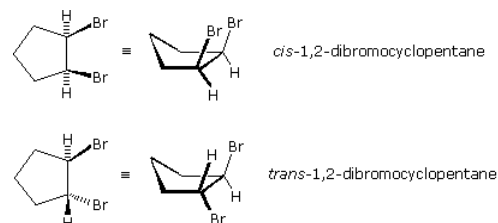


5.10: Disubstituted Cycloalkanes

Configurational Stereoisomers of Cycloalkanes

Stereoisomers are also observed in certain disubstituted (and higher substituted) cyclic compounds. Unlike the relatively flat molecules of alkenes, substituted cycloalkanes must be viewed as three-dimensional configurations in order to appreciate the spatial orientations of the substituents. By agreement, chemists use heavy, **wedge-shaped** bonds to indicate a substituent located above the average plane of the ring (note that cycloalkanes larger than three carbons are not planar), and a **hatched line** for bonds to atoms or groups located below the ring. As in the case of the 2-butene stereoisomers, disubstituted cycloalkane stereoisomers may be designated by nomenclature prefixes such as *cis* and *trans*. The stereoisomeric 1,2-dibromocyclopentanes shown to the right are an example.



Many of the stereochemical concepts we have covered are illustrated nicely by looking at disubstituted cyclohexanes. We will now examine several dichlorocyclohexanes.

The 1,1-dichloro isomer has no centers of chirality. The 1,2- and 1,3-dichlorocyclohexanes each have two centers of chirality, bearing the same set of substituents. The *cis* & *trans*-1,4-dichlorocyclohexanes do not have any chiral centers, since the two ring groups on the substituted carbons are identical.

There are three configurational isomers of 1,2-dichlorocyclohexane and three configurational isomers of 1,3-dichlorocyclohexane. These are shown below:

1,2-substitution

1,3-substitution

All the 1,2-dichloro isomers are constitutional isomers of the 1,3-dichloro isomers. In each category (1,2- & 1,3-), the (R,R)-*trans* isomer and the (S,S)-*trans* isomer are enantiomers. The *cis* isomer is a diastereomer of the *trans* isomers.

Finally, all of these isomers may exist as a mixture of two (or more) conformational isomers. The chair conformer of the *cis* 1,2-dichloro isomer *appears* to be chiral. However, it exists as a 50:50 mixture of chair conformations, which interconvert so rapidly they cannot be resolved (ie. separated). In fact, a boat conformation can be constructed in which there exists a plane of symmetry, therefore the *cis* isomer is, over, achiral. Since the *cis* isomer has two centers of chirality (asymmetric carbons) but is achiral, it is a meso-compound. The corresponding *trans* isomers also exist as rapidly interconverting chiral conformations, but they are chiral. The diequatorial conformer predominates in each case, the (R,R) conformations being mirror images of the (S,S) conformations. All these conformations are diastereomeric with the *cis* conformations.

The diequatorial chair conformer of the *cis* 1,3-dichloro isomer is achiral. It is the major component of a fast equilibrium with the diaxial conformer, which is also achiral. This isomer is also a meso compound. The corresponding *trans* isomers also undergo a rapid conformational interconversion. For these isomers, however, this interconversion produces an identical conformer, so each enantiomer (R,R) and (S,S) has predominately a single chiral conformation. These enantiomeric conformations, both of which are chiral, are diastereomeric with the *cis* (meso) isomer.

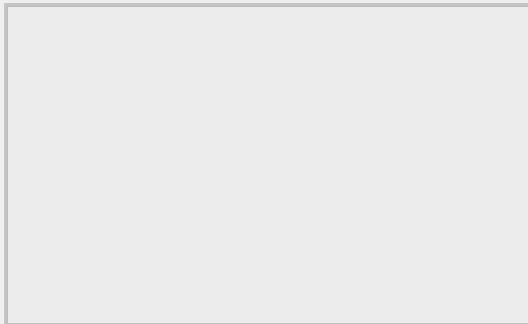
Cyclic compounds can also be *meso*. One of many such examples is *cis*-1,2-dihydroxycyclohexane. Note, however, that if the hydroxyl groups are *trans* to each other, the molecule is chiral.



Fortunately for overworked organic chemistry students, the *meso* compound is a very special case, and it is difficult to find many naturally occurring examples. They do, however, seem to like showing up in organic chemistry exam questions.

Example

Exercise: Which of the molecules shown below are *meso*? Which are chiral? Which are achiral, but not *meso*?



Exercise: Draw the structure of another dimethylcyclopentane isomer that is *meso* (do not use structures from the previous problem).

[Solutions](#)

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