

4.S: ORGANIC COMPOUNDS- CYCLOALKANES AND THEIR STEREOCHEMISTRY (SUMMARY)

CONCEPTS & VOCABULARY

4.1: Naming Cycloalkanes

- Cycloalkanes are saturated hydrocarbons that have the generic formula C_nH_{2n} , where **n** is the number of carbons in the ring.
- The IUPAC rules for naming cycloalkanes is very similar to the rules used for naming alkanes.

4.2: Cis-Trans Isomerism in Cycloalkanes

- Stereoisomers** are molecules that have the same molecular formula, the same atom connectivity, but they differ in the relative spatial orientation of the atoms.
- Di-substituted cycloalkanes exhibit *cis*- / *trans*- stereoisomerism. The *cis*- isomer has both substituents on the same face of the ring, while the *trans*- isomer has groups on opposite faces of the ring.

4.3: Stability of Cycloalkanes - Ring Strain

- Ring strain** is the total strain in a ring due to **torsional strain**, **steric strain** and **angle strain**.
- Angle strain is when the C-C-C bond angles in rings are different than 109.5° , the optimal bond angle for sp^3 hybridized carbons.
- Ring strain causes small cycloalkanes, like cyclopropane and cyclobutane, to be much less stable than other cycloalkanes.

4.4: Conformations of Cycloalkanes

- Cyclopentane has less ring strain than cyclopropane and cyclobutane, because its ring carbons have more flexibility to rotate away from planarity, resulting in lower angle and torsional strains.

4.5: Conformations of Cyclohexane

- Cyclohexane has significantly lower ring strain than smaller cycloalkanes, because cyclohexane can adopt non-planar structures, which minimize angle strain and torsional strain.
- The common non-planar structures of cyclohexane are the boat, twist-boat, and chair conformations. The most stable, and hence, the most common, is the chair conformation.

4.6: Axial and Equatorial Bonds in Cyclohexane

- The two chair conformations of cyclohexane interconvert rapidly at room temperature in a process called **chair flip** or **ring flip**.
- In the chair conformation of cyclohexane, of the two groups attached to each ring carbon, one of the groups occupies the **axial** position, while the other group occupies the **equatorial** position.
- A group that was axial will switch to the equatorial position during a ring flip, and vice versa.

4.7: Conformations of Monosubstituted Cyclohexanes

- To minimize the steric effects of **1,3-diaxial interactions**, the single group on a monosubstituted cyclohexane ring will prefer to be in the equatorial position over the axial position. The larger the group, the greater is the preference shifts.

4.8: Conformations of Disubstituted Cyclohexanes

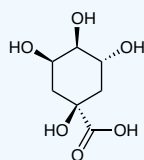
- The preference for large groups to be in the equatorial position effects the relative stability of the *cis* and *trans* isomers of disubstituted cyclohexanes. **Conformational analysis** is the process used to determine which isomer, *cis* or *trans*, is most stable.

4.9: Conformations of Polycyclic Molecules

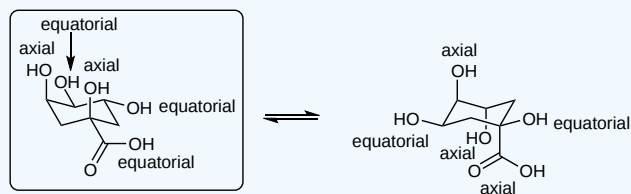
SUMMARY PROBLEMS

? EXERCISE 4.S.1

The following molecule, quinic acid, is a natural product that can be obtained from a variety of sources including the coffee bean. Draw both chair conformations for this molecule, identify each substituent in both structures as axial or equatorial, and clearly indicate which chair conformation is the most stable.



Answer

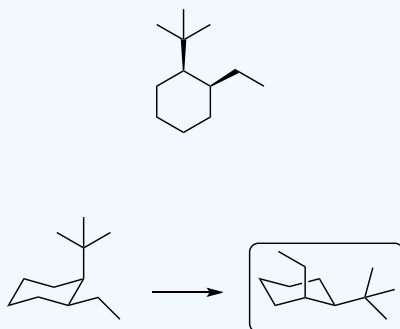


The circled conformation is more stable because it has more equatorial substituents (3 versus 2) and the largest group (the carboxylic acid) is equatorial.

? EXERCISE 4.S. 2

Convert the following name to a skeletal structure: *cis*-1-*t*-butyl-2-ethylcyclohexane. Then, draw this molecule in a chair conformation and perform a ring flip. Circle the most stable of the two conformations.

Answer

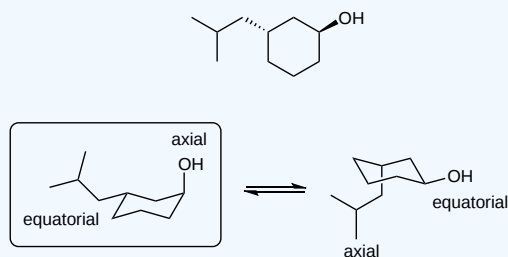


Remember that, due to its large size, the *t*-butyl substituent locks the cyclohexane ring into one conformation with the *t*-butyl in the equatorial position. Thus, this isn't an equilibrium. It exists only as the circled conformation.

? EXERCISE 4.S. 3

Convert the following name to a skeletal structure: *trans*-3-isobutylcyclohexanol. Then, draw the two chair conformations, label substituents as axial or equatorial, and circle the more stable conformation.

Answer



The circled molecule is most stable because the larger substituent is equatorial.

SKILLS TO MASTER

- Skill 4.1 Be able to name and draw cycloalkanes
- Skill 4.2 Identify and draw the *cis*- and *trans*- stereoisomers of disubstituted cycloalkanes.
- Skill 4.3 Determine the effects of torsional strain, steric strain, and angle strain on the overall ring strain of a cycloalkane.

- Skill 4.4 Draw the chair conformers of cyclohexane.
- Skill 4.5 Draw and identify the axial and equatorial positions in a chair conformer of cyclohexane and its ring-flip conformer.
- Skill 4.6 Use conformational analysis to determine the most stable stereoisomer in disubstituted and polysubstituted cyclohexanes.

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