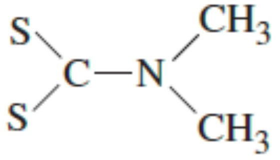
Problems

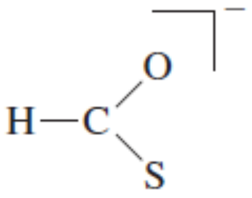
3.1 The dimethyldithiocarbamate ion, $[S_2CN(CH_3)_2]^-$, has the following skeletal structure:



a. Give the important resonance structures of this ion, including any formal charges where necessary. Select the resonance structure likely to provide the best description of this ion.
b. Repeat for the dimethylthiocarbamate ion, $[OSCN(CH_3)_2]^-$.

3.2 Several resonance structures are possible for each of the following ions. For each, draw these resonance structures, assign formal charges, and select the resonance structure likely to provide the best description for the ion.

a. Selenocyanate ion, $SeCN^-$
b. Thioformate ion,



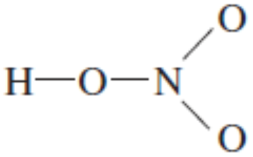
c. Dithiocarbonate, $[S_2CO]^{2-}$ (C is central)

3.3 Draw the resonance structures for the isoelectronic ions NSO^- and SNO^-, and assign formal charges. Which ion is likely to be more stable?

3.4 Three isomers having the formula N_2CO are known: ONCN (nitrosyl cyanide), ONNC (nitrosyl isocyanide), and NOCN (isonitrosyl cyanide). Draw the most important resonance structures of these isomers, and determine the formal charges. Which isomer do you predict to be the most stable (lowest energy) form? (See G. Maier, H. P. Reinsenauer, J. Eckwert, M. Naumann, M. De Marco, *Angew. Chem., Int. Ed.,* **1997** , *36* , 1707.)

3.5 Show the possible resonance structures for nitrous oxide, N_2O (the central atom is nitrogen). Indicate nonzero formal charges where they are present. Which resonance structure gives the best representation of this molecule?

3.6 Nitric acid, which exists as HNO_3 molecules in the absence of water, has the skeletal structure shown. Show the important resonance structures of HNO_3, and designate the formal charges on each atom.



3.7 L. C. Allen has suggested that a more meaningful formal charge can be obtained by taking into account the electronegativities of the atoms involved. Allen's formula for this type of charge—referred to as the *Lewis–Langmuir (L–L) charge* —of an atom, A, bonded to another atom, B, is

$$\text{L} - \text{L charge} = \underset{\text{of A}}{\text{(US) group number}} - \underset{\text{on A}}{\text{number of unshared electrons}} - 2\sum_{B} \frac{\chi_A}{\chi_A + \chi_B} \left(\begin{array}{l} \text{number of bonds} \\ \text{between A and} \\ \text{B} \end{array} \right.$$

where X_A and X_B designate the electronegativities. Using this equation, calculate the L–L charges for CO, NO_-, and HF, and compare the results with the corresponding formal charges. Do you think the L–L charges are a better representation of electron distribution? (See L. C. Allen, *J. Am. Chem. Soc.*, **1989**, *111* , 9115; L. D. Garner, T. L. Meek, B. G. Patrick, *THEOCHEM*, **2003**, *620*, 43.)

3.8 Give Lewis dot structures and sketch the shapes of the following:

a. $SeCl_4$
b. I_3^-
c. $PSCl_3$ (P is central)
d. IF_4^-
e. PH_2^-
f. TeF_4^{2-}
g. N_3^-
h. $SeOCl_4$ (Se is central)
i. PH_4^+

3.9 Give Lewis dot structures and sketch the shapes of the following:

a. ICl_2^-
b. H_3PO_3 (one H is bonded to P)
c. BH_4^-

d. $POCl_3$
e. IO_4^-
f. $IO(OH)_5$
g. $SOCl_2$
h. $ClOF_4^-$
i. XeO_2F_2

3.10 Give Lewis dot structures and sketch the shapes of the following:

a. SOF_6 (one F is attached to O)
b. POF_3
c. ClO_2
d. NO_2
e. $S2O_4^{2-}$ (symmetric, with an S—S bond)
f. N_2H_4 (symmetric, with an N—N bond)
g. $ClOF_2^+$
h. CS_2
i. $XeOF_5^-$

3.11 Explain the trends in bond angles and bond lengths of the following ions:

	X—O (pm)	**O—X—O Angle**
ClO_3^-	149	107°
BrO_3^-	165	104°
IO_3^-	181	100°

3.12 Select from each set the molecule or ion having the smallest bond angle, and briefly explain your choice:

a. NH_3, PH_3, or AsH_3

(halogen—sulfur—halogen angle)

b. NO_2^- or O_3

c. ClO_3^- or BrO_3^-

3.13

a. Compare the structures of the azide ion, N_3^-, and the ozone molecule, O_3.
b. How would you expect the structure of the ozonide ion, O_3^-, to differ from that of ozone?

3.14 Consider the series OCl_2, $O(CH_3)_2$, and $O(SiH_3)_2$, which have bond angles at the oxygen atom of 110.9°, 111.8°, and 144.1° respectively. Account for this trend.

3.15 Two ions isoelectronic with carbon suboxide, C_3O_2, are $N_5\ ^+$ and $OCNCO^+$. Whereas C_3O_2 is linear, both $N_5\ ^+$ and $OCNCO^+$ are bent at the central nitrogen. Suggest an explanation. Also predict which has the smaller outer atom— N—outer atom angle and explain your reasoning. (See I. Bernhardi, T. Drews, K. Seppelt, *Angew. Chem., Int. Ed.,* **1999** , *38* , 2232; K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem., Int. Ed* ., **1999** , *38* , 2004.)

3.16 Explain the following:

a. Ethylene, C_2H_4, is a planar molecule, but hydrazine, N_2H_4, is not.
b. $ICl_2\ ^-$ is linear, but $NH_2\ ^-$ is bent.
c. Of the compounds mercury(II) cyanate, $Hg(OCN)_2$, and mercury(II) fulminate, $Hg(CNO)_2$, one is highly explosive, and the other is not.

3.17 Explain the following:

a. PCl_5 is a stable molecule, but NCl_5 is not.
b. SF_4 and SF_6 are known, but OF_4 and OF_6 are not.

3.18 X-ray crystal structures of $ClOF_3$ and $BrOF_3$ have been determined.

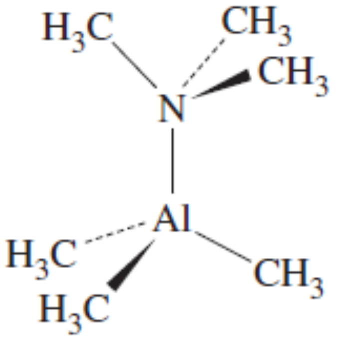
a. Would you expect the lone pair on the central halogen to be axial or equatorial in these molecules? Why?
b. Which molecule would you predict to have the smaller $F_{equatorial}$—central atom—oxygen angle? Explain your reasoning. (See A. Ellern, J. A. Boatz, K. O. Christe, T. Drews, K. Seppelt, Z. *Anorg. Allg. Chem* ., **2002** , *628* , 1991.)

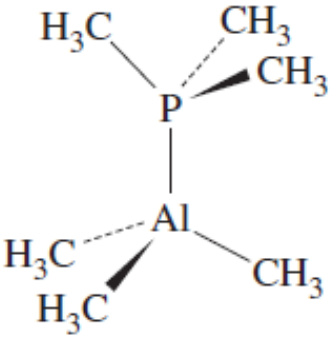
3.19 Make the following comparisons about the molecules shown next, and briefly explain your choices.

a. Which molecule has the smallerH_3C—group15 atom—CH_3 angle?

b. Which molecule has the smaller $H_3C—Al—CH_3$ angle?

c. Which molecule has the longer Al—C bond distance?





3.20 Predict and sketch the structure of the (as yet) hypothetical ion $IF_3{}^{2-}$.

3.21 A solution containing the $IO_2F_2{}^-$ ion reacts slowly with excess fluoride ion to form $IO_2F_3{}^{2-}$.

a. Sketch the isomers that might be possible matching the formula $IO_2F_3{}^{2-}$.

b. Of these structures, which do you think is most likely? Why?

c. Propose a formula of a xenon compound or ion isoelectronic with $IO_2F_3{}^{2-}$. (See J. P. Mack, J. A. Boatz, M. Gerken, *Inorg. Chem* ., **2008** , *47*, 3243.)

3.22 The $XeOF_3{}^-$ anion has been reported recently (D. S. Brock and G. J. Schrobilgen, *J. Am. Chem. Soc.* , **2010** , *133*, 6265).

a. Several structures matching this formula are conceivable. Sketch these, select the structure that is most likely, and justify your choice.

b. What is notable about the structure of this ion?

3.23 Predict the structure of $I(CF_3)Cl_2$. Do you expect the CF_3 group to be in an axial or equatorial position? Why? (See R. Minkwitz, M. Merkei, *Inorg. Chem* ., **1999** , *38* , 5041.)

3.24

a. Which has the longer axial P—F distance, $PF_2(CH_3)_3$ or $PF_2(CF_3)_3$? Explain briefly.

b. Al_2O has oxygen as central atom. Predict the approximate bond angle in this molecule and explain your answer.

c. Predict the structure of CAl_4. (See X. Li, L-S. Wang, A. I. Boldyrev, J. Simons, *J. Am. Chem. Soc* ., **1999** , *121* , 6033.)

3.25 The structures of TeF_4 and $TeCl_4$ in the gas phase have been studied by electron diffraction (S. A. Shlykov, N. I. Giricheva, A. V. Titov, M. Szwak, D. Lentz, G. V. Girichev, *Dalton Trans.* , **2010** , *39* , 3245).

a. Would you expect the Te—X (axial) distances in these molecules to be longer or shorter than than Te—X (equatorial) distances? Explain briefly.
b. Which compound would you predict to have the smaller X(axial)—Te—X(axial) angles? The smaller X(equatorial)—Te—X(equatorial) angles? Explain briefly.

3.26 $SeCl_6{}^{2-}$, $TeCl_6{}^{2-}$, and $ClF_6{}^{-}$ are all octahedral, but $SeF_6{}^{2-}$ and $IF_6{}^{-}$ are distorted, with a lone pair on the central atom apparently influencing the shape. Suggest a reason for the difference in shape of these two groups of ions. (See J. Pilmé, E. A. Robinson, R. J. Gillespie, *Inorg. Chem* ., **2006** , *45* , 6198.)

3.27 When XeF_4 is reacted with a solution of water in CH_3CN solvent, the product $F_2OXeN{\equiv}CCH_3$ is formed. Applying a vacuum to crystals of this product resulted in slow removal of CH_3CN:

$$F_2OXeN \equiv CCH_3 \rightarrow XeOF_2 + CH_3CN$$

Propose structures for $F_2OXeN{\equiv}CCH_3$ and $XeOF_2$. (See D. S. Brock, V. Bilir, H. P. A. Mercier, G. J. Schrobilgen, *J. Am. Chem. Soc* ., **2007** , *129* , 3598.)

3.28 The thiazyl dichloride ion, $NSCl_2{}^{-}$, is isoelectronic with thionyl dichloride, $OSCl_2$.

a. Which of these species has the smaller Cl—S—Cl angle? Explain briefly.
b. Which do you predict to have the longer S—Cl bond? Why? (See E. Kessenich, F. Kopp, P. Mayer, A. Schulz, *Angew. Chem., Int. Ed* ., **2001** , *40* , 1904.)

3.28 The thiazyl dichloride ion, $NSCl_2{}^-$, is isoelectronic with thionyl dichloride, $OSCl_2$.

  a. Which of these species has the smaller Cl—S—Cl angle? Explain briefly.
  b. Which do you predict to have the longer S—Cl bond? Why? (See E. Kessenich, F. Kopp, P. Mayer, A. Schulz, *Angew. Chem., Int. Ed* ., **2001** , *40* , 1904.)

- **3.29** Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.

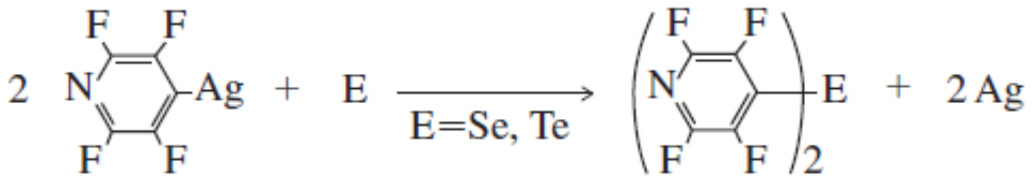
- **3.30**

  a. Are the CF_3 groups in $PCl_3(CF_3)_2$ more likely axial or equatorial? Explain briefly.
  b. Are the axial or equatorial bonds likely to be longer in $SbCl_5$? Explain briefly.

- **3.31** Of the molecules $C1SO_2CH_3$, $C1SO_2CF_3$, and $ClSO_2CCl_3$, which has the largest X—S—X angle? Explain briefly.

- **3.32** Of the molecules FSO_2F, $FSO_2(OCH_3)$, and FSO_2CH_3, which has the smallest O—S—O angle? Explain briefly.

- **3.33** Elemental Se and Te react with 4-tetrafluoropyridyl silver(I) to afford $Se(C_5F_4N)_2$ and $Te(C_5F_4N)_2$. Two independent bent molecules were found for each compound in the solid state with C—Se—C angles of 95.47(12)° and 96.16(13)°, and C—Te—C angles of 90.86(18)° and 91.73(18)°, respectively (Aboulkacem, S.; Naumann, D.; Tyrra, W.; Pantenburg, I. *Organometallics* , **2012** , *31* , 1559).



  a. Explain why the angles are more acute for the Te compound relative to the Se compound.

b. These angles are approximately 0.8° (Se) and 2.0° (Te) more acute than those in the related pentafluorophenyl (C_6F_5) compounds. The greater compression of these angles in the 4-tetrafluoropyridyl compounds has been postulated on the basis of group electronegativity differences. Explain the logic associated with this hypothesis.

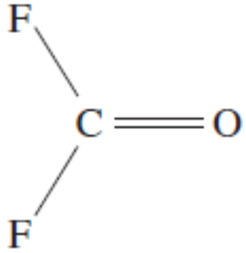
- **3.34** Which has the smaller F—P—F angle, PF_4^+ or PF_3O? Which has the longer fluorine–fluorine distance? Explain briefly.

- **3.35** Account for the trend in P—F_{axial} distances in the compounds $PF_4(CH_3)$, $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$. (See **Figure 3.19** .)

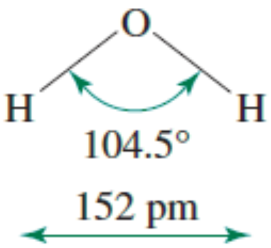
- **3.36** Although the C—F distances and the F—C—F bond angles differ considerably in $F_2C \equiv CF_2$, F_2CO, CF_4, and F_3CO^- (C—F distances 131.9 to 139.2 pm; F—C—F bond angles 101.3° to 109.5°), the F...F distance in all four structures is very nearly the same (215 to 218 pm). Explain, using the LCP model of Gillespie. (See R. J. Gillespie, *Coord. Chem. Rev* ., **2000** , *197* , 51.)

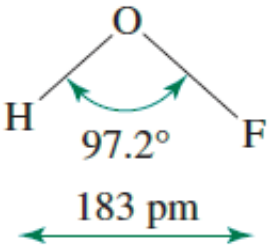
- **3.37** The Cl...Cl distance in CCl_4 is 289 pm, and the C—Cl bond distance is 171.1 pm. Using the LCP model, calculate the C—Cl distance in Cl_2CO, which has a Cl—C—Cl angle of 111.8°.

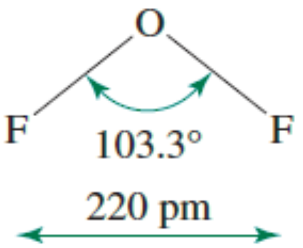
- **3.38** The F—C—F angle in F_2CO, shown here, is 109.5°; the C—F distance is 131.7 pm, and the F...F distance is 215 pm. On the basis of the LCP model, predict the C—F distance in the CF_3^+ ion.



- **3.39** Compounds in which hydrogen is the outer atom can provide challenges to theories of chemical bonding. Consider the following molecules. Using one or more of the approaches described in this chapter, provide a rationale for HOF having the smallest bond angle in this set.







- **3.40** For each of the following bonds, indicate which atom is more negative, then rank the series in order of polarity.

a. C—N
b. N—O
c. C—I
d. O—Cl
e. P—Br
f. S—Cl

- **3.41** Give Lewis dot structures and shapes for the following:

a. $VOCl_3$
b. PCl_3
c. SOF_4
d. SO_3
e. ICl_3
f. SF_6
g. IF_7
h. XeO_2F_4
i. CF_2Cl_2
j. P_4O_6

(P_4O_6 is a closed structure with overall tetrahedral arrangement of phosphorus atoms; an oxygen atom bridges each pair of phosphorus atoms.)

- **3.42** Give Lewis dot structures and sketch the shapes for the following:

a. PH_3
b. H_2Se
c. SeF_4
d. PF_5
e. IF_5
f. XeO_3
g. BF_2Cl
h. $SnCl_2$
i. KrF_2
j. $IO_2F_5{}^{2-}$

- **3.43** Which of the molecules in **Problem 3.41** are polar?

- **3.44** Which of the molecules in **Problem 3.42** are polar?

- **3.45** Provide explanations for the following:

  a. Methanol, CH_3OH, has a much higher boiling point than methyl mercaptan, CH_3SH.
  b. Carbon monoxide has slightly higher melting and boiling points than N_2 .
  c. The *ortho* isomer of hydroxybenzoic acid [$C_6H_4(OH)(CO_2H)$] has a much lower melting point than the *meta* and *para* isomers.
  d. The boiling points of the noble gases increase with atomic number.
  e. Acetic acid in the gas phase has a significantly lower pressure (approaching a limit of one half) than predicted by the ideal gas law.
  f. Mixtures of acetone and chloroform exhibit significant negative deviations from Raoult's law, which states that the vapor pressure of a volatile liquid is proportional to its mole fraction. For example, an equimolar mixture of acetone and chloroform has a lower vapor pressure than either of the pure liquids.
  g. Carbon monoxide has a greater bond-dissociation energy (1072 kJ/mol) than molecular nitrogen (945 kJ/mol).

- **3.46** Structural data for classical molecules is updated as new experiments are devised to improve precision and accuracy. Consider the trifluoromethyl compounds $E(CF_3)_3$ where E = P, As, Sb. The following C—E—C angles were determined for gas-phase $E(CF_3)_3$ by electron diffraction in the middle of the twentieth century: E = P, 99.6(25)°; E = As, 100.1(35)°; E = Sb, 100.0(35)°. (Berger, R. J. F.; Mitzel, N. W. *J. Mol. Struc.*, **2010**, *978*, 205).

a. Does the trend in these angles seem reasonable? Explain.
b. A more rigorous electron diffraction gas-phase experiment found a C—As—C angle for $As(CF_3)_3$ of 95.4(3)°, that compared favorably to the computationally determined angle of 95.9°. Which of the other two C—E—C angles seems more suspect, and should be reinvestigated using modern techniques? Explain.