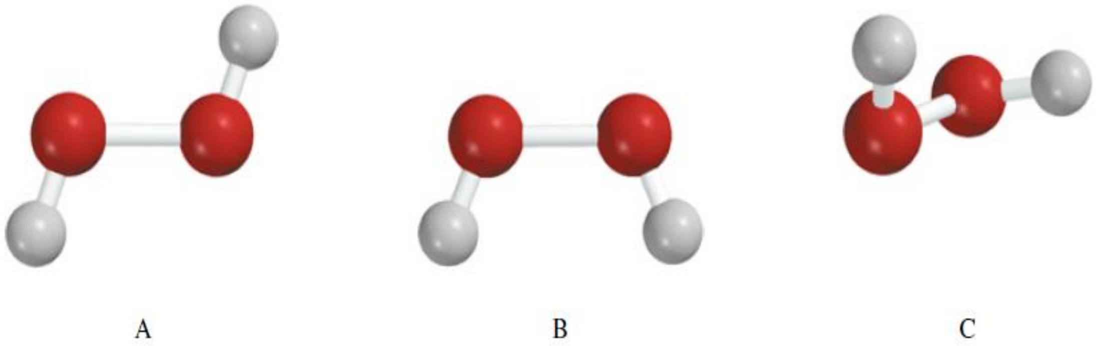
Conformation of alkanes

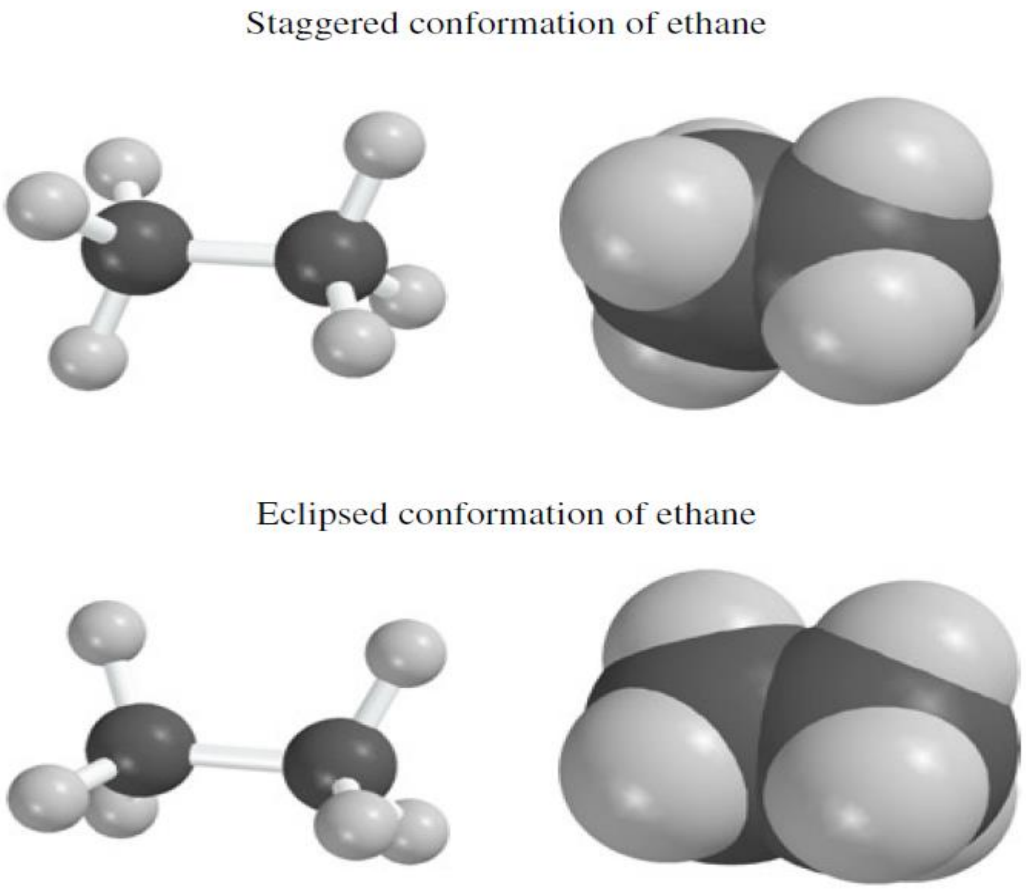
Conformers or Rotomers



Eclipsed conformation

Staggered conformation

Skew conformation

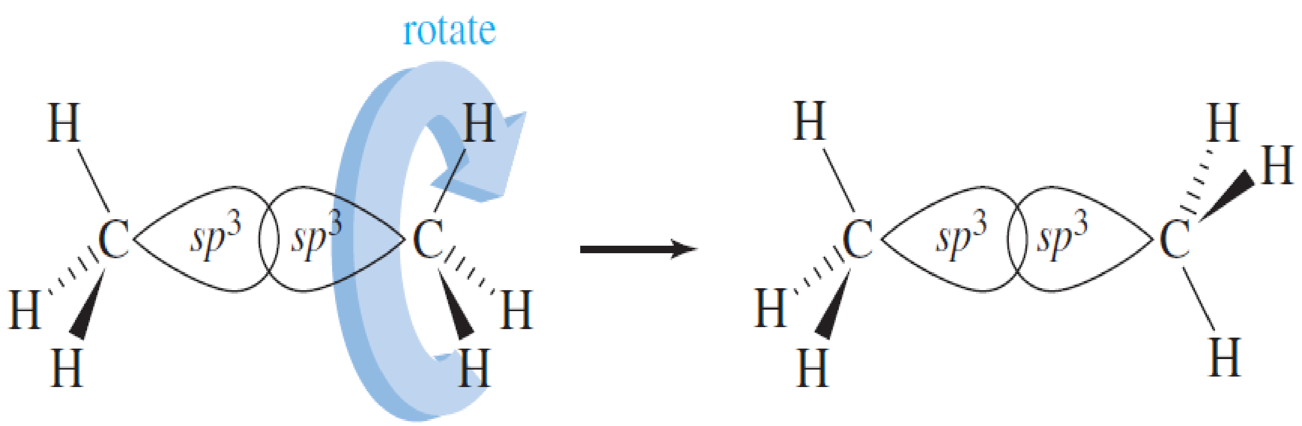


Staggered conformation of ethane

Eclipsed conformation of ethane

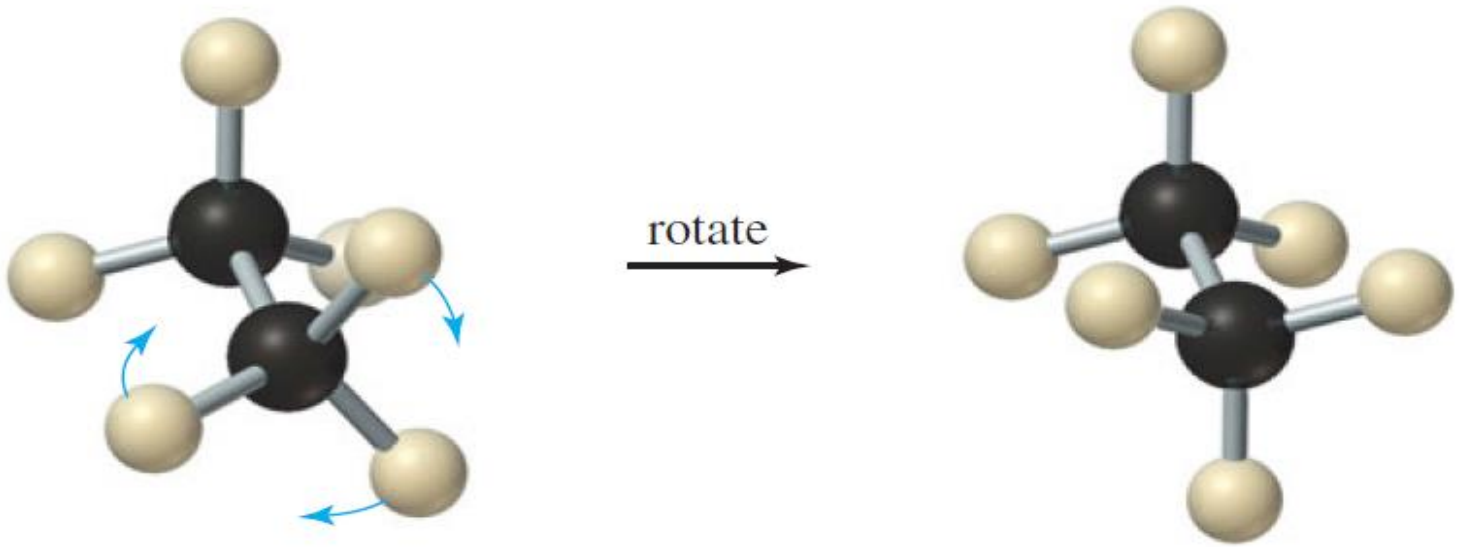
Ball-and-spoke model

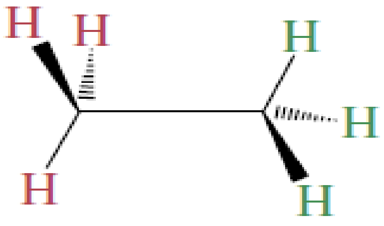
Space-filling model



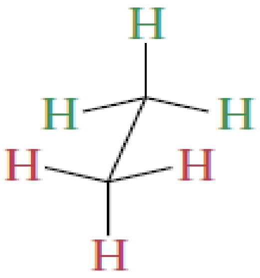
linear overlap of sigma bond

overlap maintained

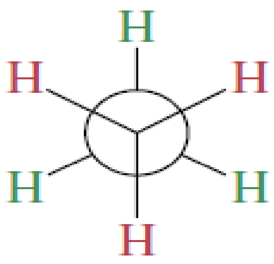




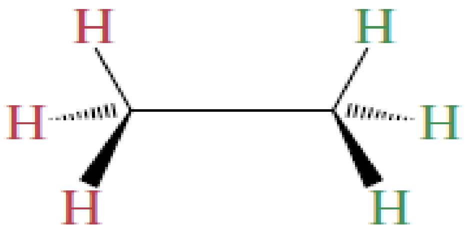
(*a*) Wedge-and-dash



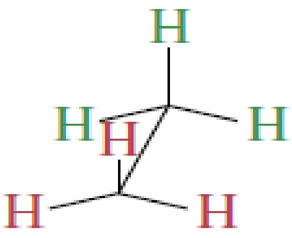
(*b*) Sawhorse



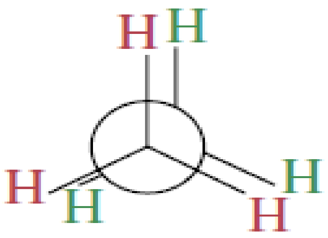
(*c*) Newman projection



(*a*) Wedge-and-dash



(*b*) Sawhorse

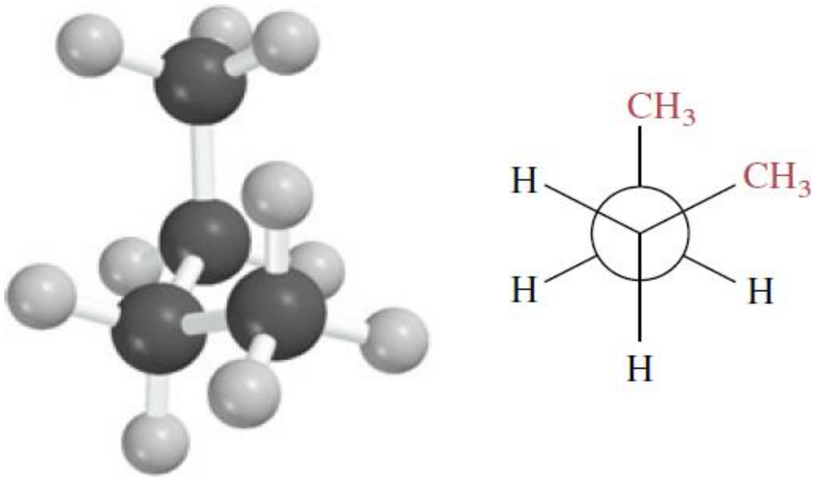


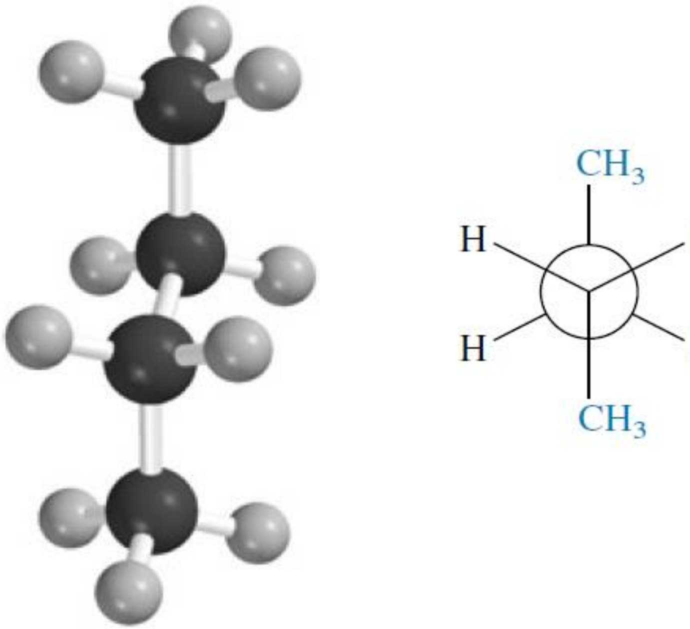
(*c*) Newman projection

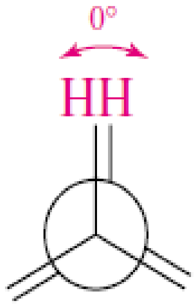
Torsional strain

Steric strain

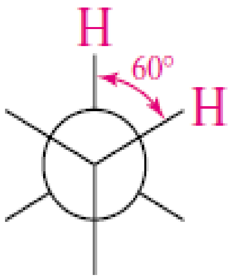
Van der Waals strain (Steric hinderence)



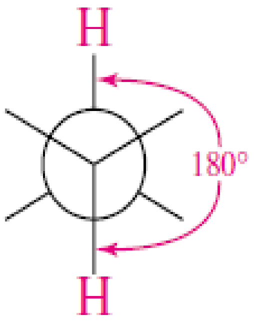




Torsion angle = 0°
Eclipsed



Torsion angle = 60°
Gauche

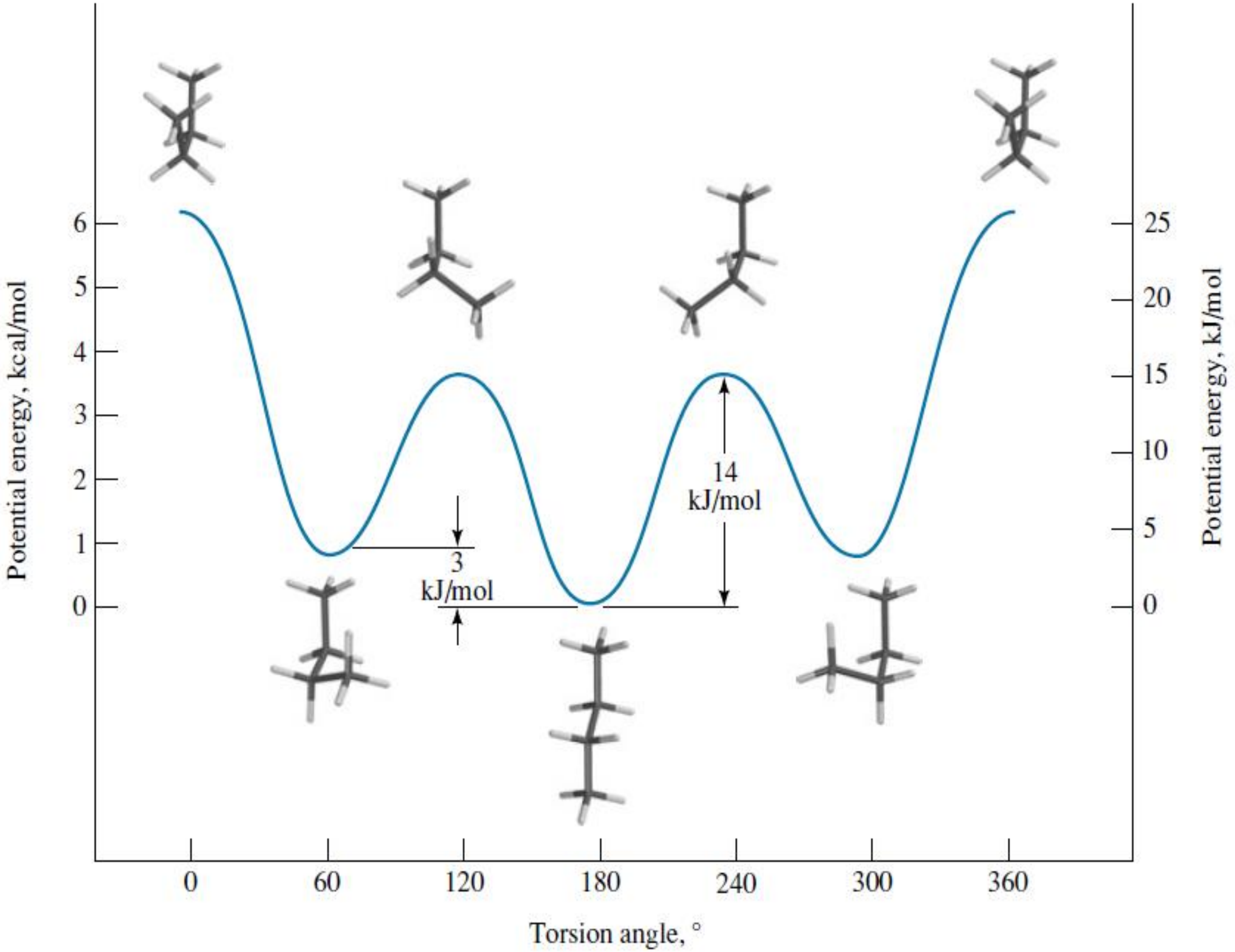


Torsion angle = 180°
Anti

Torsional strain

Steric strain

Angle strain



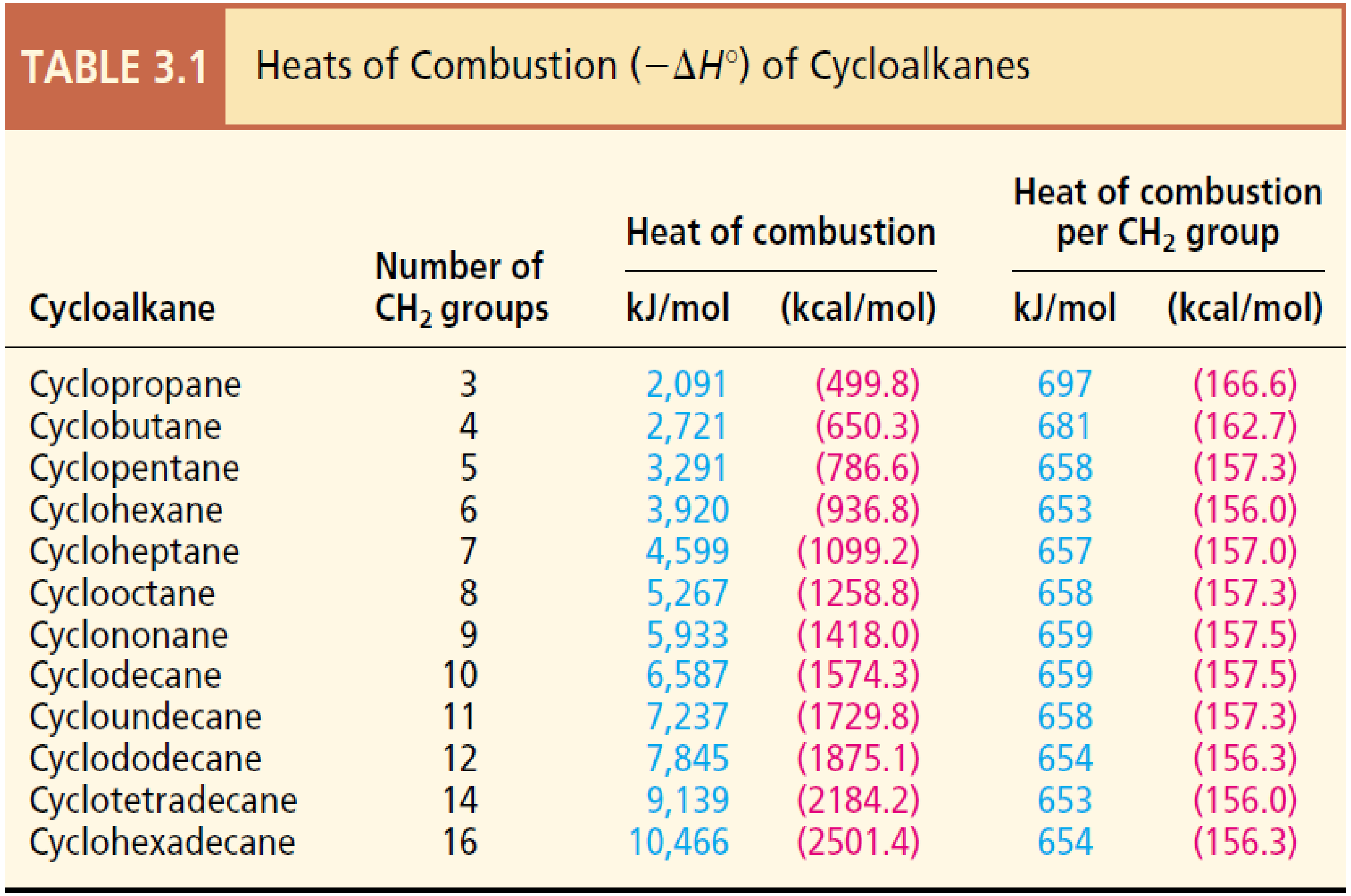
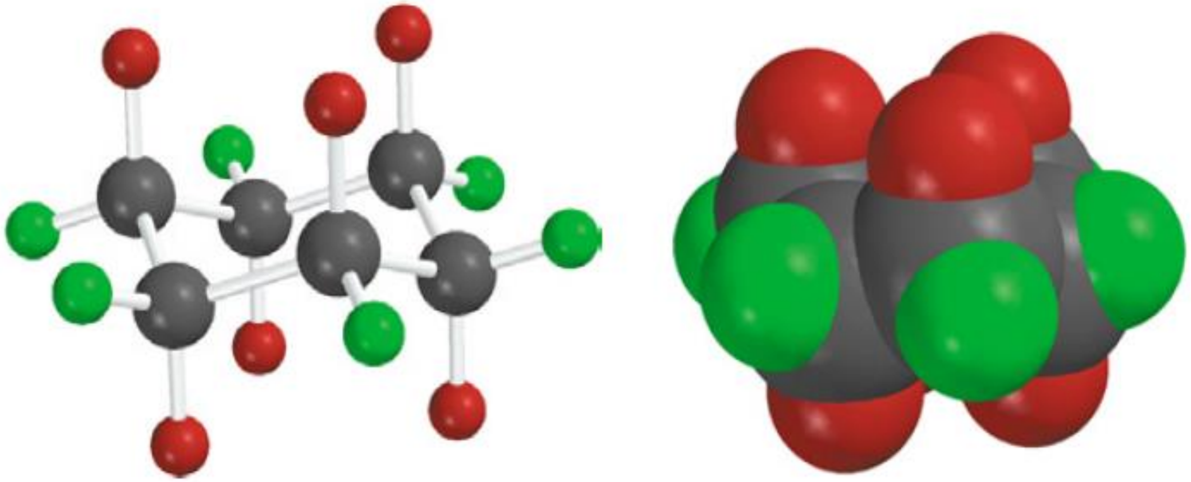


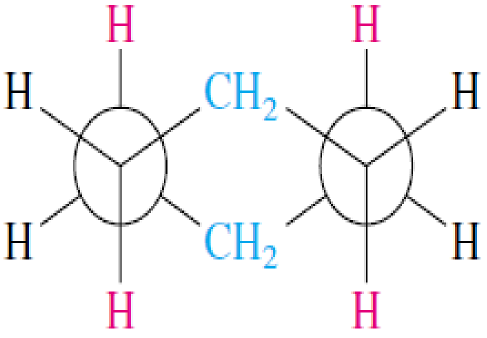
TABLE 3.1 Heats of Combustion ($-\Delta H^\circ$) of Cycloalkanes

Cycloalkane	Number of CH_2 groups	Heat of combustion		Heat of combustion per CH_2 group	
		kJ/mol	(kcal/mol)	kJ/mol	(kcal/mol)
Cyclopropane	3	2,091	(499.8)	697	(166.6)
Cyclobutane	4	2,721	(650.3)	681	(162.7)
Cyclopentane	5	3,291	(786.6)	658	(157.3)
Cyclohexane	6	3,920	(936.8)	653	(156.0)
Cycloheptane	7	4,599	(1099.2)	657	(157.0)
Cyclooctane	8	5,267	(1258.8)	658	(157.3)
Cyclononane	9	5,933	(1418.0)	659	(157.5)
Cyclodecane	10	6,587	(1574.3)	659	(157.5)
Cycloundecane	11	7,237	(1729.8)	658	(157.3)
Cyclododecane	12	7,845	(1875.1)	654	(156.3)
Cyclotetradecane	14	9,139	(2184.2)	653	(156.0)
Cyclohexadecane	16	10,466	(2501.4)	654	(156.3)

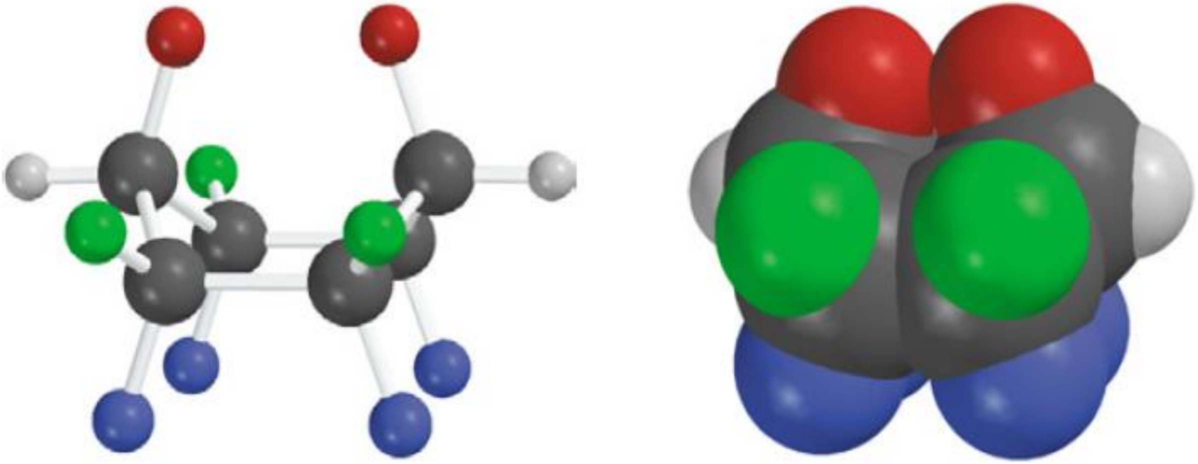


(a) (b)

Chair conformation

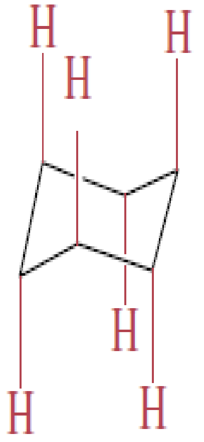


Staggered arrangement of bonds in chair conformation of cyclohexane

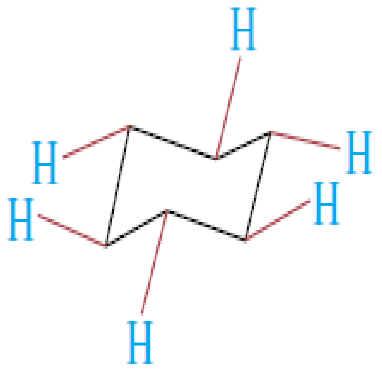


(a) (b)

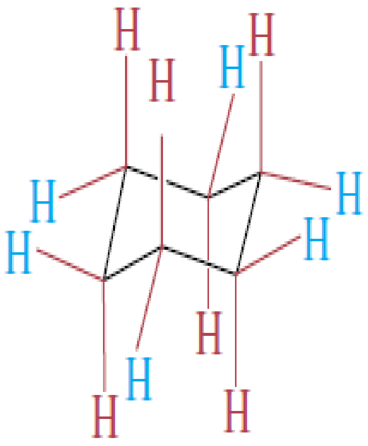
Boat conformation



Axial C—H bonds

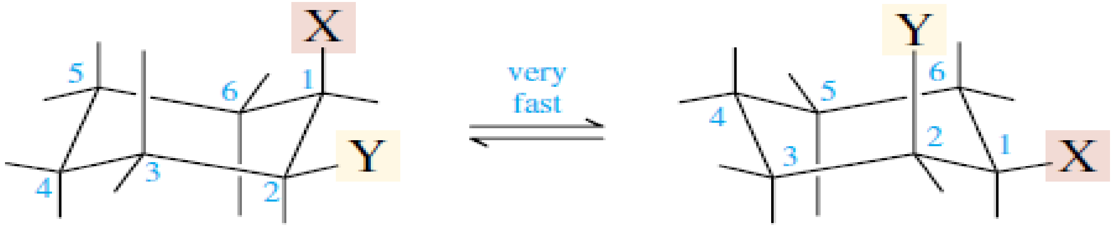


Equatorial C—H bonds



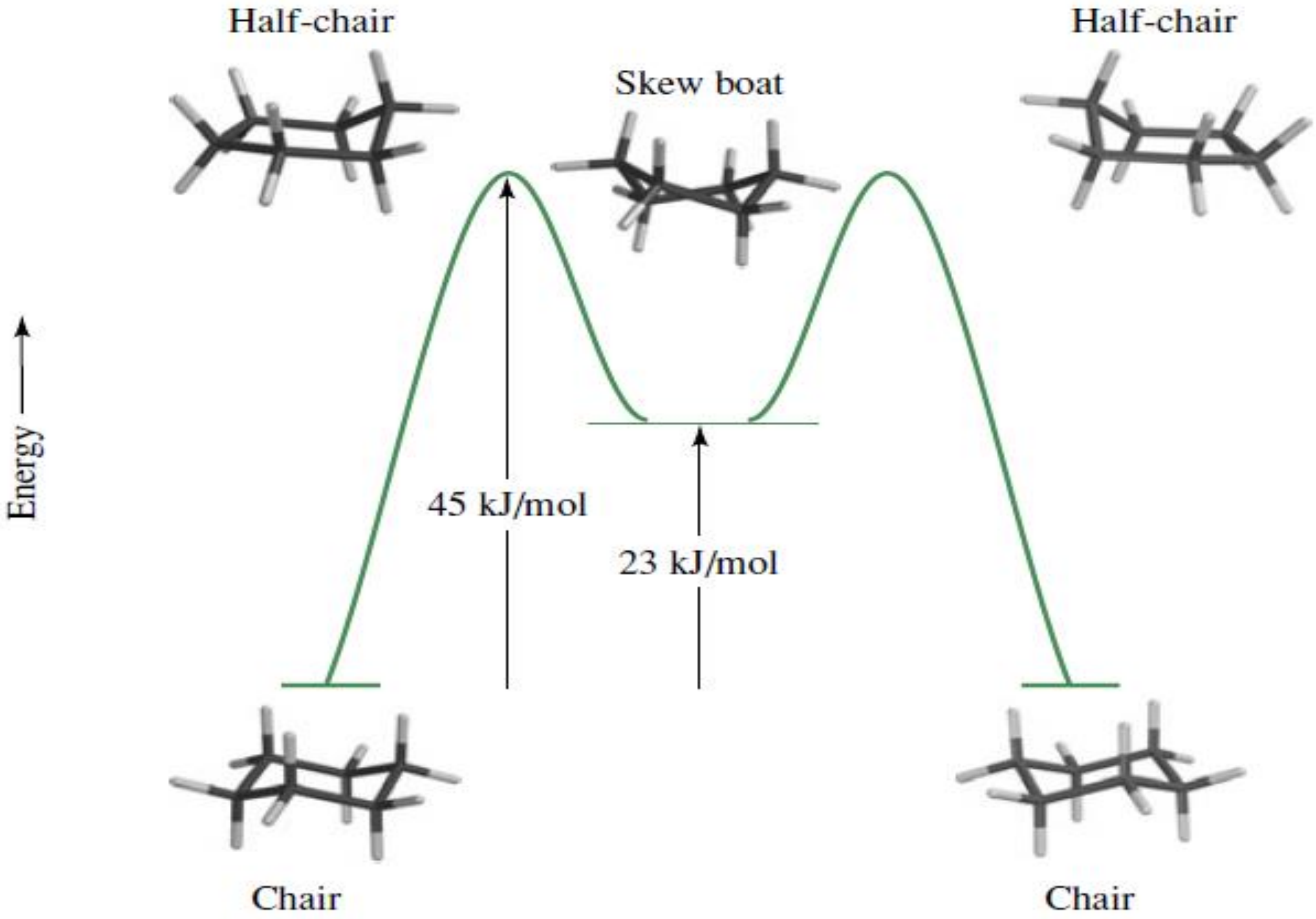
Axial and equatorial bonds together

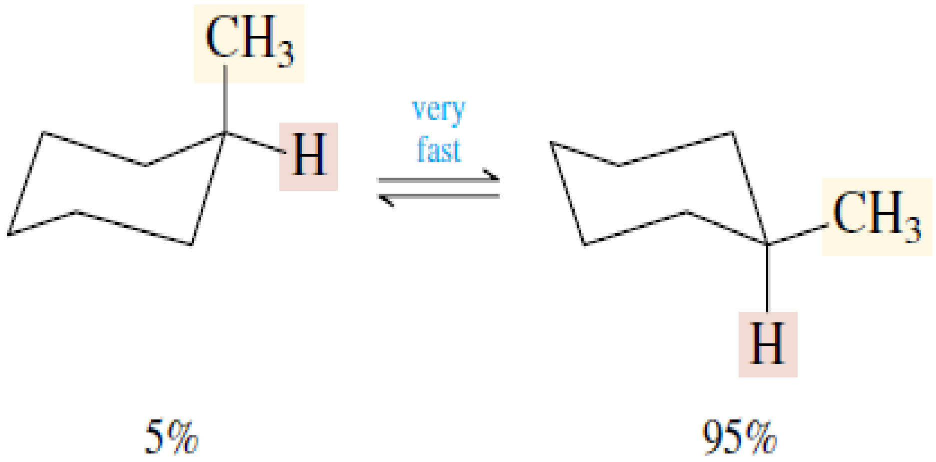
Inversion of conformation:

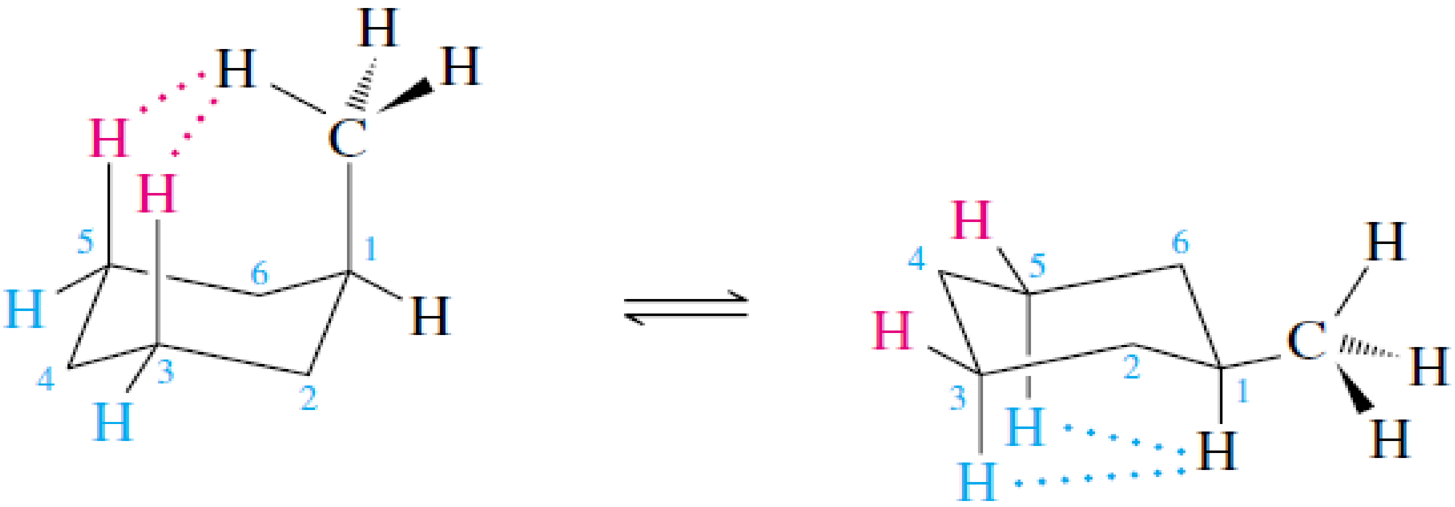


X axial; Y equatorial

X equatorial; Y axial

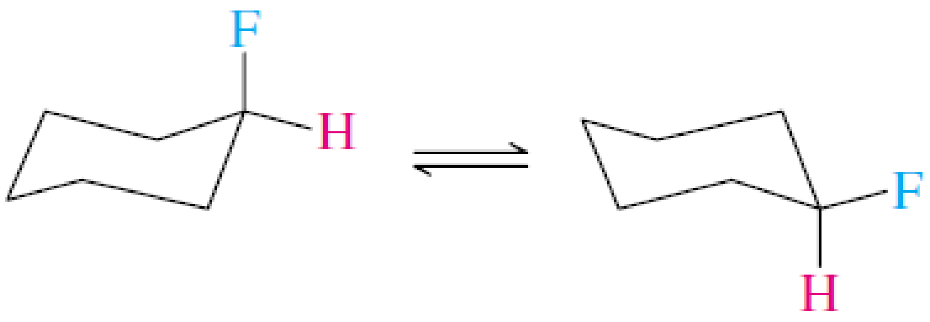

Half-chair
Skew boat
Half-chair
Energy
45 kJ/mol
23 kJ/mol
Chair
Chair





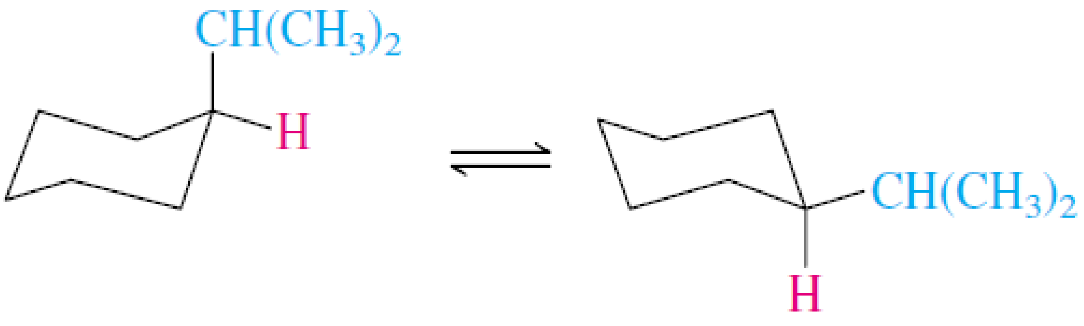
Van der Waals strain between hydrogen of axial CH_3 and axial hydrogens at C-3 and C-5

Smaller van der Waals strain between hydrogen at C-1 and axial hydrogens at C-3 and C-5



40%

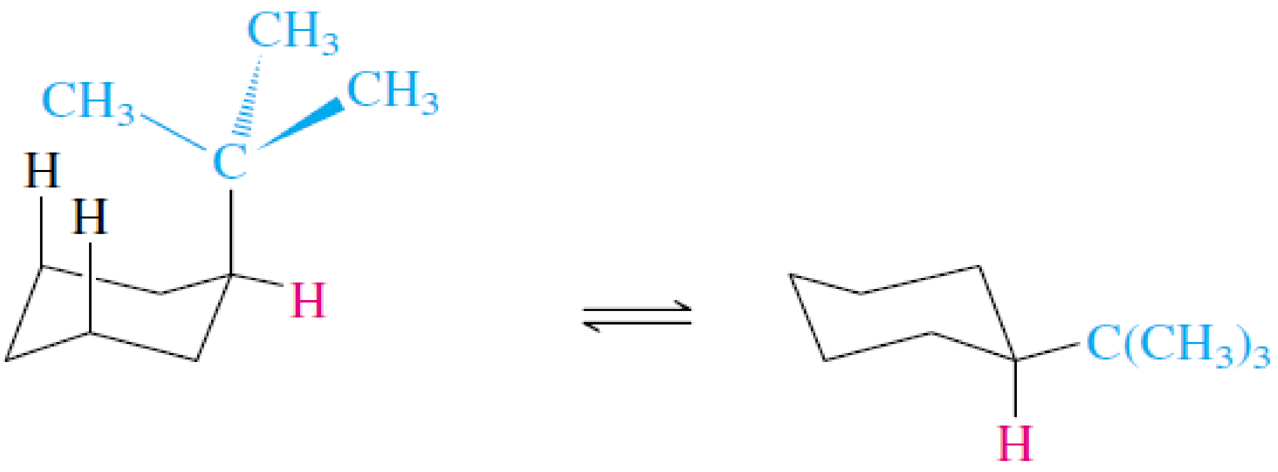
60%



3%

97%

The halogens F, Cl, Br, and I do not differ much in their preference for the equatorial position. As the atomic radius increases in the order F < Cl < Br < I, so does the carbon–halogen bond distance, and the two effects tend to cancel.



Less than 0.01%
(Serious 1,3-diaxial repulsions involving *tert*-butyl group)

Greater than 99.99%
(Decreased van der Waals strain)

FIGURE 3.16 "Bent bonds" in cyclopropane. The orbitals involved in carbon–carbon bond formation overlap in a region that is displaced from the internuclear axis. Orbital overlap is less effective than in a normal carbon–carbon σ bond, and the carbon–carbon bond is weaker.

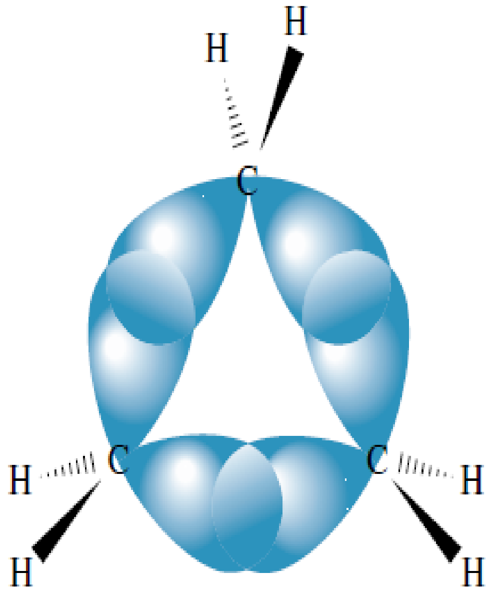
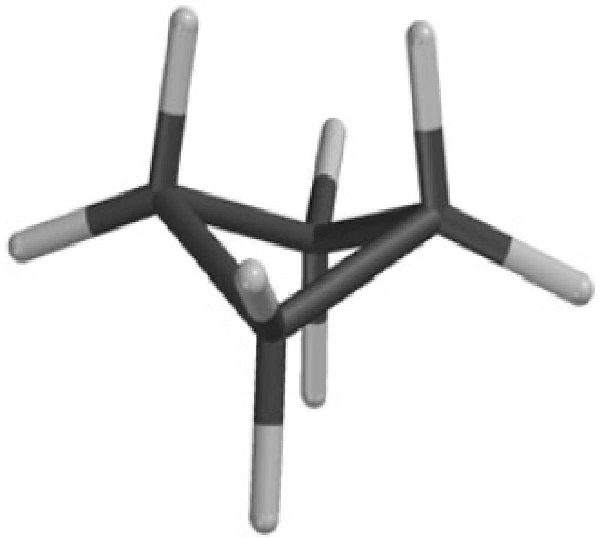
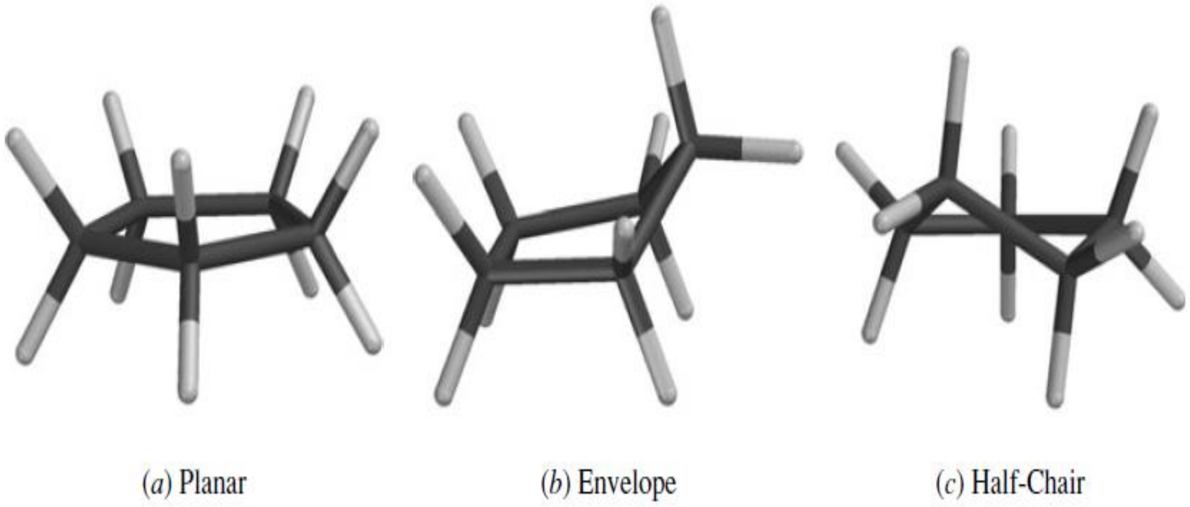


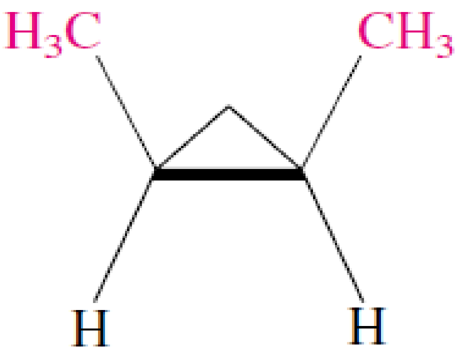
FIGURE 3.18 Nonplanar ("puckered") conformation of cyclobutane. The nonplanar conformation is more stable because it avoids the eclipsing of bonds on adjacent carbons that characterizes the planar conformation.



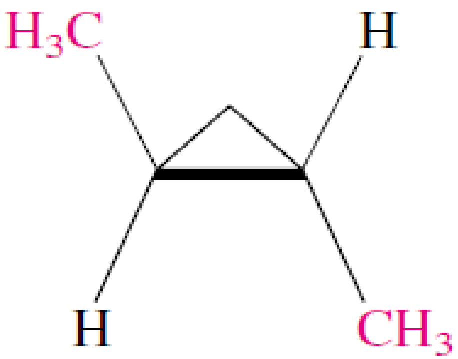


(*a*) Planar (*b*) Envelope (*c*) Half-Chair

FIGURE 3.19 The (*a*) planar, (*b*) envelope, and (*c*) half-chair conformations of cyclopentane.



cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane

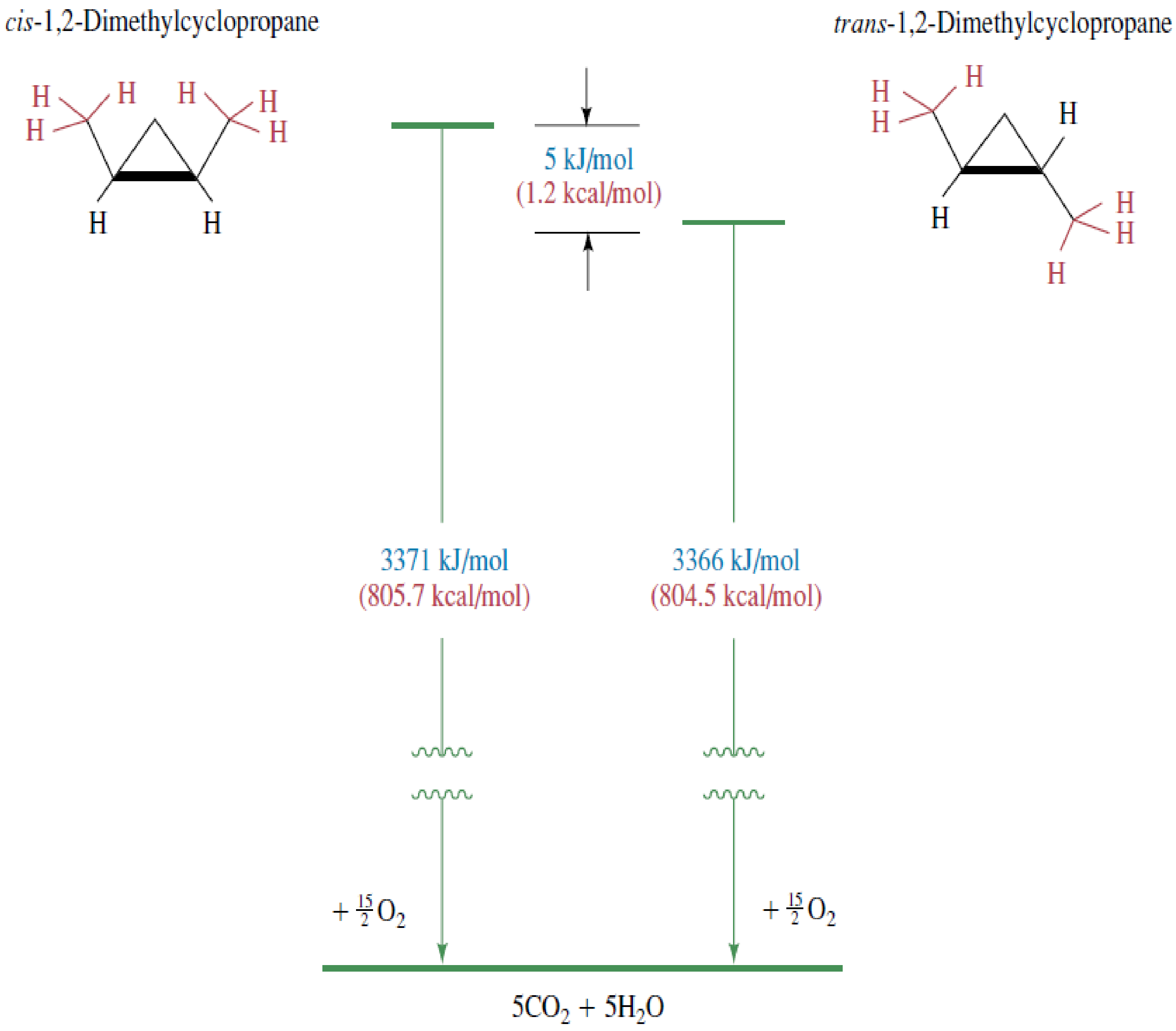
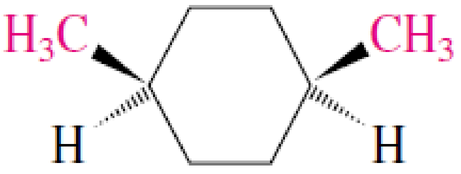
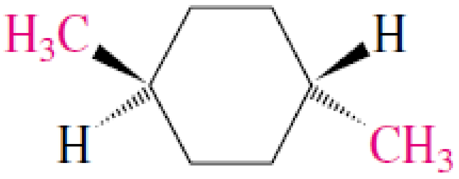


FIGURE 3.20 The enthalpy difference between *cis*- and *trans*-1,2-dimethylcyclopropane can be determined from their heats of combustion. Van der Waals strain between methyl groups on the same side of the ring makes the cis isomer less stable than the trans.



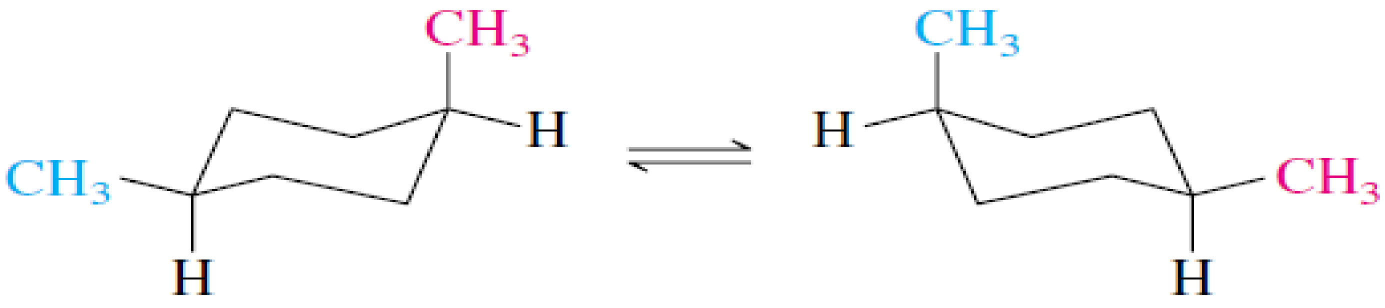
cis-1,4-Dimethylcyclohexane



trans-1,4-Dimethylcyclohexane

TABLE 3.2 Heats of Combustion of Isomeric Dimethylcyclohexanes

		Heat of combustion		Difference in heat of combustion		
Compound	**Orientation of methyl groups in most stable conformation**	**kJ/mol**	**(kcal/mol)**	**kJ/mol**	**(kcal/mol)**	**More stable stereoisomer**
cis-1,2-Dimethylcyclohexane	Axial–equatorial	5223	(1248.3)	6	(1.5)	trans
trans-1,2-Dimethylcyclohexane	Diequatorial	5217	(1246.8)			
cis-1,3-Dimethylcyclohexane	Diequatorial	5212	(1245.7)	7	(1.7)	cis
trans-1,3-Dimethylcyclohexane	Axial–equatorial	5219	(1247.4)			
cis-1,4-Dimethylcyclohexane	Axial–equatorial	5219	(1247.4)	7	(1.7)	trans
trans-1,4-Dimethylcyclohexane	Diequatorial	5212	(1245.7)			

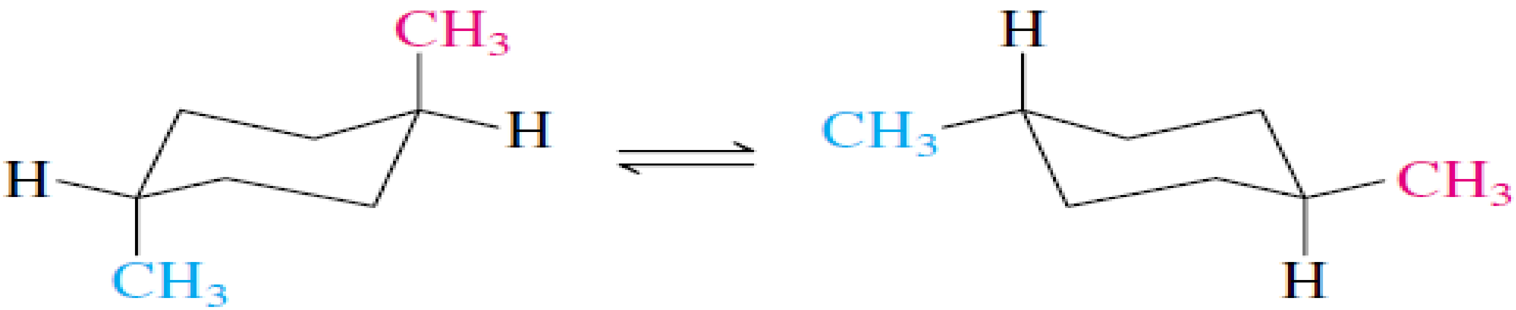


(One methyl group is axial, the other equatorial)

(One methyl group is axial, the other equatorial)

(Both methyl groups are up)

cis-1,4-Dimethylcyclohexane

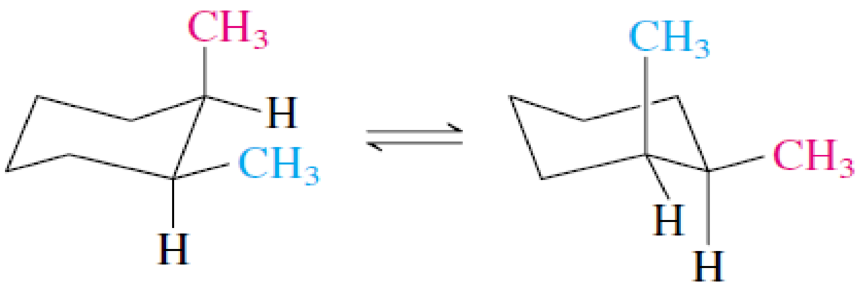


(Both methyl groups are axial: less stable chair conformation)

(Both methyl groups are equatorial: more stable chair conformation)

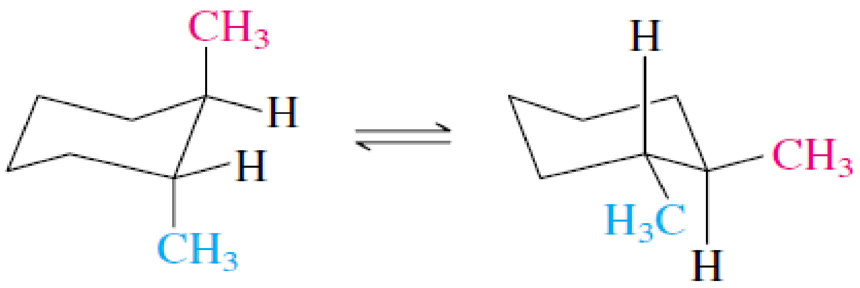
(One methyl group is up, the other down)

trans-1,4-Dimethylcyclohexane



cis-1,2-Dimethylcyclohexane

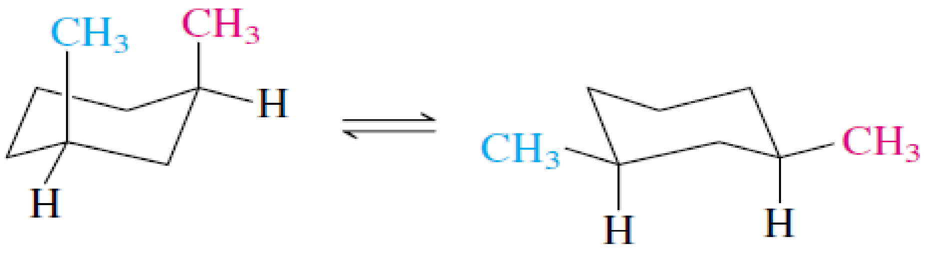
Both methyl groups are equatorial in the most stable conformation of *trans*-1,2-dimethylcyclohexane.



(Both methyl groups are axial: less stable chair conformation)

(Both methyl groups are equatorial: more stable chair conformation)

trans-1,2-Dimethylcyclohexane

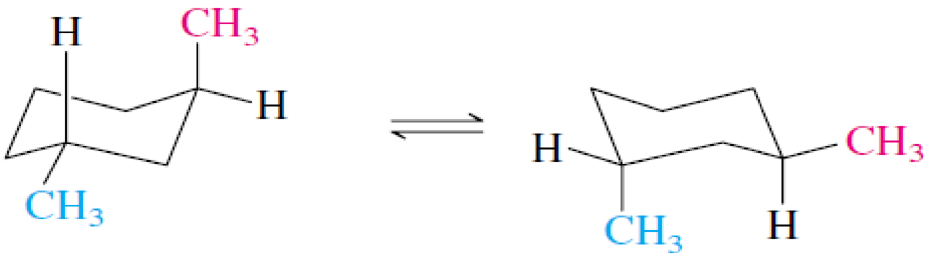


(Both methyl groups are axial: less stable chair conformation)

(Both methyl groups are equatorial: more stable chair conformation)

cis-1,3-Dimethylcyclohexane

The two chair conformations of *trans*-1,3-dimethylcyclohexane are equivalent to each other. Both contain one axial and one equatorial methyl group.

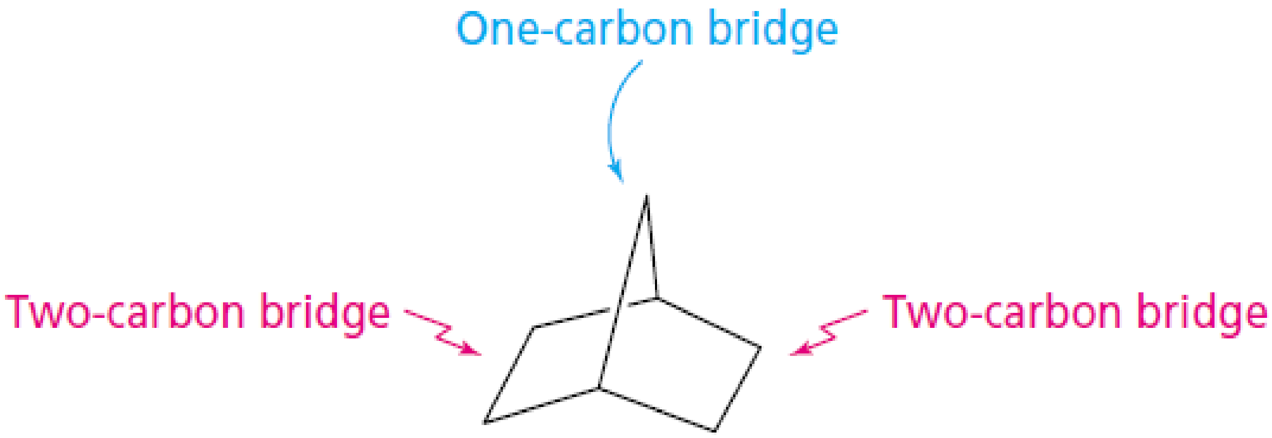


(One methyl group is axial, the other equatorial)

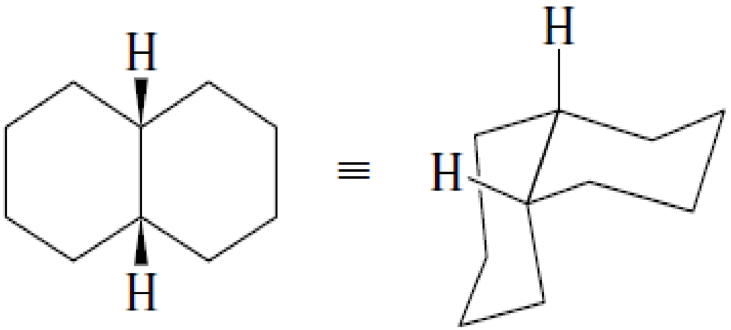
(One methyl group is axial, the other equatorial)

trans-1,3-Dimethylcyclohexane

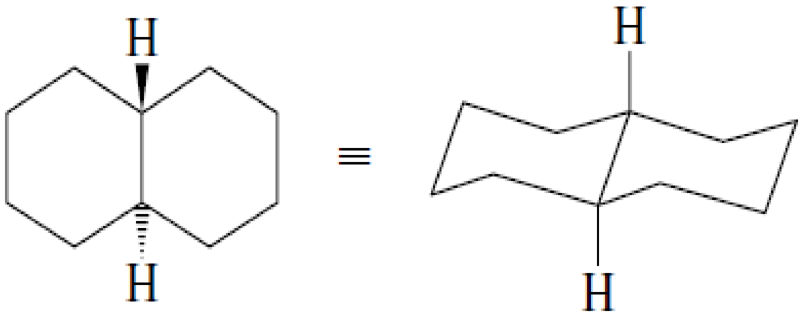
Polycyclic compounds



Bicyclo[2.2.1]heptane



cis-Bicyclo[4.4.0]decane
(*cis*-decalin)



trans-Bicyclo[4.4.0]decane
(*trans*-decalin)