

- Chem 225b - Comprehensive Organic Chemistry

Problem Set 4, Stereochemistry

Chapter 5

Due: Monday, February 18, 2008

The Borremean
Rings

Versions of this symbol date to the time of the [Vikings](#). In the 15th century, it was apparently the symbol of a tripartite alliance of the Milanese families Visconti, Sforza and Borromeo via intermarriage.

Break any (wedding?) ring and the others separate, hence the alliance is broken. The rings form a [chiral object](#) (left) that are not superimposable on their [mirror image](#).

A set of Borremean rings has been used as the logo for a certain refreshment that extols purity, body, and flavor. Is the sense of chirality of the two sets of Borremean rings the same or different? For some other discourses on



chirality, see:

[Potpourri](#)

[The Figure 8 Knot](#)

[Gentlemen's
Neckties](#)

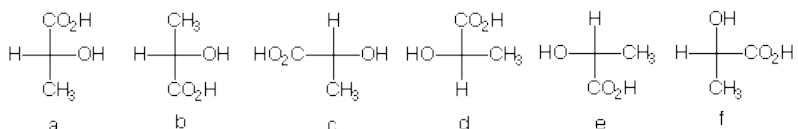
[Molecular Knots](#)

Read the [stereoisomers module](#) in the StudyAids and do the exercises. There is no need to record answers on your homework.

Don't forget the [Chirality of Shells](#) (Powerpoint).

1. When (*R*)-sec-butylbenzene, a.k.a 2-phenylbutane, undergoes free radical chlorination, four monochloro constitutional isomers are formed, the phenyl ring remaining intact. What are these structures? Draw them. Be explicit as to diastereomers, enantiomers, racemates, etc.

2. There are twelve possible Fischer projections for a given enantiomer of lactic acid. Why? (*S*)-(+)-Lactic acid, the cause of cramping during vigorous, [anaerobic physical exercise](#), was isolated from human muscle by [Berzelius](#). Which of the following Fischer projections represent (*S*)-(+)-lactic acid?



3. A mixture of enantiomers has $[\alpha]_D = -78^\circ$. If the rotation of the pure dextrorotatory enantiomer is $[\alpha]_D = +104^\circ$, what is the composition of the mixture?

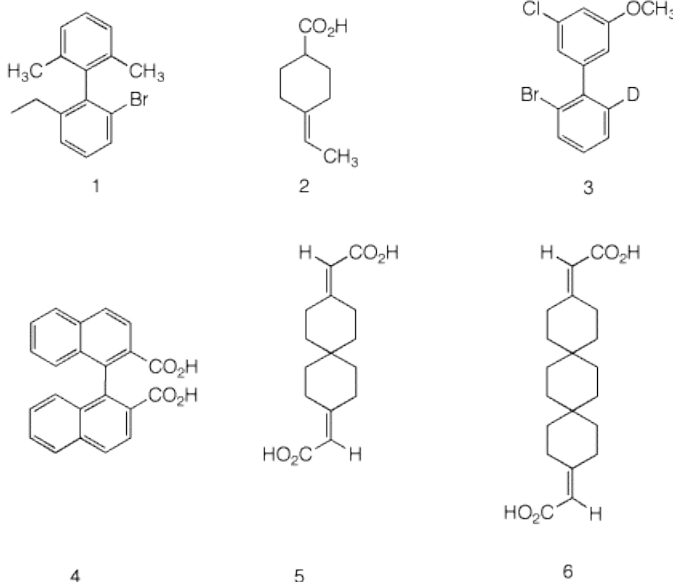
4. a) 1,2-Dibromoethane is optically inactive yet it has a dipole moment. Explain and illustrate.

b) meso-Tartaric acid exists in three staggered conformations, none of which has a [plane of symmetry](#). Yet the compound is optically-inactive. Explain and illustrate.

5. Which of the compounds on

the right are, in principle, capable of resolution? Explain and illustrate.

6. (*S*)- α -Phellandrene ($[\alpha]_D = +86^\circ$) is a monoterpene with the characteristic fragrance of dill. Monoterpenes, which are C_{10} compounds, are dimers of two identical, branched C_5 compounds. (*S*)- α -Phellandrene reacts with 2 moles of hydrogen gas in the presence of Pd to give two cyclohexanes **A** and **B**, both of which have the formula $C_{10}H_{20}$ and both of which are optically inactive. Compound **A** has an energy difference of 0.4 kcal/mol between its two chair conformations while compound **B** has a value of 3.8 kcal/mol for the same equilibrium.



a) Explain the loss of optical activity, the energy differences, and identify the structures **A** and **B**.

b) Circle the two C_5 units of (*S*)- α -phellandrene that dimerize. Ignore double bonds and stereochemistry.

5. (*R*)- α -Phellandrene has been reported to have a specific optical rotation of -217° . This observation suggests that the sample of the enantiomer used in problem 6 above is contaminated. Assume that the contaminant is the (*R*)-enantiomer and that the (*S*)-enantiomer is pure. What percentage of each enantiomer is present in the sample of problem 6? Show work.