2.2: Geometric Isomers

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 $2.2.1$.

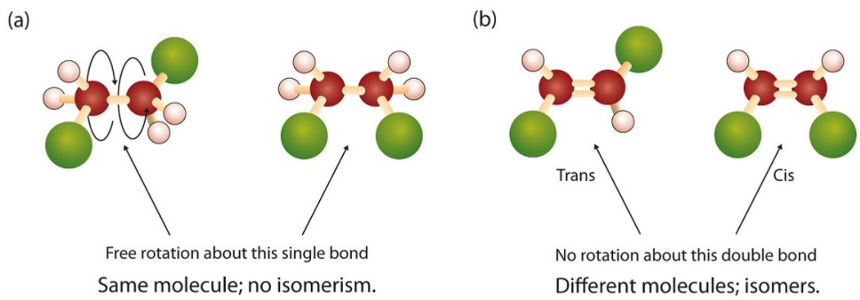


Figure $2.2.1$: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In 1,2-dichloroethane (part (a) of Figure $2.2.1$), 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:

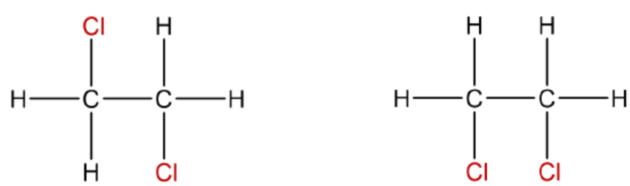


Figure $2.2.2$ Structural formulas of 1,2-dichloroethane.

In 1,2-dichloroethene (Figure $2.2.1b$), 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 $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure $2.2.3$).

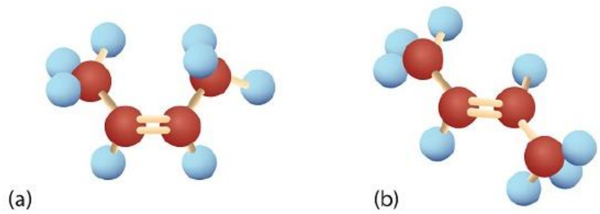


Figure 2.2.3: Models of (a) cis-2-Butene and (b) trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

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. Notice that the names of these molecules are identical except for the prefix cis or trans. Their structural formulas are as follows:

Figure 2.2.4: Structures of cis-2-Butene (left) and trans-2-Butene (right).

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 2.2.5). We can draw two *seemingly* different propenes:

Figure 2.2.5: 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 (one hydrogen and another atom/group of atoms).

In the 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 (H and CH_3), 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 $C=CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C=CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-carbon double bond.

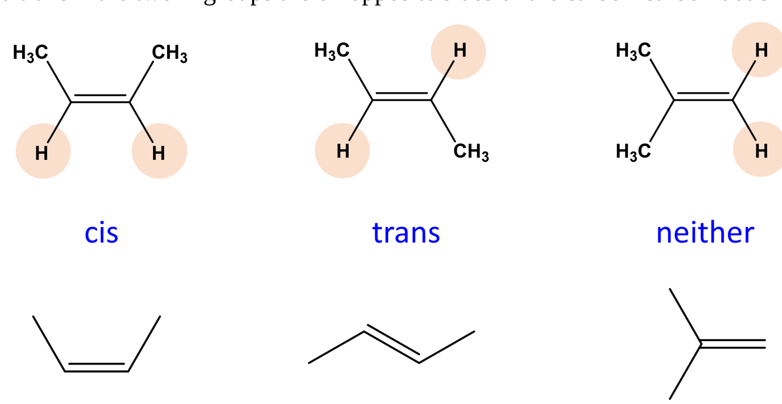


Figure 2.2.6: Structural formulas (top) and skeletal structures (bottom) of cis-trans isomers. DrTOsborne, CC BY 4.0, via Wikimedia Commons

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the carbon–carbon bonds in the ring. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). The orientation of the substitutents will be designated with either a solid and/or dashed wedge to indicate the 3-dimensional arrangement or as a Haworth projection to indicate positions above and below the plane of the ring plane (Figure 2.2.7).

Figure 2.2.7. Indication of the 3-dimensional structure (left) and Haworth projection (right) of cis-1,2-dimethylcyclopropane (left structure of both pair) and trans-1,2-dimethylcyclopropane (right structure of both pair).

Example 2.2.1

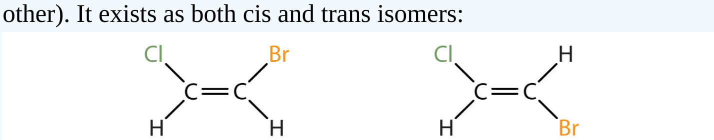
Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. CHCl=CHBr
2. CH_2=$CBrCH_3$
3. $(CH_3)_2C$=$CHCH_2CH_3$
4. CH_3CH=$CHCH_2CH_3$

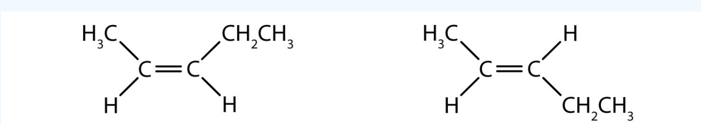
Solution

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:



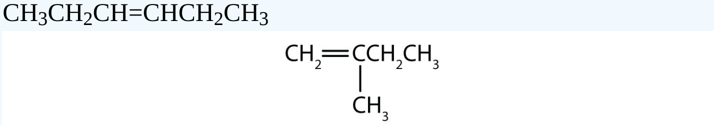
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



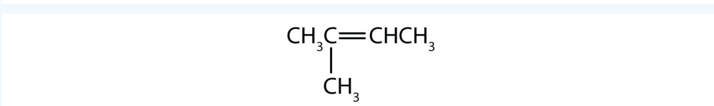
Exercise 2.2.1

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

a. CH_2=$CHCH_2CH_2CH_3$
b. CH_3CH=$CHCH_2CH_3$
c. CH_3CH_2CH=$CHCH_2CH_3$
d.

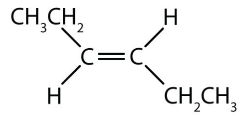


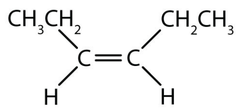
e.



✓ Example 2.2.2

Classify each compound as a cis isomer, a trans isomer, or neither. Provide the IUPAC name of the molecule.

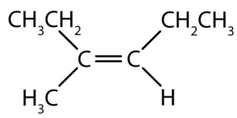
1. 

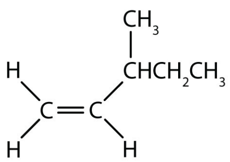
2. 

Solution

1. This compound meets rule 1 (restricted rotation due to the double bond) and rule 2 (it has two nonidentical groups on *each* carbon atom: H and CH_2CH_3). Since the H are on opposite sides of the molecule, this is a trans isomer. Using the rules for naming alkenes, the longest continuous chain has six carbon atoms with a double bond between carbons 3 and 4. This means that the parent name is 3-hexene. Putting this together indicates that the IUPAC name of the molecule is trans-3-hexene.
2. This compound meets rule 1 (restricted rotation due to the double bond) and rule 2 (it has two nonidentical groups on *each* carbon atom: H and CH_2CH_3). Since the H are on the same side of the molecule, this is a cis isomer. Using the rules for naming alkenes, the longest continuous chain has six carbon atoms with a double bond between carbons 3 and 4. This means that the parent name is 3-hexene. Putting this together indicates that the IUPAC name of the molecule is cis-3-hexene.

? Exercise 2.2.2

1. Classify each compound as a cis isomer, a trans isomer, or neither. Provide the IUPAC name of the molecule.
   a. 

   b. 

2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene

Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.
- The IUPAC naming is the same as alkene except for the addition of the cis or trans prefix.