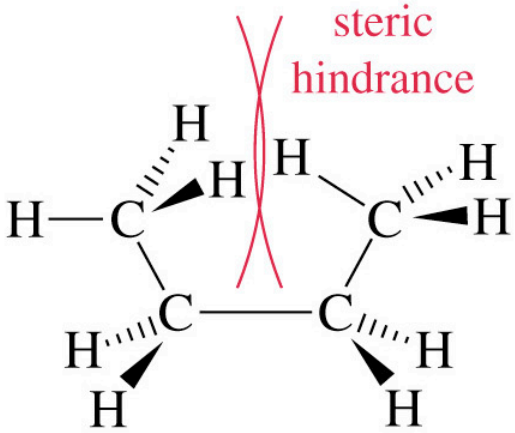


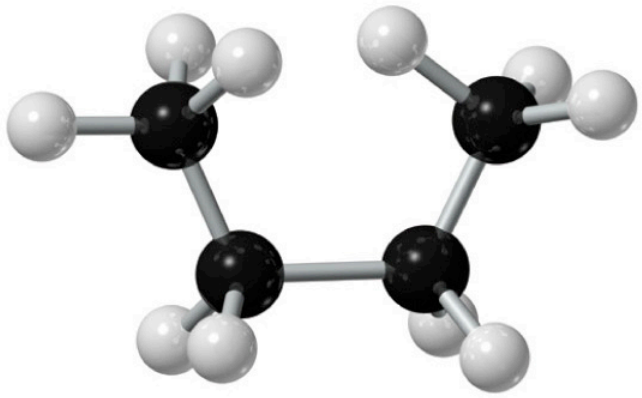
Strain Energy can be Quantified

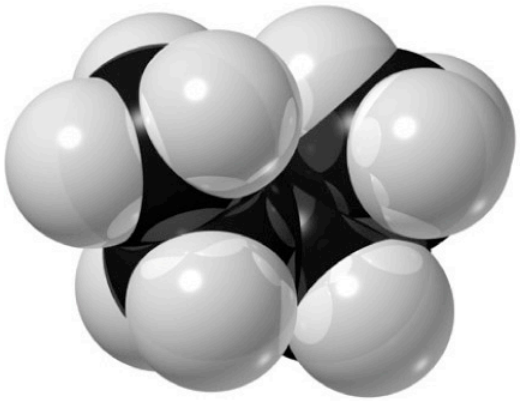
TABLE 4.1 Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost (kJ/mol)	Energy cost (kcal/mol)
H ↔ H eclipsed	Torsional strain	4.0	1.0
H ↔ CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3 ↔ CH_3 eclipsed	Torsional plus steric strain	11	2.6
CH_3 ↔ CH_3 gauche	Steric strain	3.8	0.9

Butane has Steric and Torsional Strain When Eclipsed

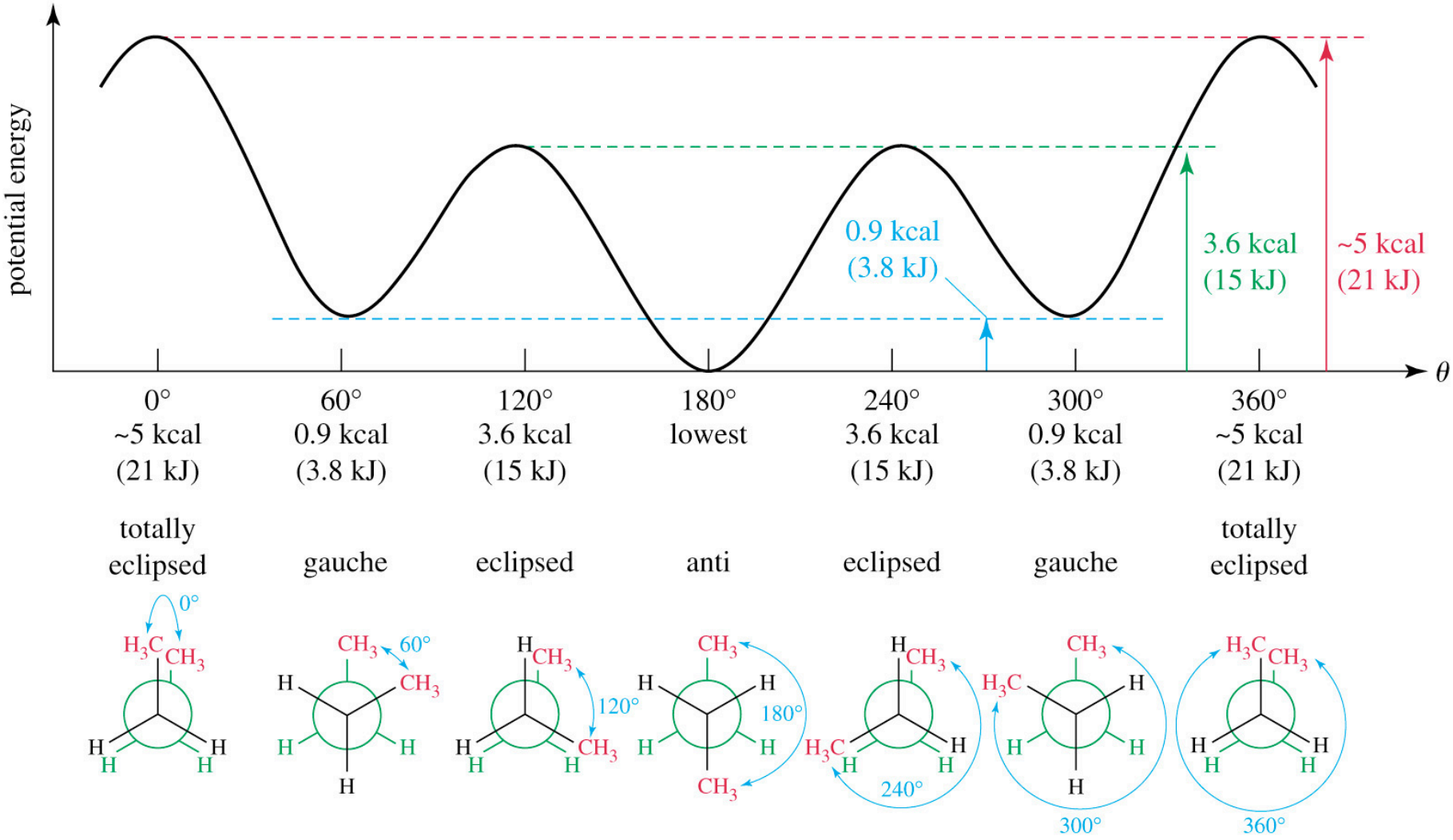




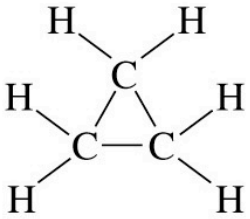


Totally eclipsed conformation of butane

PE Diagram for Butane

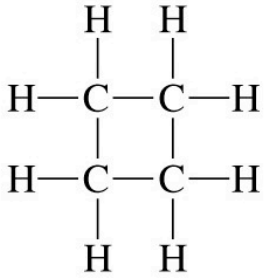


Saturated Cyclic Compounds



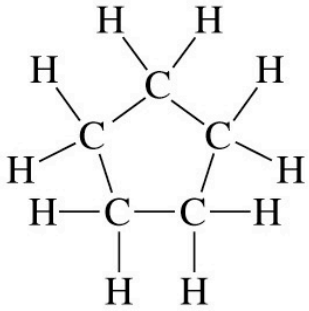
or

cyclopropane
C_3H_6

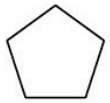


or

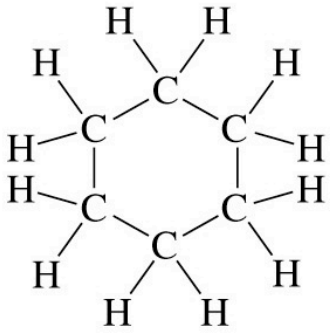
cyclobutane
C_4H_8



or

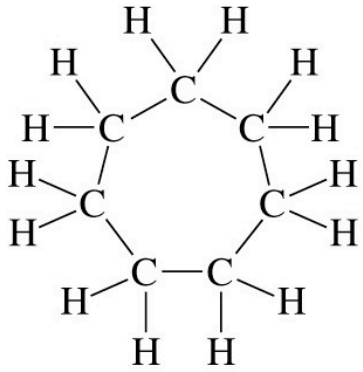


cyclopentane
C_5H_{10}



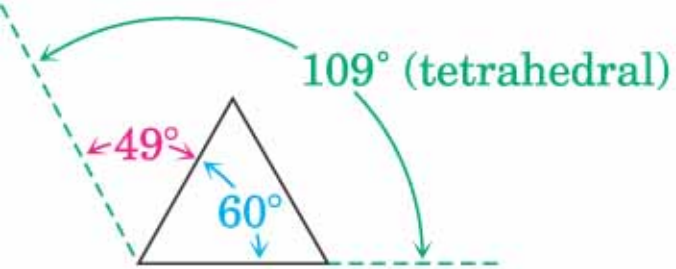
or

cyclohexane
C_6H_{12}

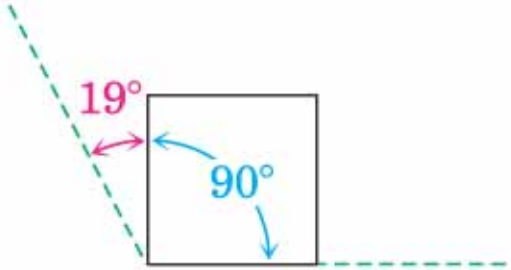


or

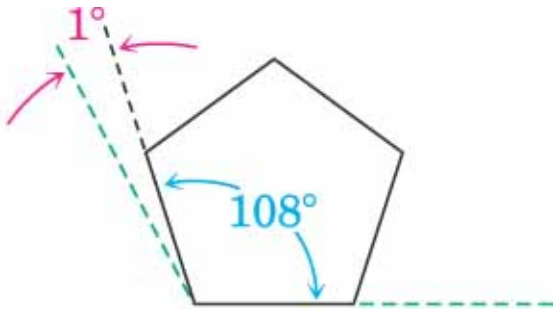
cycloheptane
C_7H_{14}



Cyclopropane



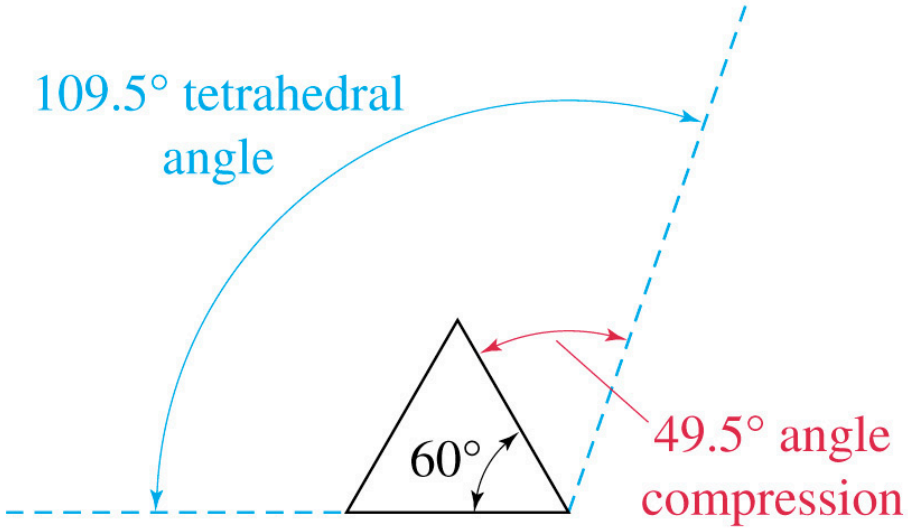
Cyclobutane

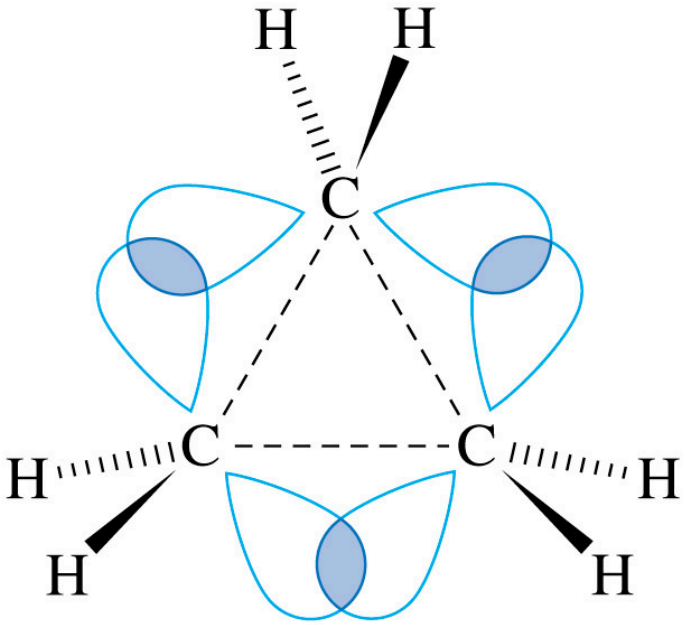


Cyclopentane

Cyclopropane

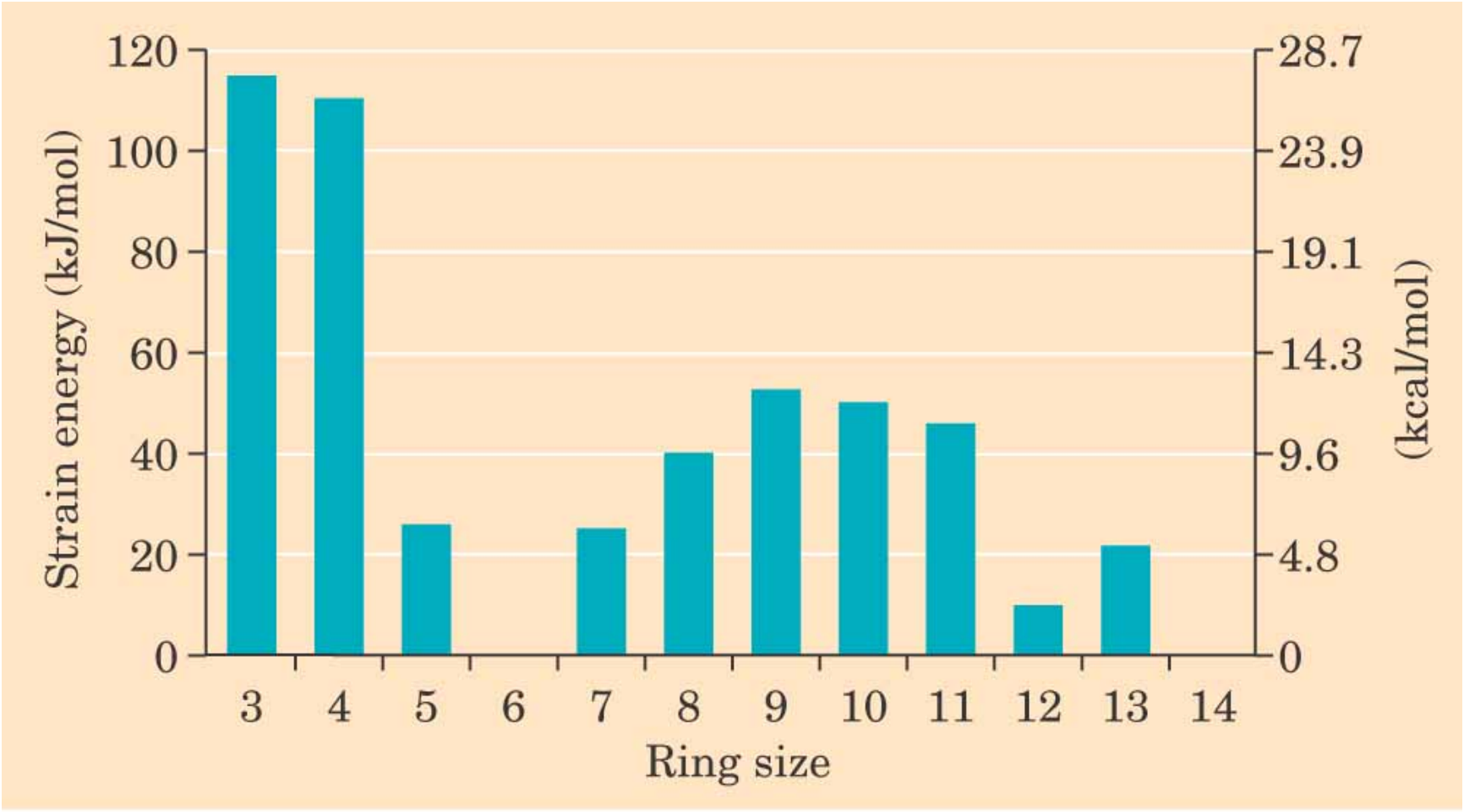
Angle and Torsional Strain



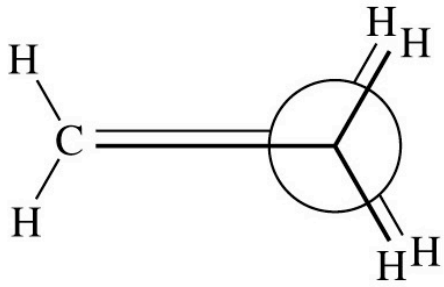


"bent bonds"
nonlinear overlap

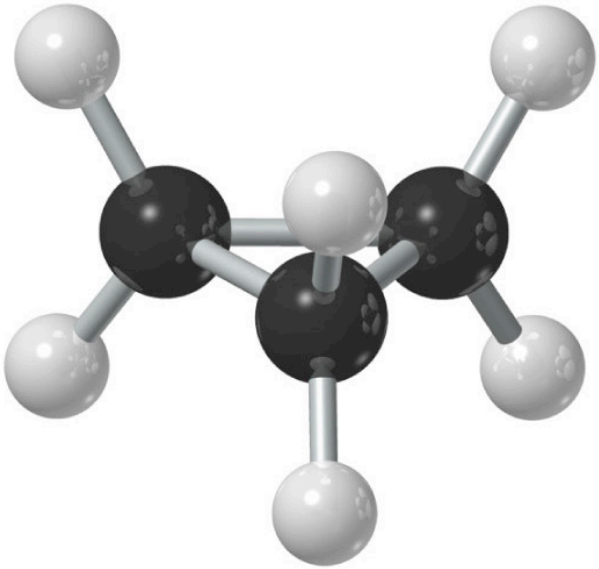
$$(CH_2)_n + \frac{3n}{2} O_2 \longrightarrow n\,CO_2 + n\,H_2O + \text{Heat}$$

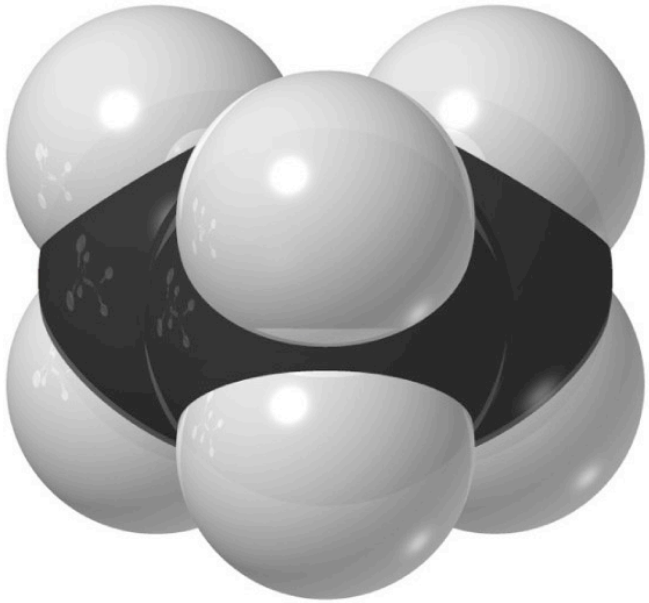


All dihedral angles = 0°

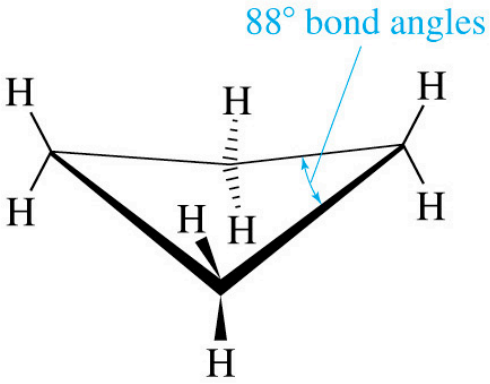


Newman projection
of cyclopropane

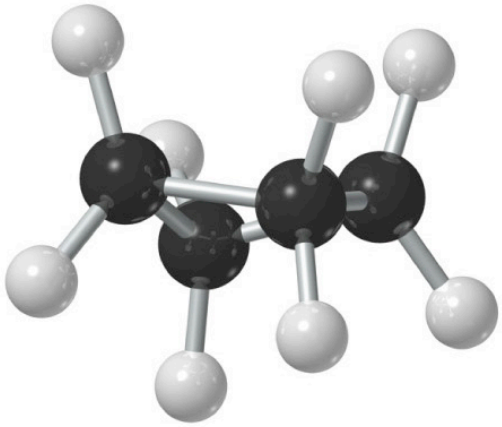


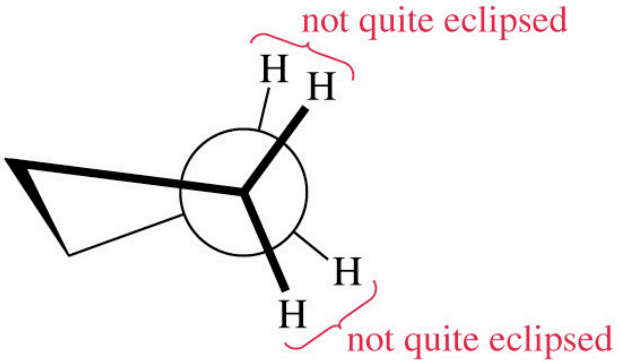


Cyclobutane **is not planar**



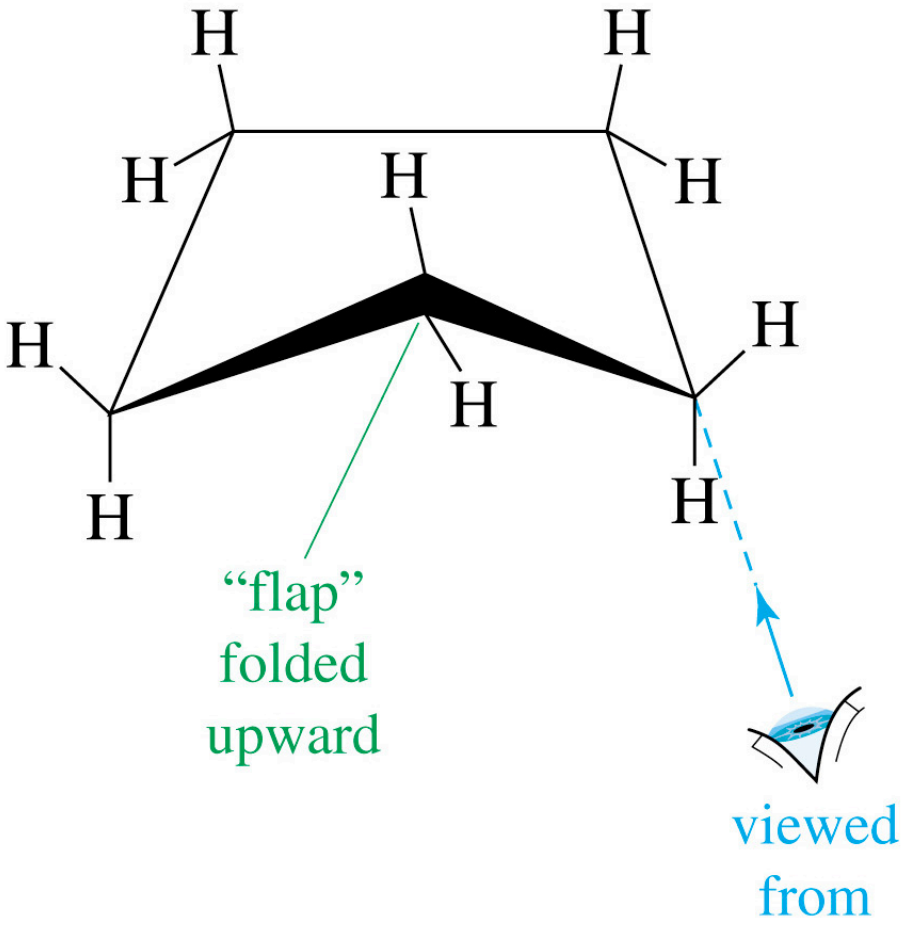
slightly folded conformation

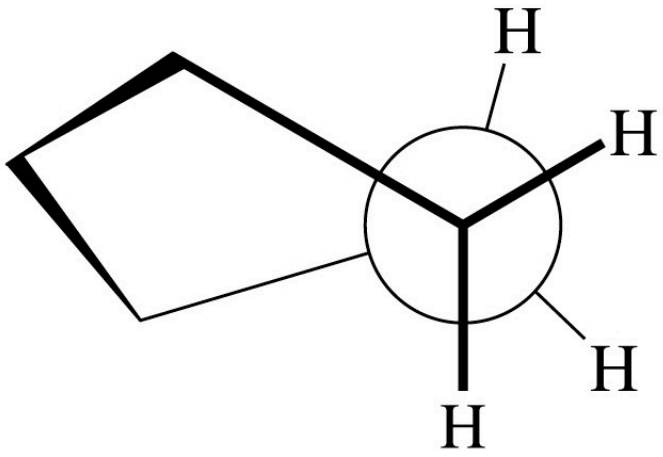




Newman projection of one bond

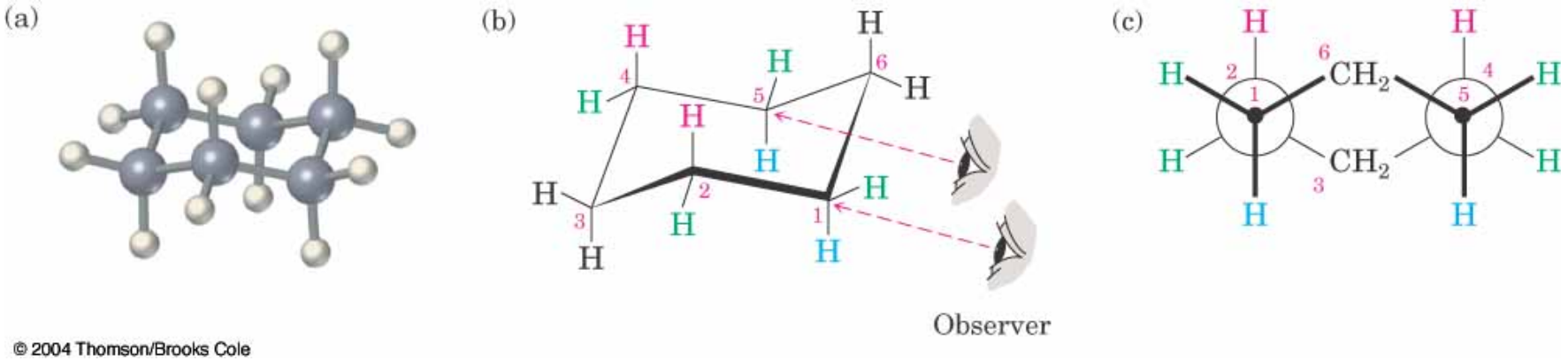
Cyclopentane



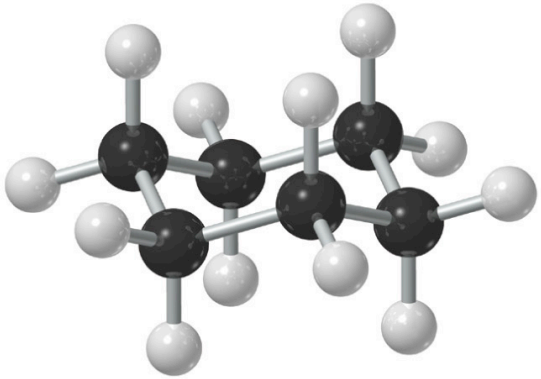


Newman projection showing relief of eclipsing of bonds

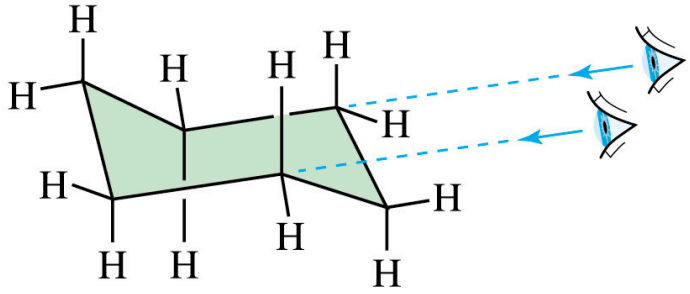
Cyclohexane



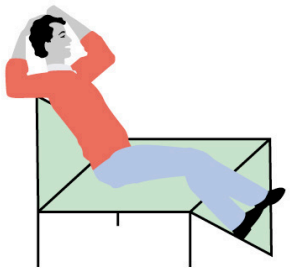
chair conformation

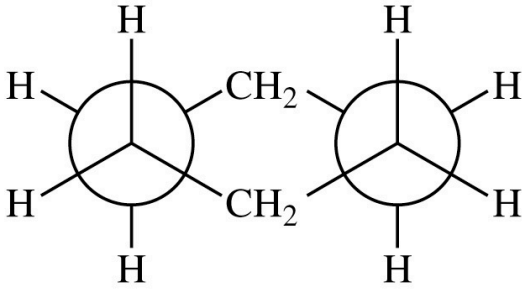


chair conformation



viewed along the “seat” bonds





Newman projection

Tabella 2.9 Calori di formazione ed energie di tensione dei cicloalcani

	Calore di formazione (kcal/mol)	Calore di formazione "privo di tensione" (kcal/mol)	Energia totale di tensione (kcal/mol)	Energia di tensione per i gruppi CH_2 (kcal/mol)
Ciclopropano	+12.7	-14.6	27.3	9.1
Ciclobutano	+6.8	-19.7	26.5	6.6
Ciclopentano	-18.4	-24.6	6.2	1.2
Cicloesano	-29.5	-29.5	0	0
Cicloeptano	-28.2	-34.4	6.2	0.9
Cicloottano	-29.7	-39.4	9.7	1.2
Ciclononano	-31.7	-44.3	12.6	1.4
Ciclodecano	-36.9	-49.2	12.3	1.2
Cicloundecano	-42.9	-54.1	11.2	1.0

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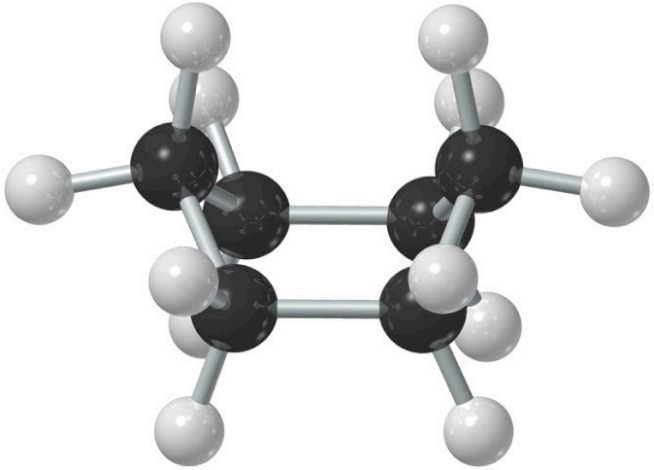
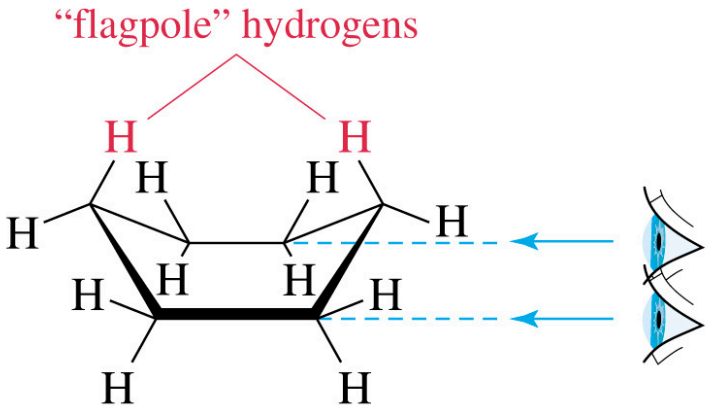
calore di formazione del cubano: 144 Kcal/mol
strain energy: 166 Kcal/mol
(*Angew. Chem.* **1992**, *31*, 1421)

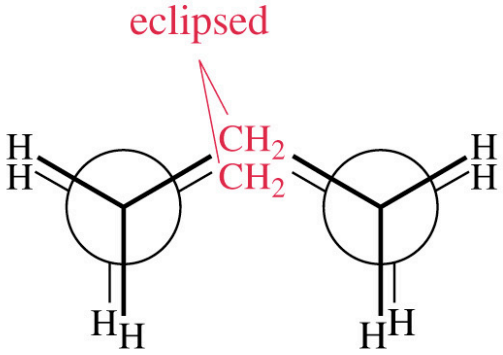
Boat Conformation



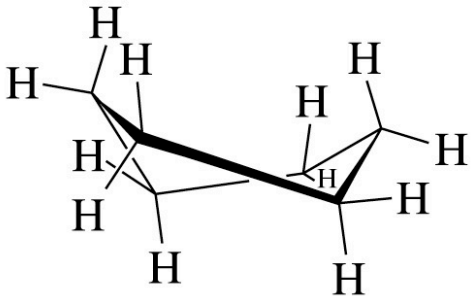
boat conformation



symmetrical boat

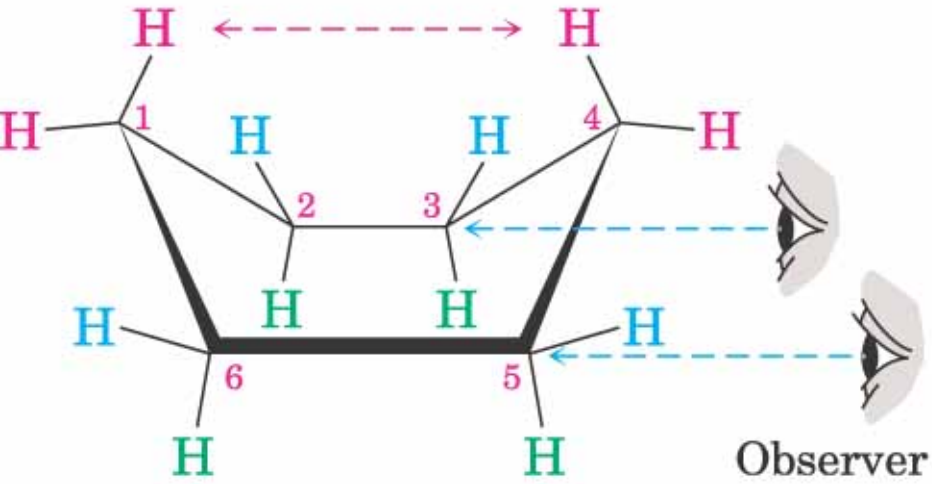


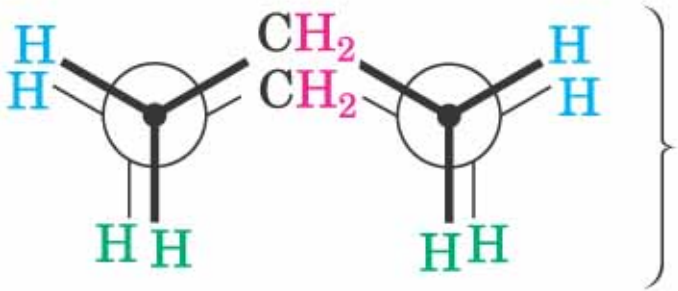
Newman projection

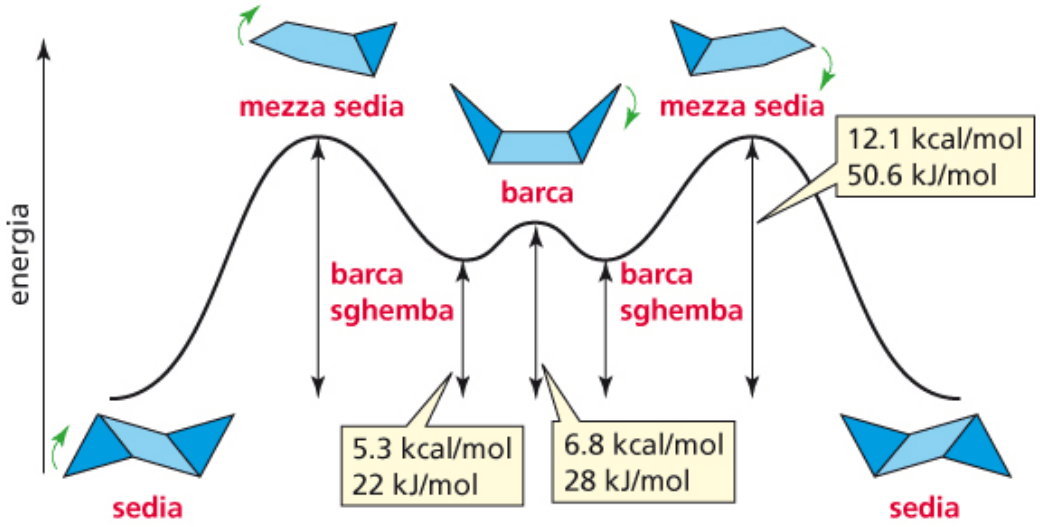


"twist" boat

Steric strain of hydrogens
at C1 and C4







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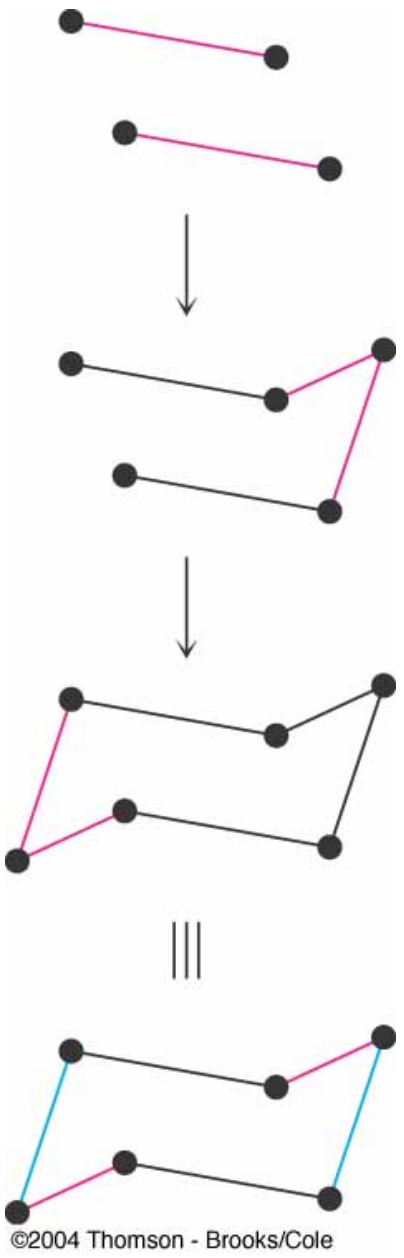
◀ Figura 2.10
I conformeri del cicloesano e le loro energie relative quando uno dei conformeri a sedia si trasforma nell'altro conformero a sedia

10^5 inversioni d'anello al secondo

how to draw a chair conformation

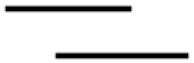
all opposite bonds are parrallel

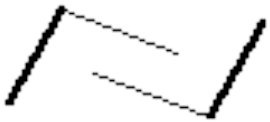


adding "wedges" helps show the 3D structure

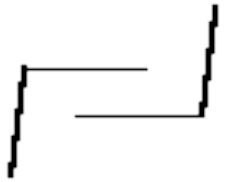
The chair can be obtained by drawing opposite sides as 3 sets of parallel lines

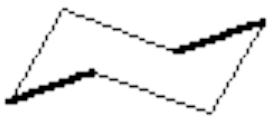
First draw the sides of the middle portion



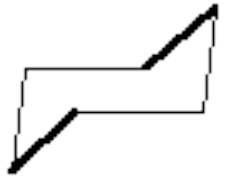


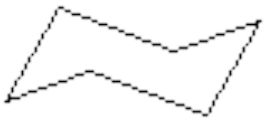
Next draw in the first half of each end



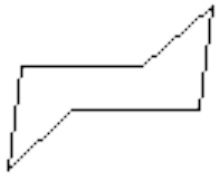


Finally complete the two ends



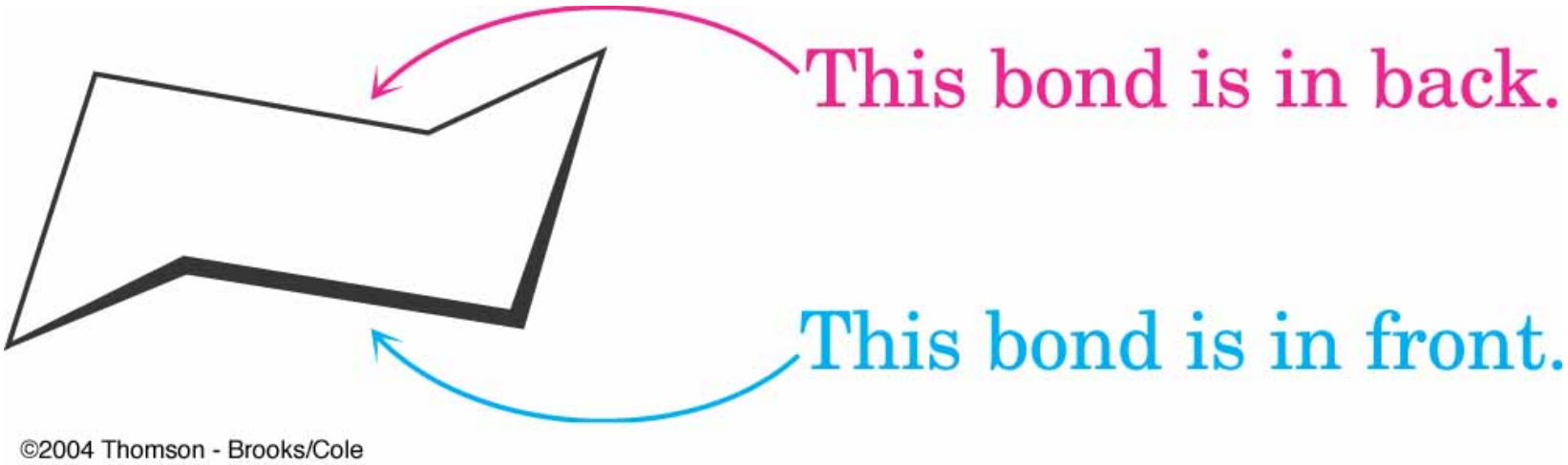


Done !



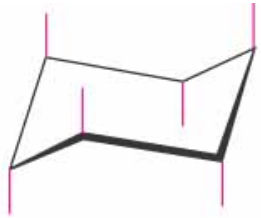
angled

horizontal



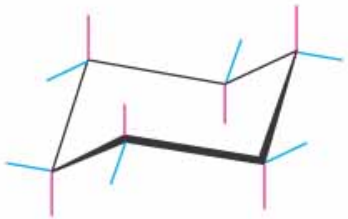
Axial bonds and Equatorial bonds

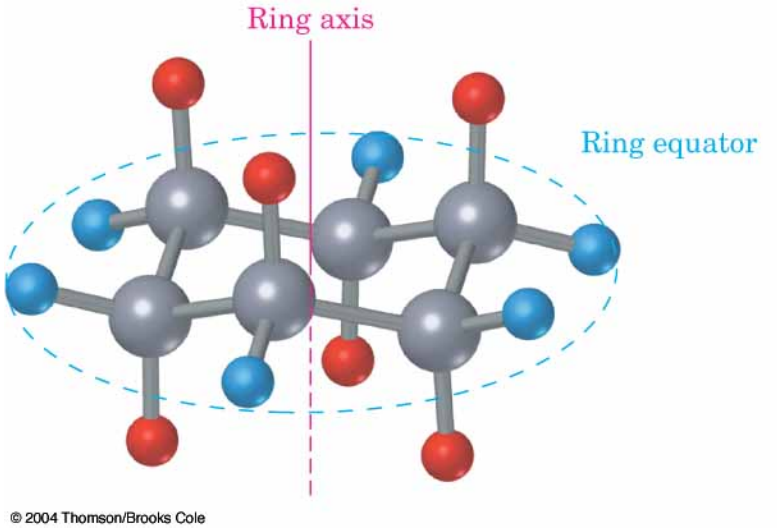
Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up–down.

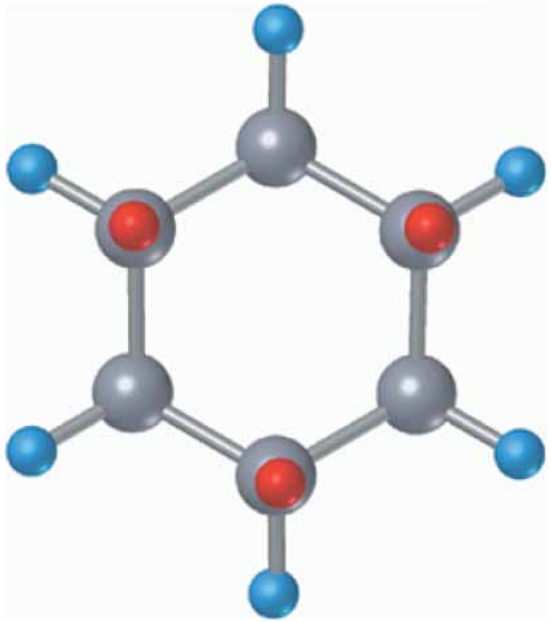


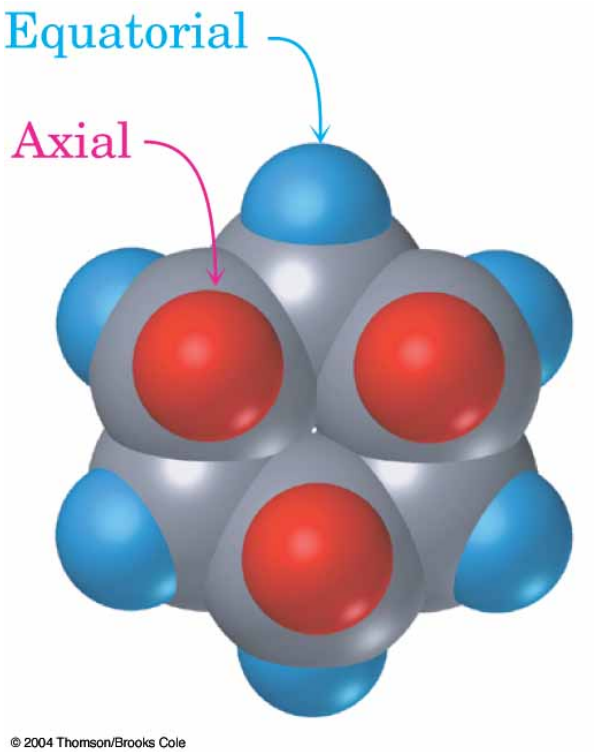
Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

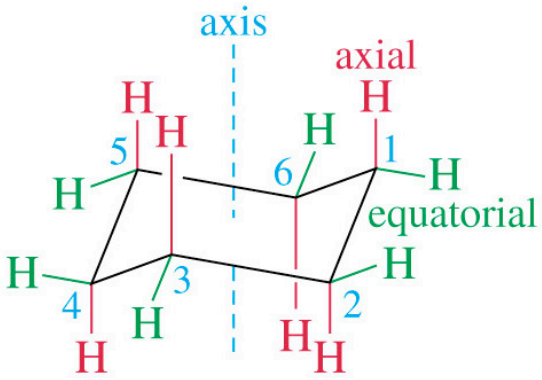
Completed cyclohexane

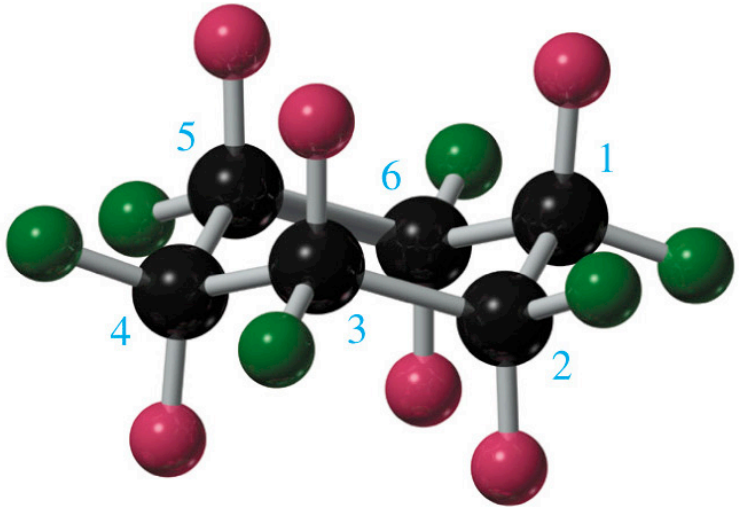


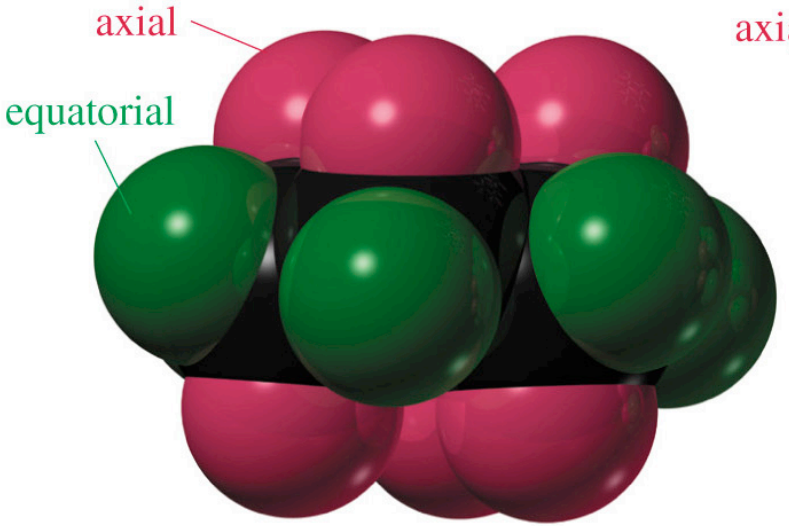




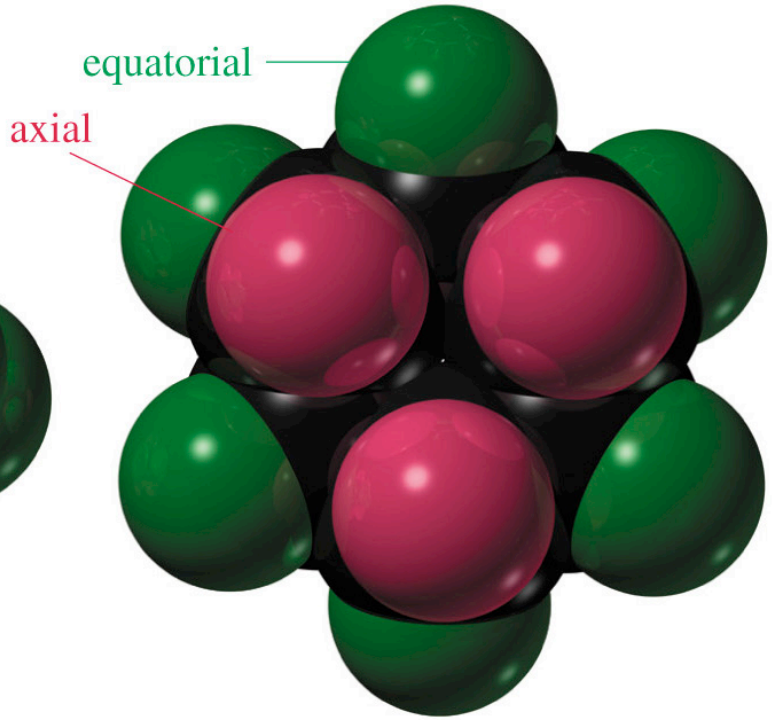






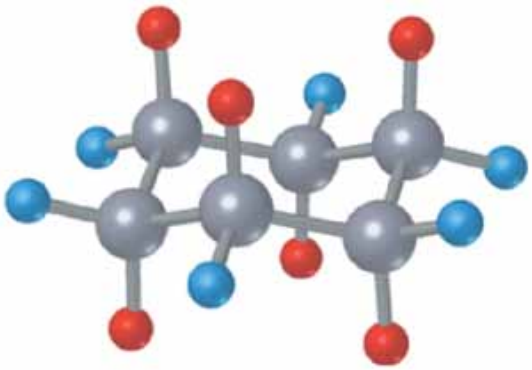


seen from the side

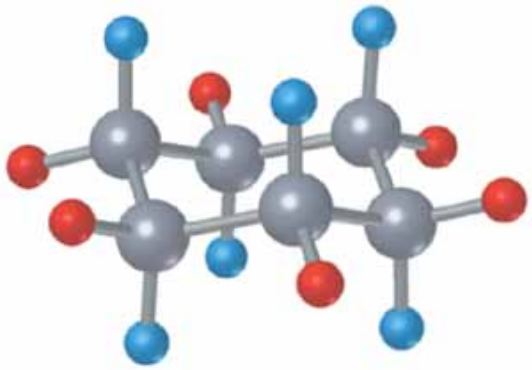


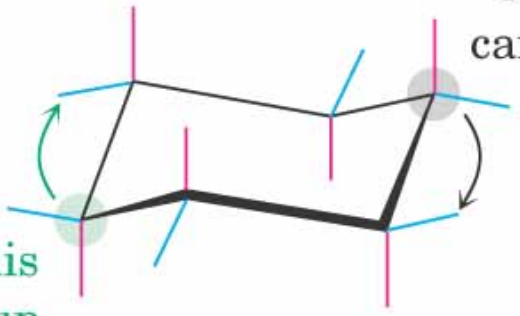
seen from above

Rings can Flip from one Chair Conformation to Another

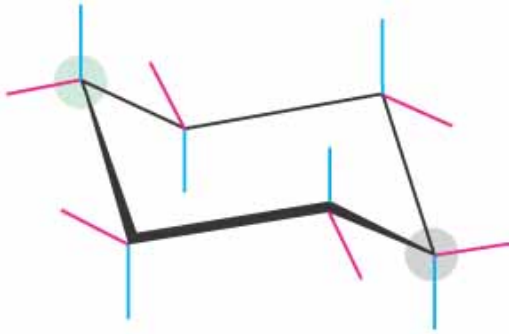


Ring-flip



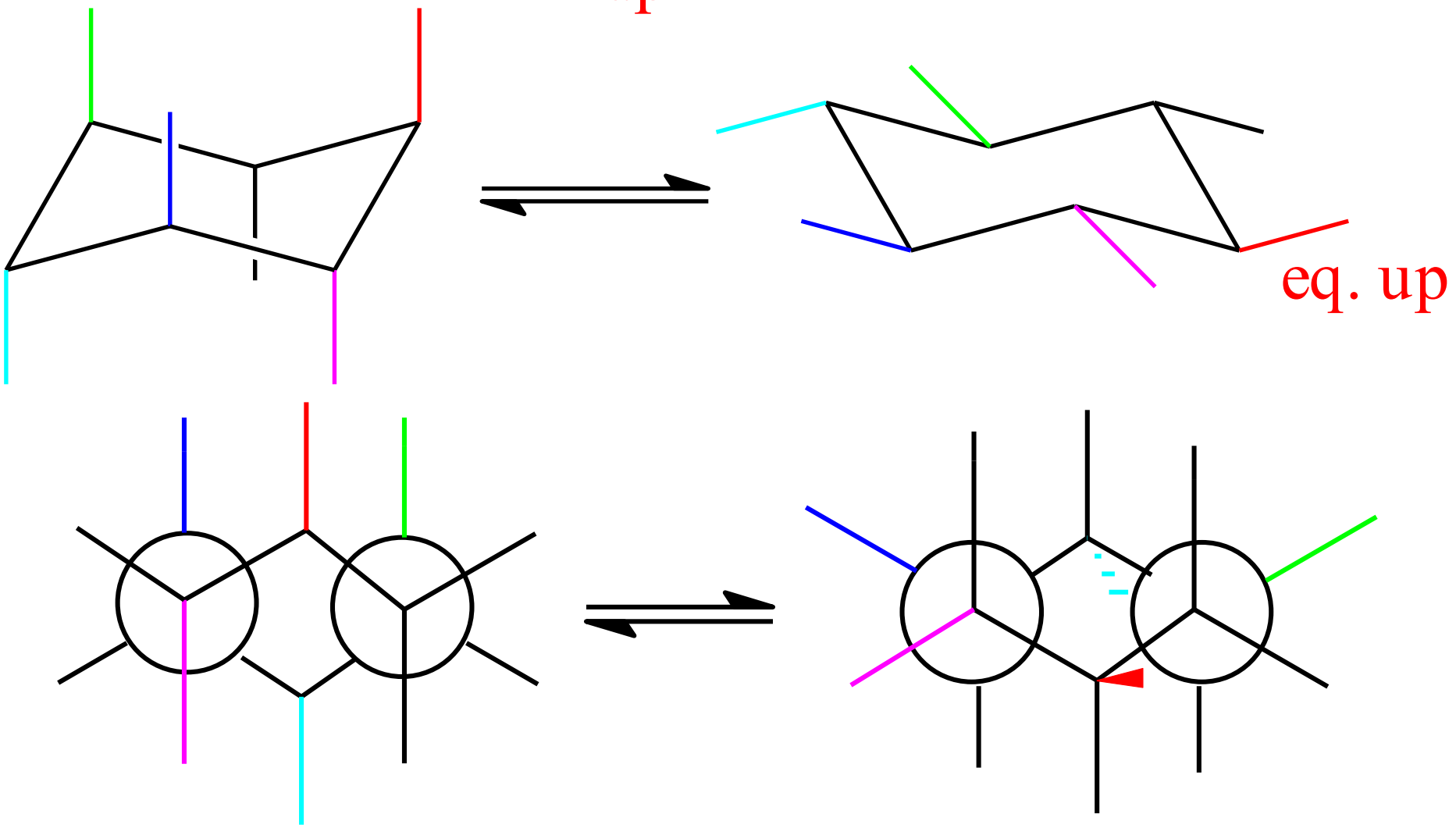


Ring-flip

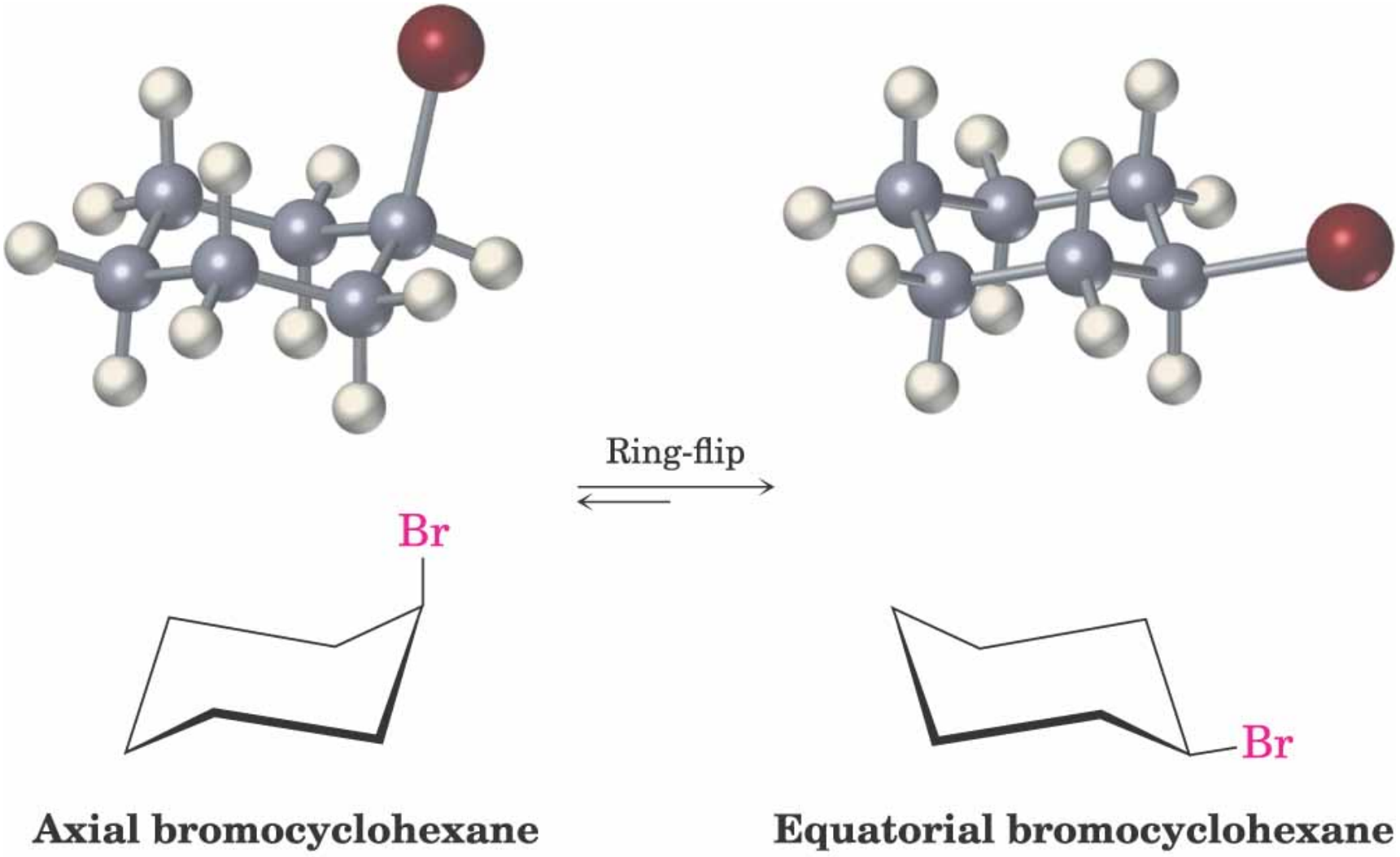


Flipping Chair Conformations

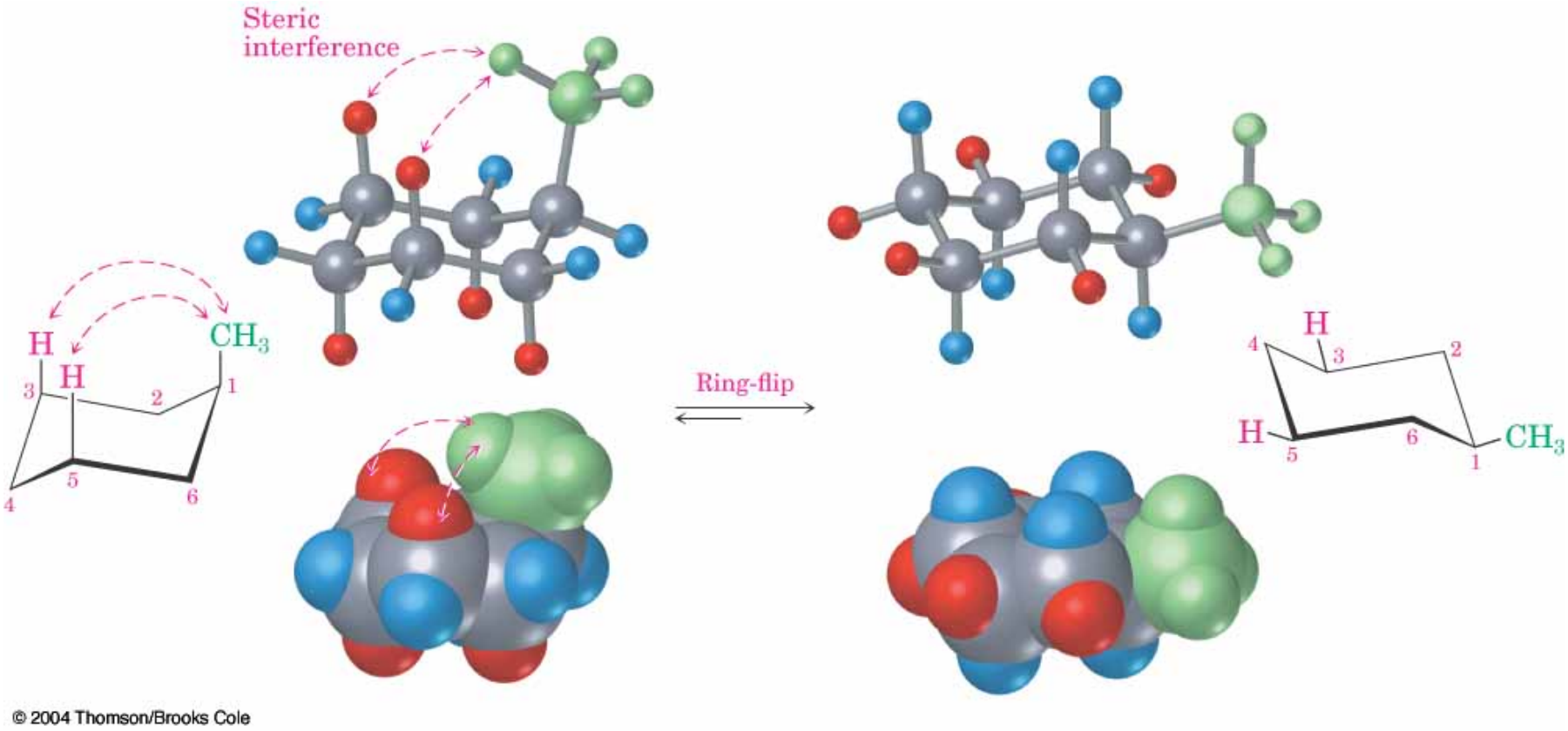
- All axial bonds become equatorial
- All equatorial bonds become axial
- All “up” bonds stay up
- All “down” bonds stay down


axial up
eq. up

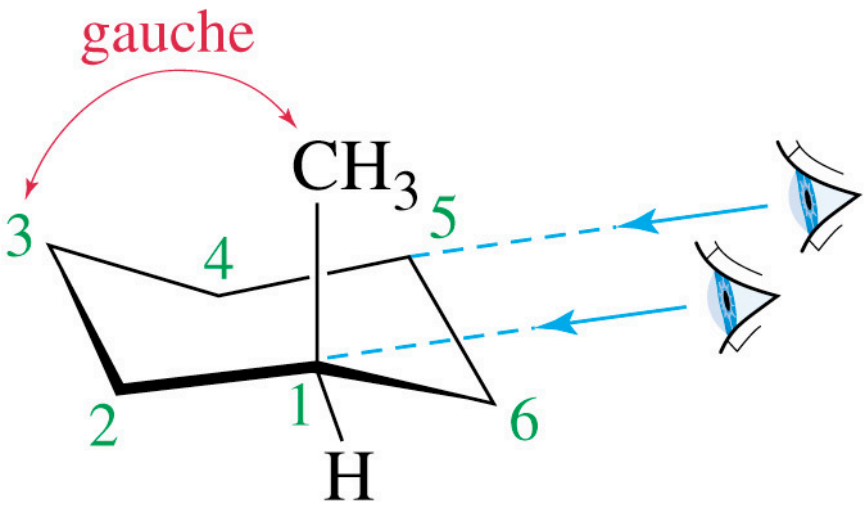
Axial-up becomes Equatorial-up

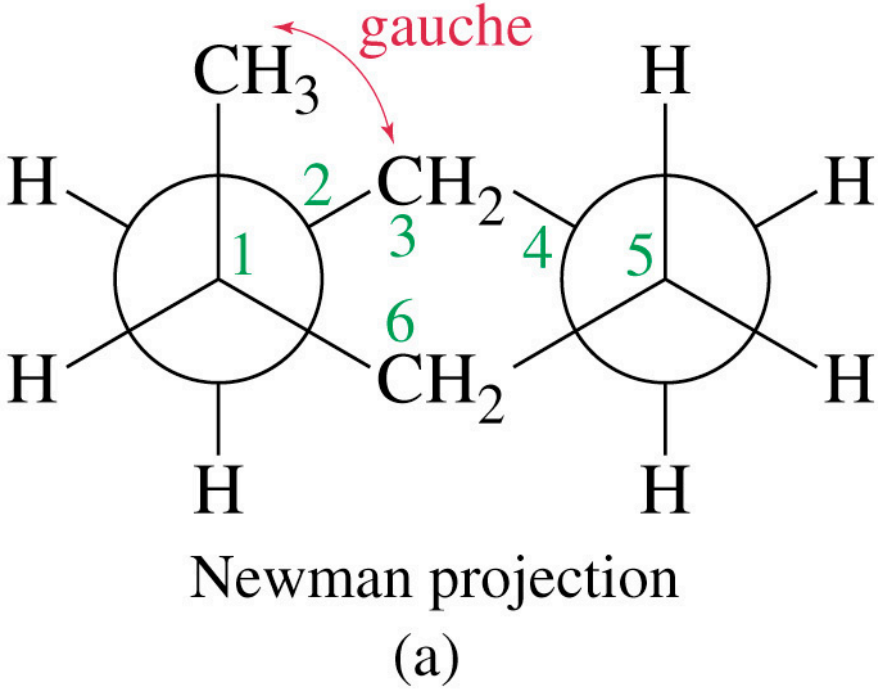


Equatorial Conformation is Preferred



Axial Methyl group is Gauche to C_3 in the ring



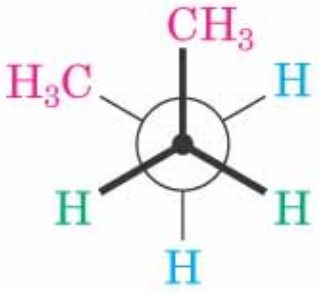


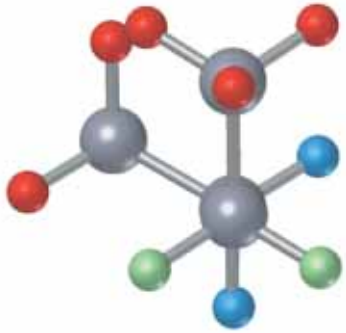
Newman projection

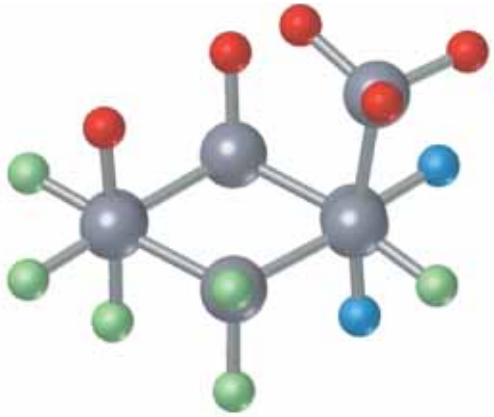
(a)

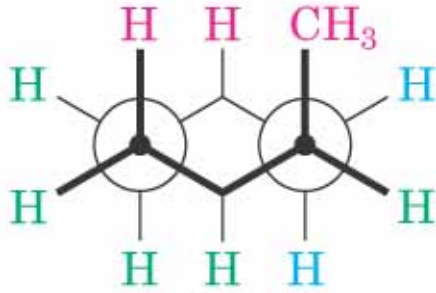
Gauche Interactions are Flagged by Parallel H's

1,3-Diaxial Interactions





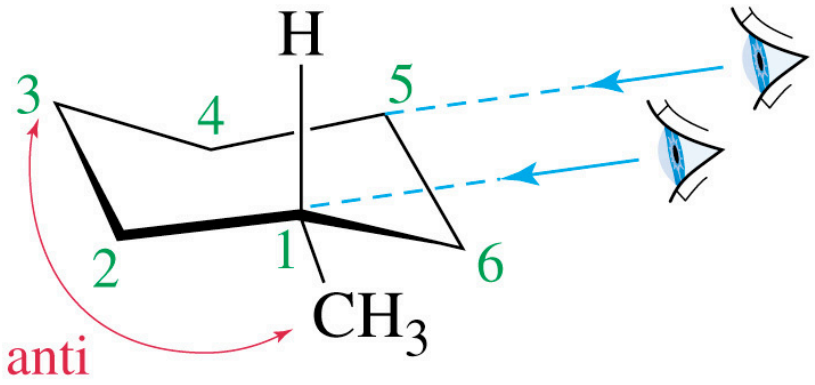


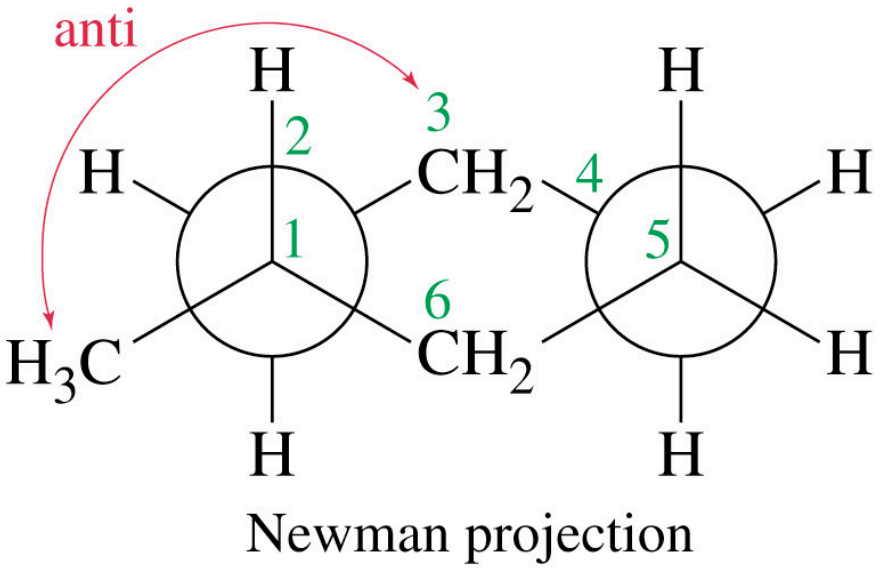


Gauche butane (3.8 kJ/mol strain)

Axial methylcyclohexane (7.6 kJ/mol strain)

Equatorial Methyl Group is Anti to C_3 in the ring





Newman projection

Tabella 2.10 Costanti di equilibrio per alcuni cicloesani monosostituiti a 25°C

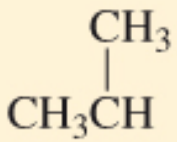
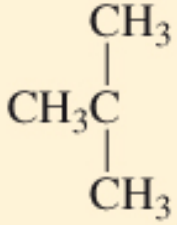
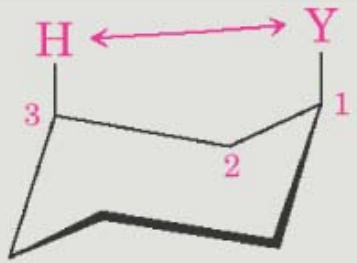
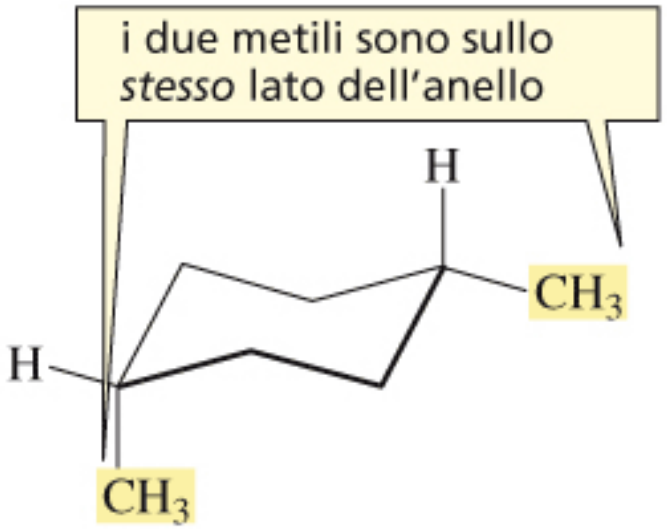
Sostituente	Assiale $\overset{K_{eq}}{\rightleftharpoons}$ Equatoriale	Sostituente	Assiale $\overset{K_{eq}}{\rightleftharpoons}$ Equatoriale
H	1	CN	1.4
CH_3	18	F	1.5
CH_3CH_2	21	Cl	2.4
	35	Br	2.2
	4800	I	2.2
		HO	5.4

TABLE 4.2 Steric Strain in Monosubstituted Cyclohexanes

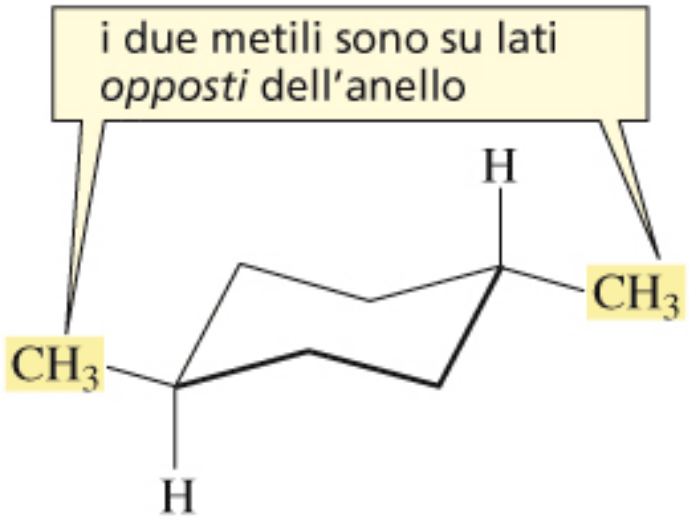


Y	Strain of one H–Y 1,3-diaxial interaction (kJ/mol)	(kcal/mol)
—F	0.5	0.12
—Cl	1.0	0.25
—Br	1.0	0.25
—OH	2.1	0.5
—CH_3	3.8	0.9
—CH_2CH_3	4.0	0.95
—$CH(CH_3)_2$	4.6	1.1
—$C(CH_3)_3$	11.4	2.7
—C_6H_5	6.3	1.5
—CO_2H	2.9	0.7
—CN	0.4	0.1

cicloesani disostituiti



cis-1,4-dimetilcicloesano



trans-1,4-dimetilcicloesano

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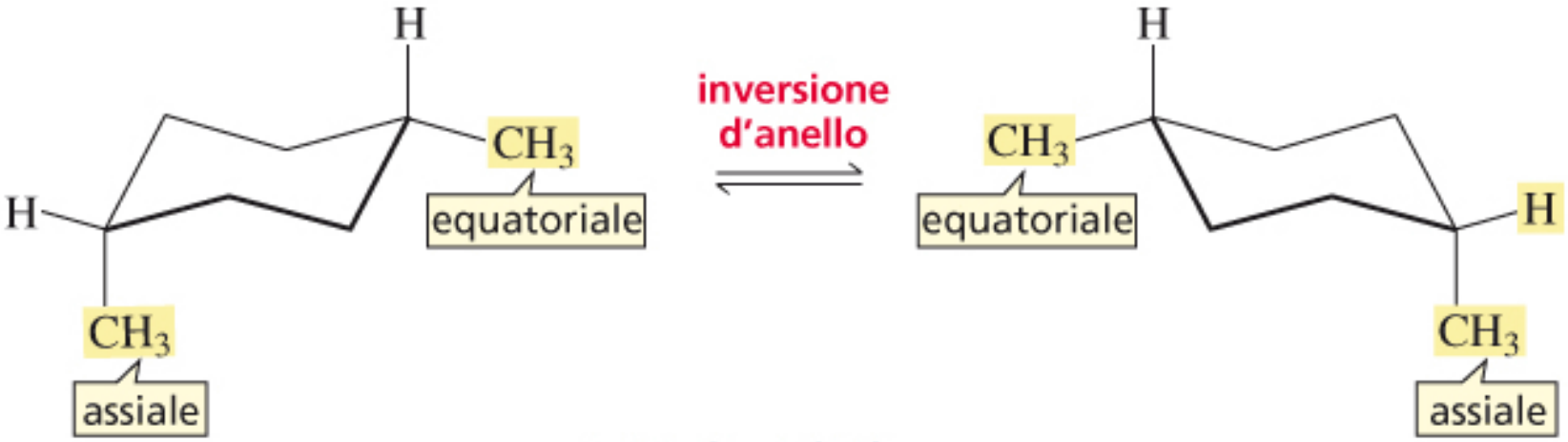

cis-1,4-dimetilcicloesano

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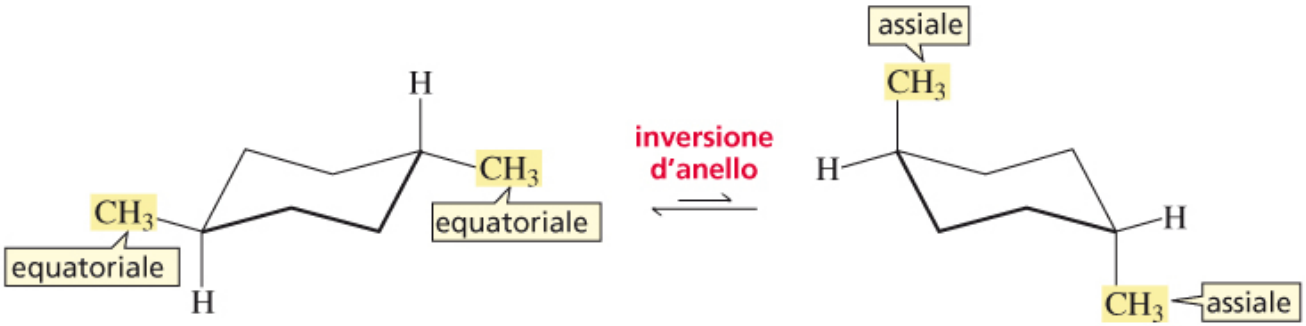
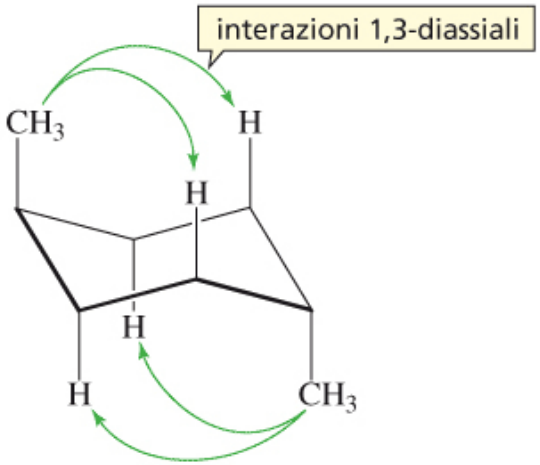


più stabile

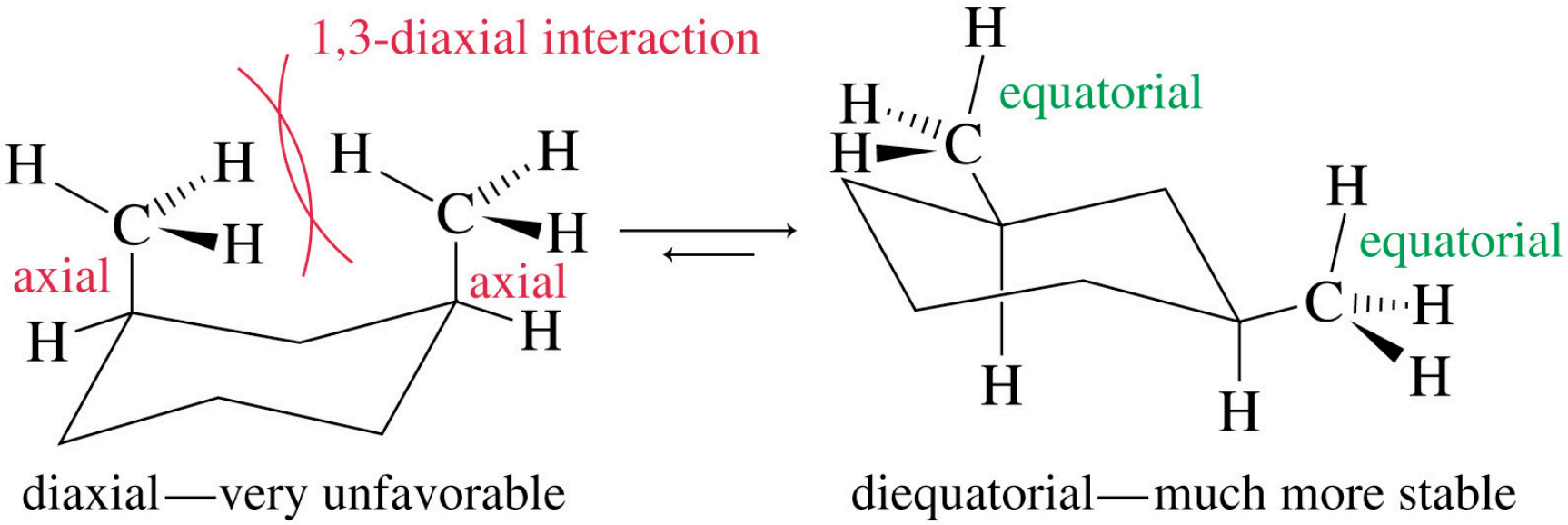
meno stabile

trans-1,4-dimetilcicloesano



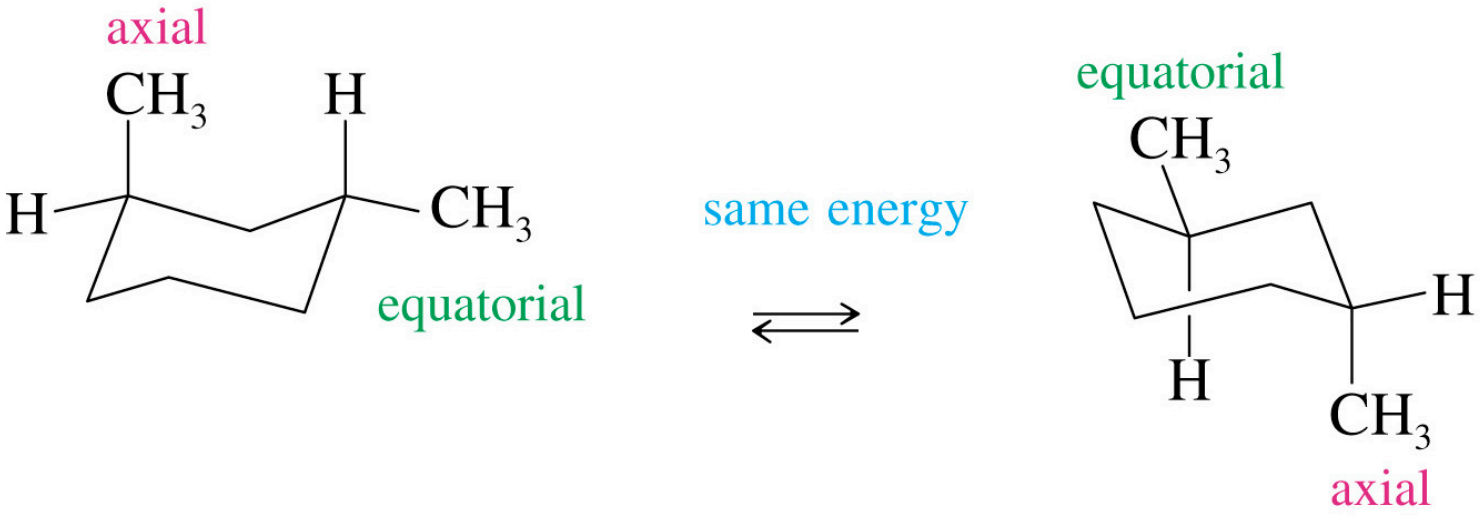
questo conformero a sedia ha quattro interazioni 1,3-diassiali

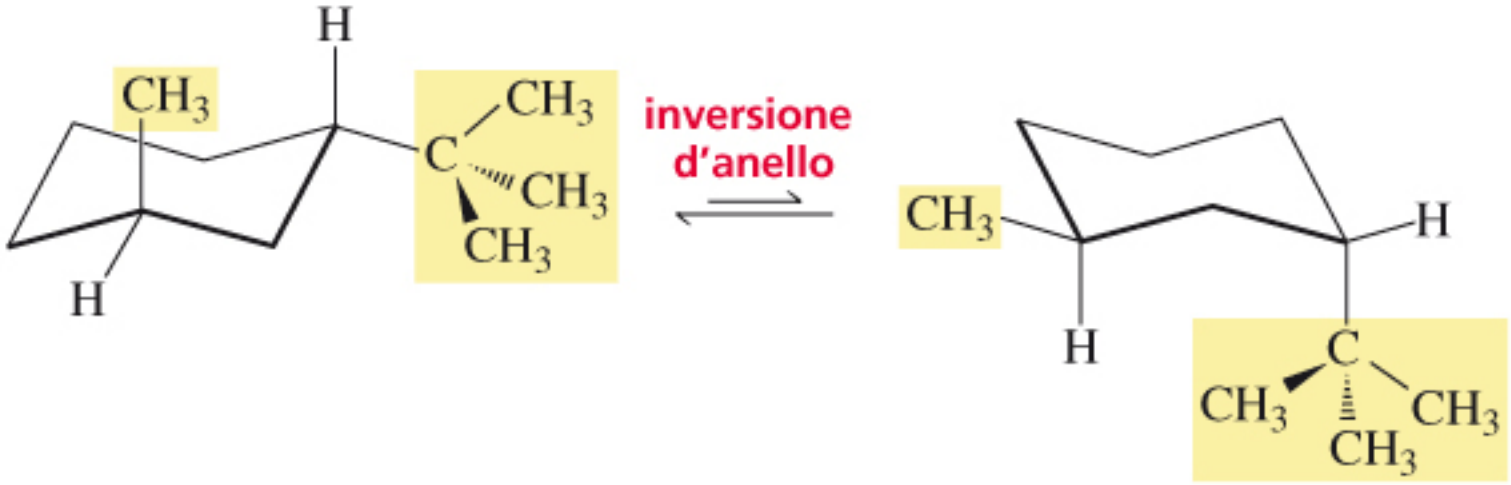
cis 1,3-Dimethylcyclohexane



trans 1,3-dimethylcyclohexane

Chair conformations of trans-*1,3-dimethylcyclohexane*





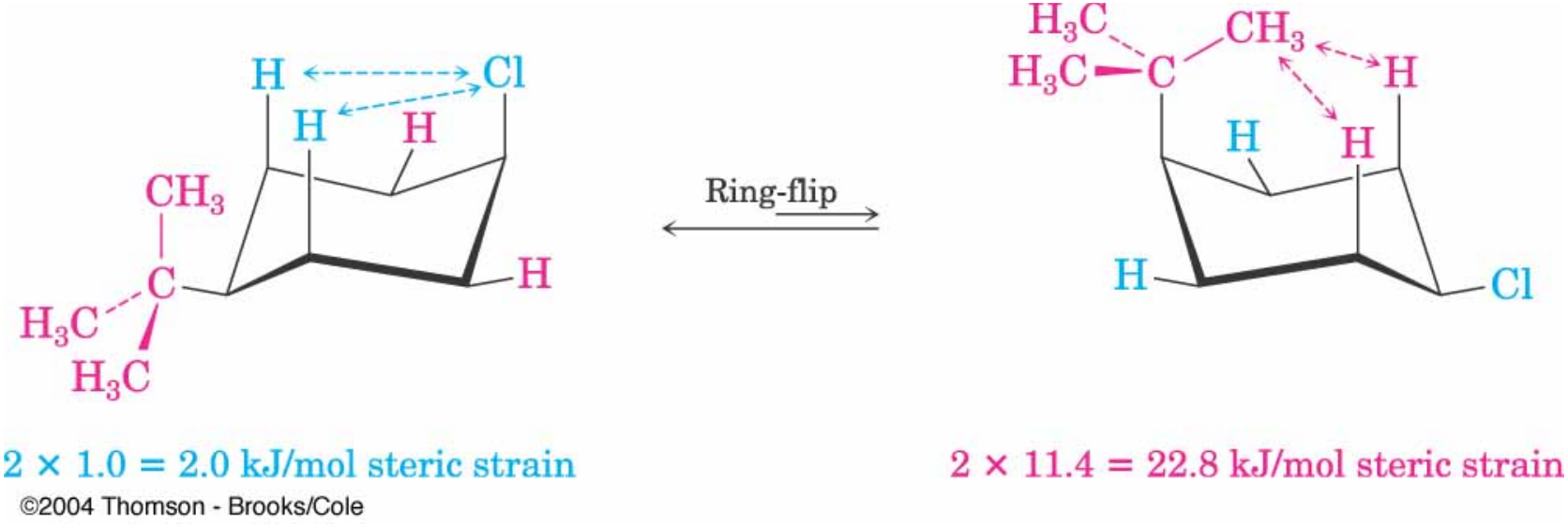
più stabile

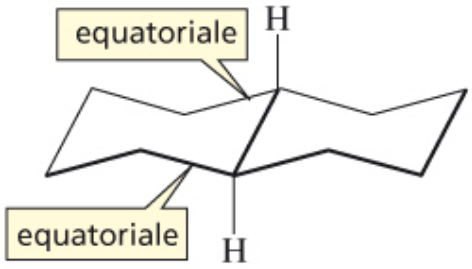
meno stabile

trans-1-*terz*-butil-3-metilcicloesano

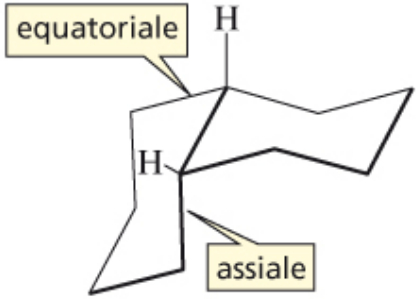
Bruice
Chimica Organica, II Ed.
EdiSES

cis 1-Chloro-4-*t*-butylcyclohexane

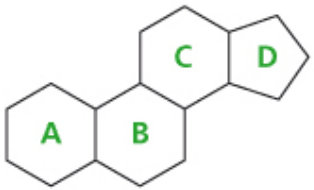




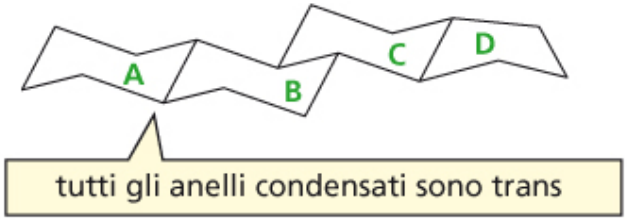
giunzione *trans*
più stabile

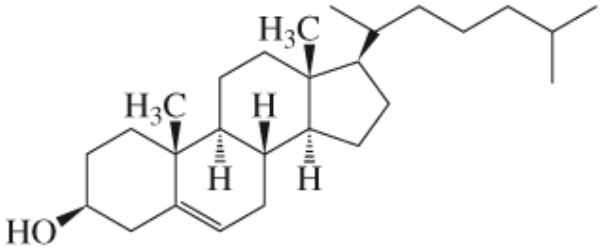


giunzione *cis*
meno stabile



struttura di uno steroide





colesterolo