5.7: Optical Rotation

- An equal mixture of two enantiomers is called a racemic mixture or racemate.
- If two enantiomers rotate plane-polarized light in opposite directions, a racemate will not rotate light at all. The effects of the two enantiomers will cancel out.

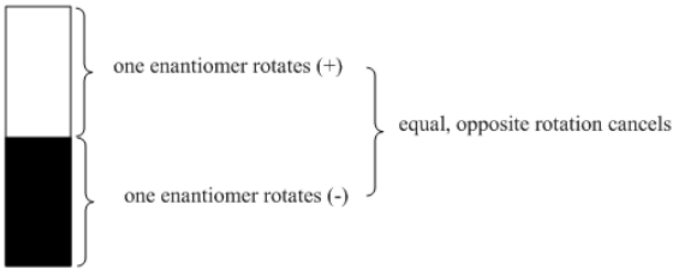


Figure 5.7.1: Optical rotation canceled out in a racemic mixture.

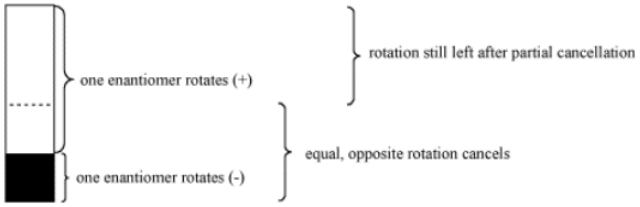


Figure 5.7.2: Optical rotation only partially canceled in a non-racemic mixture of enantiomers

e "optical purity" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer. It is expressed as a percentage. If the sample only rotates plane-polarized light half as much as expected, the optical purity is 50%.

Optical purity also corresponds to "enantiomeric excess". If the unknown sample rotates light 50% as much as a sample of pure enantiomer, it must contain 50% enantiomeric excess; the other 50% is a racemic mixture. In other words, if the sample is 75% of one enantiomer and 25% of the other, 50% of the mixture will simply cancel out in terms of optical activity. The remaining 50% will still exert optical activity, but only half as much as if the sample were 100% of that enantiomer.

These relationships could be expressed in formulae:

$$\text{Optical purity (op)} = \frac{\text{(optical rotation of pure compound)}}{\text{(optical rotation of pure enantiomer)}} \times 100\%$$

Enantiomeric excess (ee) = optical purity (that is, these numbers are always the same, although they represent different things)

$$\%\text{major enantiomer} = \text{enantiomeric excess} + \frac{100 - \text{enantiomeric excess}}{2} = 50 + \frac{\text{enantiomeric excess}}{2}$$

$$\%\text{minor enantiomer} = 100 - \%\text{ major enantiomer}$$

Exercise 5.7.1

The (+) enantiomer of compound A has an optical rotation of 75°. If a sample containing only compound A has an optical rotation of 50°, what is the composition of the sample?

Answer

A pure sample of A would have $[\alpha] = 75^o$

Optical purity or enatiomeric excess $= \frac{50}{75} = 66\%$

% major enantiomer $= 66 + \frac{34}{2} = 83\%$

% minor enantiomer $= 100 - 83 = 17\%$

Exercise 5.7.2

The (+) enantiomer of compound B has an optical rotation of 50º. If a sample containing only B contains 10% of the (+) enantiomer and 90% of the (-) enantiomer, what is the optical rotation value?

Answer

$$\%major = 90\%$$

$$\%minor = 10\%$$

Optical purity or enantiomeric excess $= \frac{X}{-50} = 90 - 10 - 80\%$

Solve for X.

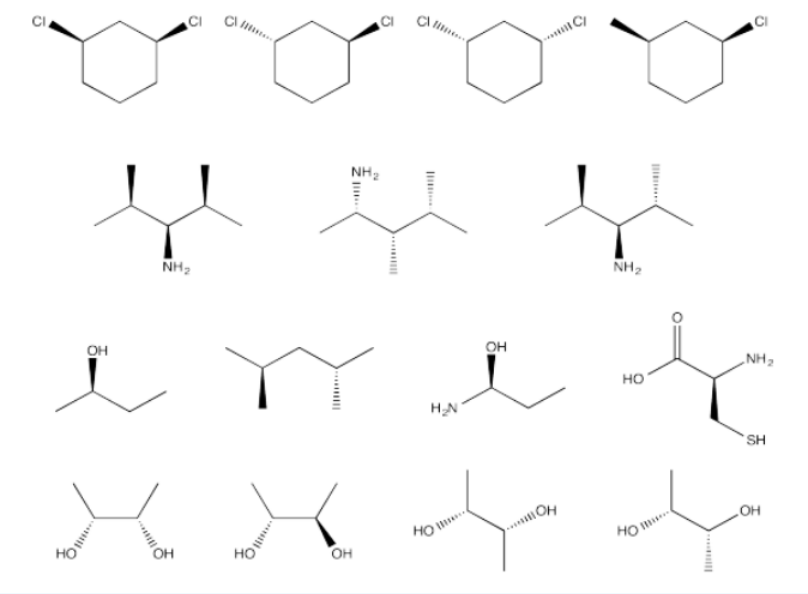
$$X = -40^{\circ}$$

Exercise 5.7.3

The (-) enantiomer of compound C has an optical rotation of -60. A sample of compound C is shown by chiral gas chromatography to contain only (-) C and no (+) C, but NMR analysis suggests the sample is about 50% ethyl acetate by weight. Predict the measured optical rotation of a 1 g/mL solution in dichloromethane, measured in a 1 dm cell.

Exercise 5.7.4

Which of the following compounds are optically active?



Answer