1) (8 pts total) Several compounds of the formula C₄H₆F₄ are drawn below in various different representations. To facilitate comparisons you may want to redraw/reorient the structures, but credit will be given only for correct answers to the questions below.

(a) (2 pts) Provide IUPAC names for just two (your choice) of compounds A-E in the spaces below. Don’t forget to include R/S labels where needed.

Label A Name (2S,3S)1,2,3,4-tetrafluorobutane
Label B Name (2R,3S)1,2,3,4-tetrafluorobutane
Label C Name (2S)1,1,1,3-tetrafluoro-2-methylpropane
Label D Name 1,1,1,2-tetrafluoro-2-methylpropane
Label E Name (2R)1,1,1,3-tetrafluoro-2-methylpropane

(b) (3 pts) Which of compounds A-E are chiral (optically active)? Please circle your answers.

A B C D E

(c) (1 pts) Find a meso compound among A-E. Please circle your answer.

A B C D E

(d) (1 pts) Which two compounds are a pair of enantiomers? Please circle your answers.

A B C D E

(e) (1 pts) Which two compounds are a pair of diastereomers? Please circle your answers.

A B C D E

2) (12 pts total + 3 Extra credit) Consider the following chair cyclohexanes. All but the first two are dimethyl substituted, and are therefore isomers. Their ∆H_f values in kcal/mol are shown below the structures.

(a) (4 pts) Draw the correct structures for the chair-chair flipped conformations in the boxes provided below. Be careful not to enantiomerize your compounds.

Labels

D -29.6 Labels

C -37.1

E -42.8 Labels

F -44.6

A -41.7 Labels

B -43.5

D -35.3

C -39.2

E -41.0

B -40.9
(b) (2 pts) Of the dimethylcyclohexanes A-F below, which two are chiral? Please circle your answers.

A  B  C  D  E  F

(c) (3 pts) First, assign the labels A-F to the above chair structures in the boxes provided. Now, among A-F, which three exist primarily in a single conformation? Don't forget that chair-chair flips (which you didn't draw) also can happen for the chair drawings in the left-hand column above; think about their energetics.

A  B  C  D  E  F

(d) (3 pts) Explain why compounds C and F have the same ∆H_f (-44.6 kcal/mol) and are more stable than any of the others. Is this the ∆H_f value you would have predicted from the energetics of the unsubstituted and monomethylated cyclohexanes?

Yes. The ∆H_f values for cyclohexane and methylcyclohexane are −29.6 and −37.1 kcal/mol, so we can say that adding a methyl in the equatorial position on cyclohexane changes the ∆H_f by −7.5 kcal/mol — i.e. −29.6 −7.5 = −37.1 kcal/mol. If we put another methyl group on, also equatorial and with no other interactions (i.e. not bumping into the first methyl), the ∆H_f should decrease again by the same increment — i.e. −37.1 −7.5 = −44.6, the energy of cis-1,3-dimethylcyclohexane C, and trans-1,4-dimethylcyclohexane F. The methyl groups have been added in their most stable (equatorial) orientations with no extra bumping, so these two are the lowest in energy of all the dimethylcyclohexanes.

(e) (3 pts EXTRA CREDIT) From the ∆∆H_f for the chair-chair flips you drew in (a), you can see that for methylcyclohexane the energy difference is 1.8 kcal/mol (the book said 1.74 but we’re rounding here) while that for 1,4-dimethylcyclohexane is exactly double this value, 3.6 kcal/mol. Why is the same not true for the 1,3- and 1,2-dimethylcyclohexanes, (∆∆H_f values are 5.4 and 2.6 kcal/mol, respectively).

Only in the 1,4 dimethyl substituted cases (both cis and trans) is there no interaction between the methyl groups in both conformations of the compound.

For cis-1,3-dimethylcyclohexane C, the diaxial conformation has extra bumping between the methyls, increasing the cost of putting them in axial positions to 5.4, an extra 1.8 kcal/mol beyond the 3.6 kcal/mol = 2 x 1.8, the sum of the energy costs of two methyls becoming axial.

For trans-1,2-dimethylcyclohexane B, the methyl-methyl interaction appears in the diequatorial form, where the two methyls are gauche. This is why the ∆H_f of B is about 1 kcal/mol higher than those of C and F, even though they’re all diequatorial. In the diaxial form, they have no interaction, and that conformation’s energy is essentially the same as in diaxial trans-1,4-dimethylcyclohexane F (∆H_f = -41.0 and -40.9 kcal/mol, respectively).