CHEMISTRY 273
PROBLEMS

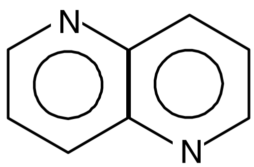
10. Read about assigning point groups: Carter, pp. 21-33; Cotton, chapter 3; Lowe, Appendix 13 (handout).

Assign point groups to the following molecules:

a. SF_5Cl

b. 1,3,5-Trichlorobenzene

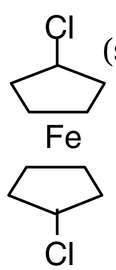
c. *trans*-$[CrCl_2(H_2O)_4]^+$ (ignore H atoms)

d. 

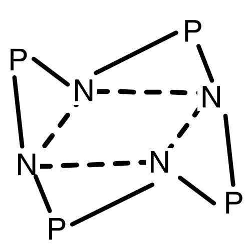
e. $OPCl_3$

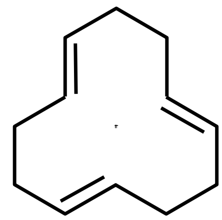
f. *trans*-$Pt(NH_3)_2Cl_2$ (ignore H atoms)

g. BIClF

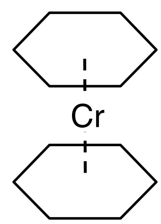
h. 

(sandwich)

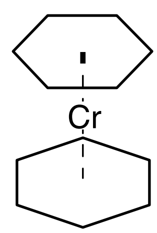
i. 

j. 

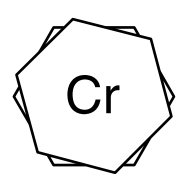
k. 1,3 -Dichloroallene

l. 

(sandwich)

m. 

(sandwich)

n. 

(sandwich)

o. A tennis ball (including the seam)

Selected answers: **b.** D_{3h} ; **e**. C_{3v} ; **i.** C_{2h} ; **o.** D_{2d}

11. Although we have not had time to go through many of the details of *ab initio* SCF calculations, I wanted to provide some experience in running GAUSSIAN and interpreting the output for an "all electron" calculation.

The commands for executing a STO-3G calculation for formaldehyde using G94 are on the handout. From the output:

(a) Indicate on a drawing the bond angles and bond lengths used in this calculation.

(b) How many electrons and how many occupied m.o.'s are there in H_2CO?

(c) Do you expect degenerate m.o.'s?

(d) What are the eigenvalues of the m.o.'s which most closely correspond to the:

(a) occupied π orbital

(b) unoccupied π^* orbital

(c) the two lone-pair n-orbitals on oxygen.

(e) What is the *total* energy calculated for H_2CO?

WE ARE GREATLY INDEBTED TO PHIL WENZEL for preparing this calculation.

12. Suppose $\underline{\underline{\mathbf{H}}}$ and $\underline{\underline{\mathbf{R}}}$ commute and $\underline{\underline{\mathbf{C}}}$ is a unitary transformation which diagonalizes $\underline{\underline{\mathbf{R}}}$:

$$\underline{\underline{\tilde{C}}}\,\underline{\underline{\mathbf{R}}}\,\underline{\underline{C}} = \underline{\underline{\mathbf{R}}}^{D} = \begin{pmatrix} r_{11} & 0 & 0 \\ 0 & r_{22} & 0 \\ 0 & 0 & \ddots \end{pmatrix}$$

and $\underline{\underline{\tilde{\mathbf{C}}}} = \underline{\underline{\mathbf{C}}}^{-1}$.

If all of the elements of $\underline{\underline{\mathbf{R}}}^{\mathbf{D}}$ are distinct (all r_{ii}'s unequal), show that $\underline{\underline{\tilde{\mathbf{C}}}}\,\underline{\underline{\mathbf{H}}}\,\underline{\underline{\mathbf{C}}} = \underline{\underline{\mathbf{D}}}$ a diagonal matrix. (*Hint:* To show that $\underline{\underline{\mathbf{C}}}$ diagonalizes $\underline{\underline{\mathbf{H}}}$, you will have to *explicitly* show $D_{ij} = 0$ for $i \neq j$.)