

1. Geometric Isomers

Introduction

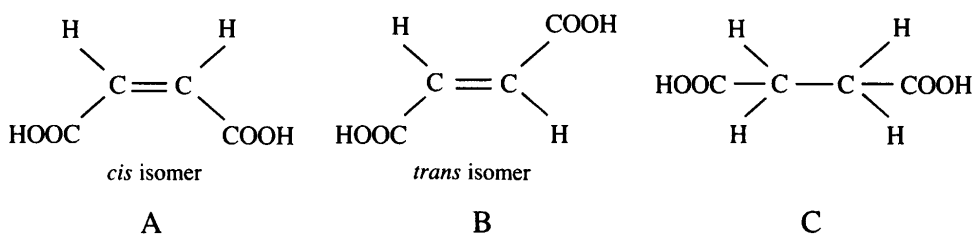
The existence of geometric or *cis-trans* isomers is a consequence of the lack of rotation about double bonds. The *cis* and *trans* isomers of 1,2-dichloroethene (pictured in Ebbing/Gammon, opening of Chapter 10) are examples. Maleic and fumaric acids, whose structures are shown in Figure 1.1 in this experiment, are another pair of geometric isomers.

Although their molecular formulas are identical, *cis* and *trans* isomers are entirely different compounds. They are different compounds because they have different geometries and because rotation about the π bond will not occur under ordinary conditions. You will note that maleic acid, the *cis* isomer, has a more congested array of atoms than does fumaric acid, the *trans* isomer. The crowding in the *cis* isomer occurs because both carboxylic acid groups ($-\text{COOH}$) are on the same side of the double bond. In contrast, these groups are on opposite sides of the double bond in the *trans* isomer.

Purpose

You will receive two unidentified samples. One will be maleic acid, and the other will be fumaric acid. The identities of these samples will become clear as you compare some of their properties.

FIGURE 1.1
The structure of
(A) maleic acid,
(B) fumaric
acid, and
(C) succinic
acid.



Isomerization

It is often possible to convert a crowded *cis* isomer to the *trans* isomer by a chemical reaction. This reaction requires an input of energy to rupture the π bond. Rotation about the remaining σ bond then occurs, and the less crowded arrangement can be obtained. After rotation, the π bond is formed once again. The name of this type of reaction is *isomerization*.

Concept of the experiment

Maleic and fumaric acids are different compounds, so they will have entirely different properties. Their melting points and solubilities in water are compared in Table 1.1.

Table 1.1 Some Properties of Maleic and Fumaric Acids

Compound	Melting Point (°C)	Solubility in H₂O (g/1000 mL) at 25°C
Maleic acid	131	788
Fumaric acid	287	7

You will base your identification of your samples on a comparison of their melting points and their solubilities. Because you are making a comparison, however, you will not need to determine the absolute values of the melting points and solubilities of your samples. Instead, you will determine which sample has the lower melting point and which one has the lower solubility. Your conclusions from this comparison should be confirmed when you determine which sample will undergo isomerization.

Procedure

Getting started

1. Your laboratory instructor may ask you to work with a partner.
2. Make sure that you have read and understood the description of suction filtration in the Introduction to this manual.
3. Obtain your unknown samples and 2 small test tubes.

Examining the samples' properties

1. Mark the 2 small test tubes so that you can recognize each sample. Place a pea-sized portion of one sample in the appropriate test tube and a similar-sized portion of the other sample in the remaining test tube.
2. Light a laboratory burner. Hold each test tube in a separate test tube holder with the same hand. Heat the samples simultaneously until one of them melts. Record which sample has melted. Allow the test tubes to cool before cleaning them.
3. Wash your test tubes, rinse them with distilled water, and dry them.
4. Repeat Step 1. Add 2 mL of distilled water to each test tube and shake the tube gently for about 1 min. Record which sample has dissolved.
5. You should be able to identify each sample at this point by comparing your data with those shown in Table 1.1. The results of the next test should confirm the identities.

Attempting isomerization

1. Obtain the mass of a piece of weighing paper, using either a platform balance, triple beam balance, or an electronic top-loading balance. Your laboratory instructor will give you directions for using either of these balances. Add 1.0 g of the more soluble sample to this paper. Transfer this portion of the sample to a 250-mL Erlenmeyer flask.
2. Add 10 mL of distilled water to this flask and swirl gently.

3. Set up a ring stand with an iron ring, and put a piece of wire gauze on the ring. If possible, put this apparatus in a hood. If a hood is not available, use an inverted conical filter funnel connected by rubber tubing to a water aspirator to suck away HCl vapor, which will be generated in Steps 6 and 7.
4. Place a laboratory burner under the wire gauze and adjust the height of the iron ring so that the wire gauze will be approximately in the hottest part of the flame. Do not light the burner until this adjustment has been made.

CAUTION: Avoid burning your fingers. Do not touch the iron ring or the wire gauze at any time during heating.

5. Place the flask on the wire gauze and heat until the water boils.
6. Measure 10 mL of concentrated hydrochloric acid in a graduated cylinder.

CAUTION: Concentrated acids must be handled carefully because they can cause severe chemical burns in addition to ruining your clothes. If you spill an acid on you, wash the contaminated area thoroughly with tap water and report the incident to your laboratory instructor. You may require further treatment.

7. Add the acid *very slowly* and *cautiously* to the boiling water and continue to boil for another minute. Record any observation of note during this time. Remove the heat. Use crucible tongs to remove the flask from the wire gauze. Set the flask aside for 10 min to allow the reaction, if any, to continue. Note and record any changes that occur.
8. Cool 20 mL of distilled water in an ice bath during this time.
9. When 10 min has elapsed, cool the flask in the ice bath. Filter the solid using suction. (This technique is described in the Introduction.) Wash the solid with the ice-cold water. Continue drawing air through the solid for about 5 min to remove most of the water.
10. After 5 min, remove the filter paper and the solid from the funnel. Place the filter paper on a paper towel that is appropriately marked so that you will not forget the identity of this sample.
11. Repeat Steps 1, 2, and 5 through 10 using the other sample.
12. Wash your test tubes, rinse them with distilled water, and dry them.
13. Test the solubility of each filtered solid using a pea-sized portion of the solid and 2 mL of distilled water. Record your observations.
14. The identities of the samples should now be confirmed. Even though the samples have been partially dried, they are still too wet for their exact melting behavior to be meaningful.

CAUTION: Before you leave the laboratory, make sure that your gas outlet and those of your neighbors are closed.

Geometric Isomers

Date: Student name:
Course: Team members:
Section:
Instructor:

Prelaboratory assignment

1. Define the following terms:

a. σ bond

b. Single bond

c. π bond

d. Double bond

e. Geometric isomers

f. Isomerization

2. a. What geometric isomers will be examined during this experiment?
Show their structures and give their names.
- b. Why are these isomers different compounds?
- c. What prevents these isomers from being only one compound?
- d. How do the properties of these isomers differ?

Student name: Course/Section: Date:

3. What safety precautions are cited in this experiment?

Geometric Isomers

Date:

Student name:

Course:

Team members:

Section:

Instructor:

Results

	Sample 1	Sample 2
Behavior on heating		
Behavior in water		
Behavior during attempted isomerization		
Behavior in water after attempted isomerization		

Questions

1. Identify each sample and describe your reasoning in making your identification.
2. Although maleic and fumaric acids are geometric isomers, *cis* and *trans* isomers of succinic acid (Figure 1.1C) do not exist. Explain.
3. Build molecular models of maleic, fumaric, and succinic acids (optional).
 - a. Do the models show why these are not identical compounds? If so, describe below.
 - b. Compare the rotation, if any, about the carbon–carbon double bonds in maleic and fumaric acids and about the corresponding carbon–carbon single bond in succinic acid.

