4.2: CIS-TRANS ISOMERISM IN CYCLOALKANES

OBJECTIVES

After completing this section, you should be able to

- draw structural formulas that distinguish between *cis* and *trans* disubstituted cycloalkanes.
- construct models of *cis* and *trans* disubstituted cycloalkanes using ball-and-stick molecular models.

KEY TERMS

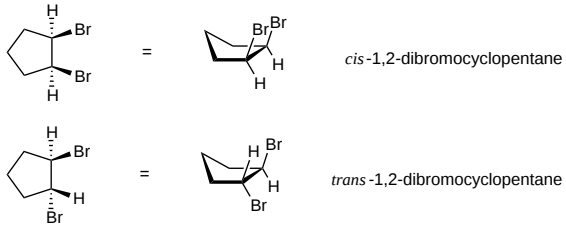
Make certain that you can define, and use in context, the key terms below.

- constitutional isomer
- stereoisomer
- *cis*-*trans* isomers

Previously, constitutional isomers have been defined as molecules that have the same molecular formula, but different atom connectivity. In this section, a new class of isomers, stereoisomers, will be introduced. **Stereoisomers** are molecules that have the same molecular formula, the same atom connectivity, but they differ in the relative spatial orientation of the atoms.

Cycloalkanes are similar to open-chain alkanes in many respects. They both tend to be nonpolar and relatively inert. One important difference, is that cycloalkanes have much less freedom of movement than open-chain alkanes. As discussed in Sections 3.6 and 3.7, open-chain alkanes are capable of rotation around their carbon-carbon sigma bonds. The ringed structures of cycloalkanes prevent such free rotation, causing them to be more rigid and somewhat planar.

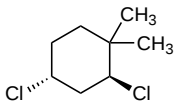
Di-substituted cycloalkanes are one class of molecules that exhibit stereoisomerism. 1,2-dibromocyclopentane can exist as two different stereoisomers: *cis*-1,2-dibromocyclopentane and *trans*-1,2-dibromocyclopentane. The *cis*-1,2-dibromocyclopentane and *trans*-1,2-dibromocyclopentane stereoisomers of 1,2-dibromocyclopentane are shown below. Both molecules have the same molecular formula and the same atom connectivity. They differ only in the relative spatial orientation of the two bromines on the ring. In *cis*-1,2-dibromocyclopentane, both bromine atoms are on the same "face" of the cyclopentane ring, while in *trans*-1,2-dibromocyclopentane, the two bromines are on opposite faces of the ring. Stereoisomers require an additional nomenclature prefix be added to the IUPAC name in order to indicate their spatial orientation. Di-substituted cycloalkane stereoisomers are designated by the nomenclature prefixes ***cis*** (Latin, meaning on this side) and ***trans*** (Latin, meaning across).

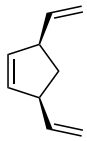


REPRESENTING 3D STRUCTURES

By convention, chemists use heavy, wedge-shaped bonds to indicate a substituent located above the plane of the ring (coming out of the page), a dashed line for bonds to atoms or groups located below the ring (going back into the page), and solid lines for bonds in the plane of the page.

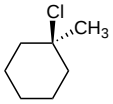
cis-1,3-dimethylcyclobutane *trans*-5-bromo-1,4,6-trimethyl-1,3-cycloheptadiene





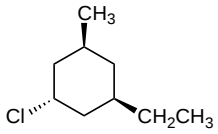
trans-2,4-dichloro-1,1-dimethylcyclohexane *cis*-3,5-divinylcyclopentene

In general, if any two sp^3 carbons in a ring have two different substituent groups (not counting other ring atoms) cis/trans stereoisomerism is possible. However, the cis/trans designations are not used if both groups are on the same carbon. For example, the chlorine and the methyl group are on the same carbon in 1-chloro-1-methylcyclohexane and the *trans* prefix should not be used.



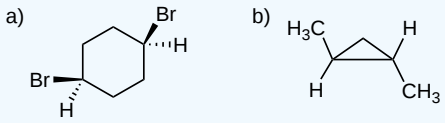
1-chloro-1-methylcyclohexane

If more than two ring carbons have substituents, the stereochemical notation distinguishing the various isomers becomes more complex and the prefixes *cis* and *trans cannot be used to formally name the molecule*. However, the relationship of any two substituents can be informally described using *cis* or *trans*. For example, in the tri-substituted cyclohexane below, the methyl group is *cis* to the ethyl group, and also *trans* to the chlorine. However, the entire molecule cannot be designated as either a *cis* or trans *isomer*. Later sections will describe how to name these more complex molecules (5.5: Sequence Rules for Specifying Configuration)



EXAMPLE 4.2.1

Name the following cycloalkanes:



Solution

These two example represent the two main ways of showing spatial orientation in cycloalkanes.

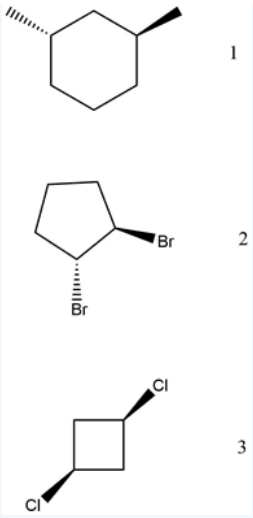
a. In example "a" the cycloalkane is shown as being flat and in the plane of the page. The positioning of the substituents is shown by using dash-wedge bonds. Cis/trans positioning can be determined by looking at the type of bonds attached to the substituents. If the substituents are both on the same side of the ring (Cis) they would both have either dash bonds or wedge bonds. If the the substituents are on opposite side of the ring (Trans) one substituent would have a dash bond and the other a wedge bond. Because both bromo substituents have a wedge bond they are one the same side of the ring and are cis. The name of this molecule is cis-1,4-Dibromocyclohexane.
b. Example "b" shows the cycloalkane ring roughly perpendicular to the plane of the page. When this is done, the upper and lower face of the ring is defined and each carbon in the ring will have a bond one the upper face and a bond on the lower face. Cis substituents will either both be on the upper face or the lower face. Trans substituents will have one on the upper face and one one the lower face. In example "b", one of the methyl substituents is on the upper face of the ring and one is on the lower face which makes them trans to each other. The name of this molecule is *trans*-1,2-Dimethylcyclopropane.

EXERCISE 4.2.2

Draw the following molecules:

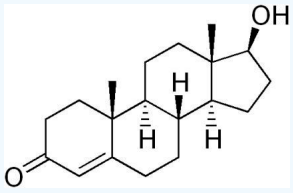
1. *trans*-1,3-dimethylcyclohexane
2. *trans*-1,2-dibromocyclopentane
3. *cis*-1,3-dichlorocyclobutane

Answer



EXERCISE 4.2.3

Cis/Trans nomenclature can be used to describe the relative positioning of substituents on molecules with more complex ring structures. The molecule below is tesosterone, the primary male sex hormone. Is the OH and the adjacent methyl group cis or trans to each other? What can you deduce about the relative positions of the indicated hydrogens?

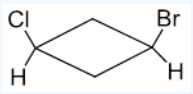


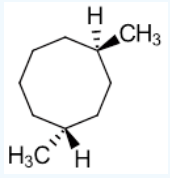
Answer

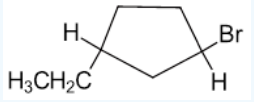
Both the OH and the methyl group have wedge bonds. This implies that they are both on the same side of the testosterone ring making them cis. Two of the hydrogens have wedge bonds while one has a wedge. This means two of the hydrogens are on one side of the testosterone ring while one is on the other side.

EXERCISE 4.2.4

Name the following compounds:







Answer

Cis-1-Bromo-3-Chlorocyclobutane

Trans-1,4-Dimethylcyclooctane

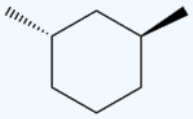
Trans-1-Bromo-3-ethylcyclopentane

EXERCISE 4.2.5

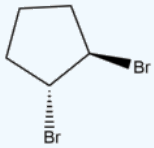
Draw the following molecules:

a. *trans*-1,3-dimethylcyclohexane
b. *trans*-1,2-dibromocyclopentane
c. *cis*-1,3-dichlorocyclobutane

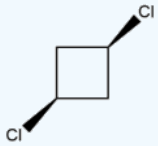
Answer



1



2



3