

Problem Set 4

Chapter 5

Due: Monday, February 13, 2006

[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](#)

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)-1-chloro-2-methylbutane is subjected to free radical chlorination, five dichloro constitutional isomers are possible.

- Draw them and name them with the appropriate R,S-descriptors.
- Two of the dichlorides are optically inactive. Which ones are they? Explain why and illustrate.

2. An optically-active compound **A** ($C_{10}H_{16}$, $[\alpha]_D = +124^\circ$) reacts with H_2 in the presence of a catalyst to provide compounds **B** and **C**. [Note: Hydrogen adds to double bonds under these conditions. Thus, ethylene is converted into ethane.] Both **B** and **C** show no optical rotation, even when the solutions are diluted, both compounds have the formula $C_{10}H_{20}$, and both compounds are 1,4-disubstituted cyclohexanes. Compound **B** has an energy difference of 3.9 kcal/mol between its two chair conformations.

- Determine the structures of **B** and **C**. Show your reasoning.
- What is the energy difference between the two chair conformations of **C**? Show work.
- The structure of **A** cannot be determined from the information provided. There are eight structures?, exclusive of which enantiomer is dextrorotatory, that fit the other data. Two of them are diastereomers. Draw the structures with at least one center of the (R)-configuration.
- A sample of **A** is isolated from mandarin oranges and it is found to have $[\alpha]_D = +31^\circ$. How much of the l-enantiomer is present in the sample? Show work.

3. Enriched **A** has an optical purity of 20% while **B** has an enantiomeric excess of 50%. Both compounds are rich in the (R)-enantiomer. Compounds **A** and **B** react to form two diastereomers $A_R B_R : A_S B_S$ and $A_R B_S : A_S B_R$. One diastereomer is 64% optically pure while the other one is only 33% optically pure.

- How much of each enantiomer is present in **A** and **B**? Show work.
- What are the percentages of each diastereomer? Show work.
- Show how the ee of each diastereomer is obtained.
- What is the optical purity of each diastereomer? Show work.

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.

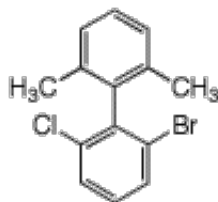
Explain and illustrate.

5. Which of the compounds on the right are, in principle, capable of resolution? Explain and illustrate.

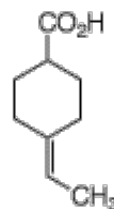
6. A mixture of enantiomers contains 1-1/2 times more of one and shows $[\alpha]_D -25.0^\circ$. What are the rotations of the pure enantiomers? Which one is in excess?

7. On the Lighter Side: The last eleven US Presidents (33-43) are shown below in order of service in addition to their party affiliation and their handedness. [Handedness is "officially" designated as how you write. Ford throwing out the "first pitch" indicates he is a rightie and not a southpaw (leftie). By the way, no photo has been converted to its mirror image by me but I found Truman as both "enantiomers".]

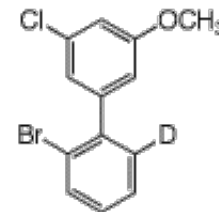
Everyone of these photos has something in common. Place that something (L or R) in the last column and then separate the last two columns as diastereomers and enantiomers. If you can correlate their diastereoisomerism with party affiliation, you are better than I am.



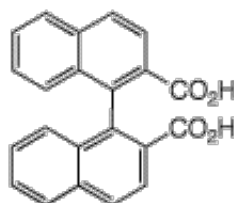
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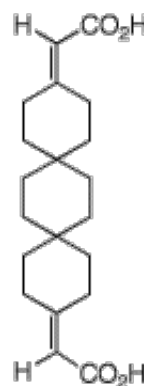
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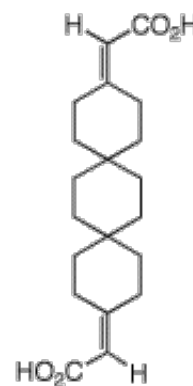
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4



5



6

President

Affiliation (D = Democrat; R = Republican)

Handedness

Chirality

Truman

D

L

Eisenhower

R

R

Kennedy

D

R

Johnson

D

R

Nixon
Ford
Carter
Reagan
Bush 41
Clinton
Bush 43

R
R
D
R
R
D
D
R

R
"R"
R
R
L
L
L
R

