- Chem 220 - Organic Chemistry

Problem Set 4, Solution Set

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 other discourses on chirality, see:

Snails, Snakes and
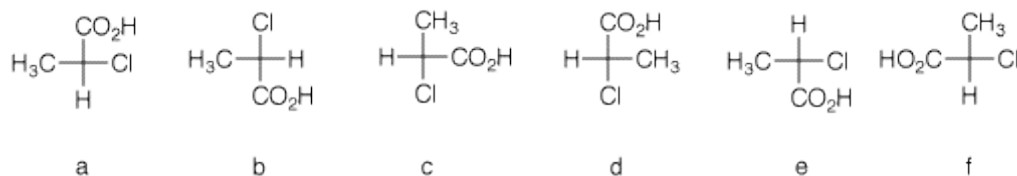Darwin (html) [1](#) [2](#)
(pdf) [1](#) [2](#)

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). Do left-handed whelks have a better survival rate than their mirror image brethren? Click [here](#).

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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. *The four constitutional isomers (same atom connectivity) are: 2, (3, 4), 5, 6 and 7. Still optically active: 6 (R), 3 (2S, 3S), 4 (2S, 3R) and 5 (R). Notice in 3 and 4, which are diastereomers, the R, S-configuration has changed altough the asymmetric center has not been altered. This is a change in group priority. #6 is racemic because abstraction of the tertiary hydrogen in the first propagation step creates a planar radical. In the second propagation step, chlorination occurs with equal facility on either face of the planar radical. #7 is achiral; two identical groups, $-CH_2Cl$, in the molecule.*
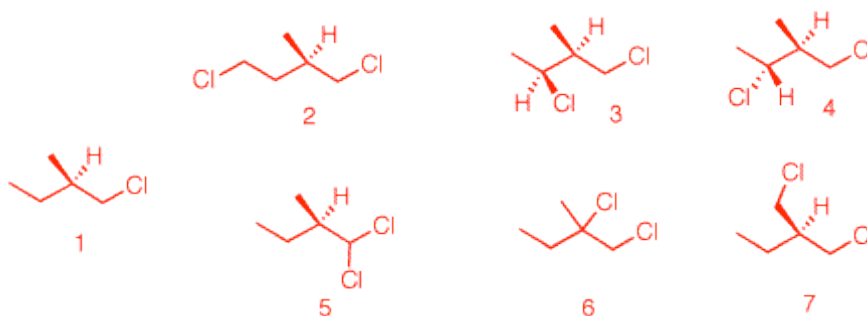
2. There are twelve possible Fischer projections for a given enantiomer of ±-chloropropionic acid. Six of the 24 of the total are shown below. Assign R,S-configurations to each one. Draw the remaining (*S*)-enantiomers.

CO₂H   Cl   CH₃   CO₂H   H   CH₃

H₃C—CI   H₃C—H   H—CO₂H   H—CH₃   H₃C—Cl   HO₂C—Cl

H   CO₂H   Cl   Cl   CO₂H   H

a   b   c   d   e   f

The configurations of a-f are shown. Row 1 illustrates what the Fischer projections mean. [See the end of the answer.] Consider the planar Fischer projection as a compass, NEWS. Convert the compass to a Fischer projection. If you think of N being in the rear, then W --> E --> S is clockwise. Think of the Fischer projection as a seatless, three-legged stool with WES as the legs and N as the spindle. Tip the Fischer projection forward to do this. If you rotate about the C-N axis, there are three different arrangements of the legs. but SEW can all occupy the position of N; four choices. For a given enantiomer of NEWS, there are 12 possible projections. Within the green box are the 12 projections for the case at hand. In 1 a-d, four different groups are at N. Reading down the four columns a-d, one has the three permutations 1-2-3.

a (S)   b (S)   c (R)   d (S)   e (R)   f (R)
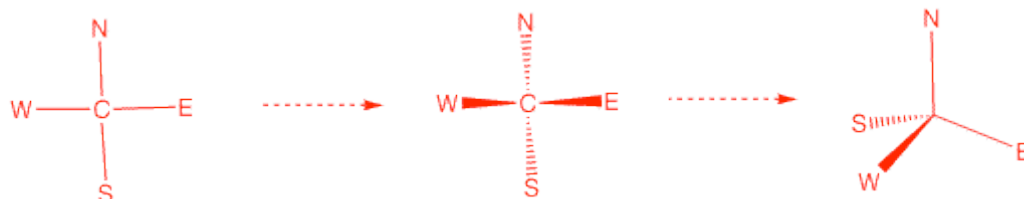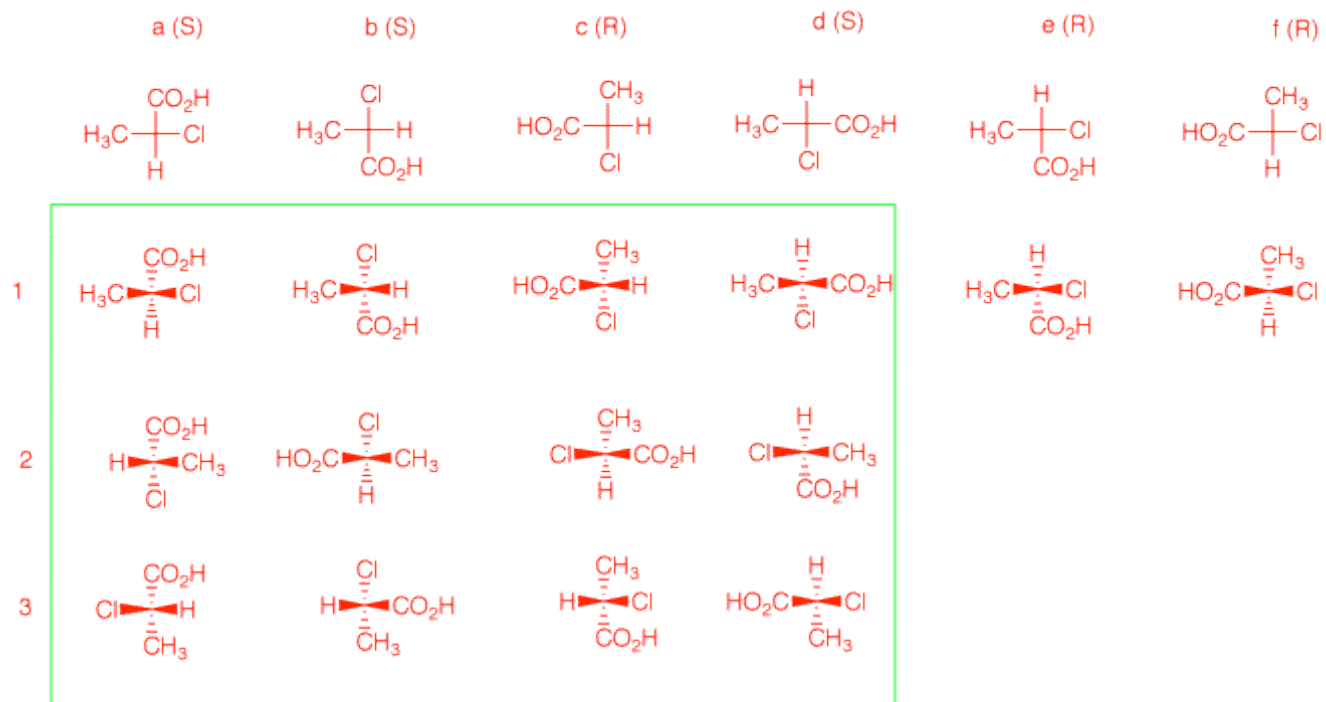
3. A 3:1 mixture of enantiomers has $[\alpha]_D$ = -60°. What is the rotation of the d- and l-enantiomers? Show work.

The major enantiomer is levorotatory based on the net negative rotation. The mixture is 3/4 levo (n_b) and 1/4 dextro (n_a). Thus,

obs. rotation = n_a (x) + n_b (-x) or, [n_a and n_b are the mole fractions; n_a + n_b = 1]

-60 = 1/4 (x) + 3/4 (-x)

-60 = -x/2

x = $[\alpha]_D$ = -120 for the levo enantiomer; $[\alpha]_D$ = +120 for the dextro enantiomer.

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.]

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

Optical activity is an algebraically additive property; dipole moments are cumulative in nature. The three staggered conformations of 1,2-dibromobutane are shown on the right in both Newman projections and sawhorse views. The anti conformation has no net dipole. The bond dipoles cancel. [Only the green *C-Br bond dipoles are shown.] The two gauche conformations have net dipoles. The vector sum of the bond dipoles gives the molecular dipole. As to optical activity, the anti conformation is achiral [center of symmetry]. The gauche conformations are chiral and form a racemate. No net optical activity.*

a   b   c

a'   b'   c'

anti   gauche 1   gauche 2

meso- tartaric acid

anti   gauche 1   gauche 2

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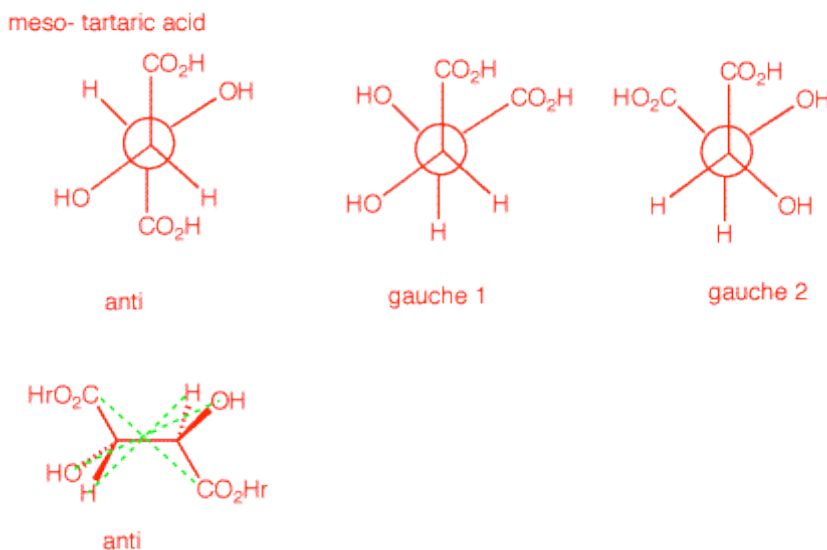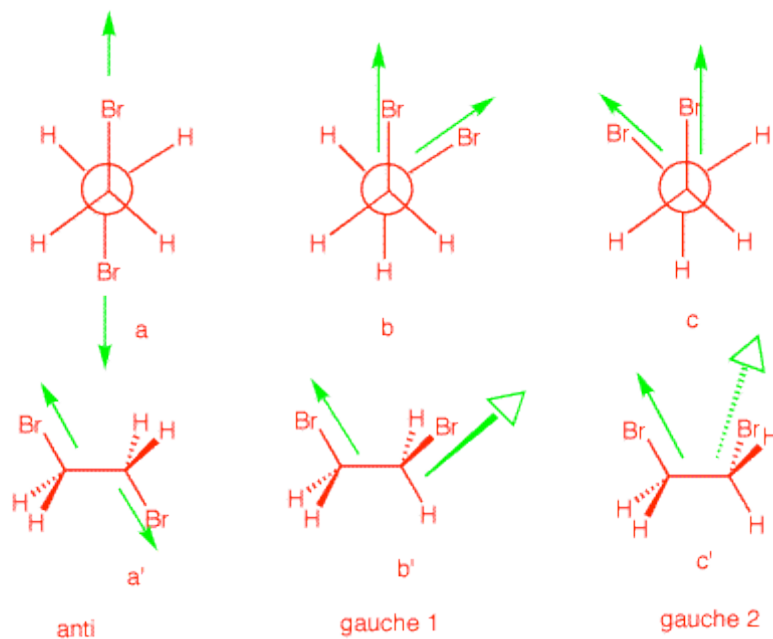
5. Which of the following compounds are, in principle, capable of resolution? Explain and illustrate. [For 3-D Jmol views of these structures click here.: 5a, 5b, 5c, 5d, 5e, 5f.]

a   b   c   d   e   f
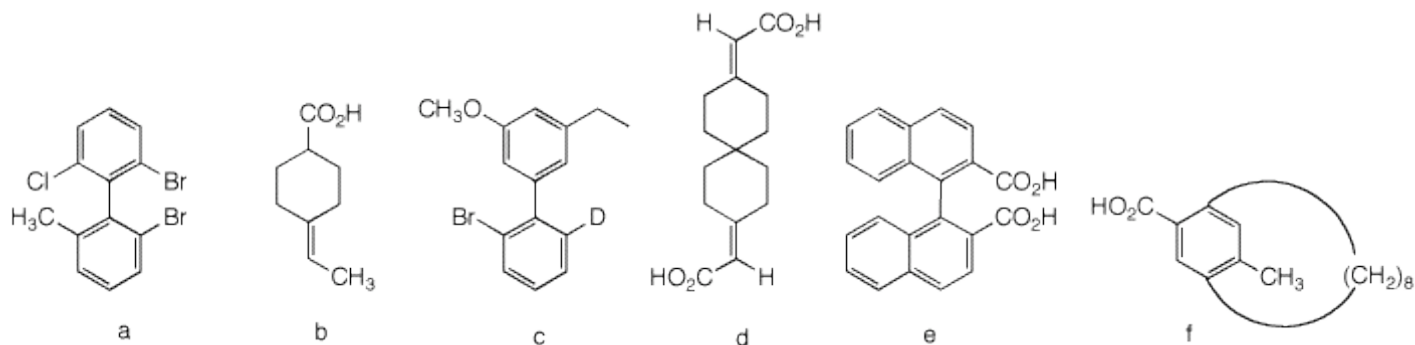
5a) This biphenyl is not planar owing to the four large groups that inhibit planarity. The two rings are orthogonal to one another thereby producing two non-superimposable mirror images.

b) This compound can be resolved. Imagine that the CO_2H group is above the plane of the molecule. Draw its mirror image. They are not superimposable. The doublebond and the 6-membered ring are an extension of the cumulated double bonds in the resolvable allenes.

c) Not resolvable. Free rotation about the biphenyl bond is too rapid for resolution.

d) This is an extension of 5b. It is resolvable. An even nummber of contiguous double bonds or 6-membered rings the compound is resolvable; odd number, not resolvable.

e) Resolvable. Same as 5a.

f) Eight CH_2 groups in a row are just enough to span the aromatic ring. Neither the CO_2H nor the methyl group can pass through the large ring. The compound is resolvable.

6. (S)-α-Phellandrene ([α]$_D$ = +86º) is a monoterpene with the characteristic fragrance of dill. (S)-±-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 **A** and **B**.

6) You can look up the structure of (S)-α-phellandrene. That two equivalents of hydrogen are absorbed means that there are two double bonds. [One triple bond is a possibility but there is no where to place it.] At least one of the double bonds must be in the ring and trisubstituted including either the methyl or isopropyl group. This is true because two cyclohexanes are formed on reduction. The group not involved in the trisubstituted double bond is the center of asymmetry. You can assume that the methyl and the isopropyl group are 1,4 to one another because A and B are both achiral [Need a plane of symmetry.] A must be 1,4-cis because it has the smaller energy difference. What are two numbers whose difference is 0.3 and whose sum is 3.9.

x + y = 3.9

x - y = 0.3

2x = 4.2

x = 2.1 (isopropyl); y = 1.8 (methyl)
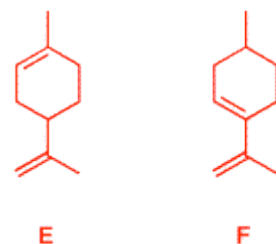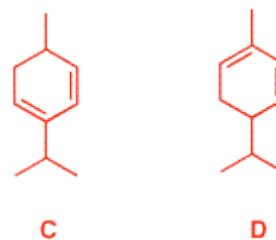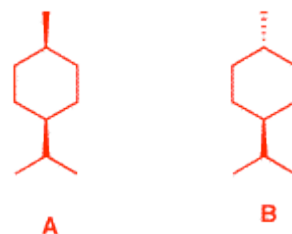
Given the information in the problem, there are only 4 possible

structures for α -phellandrene: C, D, E and F.

7. (*R*)-*α*-Phellandrene has been reported to have a specific optical rotation of -217º. 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.

In #3 we solved for the rotation. Here we calculate the % of each enantiomer. Pure (R)-(-) = [α]$_D$ = -217º; pure (S)-(+) = [α]$_D$ = +217º; impure (S) = [α]$_D$ = +86º.

obs. rotation = n$_+$ (rot +) + n$_-$ (rot -). Since n$_+$ + n$_-$ = 1, then n$_-$ = 1 - n$_+$, or

obs. rotation = n$_+$ (rot+) + (1-n$_+$) (rot-), or n$_+$ (rot+) - (n$_+$-1) (rot+), then factoring

obs. rotation = (rot+)(2n$_+$- 1), or

obs. rotation/(rot+) = (2n$_+$- 1) = ee (enantiomeric excess) = op (optical purity)

op = ee = 86/217 = 0.396 = 40%

Solving for n$_+$:

n$_+$ = (1 + 0.40)/2 = 0.70, then

n$_-$ = 1- 0.70 = 0.30.

(S)-*α*-Phellandrene = 70%; (R)-*α*-Phellandrene = 30%