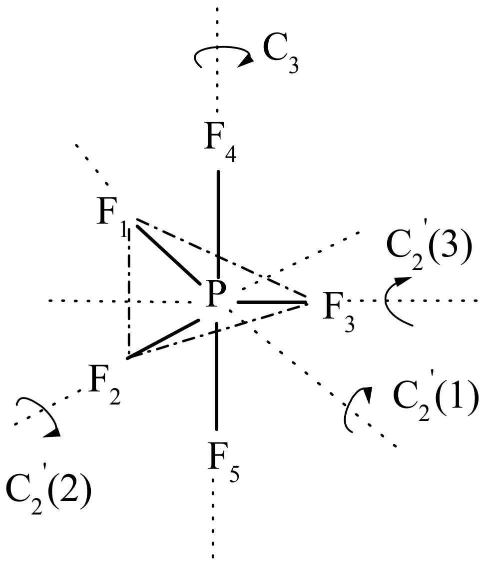
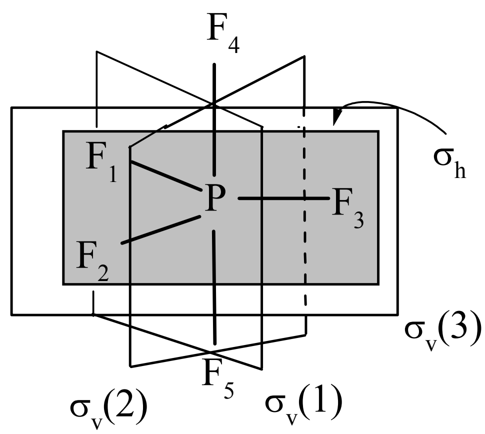
Chemistry 734b 2008

Problem Set 2 Due: February 13, 2008

This problem set covers a lot of the basics in symmetry operations, matrix algebra, and determining point groups. Like most things in group theory this problem set is pretty long so don't wait until the last moment. Show all your work.

1.) Consider the symmetry operations of PF_5 shown in the figures below:



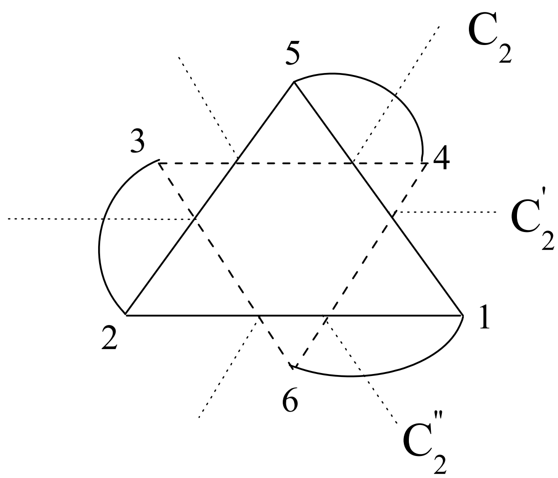


To which single symmetry operation of PF_5 are the following combinations equivalent?

a) $C_2'(1)\sigma_h$; b) $C_3^2C_2'(2)$ c) $S_3^1\sigma_v(1)$ d) $C_3^1C_2'(2)\sigma_v(2)$ e) $\sigma_h\sigma_v(1)C_2'(2)$?

2.) Identify all the independent symmetry operators associated with the molecule trans-N_2F_2. Use stereograms to set up a multiplication table for these operators to show that they do indeed form a group. *(It may help to spatially orientate the molecule by placing the y-axis along the N=N bond and the x-axis in the plane of the molecule. The z-axis then lies perpendicular to the plane of the molecule.*

3.) Consider the stylized drawing of tris-(ethylenediamine) cobalt (III) below:

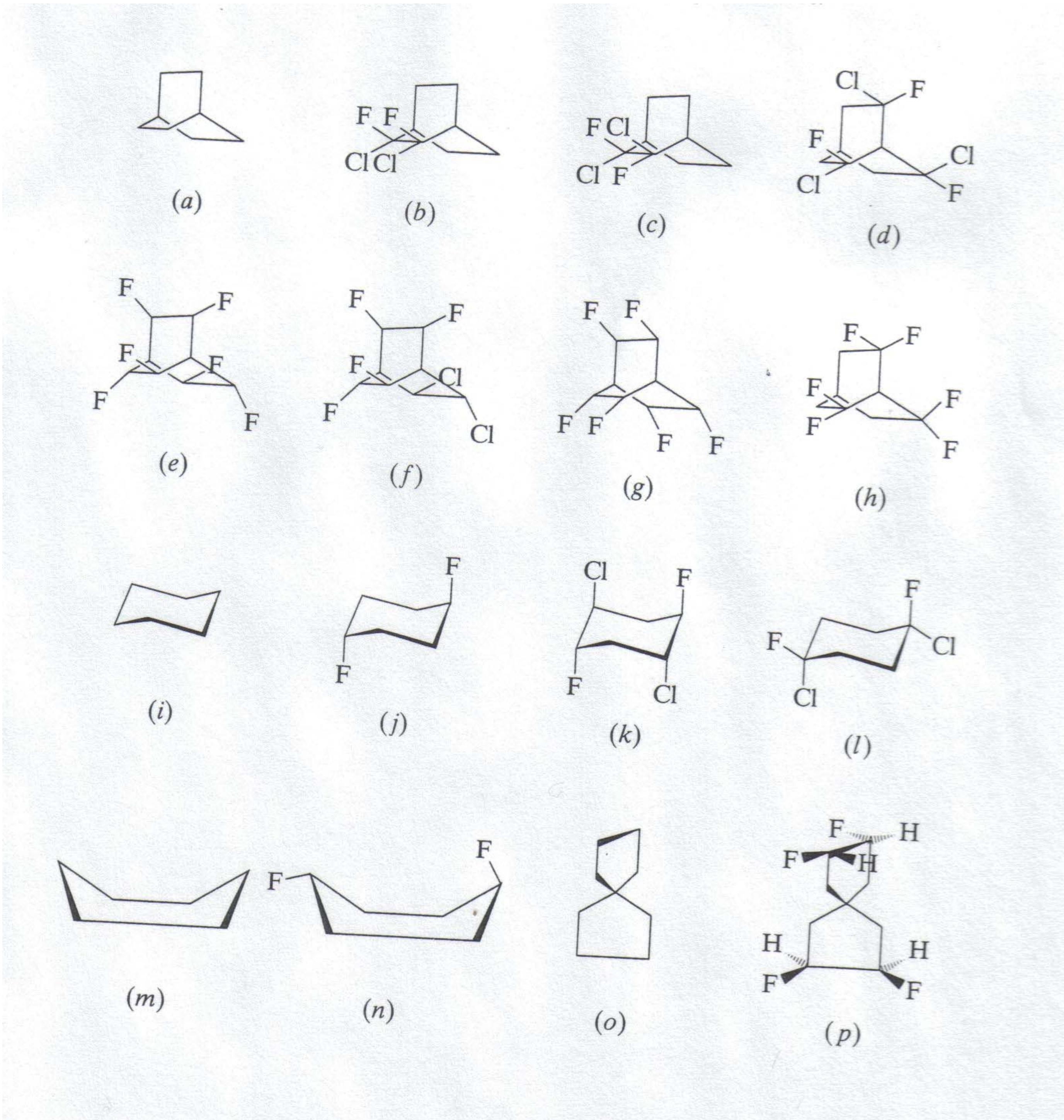


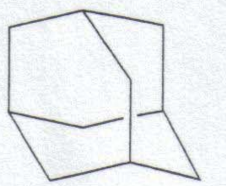
The symmetry operations for this species are E, C_3, C_3^2, C_2, C_2', and C_2''. The C_3 axis is perpendicular to the plane of the molecule as drawn on the page.

a) Construct a multiplication table for these operators. To show your work you need only manipulate the numbers labeling the ligands to determine the products.

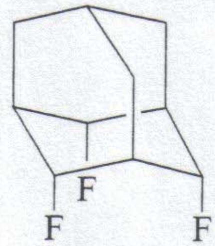
b) Divide the operations into classes by means of similarity transformations.

4.) Identify the point group of each of the molecules. To get full marks you must briefly but clearly indicate your reasoning for your choice of point group each structure.

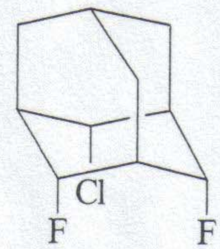




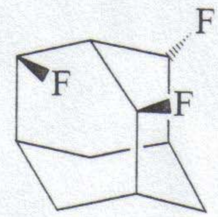
(q)



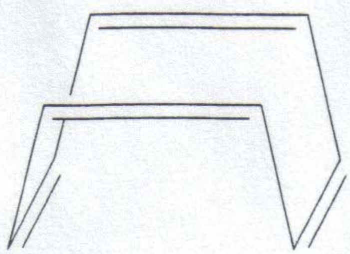
(r)



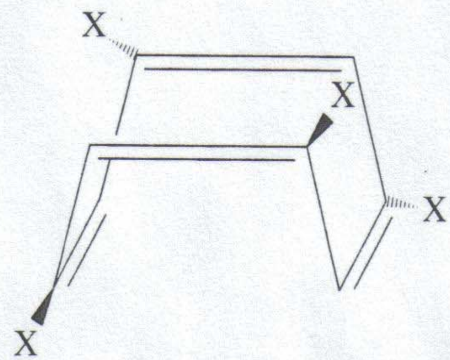
(s)



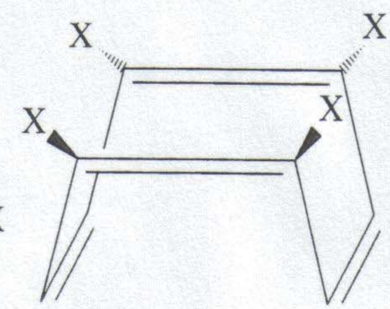
(t)



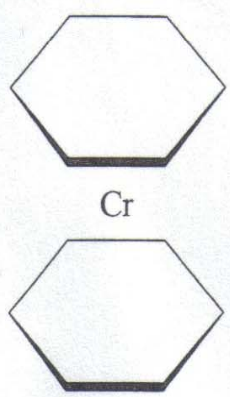
(u)



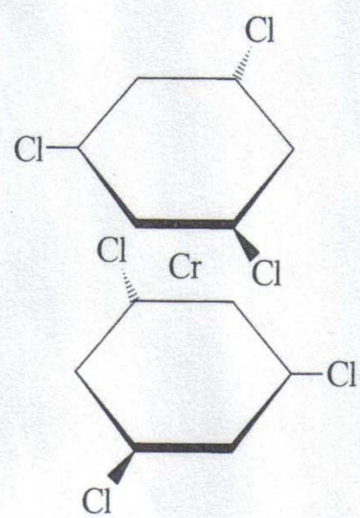
(v)



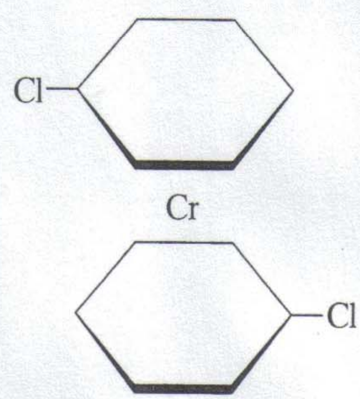
(w)



(x)



(y)



(z)

5.) For the following problem let

$$\widetilde{A} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 23 \\ 4 & 3 & 2 \end{pmatrix} \quad and \quad \widetilde{B} = \begin{pmatrix} 1 & 0 & 1 \\ 3 & -1 & -2 \\ 2 & 3 & 2 \end{pmatrix}$$

a) Calculate $\widetilde{A}+\widetilde{B},\ \widetilde{A}-\widetilde{B},\ \widetilde{A}\cdot\widetilde{B},\ \widetilde{B}\cdot\widetilde{A}$

b) Show that $\left(\widetilde{A}\cdot\widetilde{B}\right)^T = \widetilde{B}^T\cdot\widetilde{A}^T$

c) Find $\det(\widetilde{A})$, $\det(\widetilde{B})$, $\det(\widetilde{A}\cdot\widetilde{B})$, and $\det(\widetilde{B}\cdot\widetilde{A})$

d) Find $\widetilde{A}\otimes\widetilde{B}$

6.) Instead of using unit vectors along the x, y, and z-directions, one can generate a set of 3x3 matrix representations of the operators for the C_{3v} point group: {E, C_3, C_3^2, σ_v, σ_v', σ_v''} by using the figure below. For example, to generate a representation of C_3, we note that the C_3 operation takes atom 1 to 2, 2 to 3, and 3 to 1. In matrix notation this can be written as

$$C_3\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}\cdot\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 2 \\ 3 \\ 1 \end{pmatrix}$$

Write out the matrix representations for the other operations of the C_{3v} point group.