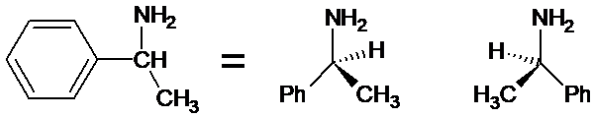
Experiment 4

# Isolating the Enantiomers of 1-Phenylethylamine by Fractional Crystalization

Enantiomers are pairs of stereoisomers that have the same atom connectivity, yet they are non-superimposable mirror images. They exhibit identical physical properties (e.g., melting point and boiling point) and cannot be distinguished by most spectroscopic techniques. This means that it is impossible to separate enantiomers using common organic techniques such as distillation and extraction. They do, however, exhibit two key differences. First, the two enantiomers rotate plane-polarized light in opposite directions and so are called "optically active." Second, they show different behavior in the presence of other optically active compounds. The first of these is important for identifying these compounds and the second is important for separating them.

1-Phenylethylamine (i.e., α-methylbenzylamine) is a chiral compound that can exist as one of two enantiomers:




*S-(–)* *R-(+)*

*Figure 1 Enantiomers of 1-phenylethylamine*

This compound can be synthesized in a variety of ways. However, unless optically active precursors and careful conditions are chosen, the synthesis will yield a 50:50 mixture of the two enantiomers. This is called a racemic mixture, which will not rotate plane-polarized light because one enantiomer cancels the rotating effect of the other. Thus, optical activity only results if the enantiomers are present in unequal amounts. In this lab, you will separate the two stereoisomers of 1-phenylethylamine and use polarimetry to explore their optical activity.

Polarimetry is a common technique for distinguishing between optically active stereoisomers (i.e., enantiomers). This makes it a very important tool in organic chemistry because the optical rotation of a molecule can dictate what reactions it will undergo. This is true for most chiral molecules, including organic, inorganic, and biological compounds. An enantiomer will consistently have the same specific rotation under identical experimental conditions. To determine the specific rotation of the sample, use Biot's law:

$$\alpha = [\alpha]\ \ell\ c$$

where α is the observed optical rotation in units of degrees, [α] is the specific rotation in units of degrees (the formal unit for specific rotation is degrees $dm^{-1}$ mL $g^{-1}$, but scientific literature uses just degrees), ℓ is the length of the cell in units of dm, and c is the sample concentration in units of grams per milliliter.

## OBJECTIVES

- Isolate the stereoisomers of 1-phenylethylamine from the racemic mixture.
- Confirm the identity of each stereoisomer using a Polarimeter.
- Determine the optical purity of your isolation using polarimetry.

## MATERIALS

One of the following
- Chromebook, computer, **or** mobile device with Vernier Instrumental Analysis app[1]
- LabQuest 2 (software is pre-installed; v2.8.7 or newer required[2])
- LabQuest 3 (software is pre-installed; v3.0.3 or newer required[2])

Go Direct Polarimeter
polarimeter sample cell
l-(+)-tartaric acid
methanol
racemic 1-phenylethylamine
dichloromethane
separatory funnel
vacuum filtration apparatus
250 mL Erlenmeyer flask
aluminum foil
ice bath
50% aqueous NaOH
$Na_2SO_4$
gravity filtration apparatus
hot plate

## PROCEDURE

### Part I Isolation of 1-phenylethylamine enantiomers

1. Obtain and wear goggles. Protect your arms and hands by wearing a long-sleeve lab coat and gloves. Conduct this reaction in a fume hood.

2. Using a hot plate, heat a solution of 7.8 g of l-(+)-tartaric acid and 125 mL of methanol in a 250 mL Erlenmeyer flask.

3. When the solution is almost boiling, slowly add 6.25 g of racemic 1-phenylethylamine. **Caution**: Adding the amine too fast will result in the mixture boiling over.

4. Remove the flask from the hot plate and allow it to cool to room temperature undisturbed to promote crystallization. Since crystallization will occur slowly, cover the top of the flask loosely with aluminum foil, and allow it to sit overnight.

[1]Instrumental Analysis v1.2 or newer required; download the most recent version for free at www.vernier.com/ia

[2]Download the most recent version of LabQuest software at www.vernier.com/downloads

5. Prismatic crystals should have crystallized out of the solution. Note: If needle crystals form instead of prismatic crystals, you must redissolve them with careful heating. Then allow them to slowly cool again, undisturbed. Needles will result in product that is not optically pure.

6. Collect the crystals using a vacuum filtration apparatus.

7. After removing the filtrate, rinse the crystals with a small amount of cold methanol.

8. Partially dissolve the crystals in 25 mL of water and treat with 4 mL 50% aqueous NaOH to pH 13. The amine salt should now be converted to the organic-soluble free amine.

9. Transfer the mixture to a separatory funnel and extract three times with 10 mL of dichloromethane.

10. Dry the organic extracts over $Na_2SO_4$, filter using gravity filtration.

11. Remove the dichloromethane using rotary evaporation or similar process. Record your yield.

12. Dissolve your product in a minimal amount of methanol to use in measuring its optical rotation (Part II). Record the exact concentrations in the table below.

**Part II Measuring the optical rotation**

13. In addition to your product from Part I, prepare a solution of 2 g of racemic 1-phenylethylamine in 25 mL methanol to use in measuring its optical rotation.

14. Set up the Go Direct Polarimeter by following the directions for your equipment:
    - Instrumental Analysis: Launch Instrumental Analysis. Connect the Go Direct Polarimeter to your Chromebook, computer, or mobile device.
    - LabQuest: Connect the Go Direct Polarimeter to your LabQuest 2 or LabQuest 3.

15. Calibrate the polarimeter.
    a. Pour distilled water in the polarimeter cell to a height of 10 cm. It is important to read the height to the nearest 0.1 cm. Read to the bottom of the meniscus.
    b. Place the cell in the polarimeter, then follow the appropriate steps:
        - Instrumental Analysis: Click or tap Finish Calibration. When the polarimeter is ready, click or tap Done.
        - LabQuest: Select Calibrate from the Sensors menu. Tap Calibrate Now and follow the instructions on the screen. When the polarimeter is ready, tap OK.

16. You are now ready to add the optically active sample into the polarimeter cell.
    a. Pour the sucrose solution in the polarimeter cell to a height of 10 cm. Record this value to the nearest 0.1 cm in Table 1.
    b. Place the sample cell in the polarimeter.
    c. Start data collection. Data collection will stop automatically.

d. Store the data, if necessary:
   - Instrumental Analysis: Data are stored automatically. Continue to the next step.
   - LabQuest: To store the data, tap the File Cabinet icon. Then, continue to the next step.

17. Use the Statistics or Curve Fit tool to determine the angle closest to 0° where the illumination is at a maximum. This is the observed angle of rotation of the plane of polarized light for the optically active sample. Record this value in Table 2.

    To access the Statistics or Curve Fit tools, follow the appropriate steps:

    - Instrumental Analysis: Highlight the peak of interest, if applicable. Then, click or tap Graph Tools, .
    - LabQuest: Highlight the peak of interest, if applicable. Then, tap Analyze.

18. Empty the polarimeter cell and rinse with a small amount of racemic 1-phenylethylamine. Then, repeat Steps 16–17 for the racemic 1-phenylethylamine.

## DATA TABLES

**Part I Isolation of 1-phenylethylamine**

| | |
|---|---|
| Weight of starting material (g) | |
| Weight of product (g) | |

**Part II Measuring the optical rotation**

| | Starting material | Product |
|---|---|---|
| Height (cm) | | |
| Concentration (g/mL) | | |
| Angle of rotation, α (°) | | |

## DATA ANALYSIS

1. Calculate the percent yield of the product.
2. Calculate the specific rotation of the starting material.
3. What stereoisomer of 1-phenylethylamine did you isolate as your product? Explain.
4. Using the literature value for the specific rotation of S-(–)-1-phenylethylamine, calculate your product purity.