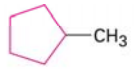
Nomenclature of Cycloalkanes

Draw skeletal structures for

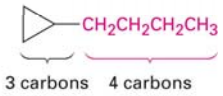
Chapter 4 in McMurry;
Chapter 4 in Vollhardt

cyclopropane cyclobutane cyclopentane cyclohexane

• When there are substituents that are simple, name the ring as the Parent part:



Methylcyclopentane

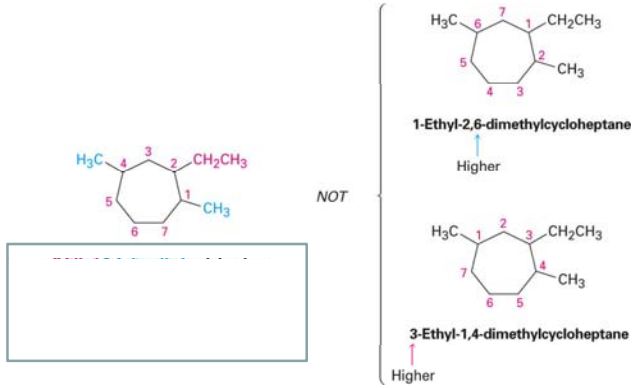


1-Cyclopropylbutane

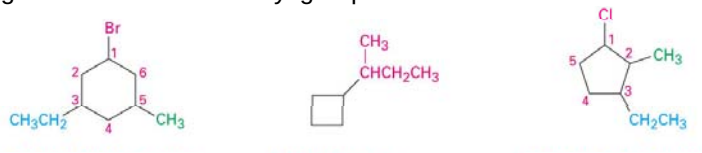
• When there are two or more substituents, choose one attachment as carbon 1 so that the second substituent has a lower number :

Name:

Nomenclature of Cycloalkanes



• Halogens are treated like alkyl groups

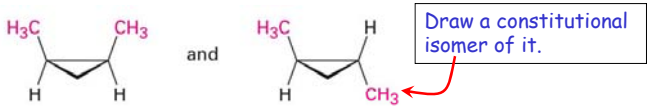


(1-Methylpropyl)cyclobutane
or *sec*-butylcyclobutane

Stereoisomerism

Constitutional isomers (different connections between atoms)

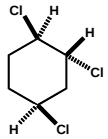
Stereoisomers (same connections but different three-dimensional geometry)



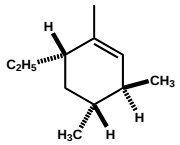
cis-1,2-dimethylcyclopropane *trans*-1,2-dimethylcyclopropane

Configurational isomers are stereoisomers that *cannot* be interconverted by rotation around a single bond (cf. conformational isomers).

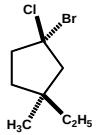
(Interconversion between configurational isomers *usually* involves breaking a bond. Thus, configurational isomers are usually not readily interconverted at rt and can, in principle at least, be separated.)



r-1,t-2,c-4-trichlorocyclohexane

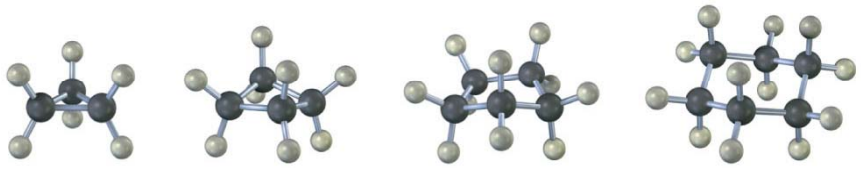


t-6-ethyl-1,r-3,t-4-trimethylcyclohexene



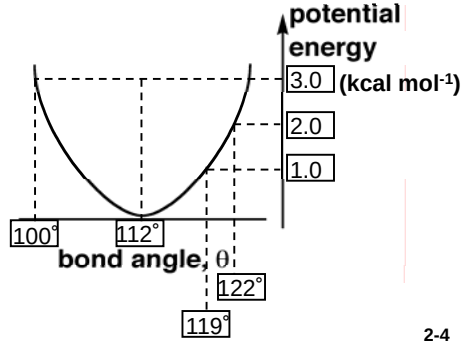
r-1-bromo-1-chloro-t-3-ethyl-3-methylcyclopentane

Structures of Cycloalkanes

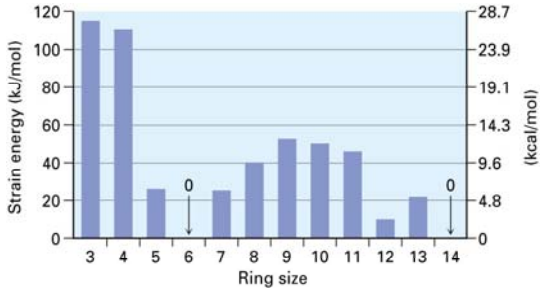


The ideal bond angle of an sp^3 carbon: 109.5°

The C-C-C bond angle of cyclopropane: 60°. The deviation of the bond angle from the ideal value raises a molecule's internal energy because of angle strain. Just as there was a potential energy surface associated with bond rotation, there is also one associated with bond angle deformation.



Heat of Combustion and Strain Energy of Cycloalkanes

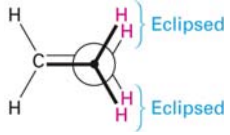


Ring strain energy calculated by cycloalkane heat of combustion per CH_2 unit, subtracted by acyclic alkane heat of combustion per CH_2, and multiplying by the number of CH_2 units in a ring.

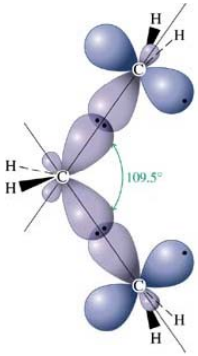
Conformations of the Cycloalkanes

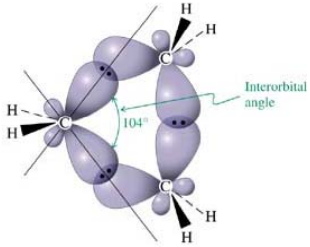
Cyclopropane is planar but the other alkanes adopt non-planar conformations to minimize:

- Angle strain - expansion or compression of bond angles away from most stable state
- Torsion strain - eclipsing of bonds on neighboring atoms
- Steric strain - repulsive interactions between nonbonded atoms in close proximity

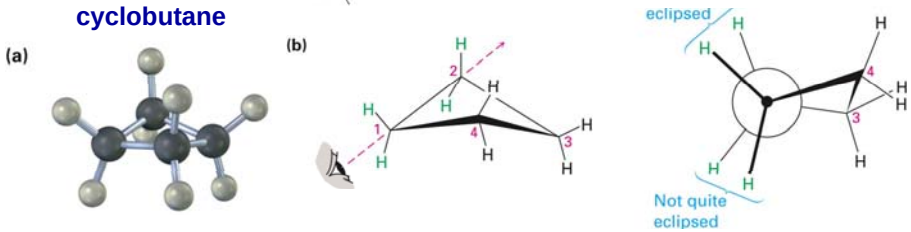


Conformations of the Cycloalkanes



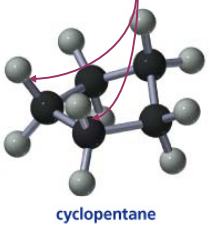


cyclobutane



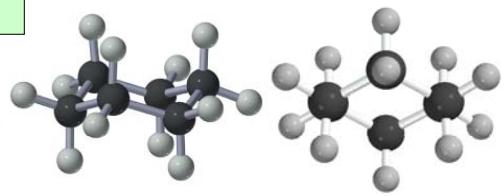
Conformations of the Cycloalkanes

eclipsing interaction

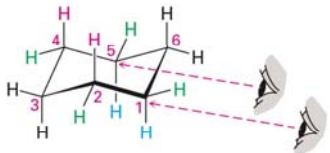


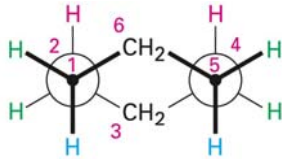
An envelope-like conformation

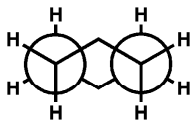
The chair conformation of cyclohexane is nearly strain-free.



Drawing cyclohexane - an important skill







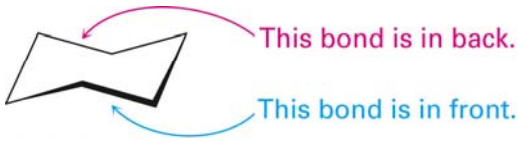
Newman projection

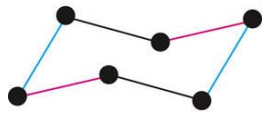
Draw a Chair Conformation of Cyclohexnane

Step 1 Draw two parallel lines, slanted downward slightly off-set from each other;

Step 2 Draw another two parallel lines from two carbons far away from each other;

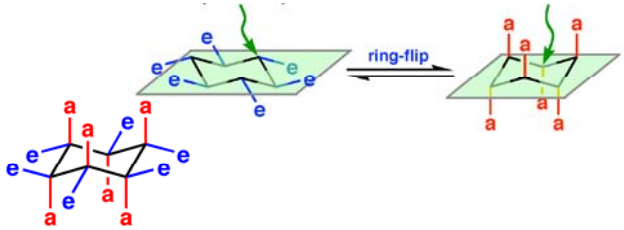
Step 3 Connect the rest two bonds (also parallel with each other).



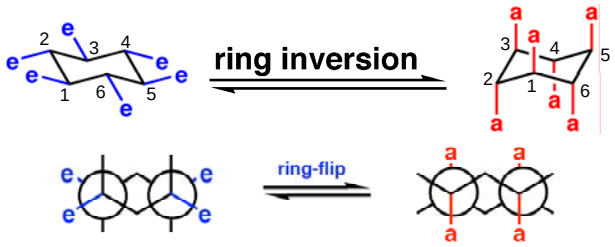


Cyclohexane Substituents

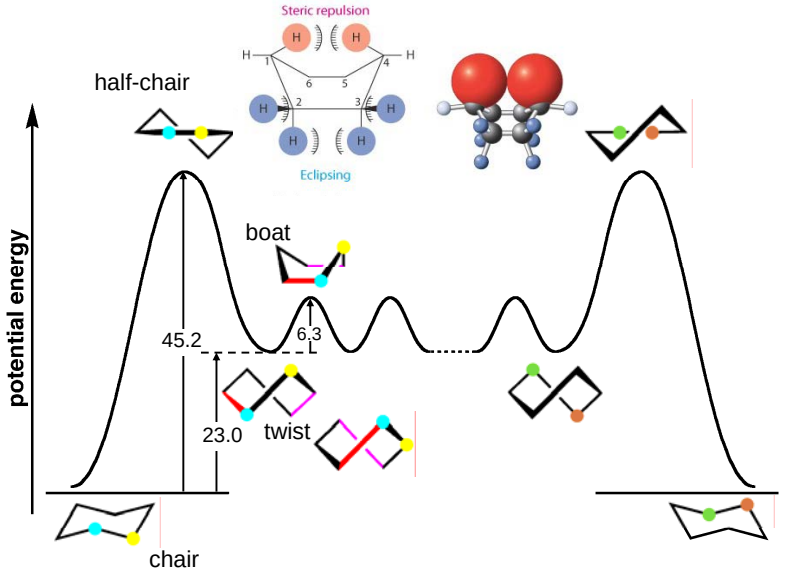
Draw the axial and equatorial bonds at each carbon



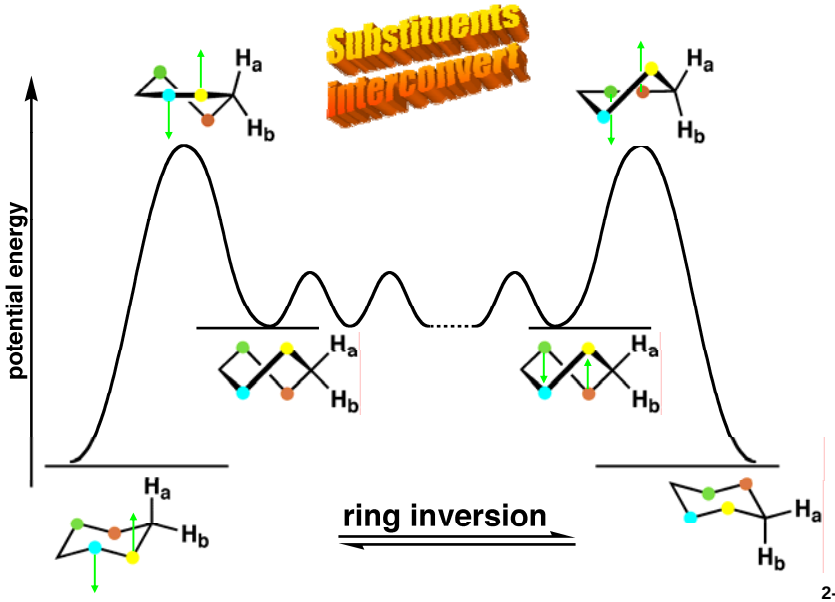
Cyclohexane can undergo a conformational transition known as the ring-inversion (ring-flip) in which each axial bond becomes equatorial and each equatorial bond becomes axial



Ring Inversion (Flipping) of Cyclohexane

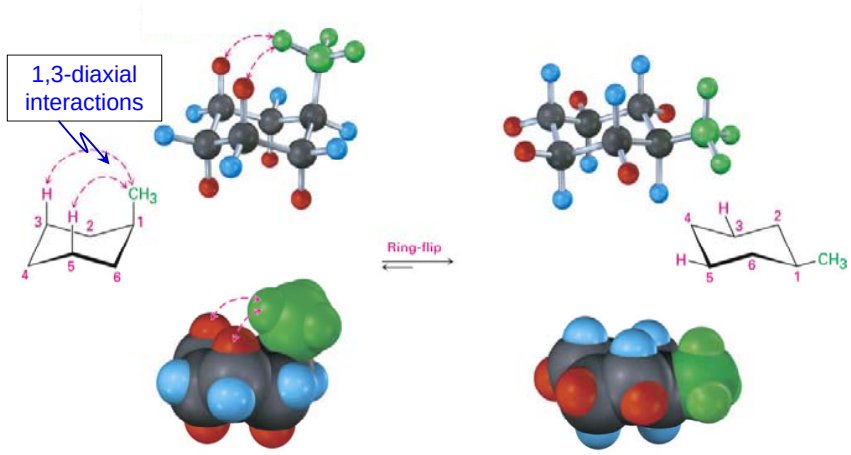


Atomic Motions Involved in Ring Inversion

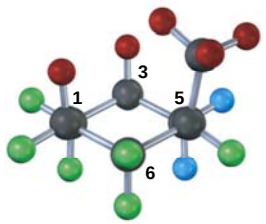


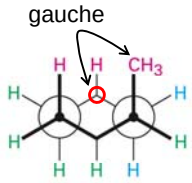
Substituted Cyclohexanes

Substituents prefer equatorial positions to avoid unfavorable 1,3-diaxial interactions (a type of steric strain).



Substituted Cyclohexanes





Axial methylcyclohexane (7.6 kJ/mol strain)

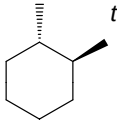
TABLE 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial

Substituent	G [kcal mol^{-1} (kJ mol^{-1})]	Substituent	G [kcal mol^{-1} (kJ mol^{-1})]
H	0 (0)	F	0.25 (1.05)
CH_3	1.70 (7.11)	Cl	0.52 (2.18)
CH_3CH_2	1.75 (7.32)	Br	0.55 (2.30)
$(CH_3)_2CH$	2.20 (9.20)	I	0.46 (1.92)
$(CH_3)_3C$	5 (21)	HO	0.94 (3.93)
$HO-\overset{O}{\overset{\|}{C}}$	1.41 (5.90)	CH_3O	0.75 (3.14)
$CH_3O-\overset{O}{\overset{\|}{C}}$	1.29 (5.40)	H_2N	1.4 (5.9)

Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

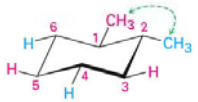
Disubstituted Cyclohexanes

trans-1,2-dimethylcyclohexane

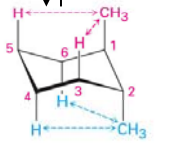


One gauche interaction

3.8 kJ/mol

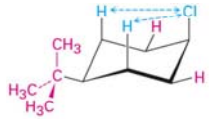


ring-flip



Two axial methyl groups

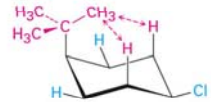
7.6 × 2 kJ/mol



axial -Cl: 2.2 kJ/mol

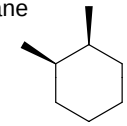
Ring-flip

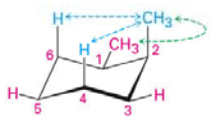
What's the relative ratio of the two conformers at 25 °C?



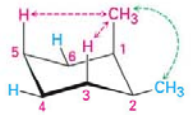
axial *t*-Bu: 21 kJ/mol

cis-1,2-dimethylcyclohexane

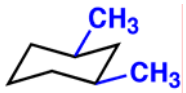




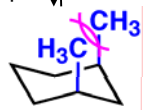
ring-flip



One gauche interaction and one axial methyl group



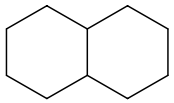
ring-flip



CH_3–CH_3 diaxial interaction

Polycyclic Alkanes and Spiroalkanes

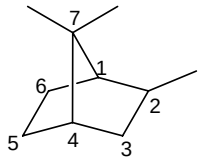
Give IUPAC names



decalin

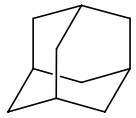
decahydronaphthalene

norbornane

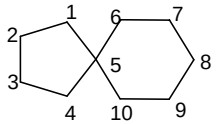


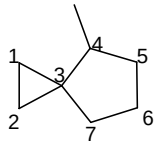
C1 and C4 are bridgehead carbons

Cubane

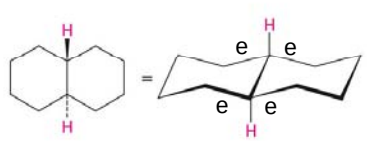


adamantane

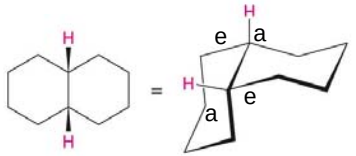




Cis- and Trans-Decalins



***trans*-Decalin**



***cis*-Decalin**