

4.10: CONFORMATIONS OF DISUBSTITUTED CYCLOHEXANES

Learning Objective

- draw di-substituted cyclohexane conformers (chair only)
- correlate energies of conformations with rotational energy diagrams and predict the most stable conformations for disubstituted cyclohexanes

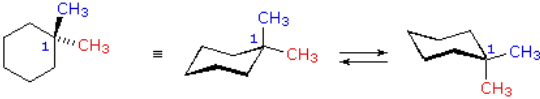
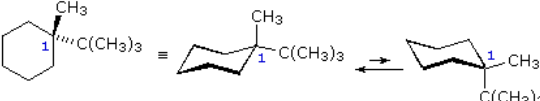
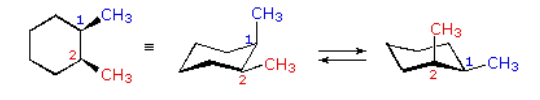
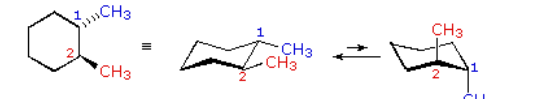
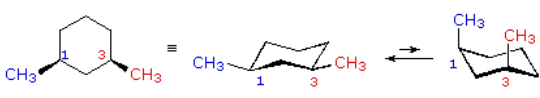
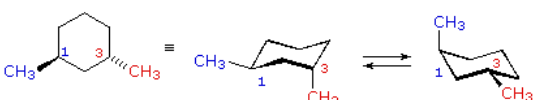
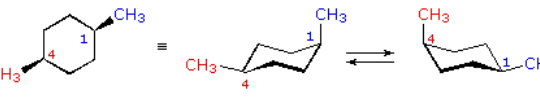
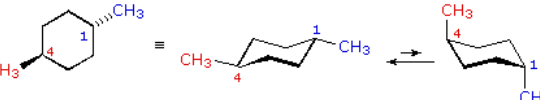
Conformational Structures of Disubstituted Cyclohexanes

In a sample of cyclohexane, the two identical chair conformers are present in equal concentration, and the hydrogens are all equivalent (50% equatorial & 50% axial) due to rapid interconversion of the conformers. When the cyclohexane ring bears a substituent, the two chair conformers are not the same. In one conformer the substituent is axial, in the other it is equatorial. Due to steric hindrance in the axial location, substituent groups prefer to be equatorial and that chair conformer predominates in the equilibrium.

When cycloalkanes have two substituents on different ring carbon atoms, then a pair of configurational stereoisomers exist. Now we must examine the way in which favorable ring conformations influence the properties of the configurational isomers. Remember, configurational stereoisomers are stable, unique chemical compounds, whereas, conformational isomers are different rotations of the same compound. In examining possible structures for disubstituted cyclohexane, it is useful to follow two principles:

1. Substituents on chair conformers prefer to occupy equatorial positions due to the increased steric hindrance of axial locations.

The following equations and formulas illustrate how the presence of two or more substituent on a cyclohexane ring perturbs the interconversion of the two chair conformers in ways that can be predicted. When there is a potential energy difference between the conformers, then the lower energy conformation is favored as indicated by the equilibrium reaction arrows.

1,1-dimethylcyclohexane	
1-t-butyl-1-methylcyclohexane	
cis-1,2-dimethylcyclohexane	
trans-1,2-dimethylcyclohexane	
cis-1,3-dimethylcyclohexane	
trans-1,3-dimethylcyclohexane	
cis-1,4-dimethylcyclohexane	
trans-1,4-dimethylcyclohexane	

In the case of 1,1-disubstituted cyclohexanes, one of the substituents must necessarily be axial and the other equatorial, regardless of which chair conformer is considered. Since the substituents are the same in 1,1-dimethylcyclohexane, the two conformers are

identical and present in equal concentration. In 1-t-butyl-1-methylcyclohexane the t-butyl group is much larger than the methyl, and that chair conformer in which the larger group is equatorial will be favored in the equilibrium ($> 99\%$). Consequently, the methyl group in this compound is almost exclusively axial in its orientation.

In the cases of 1,2-, 1,3- and 1,4-disubstituted compounds the analysis is a bit more complex. It is always possible to have both groups equatorial, but whether this requires a cis-relationship or a trans-relationship depends on the relative location of the substituents. As we count around the ring from carbon #1 to #6, the uppermost bond on each carbon changes its orientation from equatorial (or axial) to axial (or equatorial) and back. It is important to remember that the **bonds on a given side of a chair ring-conformation always alternate in this fashion**. Therefore, it should be clear that for cis-1,2-disubstitution, one of the substituents must be equatorial and the other axial; in the trans-isomer both may be equatorial. Because of the alternating nature of equatorial and axial bonds, the opposite relationship is true for 1,3-disubstitution (cis is all equatorial, trans is equatorial/axial). Finally, 1,4-disubstitution reverts to the 1,2-pattern.

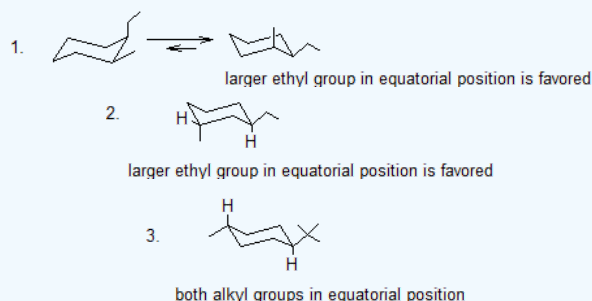
The conformations of some substituted cyclohexanes may be examined as interactive models by [Clicking Here](#).

It can be helpful to add the hydrogen atoms at the axial positions to help recognize the equatorial position.

Exercise

1. Draw the two chair conformations for cis-1-ethyl-2-methylcyclohexane using bond-line structures and indicate the more energetically favored conformation.
2. Draw the most stable conformation for trans-1-ethyl-3-methylcyclohexane using bond-line structures.
3. Draw the most stable conformation for trans-1-t-butyl-4-methylcyclohexane using bond-line structures.

Answer



CONTRIBUTORS

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)