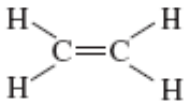
Problems

4.1 Determine the point groups for

a. Ethane (staggered conformation)
b. Ethane (eclipsed conformation)
c. Chloroethane (staggered conformation)
d. 1,2-Dichloroethane (staggered *anti* conformation)

4.2 Determine the point groups for

a. Ethylene



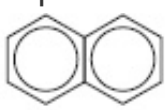
b. Chloroethylene
c. The possible isomers of dichloroethylene

4.3 Determine the point groups for

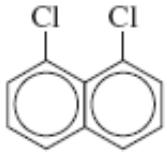
a. Acetylene
b. H—C ≡ C—F
c. H—C ≡ C—CH_3
d. H—C ≡ C—CH_2Cl
e. H—C ≡ C—Ph (Ph = phenyl)

4.4 Determine the point groups for

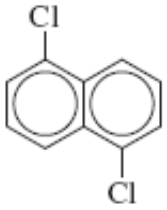
a. Naphthalene



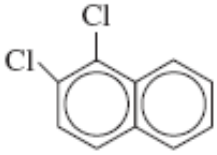
b. 1,8-Dichloronaphthalene



c. 1,5-Dichloronaphthalene

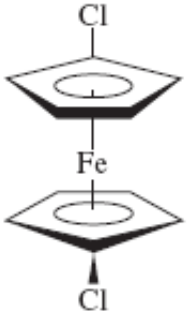


d. 1,2-Dichloronaphthalene

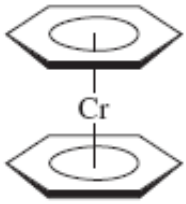


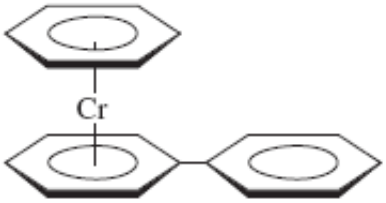
4.5 Determine the point groups for

a. 1,1' – Dichloroferrocene



b. Dibenzenechromium (eclipsed conformation)



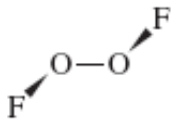


c.

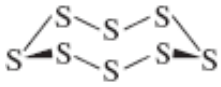
d. H_3O^+

e. O_2F_2

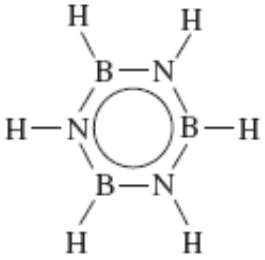
f. Formaldehyde, H_2CO



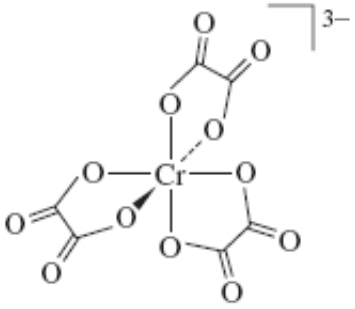
g. S_8 (puckered ring)



h. Borazine (planar)



i. $[Cr(C_2O_4)_3]^{3-}$

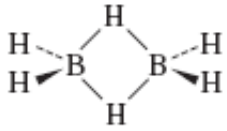


j. A tennis ball (ignoring the label, but including the pattern on the surface)

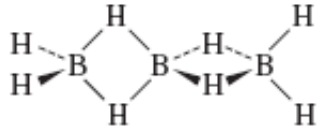
4.6 Determine the point groups for

a. Cyclohexane (chair conformation)

b. Tetrachloroallene $Cl_2C=C=CCl_2$
c. SO_4^{2-}
d. A snowflake
e. Diborane



f. The possible isomers of tribromobenzene
g. A tetrahedron inscribed in a cube in which alternate corners of the cube are also corners of the tetrahedron.
h. B_3H_8



i. A mountain swallowtail butterfly.
j. The Golden Gate Bridge, in San Francisco, CA

4.7 Determine the point groups for
a. A sheet of typing paper
b. An Erlenmeyer flask (no label)
c. A screw
d. The number 96
e. Five examples of objects from everyday life; select items from five different point groups
f. A pair of eyeglasses, assuming lenses of equal strength
g. A five-pointed star
h. A fork with no decoration
i. Wilkins Micawber, *David Copperfield* character who wore a monocle
j. A metal washer

4.8 Determine the point groups for
a. A flat oval running track
b. A jack (child's toy)

c. A person's two hands, palm to palm
d. A rectangular towel, blue on front, white on back
e. A hexagonal pencil with a round eraser
f. The recycle symbol, in three dimensions

g. The meander motif

h. An open, eight-spoked umbrella with a straight handle
i. A round toothpick
j. A tetrahedron with one green face, the others red

4.9 Determine the point groups for

a. A triangular prism
b. A plus sign
c. A t-shirt with the letter T on the front
d. Set of three wind turbine blades
e. A spade design (as on a deck of playing cards)
f. A sand dollar

g. Flying Mercury sculpture, by Giambologna at the Louvre in Paris, France
h. An octahedron with one blue face, the others yellow
i. A hula hoop
j. A coiled spring

4.10 Determine the point groups for the examples of symmetry in **Figure 4.1** .

4.11 Determine the point groups of the molecules in the following end-of-chapter problems from **Chapter 3** :

a. **Problem 3.40**
b. **Problem 3.41**

4.12 Determine the point groups of the molecules and ions in

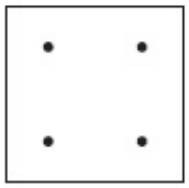
a. **Figure 3.8**
b. **Figure 3.15**

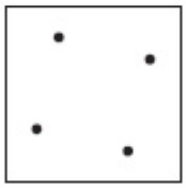
4.13 Determine the point groups of the following atomic orbitals, including the signs on the orbital lobes:

a. p_x
b. d_{xy}
c. $d_{x^2-y^2}$
d. d_{z^2}
e. f_{xyz}

4.14

a. Show that a cube has the same symmetry elements as an octahedron.
b. Suppose a cube has four dots arranged in a square on each face as shown. What is the point group?
c. Suppose that this set of dots is rotated as a set 10° clockwise on each face. Now what is the point group?





4.15 Suppose an octahedron can have either yellow or blue faces.

a. What point groups are possible if exactly two faces are blue?
b. What points are possible if exactly three faces are blue?
   Now suppose the faces have four different colors.
c. What is the point group if pairs of opposite faces have identical colors?

4.16 What point groups are represented by the symbols of chemical elements?

4.17 Baseball is a wonderful game, particularly for someone interested in symmetry. Where else can one watch a batter step from an on-deck circle of **a** symmetry to a rectangular batter's box of **b** symmetry, adjust a cap of **c** symmetry (it has OO on the front, for the Ozone City Oxygens), swing a bat of **d** symmetry (ignoring the label and grain of the wood) across a home plate of **e** symmetry at a baseball that has **f** symmetry (also ignoring the label) that has been thrown by a chiral pitcher having **g** symmetry, hit a towering fly ball that bounces off the fence, and race around the bases, only to be called out at home plate by an umpire who may have no appreciation for symmetry at all.

4.18 Determine the point groups for the following flags or parts of flags. You will need to look up images of flags not shown.

a. Botswana

b. Finland

c. Honduras

d. Field of stars in flag of Micronesia

e. Central design on the Ethiopian flag:

f. Turkey
g. Japan
h. Switzerland
i. United Kingdom (be careful!)

4.19 Prepare a representation flowchart according to the format of **Table 4.8** for SNF_3.

4.20 For *trans*-1,2-dichloroethylene, which has C_{2h} symmetry,

a. List all the symmetry operations for this molecule.
b. Write a set of transformation matrices that describe the effect of each symmetry operation in the C_{2h} group on a set of coordinates x, y, z for a point (your answer should consist of four 3 × 3 transformation matrices).

c. Using the terms along the diagonal, obtain as many irreducible representations as possible from the transformation matrices. You should be able to obtain three irreducible representations in this way, but two will be duplicates. You may check your results using the C_{2h} character table.
d. Using the C_{2h} character table, verify that the irreducible representations are mutually orthogonal.

4.21 Ethylene has D_{2h} symmetry.

a. List all the symmetry operations of ethylene.
b. Write a transformation matrix for each symmetry operation that describes the effect of that operation on the coordinates of a point x, y, z.
c. Using the characters of your transformation matrices, obtain a reducible representation.
d. Using the diagonal elements of your matrices, obtain three of the D_{2h} irreducible representations.
e. Show that your irreducible representations are mutually orthogonal.

4.22 Using the D_{2d} character table,

a. Determine the order of the group.
b. Verify that the E irreducible representation is orthogonal to each of the other irreducible representations.
c. For each of the irreducible representations, verify that the sum of the squares of the characters equals the order of the group.

- For each of the irreducible representations, verify that the sum of the squares of the characters equals the order of the group.

- Reduce the following representations to their component irreducible representations:

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_1	6	0	2	2	2
Γ_1	6	4	6	2	0

- **4.23** Reduce the following representations to irreducible representations:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	6	3	2
Γ_2	5	-1	-1

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

- **4.24** For D_{4h} symmetry use sketches to show that d_{xy} orbitals have B_{2g} symmetry and that $d_{x^2-y^2}$ orbitals have B_{1g} symmetry. (Hint: you may find it useful to select a molecule that has D_{4h} symmetry as a reference for the operations of the D_{4h} point group. Observe how the signs on the orbital lobes change as the symmetry operations are applied.)

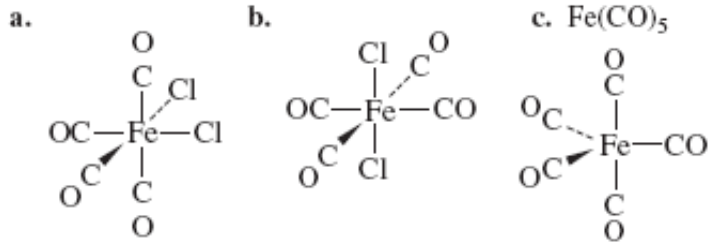
- **4.25** Which items in **Problems 4.5** through **Problem 4.9** are chiral? List three items *not* from this chapter that are chiral.

- **4.26** $XeOF_4$ has one of the more interesting structures among noble gas compounds. On the basis of its symmetry,

  a. Obtain a representation based on *all* the motions of the atoms in $XeOF_4$.
  b. Reduce this representation to its component irreducible representations.
  c. Classify these representations, indicating which are for translational, rotational, and vibrational motion.
  d. Determine the irreducible representation matching the xenon–oxygen stretching vibration. Is this vibration IR active?

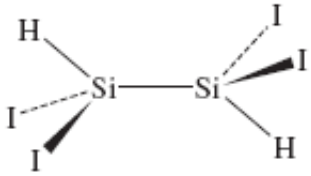
- **4.27** Repeat the procedure from the previous problem, parts a through c, for the SF_6 molecule and determine which vibrational modes are IR active.

- 4.28 For the following molecules, determine the number of IR-active C—O stretching vibrations:



- **4.29** Repeat **Problem 4.28** to determine the number of Raman-active C—O stretching vibrations.

- **4.30** The structure of 1,1,2,2-tetraiododisilane is shown here. (Reference: T. H. Johansen, K. Hassler, G. Tekautz, K. Hagen, J. *Mol. Struct*., **2001**, *598*, 171.)

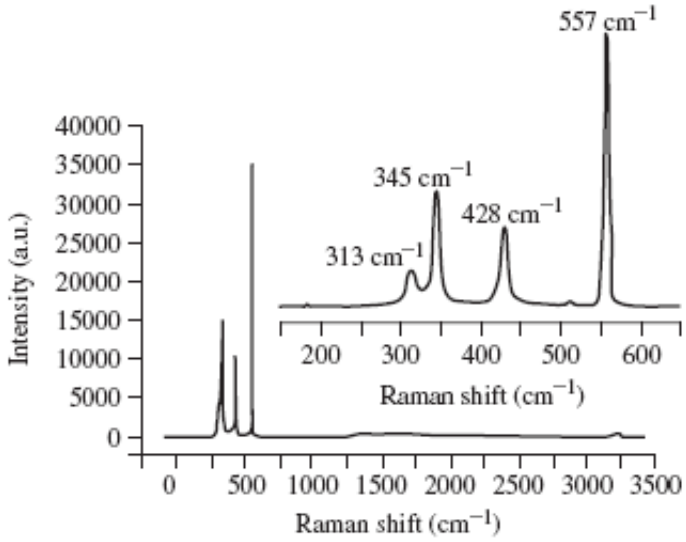


  a. What is the point group of this molecule?
  b. Predict the number of IR-active Si—I stretching vibrations.
  c. Predict the number of Raman-active Si—I stretching vibrations.

- **4.31** Both *cis* and *trans* isomers of $IO_2F_4^-$ have been observed. Can IR spectra distinguish between these? Explain, supporting your answer on the basis of group theory. (Reference: K. O. Christe, R. D. Wilson, C. J. Schack, *Inorg. Chem*., **1981**, *20*, 2104.)

- **4.32** White elemental phosphorus consists of tetrahedral P_4 molecules and is an important source of phosphorus for synthesis. In contrast, tetrahedral As_4 (yellow arsenic) is unstable, and decomposes to a grey As allotrope with a sheet structure. However, AsP_3, previously only observed at high temperature in the gas phase, has been isolated at ambient temperature as a white solid, where an As atom replaces one vertex of the tetrahedron.

a. The Raman spectrum of AsP_3, shown next, exhibits four absorptions. Is this consistent with the proposed structure? (Facile Synthesis of AsP_3, Brandi M. Cossairt, Mariam-Céline Diawara, Christopher C. Cummins. © 2009. The American Association for the Advancement of Science. Reprinted with permission from AAAS.)

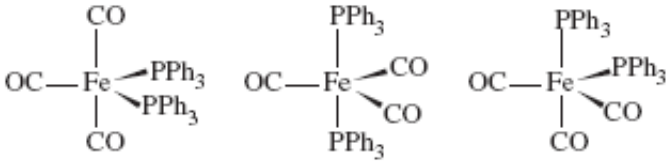


b. If As_2P_2 is ever isolated as a pure substance, how many Raman absorptions would be expected? (Reference: B. M. Cossairt, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 15501.)
c. Could a pure sample of P_4 be distinguished from pure AsP_3 simply on the basis of the number of Raman absorptions? Explain.

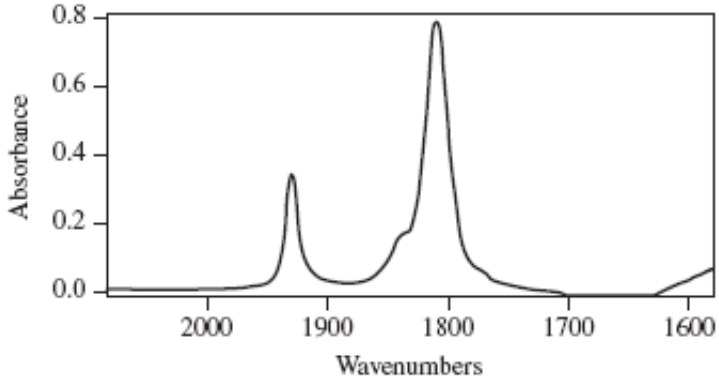
- **4.33** Complexes of the general formula $Fe(CO)_{5-x}(PR_3)_x$ are long known. The bimetallic $Fe_2(CO)_9$ reacts with triphenylphosphine in refluxing diethyl ether to afford a monosubstituted product $Fe(CO)_4(PPh_3)$ that exhibits (CO) absorptions at 2051, 1978, and 1945 cm in hexane. (N. J. Farrer, R. McDonald, J. S. McIndoe, *Dalton Trans.*, **2006**, 4570.) Can these data be used

to unambiguously establish whether the PPh_3 ligand is bound in either an equatorial or axial site in this trigonal bipyramidal complex? Support your decision by determining the number of IR-active CO stretching modes for these isomers.

- **4.34** Disubstituted $Fe(CO)_3(PPh_3)_2$ ((CO): 1883 cm; M. O. Albers, N. J. Coville, T. V. Ashworth, E. J. Singleton, *Organomet. Chem.*, **1981**, *217*, 385.) is also formed in the reaction described in **Problem 4.33** . Which of the following molecular geometries is supported by this spectrum? Support your decision by determining the number of IR-active CO stretching modes for these isomers. What does R. L. Keiter, E. A. Keiter, K. H. Hecker, C. A. Boecker, *Organometallics* **1988**, *7*, 2466 indicate about the infallibility of group theoretical CO stretching mode infrared spectroscopic prediction in the case of $Fe(CO)_3(PPh_3)_2$?



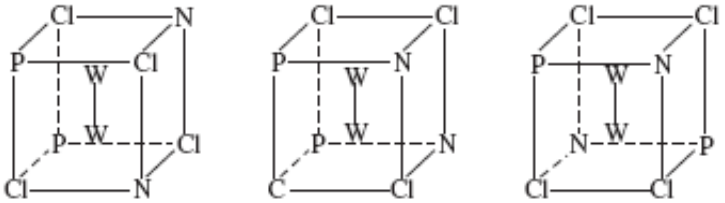
- **4.35** The reaction of $[Ti(CO)_6]^{2-}$ and chlorotriphenylmethane, Ph3CCl, results in rapid oxidation of $[Ti(CO)_6]^{2-}$ to afford a trityltitanium tetracarbonyl complex (P. J. Fischer, K. A. Ahrendt, V. G. Young, Jr., J. E. Ellis, Organometallics, 1998, 17, 13). On the basis of the IR spectrum (ν(CO)): 1932, 1810 cm^{-1}): acquired in tetrahydrofuran solution, shown next, is this complex expected to exhibit a square planar or a square pyramidal arrangement of four CO ligands bound to titanium? Does the spectrum rule out either of these possible geometries?



- **4.36** A related reaction to the one described in **Problem 4.35** , in which *cis* -$Mo(CO)_4(POPh_3)_2$ rearranges to *trans*-$Mo(CO)_4(POPh_3)_2$, has been probed mechanistically (D. J. Darensbourg, J. R. Andretta, S. M. Stranahan, J. H. Reibenspies, *Organometallics* **2007**, *26*, 6832.) When this reaction is conducted under an atmosphere of carbon monoxide, *cis*/*trans* isomerization does not occur. Instead a new complex ((CO) (hexane): 2085, 2000 (very weak),

1972, 1967 cm^{-1}) is formed (D. J. Darensbourg, T. L. Brown, *Inorg. Chem*. **1968**, *7*, 959.) Propose the formula of this Mo carbonyl complex consistent with the *v*(CO) IR spectra data. Support your answer by determining its expected number of CO stretching modes for comparison with the published spectrum.

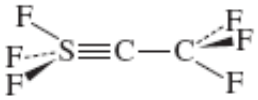
- **4.37** Three isomers of $W_2Cl_4(NHEt)_2(PMe_3)_2$ have been reported. These isomers have the core structures shown here. Determine the point group of each. (Reference: F. A. Cotton, E. V. Dikarev, W-Y. Wong, *Inorg. Chem.*, **1997**, *36*, 2670.)



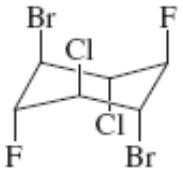
- **4.38** Derivatives of methane can be obtained by replacing one or more hydrogen atoms with other atoms, such as F, Cl, or Br. Suppose you had a supply of methane and the necessary chemicals and equipment to make derivatives of methane containing all possible combinations of the elements H, F, Cl, and Br. What would be the point groups of the molecules you could make? There are many possible molecules, and they can be arranged into five sets for assignment of point groups.

- **4.39** Determine the point groups of the following molecules:

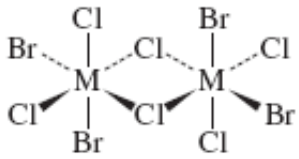
  a. F_3SCCF_3, with a triple S — C bond



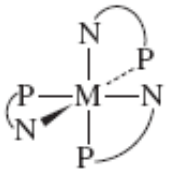
  b. $C_6H_6F_2Cl_2Br_2$, a derivative of cyclohexane, in a chair conformation



  c. $M_2Cl_6Br_4$, where M is a metal atom



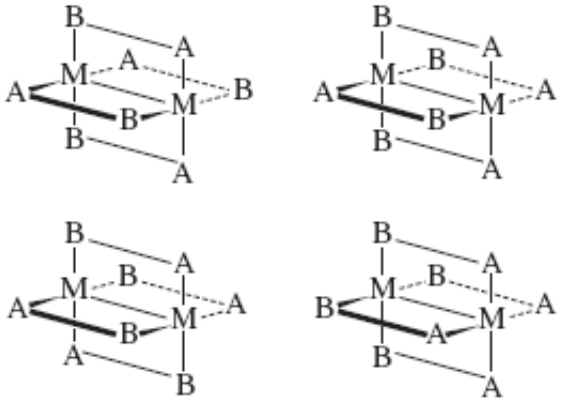
d. $M(NH_2C_2H_4PH_2)_3$, considering the $NH_2C_2H_4PH_2$ rings as planar



e. PCl_2F_3 (the most likely isomer)

•

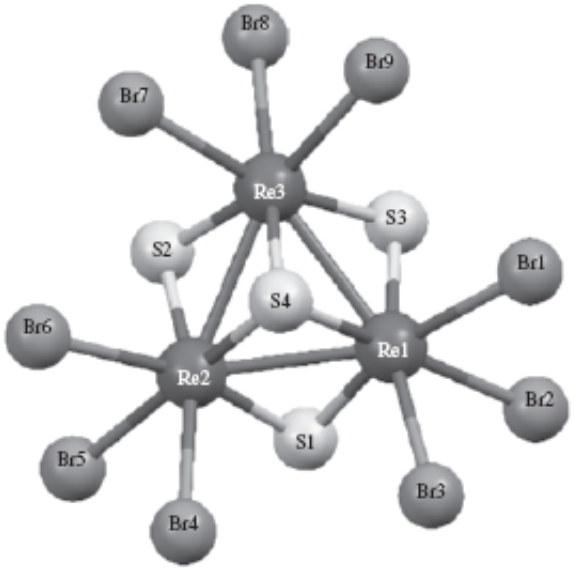
4.40 Assign the point groups of the four possible structures for asymmetric bidentate ligands bridging two metals in a “paddlewheel” arrangement: (Reference: Y. Ke, D. J. Collins, H. Zhou,



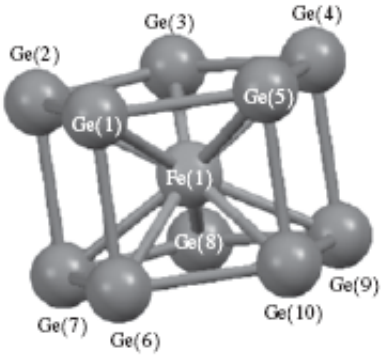
Inorg. Chem. 2005, 44, 4154.)

- **4.41** Determine the point groups of the following:

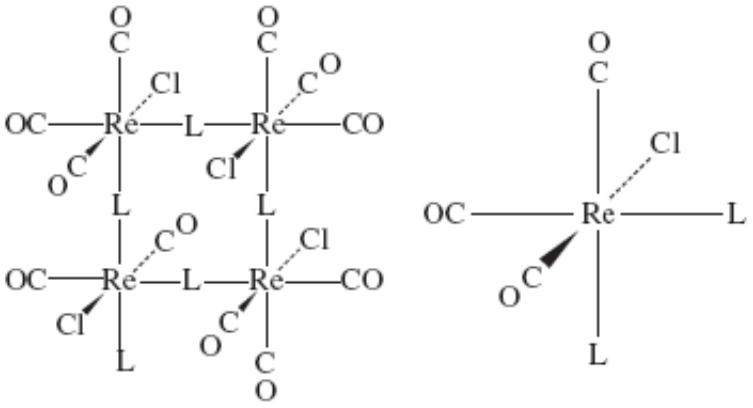
a. The cluster anion $[Re_3(\mu_3\text{ - }S)(\mu\text{ - }S)_3Br_9]^{2-}$ (Reference: H. Sakamoto, Y. Watanabe, T. Sato, Inorg. Chem., 2006, 45, 4578.)

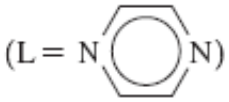


b. The cluster anion $[Fe@Ga10]^{3-}$ (Reference: B. Zhou, M. S. Denning, D. L. Kays, J. M. Goicoechea, J. Am. Chem. Soc., 2009, 131, 2802).

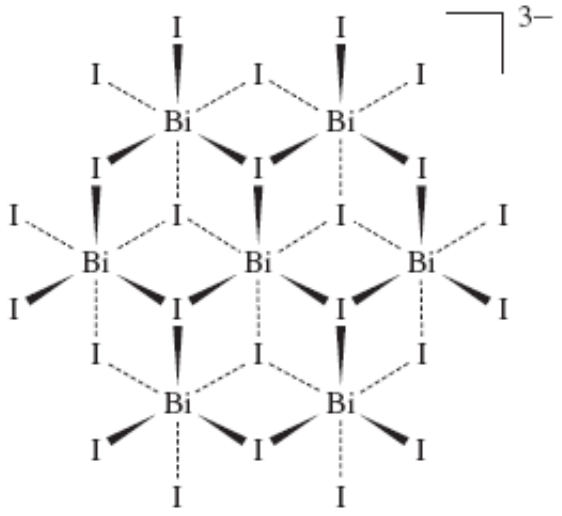


c. The “corner” and “square” structures: (Reference: W. H. Otto, M. H. Keefe, K. E. Splan, J. T. Hupp, C. K. Larive, Inorg. Chem. 2002, 41, 6172.)





d. The $[Bi_7I_{24}]^{3-}$ ion. (Reference: K.Y. Monakhov, C. Gourlaouen, R. Pattacini, P. Braunstein, Inorg. Chem., 2012, 51, 1562. This reference also has alternative depictions of this structure.



- **4.42** Use the Internet to search for molecules with the symmetry of

    a. The I_h point group
    b. The T point group
    c. The I_h point group
    d. The T_h point group

Report the molecules, the URL of the Web site where you found them, and the search strategy you used.