

13.3: The Structure of Alkenes- Cis-Trans Isomerism

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 13.3.1.

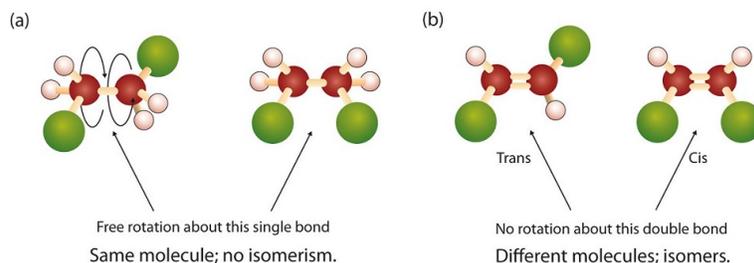


Figure 13.3.1: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In 1,2-dichloroethane (part (a) of Figure 13.3.1), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (Figure 13.3.1b), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the *cis* isomer (Latin *cis*, meaning “on this side”) and is named *cis*-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the *trans* isomer (Latin *trans*, meaning “across”) and is named *trans*-1,2-dichloroethene. These two compounds are *cis-trans* isomers (or *geometric isomers*), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $\text{CH}_3\text{CH}=\text{CHCH}_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in *cis-trans* isomerism (Figure 13.3.2).

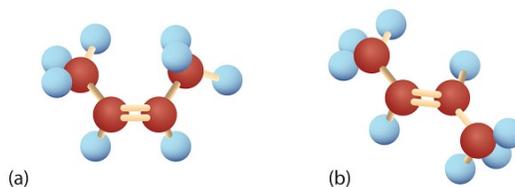


Figure 13.3.2: Ball-and-Spring Models of (a) *Cis*-2-Butene and (b) *Trans*-2-Butene. *Cis-trans* isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:

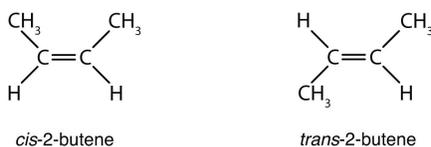


Figure 13.3.3: Models of (left) *Cis-2-Butene* and (right) *Trans-2-Butene*.

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 13.3.4). We can draw two *seemingly* different propenes:



Figure 13.3.4: Different views of the propene molecule (flip vertically). These are not isomers.

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $\text{C}=\text{CH}_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $\text{C}=\text{CR}_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type $\text{R}-\text{CH}=\text{CH}-\text{R}$ can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Advanced Note: E/Z Isomerization

If a molecule has a $\text{C}=\text{C}$ bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature described above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a $\text{C}=\text{C}$ bond, with a methyl group and a bromine on one carbon, and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced [E/Z nomenclature](#) discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon-carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



Example 13.3.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. $\text{CHCl}=\text{CHBr}$
2. $\text{CH}_2=\text{CBrCH}_3$
3. $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$
4. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$

Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:



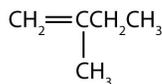
- This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
- This compound has two methyl (CH₃) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
- This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



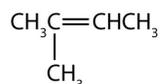
? Exercise 13.3.1

Which compounds can exist as cis-trans isomers? Draw them.

- a. CH₂=CHCH₂CH₂CH₃
- b. CH₃CH=CHCH₂CH₃
- c. CH₃CH₂CH=CHCH₂CH₃

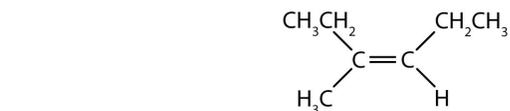
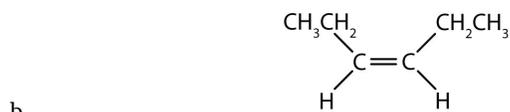
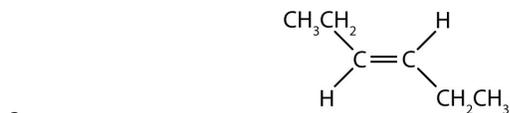


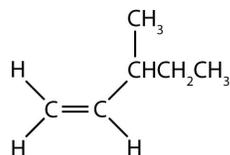
d.



Concept Review Exercises

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.





d.

Answers

1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.
2. a. trans (the two hydrogen atoms are on opposite sides)
b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
c. cis (the two ethyl groups are on the same side)
d. neither (flipping the bond does not change the molecule. There are no isomers for this molecule)

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