CHEMISTRY 273
PROBLEMS

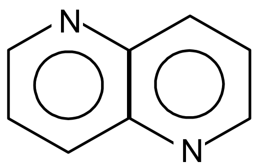
10. Read about assigning point groups: Carter, pp. 21-33; Cotton, chapter 3; Lowe, Appendix 13 (handout).

Assign point groups to the following molecules:

a. SF_5Cl

b. 1,3,5-Trichlorobenzene

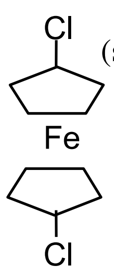
c. *trans*-$[CrCl_2(H_2O)_4]^+$ (ignore H atoms)

d. 

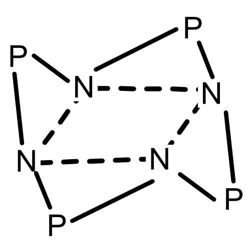
e. $OPCl_3$

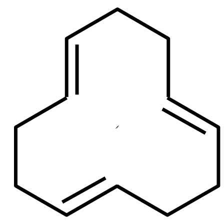
f. *trans*-$Pt(NH_3)_2Cl_2$ (ignore H atoms)

g. BIClF

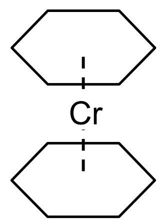
h. 

(sandwich)

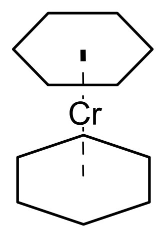
i. 

j. 

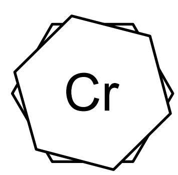
k. 1,3 -Dichloroallene

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 SPARTAN and interpreting the output for an "all electron" calculation.

    a. Conduct an STO-3G geometry optimization for formaldehyde H_2CO. Instructions accessing SPARTAN are available at:

    i. Indicate on a drawing the initial bond angles and bond lengths used in this calculation and those at the fial equilibrium geometry.

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

    iii. Do you expect degenerate m.o.'s?

    iv. What are the eigenvalues of the m.o.'s which most closely correspond to

    (a) occupied π orbital

    (b) unoccupied π^* orbital

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

    v. What is the dipole moment calculated with this basis?

    vi. For the energy of H_2CO at the equilibrium geometry give

    (a) total energy

    (b) kinetic energy

    (c) nuclear repulsion energy

    (d) nuclear-electron attraction energy

    (e) electron-electron repulsion energy

    b. Redo the calculation using 6-31G**, 6-311+G**, and a MØller Plesset MP2 calculation with a 6-311+G** basis. Compare the total energy for these calculations and the calculated dipole moments with the STO-3G in part 11.a.v and 11.a.vi.(a).

    c. Do a CI calculation for the equilibrium geometry of the first excited state of H2CO using CIS (singly excited determinants; and a 6-31G** basis.

    i. Indicate on a drawing the final geometry for the first excited singlet state.

    ii. What is the transition energy for this state?

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

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

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

If all of the elements of $\underline{\underline{\boldsymbol{R}}}^{\mathbf{D}}$ 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 $i \neq j$.)