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- Chem 220 - Organic Chemistry

Stereochemistry

Chapter 5

Due: Monday, October 5, 2009

## The Borremean Rings

Versions of this symbol date to the time of the Vikings. In the 15th century, it was 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 is not superimposable on its 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





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other discourses on chirality, see:

<u>Potpourri</u>

The Figure 8 Knot

Gentlemen's Neckties

Molecular Knots

**Snails and Crabs** 

Snails, Snakes and Darwin (html) 12 (pdf) 12

Read the <u>stereoisomers module</u> in the StudyAids and do the exercises. There is no need to record answers on your homework.

Don't forget the <u>Chirality of Shells</u> (Powerpoint). Do left-handed whelks have a better survival rate than their mirror image brethren? Click <u>here</u>.

- 1. When (R)-1-chloro-2-methylbutane undergoes free radical chlorination, five dichloro constitutional isomers are formed. 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  $\pm$ -chloropropionic acid. Six of the 24 of the total are shown below. Assign R,S-configurations to each one. Draw the remaining (S)-enantiomers.

- 3. A 3:1 mixture of enantiomers has  $[\pm]_D = -60^\circ$ . What is the rotation of the d- and l-enantiomers? Show work.
- 4. a) 1,2-Dibromoethane is optically inactive yet it has a dipole moment. Explain and illustrate. [Hint: Draw the staggered conformations and assess optical activity and dipole moment for each.]

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b) meso-Tartaric acid exists in three staggered conformations, none of which has a <u>plane of symmetry</u>. Yet the compound is optically-inactive. Indeed, the only conformation that has a plane of symmetry is quite unstable. Explain and illustrate.

5. Which of the following compounds are, in principle, capable of resolution? Explain and illustrate. [For 3-D Jmol views of these structures click here.: <u>5a</u>, <u>5b</u>, <u>5c</u>, <u>5d</u>, <u>5e</u>, <u>5f</u>.]

6. (S)- $\pm$ -Phellandrene ([ $\pm$ ]<sub>D</sub> = +86°) is a monoterpene with the characteristic fragrance of dill. (S)- $\pm$ -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 0.3 kcal/mol between its two chair conformations while compound **B** has a value of 3.9 kcal/mol for the same equilibrium.

Explain the loss of optical activity, the energy differences, and identify the structures  $\bf A$  and  $\bf B$ .

7. (R)-±-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 (R)-enantiomer is pure. What percentage of each enantiomer is present in the sample of problem 6? Show work.