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Chem 220 - Organic Chemistry

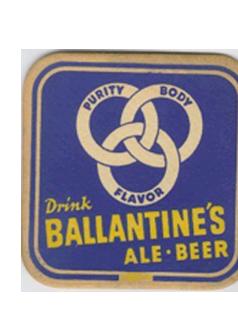
Problem Set 4

Chapter 5, Stereochemistry

Due: Monday, October 4, 2010

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 other discourses on chirality, see:





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<u>Potpourri</u>

The Figure 8 Knot

Gentlemen's Neckties

Molecular Knots

Snails and Crabs

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

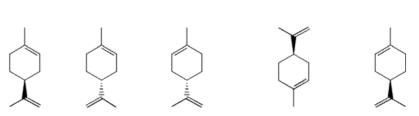
Read the <u>stereoisomers module</u> in the StudyAids and do the exercises. There is no need to record answers on your homework.

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. A 4:1 mixture of enantiomers has $[\alpha]_D = +120^{\circ}$. What is the rotation of the levorotatory enantiomer? The dextrorotatory enantiomer? Show work.
- 3. 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.]
- b) meso-2,3-Dibromobutane 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.
- 4. 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>a</u>, <u>b</u>, <u>c</u>, <u>d</u>, <u>e</u>, <u>f</u>.]

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- 5. Terpenes are naturally occurring compounds that are comprised of multiples of the C_5 unit isoprene (it looks like 2-methylbutane). Limonene is a monoterpene that occurs as both enantiomers in nature. The (R)-enantiomer has an orange, citrus-like aroma while the (S)-enantiomer has a harsher, lemony fragrance.
- a) Of the limonenes shown on the right, identify the R and S enantiomers.
- b) (R)-Limonene (d-limonene) is reported to have a rotation of $[\alpha]_D$ 123.8°. Its enantiomer is reported as $[\alpha]_D$ 101.3°. Assume that the enantiomer with the lower rotation is contaminated with the other enantiomer, calculate the percent of (+)- and (-)- enantiomers in the sample.
- c) When compounds containing double bonds are treated with H₂ in the presence of a noble metal catalyst, hydrogen is added to the double bond. In the case of (*R*)-limonene, two compounds, **A** and **B** (both C₁₀H₂₀), are formed. Are they necessarily formed in equal amounts? Explain. Is the ratio **A/B** different when (*S*)-limonene is used? Explain.



d) The energy difference between the chair conformations of **A** is greater than the energy difference of the chair conformations in **B**. What are the structures of **A** and **B**? What are the energy differences? Go here for data.