3 Symmetry

3.1 CH_3F is a trigonal pyramidal molecule. It possesses a three-fold axis and three mirror planes.

(a) Make sketches showing the positions of these symmetry elements.

(b) Is the three-fold axis the principal axis of this molecule?

(c) Giving your reasons, classify the mirror planes as σ_v, σ_h or σ_d.

(d) To which point group does this molecule belong?

3.2 CH_2Cl_2 can be thought of as having tetrahedral coordination at carbon.

(a) Identify the symmetry elements which this molecule possesses and draw sketches showing their locations.

(b) Hence determine the point group to which this molecule belongs.

(c) Would your answers be altered if the Cl–C–Cl and H–C–H bond angles were not equal? Give your reasons.

3.3 The cyclopropenyl cation, $C_3H_3^+$, is planar with the carbon atoms, and the hydrogen atoms, being located at the vertices of an equilateral triangle.

(a) Identify the principal axis, and any other rotation axes.

(b) Identify any mirror planes, classifying them as σ_v, σ_h or σ_d.

(c) This molecule also possesses a three-fold axis of improper rotation; identify the position of this axis.

(d) To which point group does this molecule belong?

3.4 In a reference work the shapes of various molecules are described by giving the point groups to which they belong. Based on the information given below, sketch the shapes of the molecules.

(a) O_3 belongs to the point group C_{2v}.

(b) N_2O belongs to the point group $C_{\infty v}$.

(c) CS_2 belongs to the point group $D_{\infty h}$.

(d) $Ni(CN)_4^{2-}$ belongs to the point group D_{4h}.

(e) $FeCl_4^{2-}$ belongs to the point group T_d.

(f) PH_3 belongs to the point group C_{3v}.

(g) ClF_3 belongs to the point group C_{2v}.

(h) $CrCl_6^{3-}$ belongs to the point group O_h.

3.5 Use symmetry arguments to explain the following statements or answer the questions.

(a) In 1,2-diiodobenzene there are two different kinds of hydrogen atoms, whereas in 2-iodochlorobenzene there are four different kinds of hydrogen atoms.

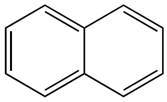
(b) In 1,4-dichlorobenzene there is only one kind of hydrogen atom.

(c) Spectroscopic data show that in a particular difluorinated benzene ($C_6H_4F_2$) there is only one type of fluorine. Giving your reasons, explain which substitution pattern or patterns are consistent with these data.

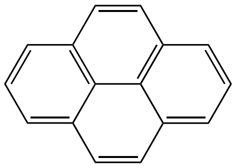
(d) Spectroscopic data show that in a particular trifluorinated benzene ($C_6H_3F_3$) there is only one type of fluorine. Which substitution pattern is consistent with these data? Give your reasons.

(e) For a different isomer of $C_6H_3F_3$ it is found that there are two different kinds of fluorine. Giving your reasons, explain which isomer this is.

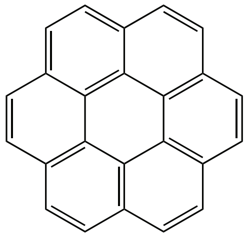
(f) Identify the number of different carbon environments there are in (i) naphthalene, (ii) pyrene, and (iii) coronene, whose structures are shown below. [Recall that the symmetry depends on the arrangement of the atoms, not the arrangement of any indicated bonds.]



naphthalene



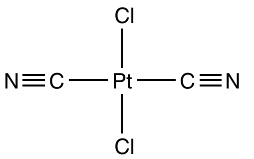
pyrene



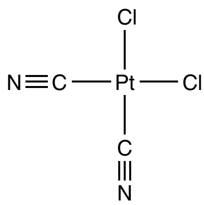
coronene

3.6 Use symmetry arguments to explain the following observations or answer the questions.

(a) All of the Cl atoms in square-planar $PtCl_4^{2-}$ are equivalent. For each of the isomers of $PtCl_2(CN)_2^{2-}$ shown below (which are based on square-planar coordination at Pt) there is only one chlorine environment.



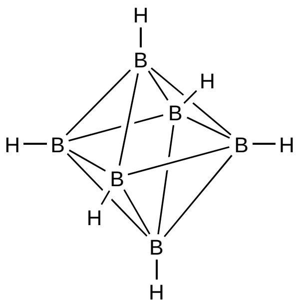
A



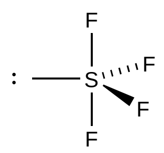
B

(b) The shape of IF_7 can be described as a pentagonal bipyramid. How many different fluorine environments are there?

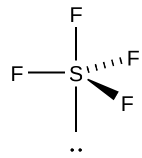
(c) All of the boron atoms in $B_6H_6^{2-}$, in which the boron atoms are arranged at the vertices of an octahedron, are equivalent.



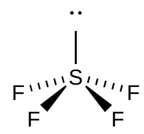
(d) Three possible structures for SF_4 are shown below; for each the position occupied by the lone pair is also shown. Structures **1** and **2** are based on a trigonal bipyramid, whereas structure **3** is based on a square-based pyramid. For each structure, how many different fluorine environments are there?



1



2



3

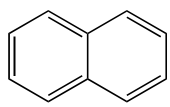
3.7 Use symmetry arguments to explain the following observations.

(a) NH_3 has a dipole pointing along its three-fold axis whereas BF_3 does not.

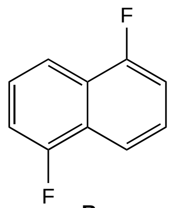
(b) CO_2 has no dipole, but OCS has a dipole parallel to its long axis (both molecules are linear).

(c) SF_6 has no dipole.

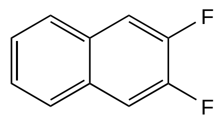
(d) Naphthalene (**A**) has no dipole, nor does the isomer of difluoronaphthalene shown in **B**, but the isomer **C** possess a dipole.



A



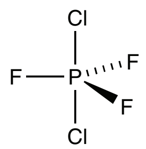
B



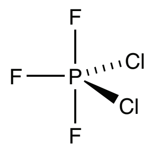
C

(e) PF_5 has no dipole despite the fact that all the fluorine atoms are not equivalent.

(f) Isomer **D** has no dipole, but isomer **E** does.



D



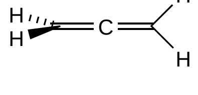
E

3.8 Use symmetry arguments to explain the following observations.

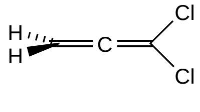
(a) None of CH_4, CH_3Cl, and CH_2ClF are chiral, but CHClFI is.

(b) No planar molecule can be chiral.

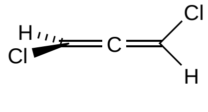
(c) Of the three allenes shown below, **A** and **B** are not chiral, whereas **C** is.



A



B



C

(d) Consider the transition metal complex $MA_2B_2C_2$ which has octahedral coordination about the central metal atom M, and where A, B and C are ligands. Draw the structures of all of the isomers of this complex and indicate which are chiral. [Hint: in drawing the isomers you simply need to consider arrangements in which the two A ligands are at either 90° or 180° to one another, and likewise for B and C.]

3.9 BeH_2 is a linear centro-symmetric molecule. It possesses a mirror plane, perpendicular to the long axis and passing through the Be; as is the usual convention, the long axis defines the z direction.

(a) Classify the following beryllium atomic orbitals as symmetric or anti-symmetric with respect to reflection in this mirror plane: $2s$, $2p_x$, $2p_y$ and $2p_z$.

(b) Construct a symmetric and an anti-symmetric symmetry orbital from the two hydrogen $1s$ AOs.

(c) Classify the AOs in (a) and the symmetry orbitals found in (b) according to reflection in the yz-plane.

3.10 OF_2 has a similar geometry to H_2O; assume that the molecule lies in the xz-plane. By considering their behaviour on reflection in the yz-plane, construct a symmetric and an anti-symmetric symmetry orbital from the two fluorine $2p_x$ AOs.

3.11 In Fig. 3.30 on page 95 we classified the oxygen AOs in H_2O according to reflection in the yz-plane. Do the same for the other symmetry operations of this molecule i.e. the C_2 rotation and reflection in the xz-plane.

Likewise, classify the two symmetry orbitals shown in Fig. 3.31 on page 96 according to these two symmetry operations.