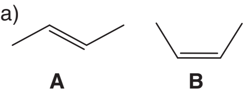
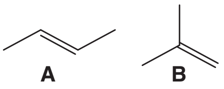
14 Organic chemistry 2: three-dimensional shapes

14.1 Describe the relationship between the following pairs of structures (e.g. whether they are enantiomers, diastereomers etc.)

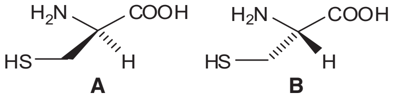
(a)



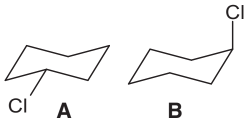
(b)



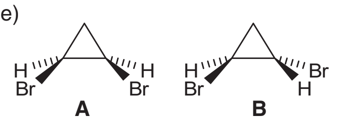
(c)



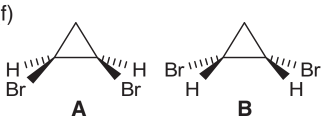
(d)



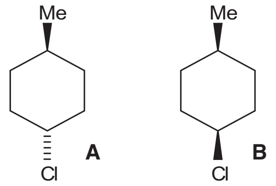
(e)



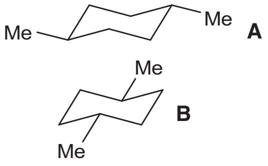
(f)



(g)

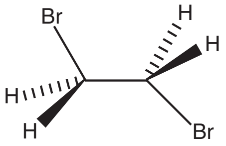


(h)

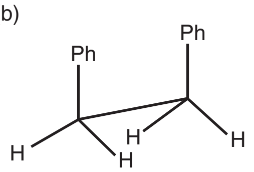


14.2 Redraw each of the following structures in the ways described in Box 14.2 on page 509, indicating the direction in which your views are taken. Describe the relationship between the substituents (other than hydrogen) on the two carbons.

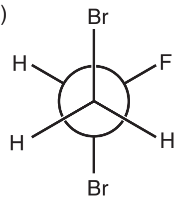
(a)



(b)



(c)



14.3 (a) Sketch (i) a graph of the energy of $BrCH_2CH_2Br$ as a function of the dihedral angle between the two C–Br bonds, and (ii) a similar graph for $BrCH_2CH_3$ as a function of the dihedral angle between the C–Br bond and one of the C–H bonds in the methyl group. Comment on the form of the two graphs.

(b) According to the Boltzmann distribution, if conformation A is higher in energy than conformation B by an amount ΔE the ratio r of the populations of the conformations is given by

$$r = \frac{\text{population of A}}{\text{population of B}} = \exp\left(\frac{-\Delta E}{RT}\right),$$

where R is the gas constant ($8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}$) and T is the absolute temperature. Use this relationship to calculate the ratio of the populations of the *gauche* and *anti* conformers of butane, the energy profile for which is shown in Fig. 14.9 on page 510, at 298 K and at 398 K.

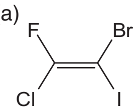
(c) If the number of molecules in conformer A is N_A and the number in conformer B is N_B, then it follows that $r = N_A/N_B$. The *fraction* of molecules which are in conformer A is given by $N_A/(N_A + N_B)$. Show that

$$\frac{N_A}{N_A + N_B} = \frac{r}{1 + r}.$$

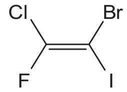
Hence work out the percentage of butane in the *gauche* and *anti* conformers at 298 K and at 398 K.

14.4 Using the CIP convention (Box 14.3 on page 515) assign *E*/*Z* labels to the double bonds in the following molecules.

(a)

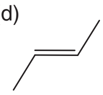


(b)

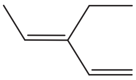


(c)

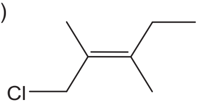
(d)



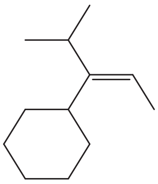
(e)



(f)

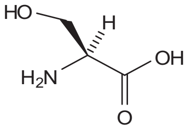


(g)



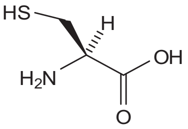
14.5 Using the CIP convention, assign *R*/*S* labels to the chiral centre or centres in the following molecules.

(a)



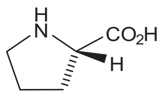
serine

(b)



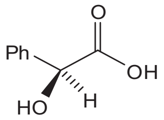
cysteine

(c)



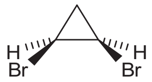
proline

(d)

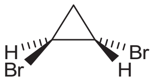


mandelic acid

(e)

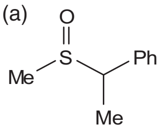


(f)

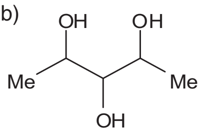


14.6 For both of the following compounds draw all possible stereoisomers, indicating which are enantiomers and which are diastereomers (use wedged and dashed bonds to differentiate the individual isomers). For which of these compounds does a *meso* isomer exist?

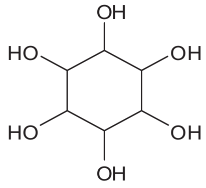
(a)



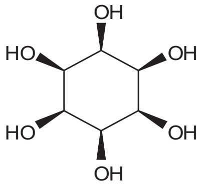
(b)



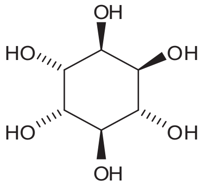
14.7 Inositol, (a), exists as nine stereoisomers, some of which are shown below.



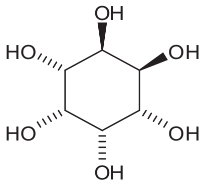
(a)



(b)



(c)



(d)

(a) Using symmetry arguments, explain why isomer (b) is achiral, and why isomer (c) is chiral.

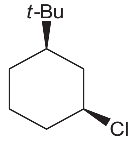
(b) Draw out the structures of all nine stereoisomers (using wedged and dashed bonds), identifying which are chiral.

(c) Draw isomer (d) with the ring in the chair conformation, being careful to place the OH groups in the correct 'up' and 'down' positions. Explain why the structure you have drawn is chiral, and consider what effect a ring flip would have on this structure.

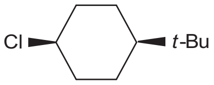
(d) Using your answer to (d), explain why it has not been possible to isolate the enantiomers of isomer (d).

14.8 Explain why the presence of a bulky substituent, such as *t*-Bu, results in a cyclohexane ring being 'locked' in a particular conformation. Draw the lowest energy conformations of (a) and (b), making it clear whether the Cl is axial or equatorial.

(a)



(b)



14.9 In the low-temperature spectrum of bromocyclohexane shown in Fig. 14.40 on page 533 the integral of the peak at 20.3 ppm was found to be 0.215 (arbitrary units) and that of the peak at 27.1 ppm was found to be 0.998 (same arbitrary units). Assuming that the integral is proportional to concentration, find the equilibrium constant for the axial $\rightleftharpoons$ equatorial equilibrium. Hence find $\Delta_r G^\circ$ for the process and the *A*-value. Compare your value with those in Table 14.2 on page 534. [Be sure to use the correct temperature.]