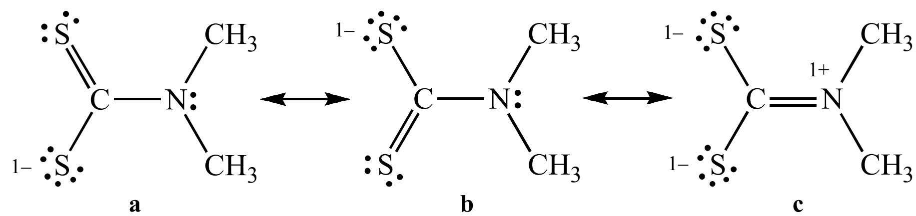
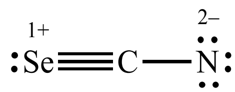
# CHAPTER 3: SIMPLE BONDING THEORY

**3.1** **a.** Structures a and b are more likely than c, because the negative formal charge is on the electronegative S. In c, the electronegative N has a positive charge.

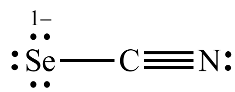


**b.** The same structures fit $(OSCN(CH_3)_2^-$. The structure with a 1– formal charge on O is most likely, since O is the most electronegative atom in the ion.

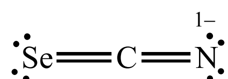
**3.2** **a.**



The formal charges are large, but match electronegativity.

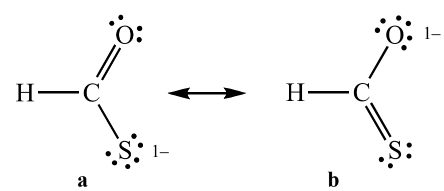


Negative formal charge of 1– on Se, a low electronegativity atom.

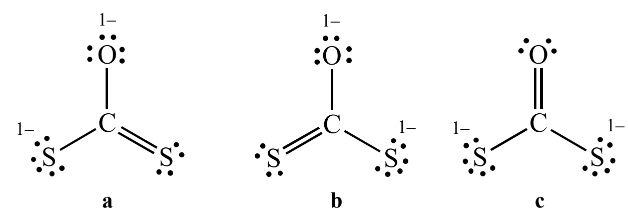


Negative formal charge on N, the most electronegative atom. Best resonance structure of the three.

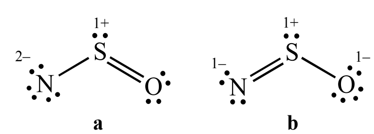
**b.** b is better than a, because the formal charge is on the more electronegative O.



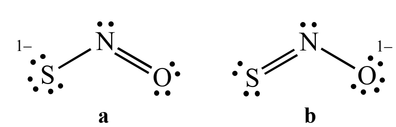
**c.** a and b are better than c, because one of the formal charges is on the more electronegative O.



**3.3** $NSO^-$: a has 2– formal charge on N, 1+ on S. Large formal charges, not very likely. b has 1– formal charges on N and O, 1+ on S, and is a better structure.



$SNO^-$: a has a 1– formal charge on S. Not very likely, doesn't match electronegativity (negative formal charge is not on most electronegative atoms). b has 1– formal charge on O, and is a better structure.

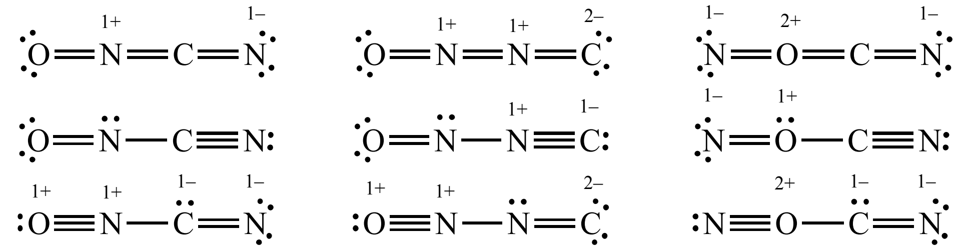


Overall, the S=N–O$^-$ structure is better based on formal charges, since it has only a negative charge on O, the most electronegative atom in the ion.

**3.4**

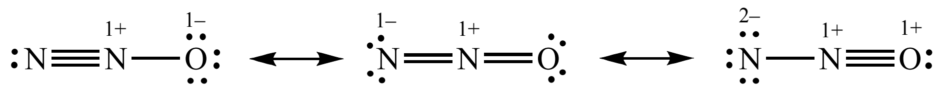
I II III

A B C



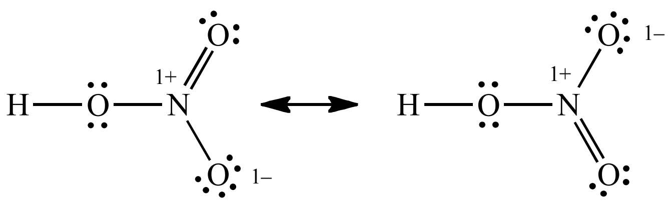
Structure IB is best by the formal charge criterion, with no formal charges, and is expected to be the most stable. None of the structures II or III are as good; they have unlikely charges (by electronegativity arguments) or large charges.

**3.5**

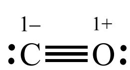
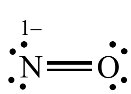
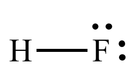


The first resonance structure, which places the negative formal charge on the most electronegative atom, provides a slightly better representation than the second structure, which has its negative formal charge on the slightly less electronegative nitrogen. Experimental measurements show that the nitrogen–nitrogen distance (112.6 pm) in $N_2O$ is slightly closer to the triple bond distance (109.8 pm) in $N_2$ than to the double bond distances found in other nitrogen compounds, and thermochemical data are also consistent with the first structure providing the best representation. The third resonance structure, with greater overall magnitudes of formal charges, is the poorest representation.

**3.6**

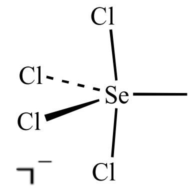


**3.7**

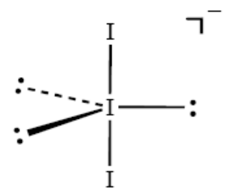
| *Molecule, Including Usual Formal Charges* | *Atom* | *Group Number* | *Unshared Electrons* | $2\left(\frac{\chi_A}{\chi_A + \chi_B}\right)$ | *Number of Bonds* | *Calculated Formal Charge* |
|---|---|---|---|---|---|---|
|  | C | 4 | 2 | $2\left(\frac{2.544}{2.544+3.61}\right)=0.83$ | 3 | –0.49 |
| | O | 6 | 2 | $2\left(\frac{3.61}{2.544+3.61}\right)=1.17$ | 3 | 0.49 |
|  | N | 5 | 4 | $2\left(\frac{3.066}{3.066+3.61}\right)=0.92$ | 2 | –0.84 |
| | O | 6 | 4 | $2\left(\frac{3.61}{3.066+3.61}\right)=1.08$ | 2 | –0.16 |
|  | H | 1 | 0 | $2\left(\frac{2.300}{2.300+4.193}\right)=0.71$ | 1 | 0.29 |
| | F | 7 | 6 | $2\left(\frac{4.193}{2.300+4.193}\right)=1.29$ | 1 | –0.29 |

Surprisingly, CO is more polar than FH, and $NO^-$ is intermediate, with C and N the negative atoms in CO and $NO^-$.

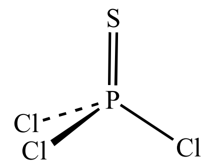
**3.8** **a.** $SeCl_4$ requires 10 electrons around Se. The lone pair of electrons in an equatorial position of a trigonal bipyramid distorts the shape by bending the axial chlorines back.



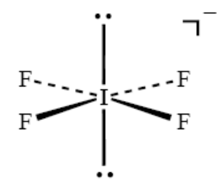
**b.** $I_3^-$ requires 10 electrons around the central I and is linear.



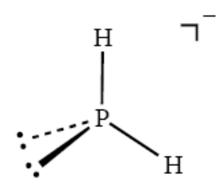
**c.** $PSCl_3$ is nearly tetrahedral. The multiple bonding in the P–S bond compresses the Cl—P—Cl angles to 101.8°, significantly less than the tetrahedral angle.



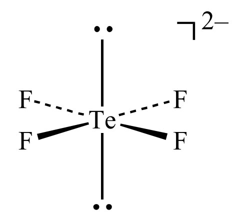
**d.** $IF_4^-$ has 12 electrons around I and has a square planar shape.



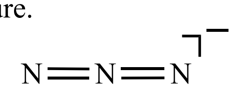
**e.** $PH_2^-$ has a bent structure, with two lone pairs.



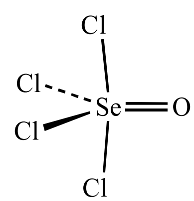
**f.** $TeF_4^{2-}$ has 12 electrons around Te, with a square planar shape.



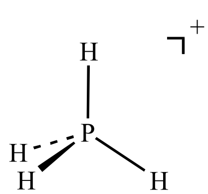
**g.** $N_3^-$ is linear, with two double bonds in its best resonance structure.



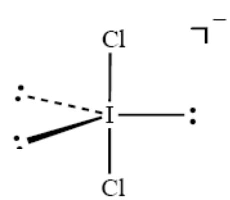
**h.** $SeOCl_4$ has a distorted trigonal bipyramidal shape with the extra repulsion of the double bond placing oxygen in an equatorial position.



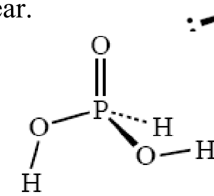
**i.** $PH_4^+$ is tetrahedral.



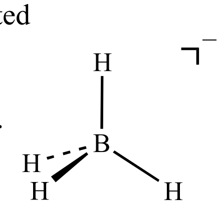
**3.9** **a.** $ICl_2^-$ has 10 electrons around I and is linear.



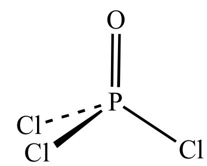
**b.** $H_3PO_3$ has a distorted tetrahedral shape.



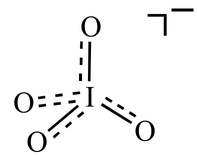
**c.** $BH_4^-$ is tetrahedral.



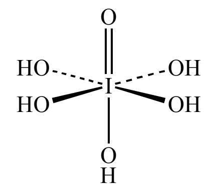
**d.** $POCl_3$ is a distorted tetrahedron. The Cl—P—Cl angle is compressed to 103.3° as a result of the P—O double bond.



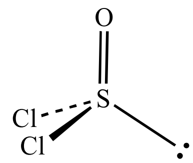
**e.** $IO_4^-$ is tetrahedral, with significant double bonding; all bonds are equivalent.



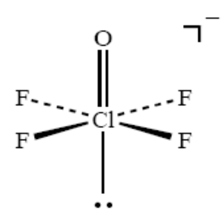
**f.** $IO(OH)_5$ has the oxygens arranged octahedrally, with hydrogens on five of the six oxygens.



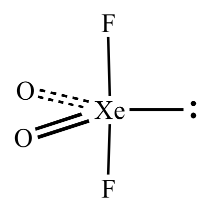
**g.** $SOCl_2$ is trigonal pyramidal, with one lone pair and some double bond character in the S–O bond.



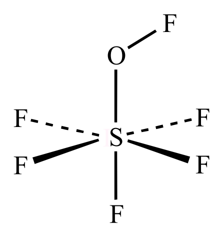
**h.** $ClOF_4^-$ is a square pyramid. The double bonded O and the lone pair occupy opposite positions.



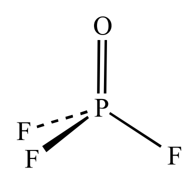
**i.** The F—Xe—F angle is nearly linear (174.7°), with the two oxygens and a lone pair in a trigonal planar configuration. Formal charges favor double bond character in the Xe–O bonds. The O—Xe—O angle is narrowed to 105.7° by *lp-bp* repulsion.



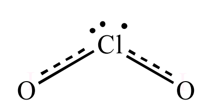
**3.10 a.** $SOF_6$ is nearly octahedral around the S.



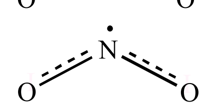
**b.** $POF_3$ has a distorted tetrahedral shape, with F—P—F angles of 101.3°.



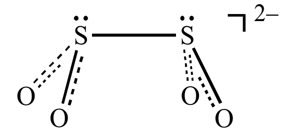
**c.** $ClO_2$ is an odd electron molecule, with a bent shape, partial double bond character, and an angle of 117.5°.



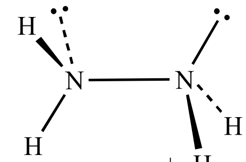
**d.** $NO_2$ is another odd electron molecule, bent, with partial double bond character and an angle of 134.25°. This is larger than the angle of $ClO_2$ because there is only one odd electron on N, rather than the one pair and single electron of $ClO_2$.



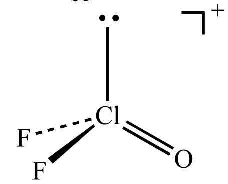
**e.** $S_2O_4^{2-}$ has $SO_2$ units with an angle of about 30° between their planes, in an eclipsed conformation.



**f.** $N_2H_4$ has a trigonal pyramidal shape at each N, and a *gauche* conformation. There is one lone pair on each N.

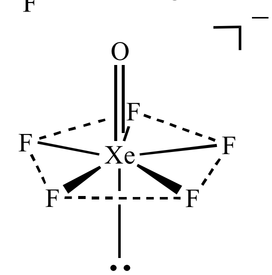


**g.** $ClOF_2^+$ is a distorted trigonal pyramid with one lone pair and double bond character in the Cl—O bond.



**h.** $CS_2$, like $CO_2$, is linear with double bonds. S═C═S

**i.** The structure of $XeOF_5^-$ is based on a pentagonal bipyramid, with a lone pair and the oxygen atom in axial positions. See K. O. Christe et al., *Inorg. Chem.*, **1995**, *34*, 1868 for evidence in support of this structure.

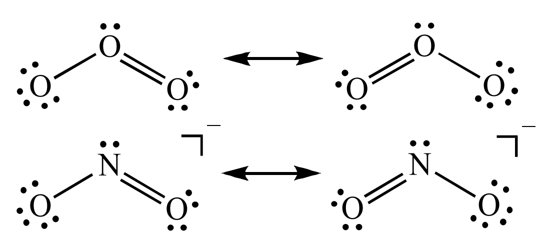


**3.11** All the halate ions are trigonal pyramids; as the central atom increases in size, the bonding pairs are farther from the center, and the lone pair forces a smaller angle. The decreasing electronegativity Cl > Br > I of the central atom also allows the electrons to be pulled farther out, reducing the *bp-bp* repulsion.

**3.12** **a.** $AsH_3$ should have the smallest angle, since it has the largest central atom. This minimizes the bond pair—bond pair repulsions and allows a smaller angle. Arsenic is also the least electronegative central atom, allowing the electrons to be drawn out farther and lowering the repulsions further. Actual angles: $AsH_3$ = 91.8°, $PH_3$ = 93.8°, $NH_3$ = 106.6°.

**b.** Cl is larger than F, and F is more electronegative and should pull the electrons farther from the S, so the F—S—F angle should be smaller in $OSF_2$. This is consistent with the experimental data: the F—S—F angle in $OSF_2$ is 92.3° and the Cl—S—Cl angle in $OSCl_2$ is 96.2°.

**c.** $NO_2^-$ has rather variable angles (115° and 132°) in different salts. The sodium salt (115.4°) has a slightly smaller angle than $O_3$ (116.8°). The N–O electronegativity difference should pull electrons away from N, reducing the *bp-bp* repulsion and the angle.

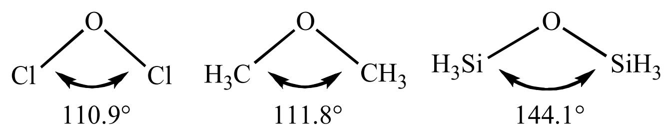


**d.** $BrO_3^-$ (104°) has a slightly smaller angle than $ClO_3^-$ (107°), since it has a larger central atom. In addition, the greater electronegativity of Cl holds the electrons closer and increases *bp-bp* repulsion.

**3.13** **a.** $N_3^-$ is linear, with two double bonds. $O_3$ is bent (see solution to 3.12.c), with one double bond and a lone pair on the central O caused by the extra pair of electrons.

**b.** Adding an electron to $O_3$ decreases the angle, as the odd electron spends part of its time on the central O, making two positions for electron repulsion. The decrease in angle is small, however, with angles of 113.0 to 114.6 pm reported for alkali metal ozonides (see W. Klein, K. Armbruster, M. Jansen, *Chem. Commun.*, **1998**, 707) in comparison with 116.8° for ozone.

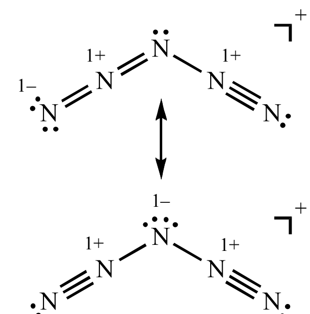
**3.14**



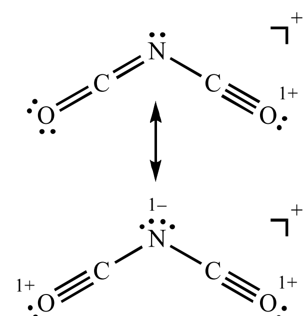

As the groups attached to oxygen become less electronegative, the oxygen atom is better able to attract shared electrons to itself, increasing the *bp-bp* repulsions and increasing the bond angle. In the case of $O(SiH_3)_2$, the very large increase in bond angle over $O(CH_3)_2$ suggests that the size of the $SiH_3$ group also has a significant effect on the bond angle.

**3.15** $C_3O_2$ has the linear structure O=C=C=C=O, with zero formal charges.

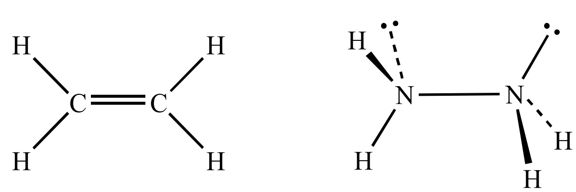
$N_5^+$ with the same electronic structure has formal charges of 1–, 1+, 1+, 1+, 1–, unlikely because three positive charges are adjacent to each other. Changing to N=N=N–N≡N results in formal charges of 1–, 1+, 0, 1+, 0, a more reasonable result with an approximately trigonal angle in the middle. With triple bonds on each end, the formal charges are 0, 1+, 1–, 1+, 0 and a tetrahedral angle. Some contribution from this would reduce the bond angle.



OCNCO$^+$ can have the structure O≡C–N–C≡O, with formal charges of 1+, 0, 1–, 0, 1+ and two lone pairs on the central N. This would result in an even smaller angle in the middle, but has positive formal charges on O, the most electronegative atom. O=C=N–C≡O has a formal charge of 1+ on the final O. Resonance would reduce that formal charge, making this structure and a trigonal angle more likely. The Seppelt reference also mentions two lone pairs on N and cites “the markedly higher electronegativity of the nitrogen atom with respect to the central atom in $C_3O_2$, which leads to a higher localization of electron density in the sense of a nonbonding electron pair.” Therefore, the bond angles should be OCCCO > OCNCO$^+$ > $N_5^+$. Literature values are 180°, 130.7°, and 108.3 to 112.3° (calculated), respectively.

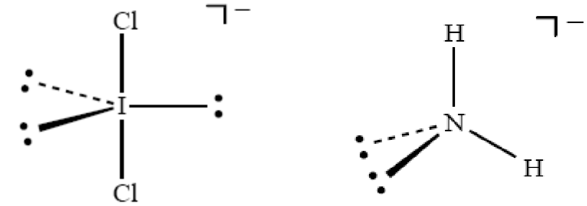


**3.16 a.**



In ethylene, carbon has *p* orbitals not involved in sigma bonding. These orbitals interact to form a pi bond between the carbons, resulting in planar geometry. (Sigma and pi bonding are discussed further in Chapter 5.) In hydrazine each nitrogen has a steric number of 4, and there is sigma bonding only; the steric number of 4 requires a three-dimensional structure.

**b.**



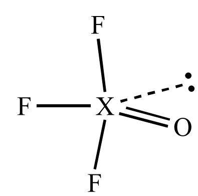

In $ICl_2^-$ the iodine has a steric number of 5, with three lone pairs in equatorial positions; the consequence is a linear structure, with Cl atoms occupying axial positions. In $NH_2^-$ the two lone pairs require a bent arrangement.

**c.** Resonance structures of cyanate and fulminate are shown in Figures 3.4 and 3.5. The fulminate ion has no resonance structures that have as low formal charges as structures A and B shown for cyanate. The guideline that resonance structures having low formal charges tend to correspond to relatively stable structures is followed here. $Hg(CNO)_2$, which has higher formal charges in its resonance structures, is the explosive compound.

**3.17 a.** $PCl_5$ has 10 electrons around P, using 3*d* orbitals in addition to the usual 3*s* and 3*p*. N is too small to allow this structure. In addition, N would require use of the 3*s*, 3*p*, or 3*d* orbitals, but they are too high in energy to be used effectively.

**b.** Similar arguments apply, with O too small and lacking in accessible orbitals beyond the 2*s* and 2*p*.

**3.18 a.** The lone pairs in both molecules are equatorial, the position that minimizes 90° interactions between lone pairs and bonding pairs.




**b.** In $BrOF_3$ the less electronegative central atom allows electrons in the bonds to be pulled toward the F and O atoms to a greater extent, reducing repulsions near the central atom and enabling a smaller bond angle. In $BrOF_3$ the $F_{eq}$–Br–O angle is approximately 4.5° smaller than the comparable angle in $ClOF_3$.

**3.19 a.** The $CH_3$—N—$CH_3$ angle is expected to be larger than the $CH_3$—P—$CH_3$ angle; *bp-bp* repulsion will be more intense at the N due to the higher electronegativity of N relative to P. The angles are 108.2° ($CH_3$—N—$CH_3$) and 103.4° ($CH_3$—P—$CH_3$).

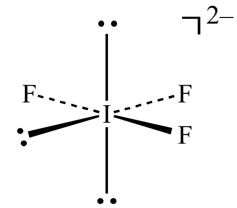
**b.** $N(CH_3)_3$ is expected to exert a greater steric influence on $Al(CH_3)_3$ relative to $P(CH_3)_3$ on the basis of a shorter Al—N bond distance (204.5 pm) than Al—P bond distance (253 pm). Therefore, $(CH_3)_3NAl(CH_3)_3$ has a more acute $CH_3$—Al—$CH_3$ angle (114.4°) than $(CH_3)_3PAl(CH_3)_3$ (117.1°).

**c.** On the basis of the steric argument applied in part b, $(CH_3)_3NAl(CH_3)_3$ should have a longer Al—C distance. However, while this distance is slightly longer in

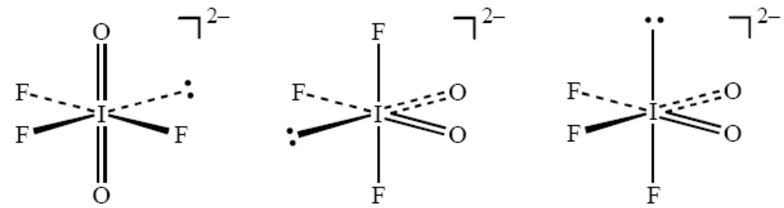
$(CH_3)_3NAl(CH_3)_3$ relative to $(CH_3)_3PAl(CH_3)_3$ (1.978 pm vs. 1.973 pm), these lengths are not statistically different when their standard deviations are considered.

Data for $(CH_3)_3NAl(CH_3)_3$ from T. Gelbrich, J. Sieler, U. Dümichen, *Z. Kristallogr.*, **2000**, *215*, 127. Data for $(CH_3)_3PAl(CH_3)_3$ from A. Almenningen, L. Fernholt, A. Haaland, J. Weidlein, *J. Organomet. Chem.*, **1978**, *145*, 109.

**3.20** $IF_3^{2-}$ has three lone pairs and three bonds. Overall, this ion is predicted to be T-shaped, with bond angles slightly less than 90°.



**3.21** **a.** There are three possibilities:

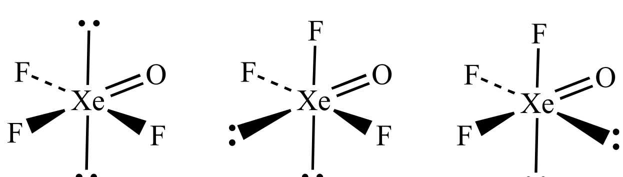


**b.** The third structure, with the lone pair and double bonds in a facial arrangement, is least likely because it would have the greatest degree of electron-electron repulsions involving these regions of high electron concentrations.

The second structure, which has fewer 90° lone pair–double bond repulsions than the first structure, is expected to be the most likely. Experimental data are most consistent with this structure.

**c.** One possibility: $XeO_2F_3^-$

**3.22** **a.** Three unique arrangements of the nonbonding pairs and the oxygen atom are possible in $XeOF_3^-$ when the octahedral electron-group geometry is considered: (1) *trans* nonbonding pairs; (2) one pair *trans* and one *cis* the oxygen atom; and (3) both pairs *cis* the oxygen atom.

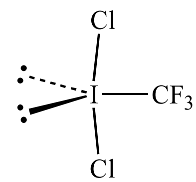


1 2 3

A square-planar structure (1) is expected to minimize *lp-lp* repulsions relative to structures 2 and 3 with unfavorable 90° *lp-lp* interactions. A low temperature Raman spectroscopic study coupled with quantum-chemical calculations of shock-sensitive salts of $XeOF_3^-$ confirms this prediction (D. S. Brock, H. P. A. Mercier, G. J. Schrobilgen, *J. Am. Chem. Soc.*, **2010**, *132*, 10935).

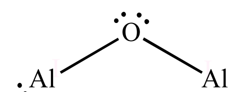
**b**. This anion is notable as the first example of a VSEPR arrangement ( $AX_3YE_2$) that features a doubly bond atom (oxygen) positioned approximately 90° to relative the domains of two nonbonding pairs.

**3.23** $I(CF_3)Cl_2$ is roughly T-shaped, with the two Cl atoms opposite each other and the $CF_3$ group and two lone pairs in the trigonal plane. The experimental Cl—I—C angles are 88.7° and 82.9°, smaller than the 90° expected if there were no extra repulsion from the lone pairs. Repulsion between the lone pairs and the larger $CF_3$ group put them in the trigonal plane, where there is more room.

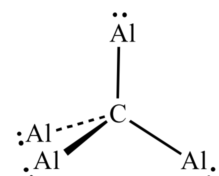



**3.24** **a.** $CF_3$ has a greater attraction for electrons than $CH_3$, so the P in $PF_2(CF_3)_3$ is more positive than the P in $PF_2(CH_3)_3$. This draws the F atoms in slightly, so the P—F bonds are shorter in $PF_2(CF_3)_3$ (160.1 pm vs. 168.5 pm).

**b.** Al—O—Al could have an angle near 109°, like water, or could have double bonds in both directions and a nearly linear structure. In fact, the angle is about 140°. The single-bonded picture is more probable; the high electronegativity of O compared to Al draws the bonding pairs closer, opening up the bond angle. A Lewis structure with zero formal charges on all atoms can be drawn for this molecule with four electrons on each Al.




**c.** $CAl_4$ is tetrahedral. Again, a Lewis structure with zero formal charges can be drawn with four electrons on each Al.



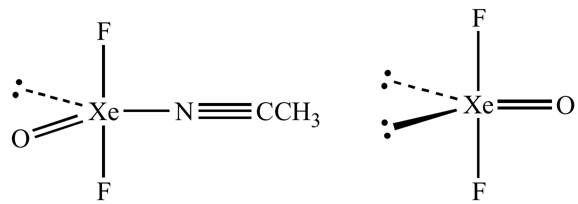

**3.25** **a.** The Te—X(axial) distances are expected to be longer than the Te—X(equatorial) distances on the basis of the increased *lp-bp* and *bp-bp* repulsion that the electron groups in the axial positions experience relative to those in the equatorial positions. The observed bond distances exhibit these features for both $TeF_4$ (Te—F(axial), 189.9 pm; Te—X(equatorial), 184.6 pm) and $TeCl_4$ (Te—Cl(axial), 242.8 pm; Te—Cl(equatorial), 228.9 pm).

**b**. These angles should both be smaller in $TeF_4$, on the basis of reduced *bp-bp* repulsion at the Te atom in $TeF_4$ due to the higher electronegativity of F relative to Cl. The angles were determined as 164.3° (F(axial)—Te—F(axial)), 176.7° (Cl(axial)—Te—Cl(axial)), 99.5° (F(equatorial)—Te—F(equatorial)), and 102.5° (Cl(equatorial)—Te—Cl(equatorial). The equatorial nonbonding pair in these complexes has a greater influence in $TeF_4$ than in $TeCl_4$.

**3.26**

| Octahedral | Distorted |
|---|---|
| $SeCl_6^{2-}$ | $SeF_6^{2-}$ |
| $TeCl_6^{2-}$ | $IF_6^{-}$ |
| $ClF_6^{-}$ | |

The distorted structures have the smallest outer atoms in comparison with the size of the central atom. In these cases, there apparently is room for a lone pair to occupy a position that can lead to distortion. In the octahedral cases there may be too much crowding to allow a lone pair to distort the shape.

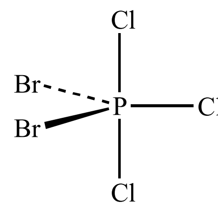
**3.27** 

In $F_2OXeN{\equiv}CCH_3$, the nitrogen–xenon bond is weak; see the reference for details on bond distances and angles.

**3.28** **a.** O is more electronegative than N and can draw the electrons more strongly away from the S. The more positive S in $OSCl_2$ consequently attracts bonding pairs in S–Cl bonds closer to sulfur, increasing *bp-bp* repulsions and increasing the Cl—S—Cl angle (96.2° in $OSCl_2$, 93.3° in $NSCl_2^-$).

**b.** Because the sulfur in $OSCl_2$ attracts the S–Cl bonding pairs more strongly, these bonds are shorter: 207.6 pm in $OSCl_2$, 242.3 pm in $NSCl_2^-$.

**3.29** The larger, less electronegative Br atoms are equatorial.



**3.30** **a.** In $PCl_3(CF_3)_2$, the highly electronegative $CF_3$ groups occupy axial positions.

**b.** The axial positions in $SbCl_5$ experience greater repulsions by bonding pairs, leading to longer Sb–Cl (axial) bonds (223.8 pm) than Sb–Cl (equatorial) bonds (227.7 pm).

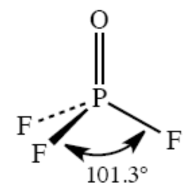
**3.31** The pertinent group electronegativity ranking is $CF_3 > CCl_3 > CH_3$. Therefore, $ClSO_2CF_3$ is expected to possess the lowest concentration of electron density near the S of the S—C bond, and $ClSO_2CH_3$ the highest concentration of electron density. The *bp-bp* repulsion that influences the Cl—S—C angles should decrease as $ClSO_2CH_3 > ClSO_2CCl_3 > ClSO_2CF_3$. Therefore, $ClSO_2CF_3$ should exhibit the smallest Cl—S—C angle, and $ClSO_2CH_3$ the largest Cl—S—C angle. The angles measured in the gas phase for these molecules are 101° ($ClSO_2CH_3$; M. Hargittai, I. Hargittai, *J. Chem. Phys.*, **1973**, *59*, 2513) , 96° ($ClSO_2CCl_3$; N. V. Alekseev, *Z. Struki. Khimii*, **1967**, *8*, 532), and 95.4° ($ClSO_2CF_3$; R. Haist, F. Trautner, J. Mohtasham, R. Winter, G. L. Gard, H. Oberhammer, *J. Mol. Struc.*, **2000**, *550*, 59).

**3.32** The $FSO_2X$ molecule with the smallest O—S—O angle is expected to be that with the greatest concentration of electron density at the S atom from the S—X bond. This molecule should exert the greatest amount of *bp-bp* repulsion between the S—F and S—X bonds, maximally hindering expansion of the O—S—O angle within this series. The pertinent group electronegativity ranking is $F > OCH_3 > CH_3$; the S—$CH_3$ bond should possess the greatest electron density at the S atom. While $FSO_2CH_3$ exhibits a smaller O—S—O angle (123.1°, I. Hargittai, M. Hargittai, *J. Mol. Struc.*, **1973**, *15*, 399) than found in $FSO_2(OCH_3)$ (124.4°, I. Hargittai, R. Seip, K. P. Rajappan Nair, C. O. Britt, J. E. Boggs, B. N. Cyvin, *J. Mol. Struc.*, **1977**, *39*, 1.), the O—S—O angle of $FSO_2F$ (123.6°, D. R. Lide, D. E. Mann, R. M. Fristrom, *J. Chem. Phys.*, **1957**, *26*, 734) is smaller than expected on the exclusive basis of group electronegativity arguments. It is noteworthy that O—S—O angles ranging from 122.6 to 130°, with rather large standard deviations (see K. Hagen, V. R. Cross, K. Hedberg, *J. Mol. Struc.,* **1978**, *44*, 187), have also been reported for $FSO_2F$.

**3.33** **a**. Because Te is less electronegative than Se, the highly electronegative $C_5F_4N$ groups draw electron density away from the Te atom more effectively than from the Se atom, rendering more effective *lp-bp* repulsion in compressing the C—group 16 atom—C angle in $Te(C_5F_4N)_2$.

**b**. As the electronegativity of the group bound to these atoms increases, *lp-bp* repulsion is expected to have increasing impact in compressing the C—group 16 atom—C angle. The pertinent group electronegativity ranking is $C_5F_4N > C_6F_5$ on the basis of theoretical calculations ( B. Hoge, C. Thösen, T. Hermann, P. Panne, I. Patenburg, *J. Flourine Chem.*, **2004**, *125*, 831).

**3.34** $PF_4^+$ has the bond angle expected for a tetrahedron, 109.5°. In $PF_3O$ the multiple bond to oxygen results in distortion away from the oxygen, leading to a smaller F–P–F angle. By the LCP approach the F···F distances should be approximately the same in these two structures. They are similar: 238 pm in $PF_4^+$ and 236 pm in $PF_3O$.




**3.35** As more (less electronegative) $CH_3$ groups are added, there is greater concentration of electrons near P, and greater electron-electron repulsion leads to longer axial P–F bonds.

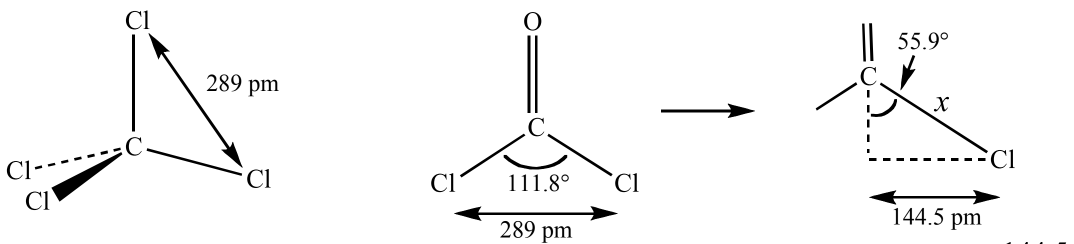
| Reported P–F distances: | $PF_4(CH_3)$ | $PF_3(CH_3)_2$ | $PF_2(CH_3)_3$ |
|---|---|---|---|
| 161 | pm | 164 pm | 168 pm |

**3.36** Bond angles and distances:

| | Steric Number | C—F (pm) | FCF angle (°) | F—F (pm) |
|---|---|---|---|---|
| $F_2C{=}CF_2$ | 3 | 133.6 | 109.2 | 218 |
| $F_2CO$ | 3 | 131.9 | 107.6 | 216 |
| $CF_4$ | 4 | 131.9 | 109.5 | 216 |
| $F_3CO^-$ | 4 | 139.2 | 101.3 | 215 |

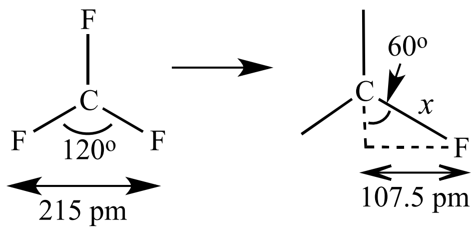
The differences between these molecules are subtle. The LCP model views the F ligands as hard objects, tightly packed around the central C in these examples. In this approach, the F···F distance remains nearly constant while the central atom moves to minimize repulsions.

**3.37** The calculation is similar to the example shown in Section 3.2.4.




$$\sin 55.9° = 0.828 = \frac{144.5}{x}$$
$$x = 174.5 \text{ pm}$$

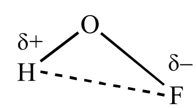
**3.38** $CF_3^+$ is expected to be trigonal planar with a 120° F—C—F angle.




$$\sin 60° = 0.866 = \frac{107.5}{x}$$
$$x = 124.1 \text{ pm}$$

The C—F bond length predicted via quantum chemical calculations is 124.4 pm, with a F···F distance of 216 pm (R. J. Gillespie and P. L. A. Popelier*, Chemical Bonding and Molecular Geometry*, Oxford, New York, 2001, p. 119).

**3.39** By the LCP approach, from the structures of HOH and FOF, the hydrogen radius would be 76 pm (half of the H···H distance) and the fluorine radius (half of the F···F distance) would be 110 pm. Because the LCP model describes nonbonded outer atoms as being separated by the sums of their radii, as if they were touching spheres, the H···F distance in HOF would therefore be the sum of the ligand radii, 76 + 110 = 186 pm, in comparison with the actual H···F distance of 183 pm. If the covalent O–H and O–F bonds in HOF are similar to the matching distances in HOH and FOF, the H–O–F angle must be smaller than the other angles because of the H···F distance.



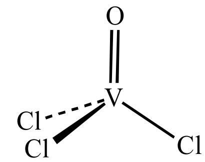

An alternative explanation considers the polarity in HOF. Because of the high electronegativity of fluorine, the F atom in HOF acquires a partial negative charge, which is attracted to the relatively positive H atom. By this approach, electrostatic attraction between H and F reduces the bond angle in HOF, giving it the smallest angle of the three compounds.

**3.40** The electronegativity differences are given in parentheses:

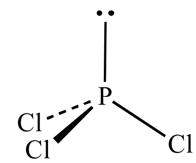
| | | | | | |
|---|---|---|---|---|---|
| **a.** | C–N | N is negative (0.522) | **d.** | O–Cl | O is negative (0.741) |
| **b.** | N–O | O is negative (0.544) | **e.** | P–Br | Br is negative (0.432) |
| **c.** | C–I | C is negative (0.185) | **f.** | S–Cl | Cl is negative (0.280) |

The overall order of polarity is O–Cl > N–O > C–N > P–Br > S–Cl > C–I.

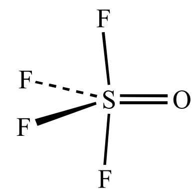
**3.41** **a.** $VOCl_3$ has a distorted tetrahedral shape, with Cl—V—Cl angles of 111°, and Cl—V—O angles of 108°.



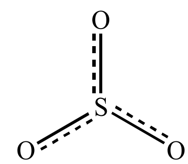
**b.** $PCl_3$ has a trigonal pyramidal shape with Cl—P—Cl angles of 100.4°.



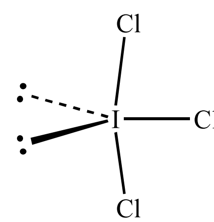
**c.** $SOF_4$ has a distorted trigonal bipyramidal shape. The axial fluorine atoms are nearly linear with the S atom; the equatorial F—S—F angle is 100°.



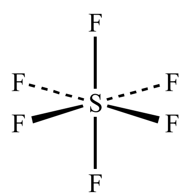
**d.** $SO_3$ is trigonal (triangular), with equal bond angles of 120°.



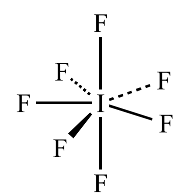
**e.** $ICl_3$ would be expected to have two axial lone pairs, causing distortion to reduce the Cl (axial)–I–Cl (equatorial) angles to < 90°. However, reaction of $I_2$ with $Cl_2$ yields dimeric $I_2Cl_6$, which readily dissociates into ICl and $Cl_2$.



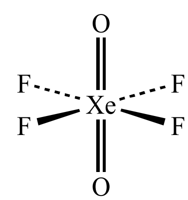
**f.** $SF_6$ is a regular octahedron.



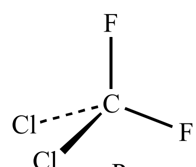
**g.** $IF_7$ is a rare example of pentagonal bipyramidal geometry.



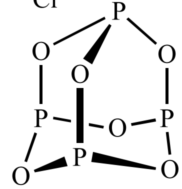
**h.** The structure of $XeO_2F_4$ is based on an octahedron, with oxygens in *trans* positions because of multiple bonding.



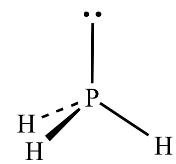
**i.** $CF_2Cl_2$, like methane, is tetrahedral.



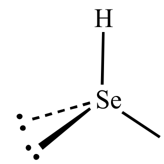
**j.** $P_4O_6$ is described in the problem. Each P has one lone pair, each O has two.



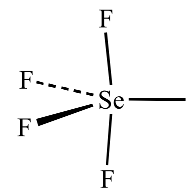
**3.42** **a.** $PH_3$ has a smaller bond angle than $NH_3$, about 93°. The larger central atom reduces the repulsion between the bonding pairs.



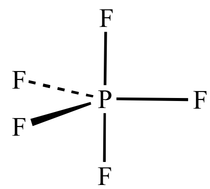
**b.** $H_2Se$ has a structure like water, with a bond angle near 90°. The larger central atom increases the distance between the S–H bonding pairs and reduces their repulsion, resulting in a smaller angle than in water.



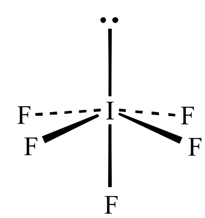
**c.** $SeF_4$ has a lone pair at one of the equatorial positions of a trigonal bipyramid, and bond angles of about 110° (equatorial) and 169° (axial). Seesaw shape.



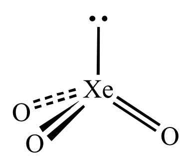
**d.** $PF_5$ has a trigonal bipyramidal structure.



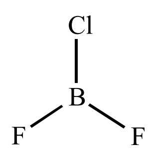
**e.** $IF_5$ is square pyramidal, with slight distortion away from the lone pair.



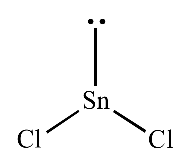
**f.** $XeO_3$ has a trigonal pyramidal shape, similar to $NH_3$, but with Xe–O double bonds.



**g.** $BF_2Cl$ is trigonal planar, with $\angle$FBCl larger than $\angle$FBF.

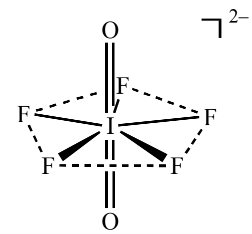


**h.** $SnCl_2$ has a bond angle of 95° in the vapor phase, smaller than the trigonal angle. As a solid, it forms polymeric chains with bridging chlorines and bond angles near 80°.



**i.** $KrF_2$ is linear: F—Kr—F . VSEPR predicts three lone pairs on krypton in equatorial positions, with the fluorine atoms in axial positions.

**j.** $IO_2F_5^{2-}$ has a steric number of 7 on iodine, with oxygen atoms occupying axial positions.



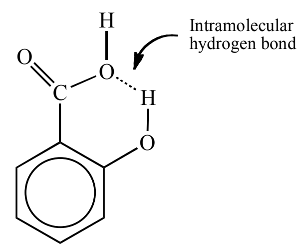
**3.43** Polar: $VOCl_3$, $PCl_3$, $SOF_4$, $ICl_3$, $CF_2Cl_2$

**3.44** Polar: $PH_3$, $H_2Se$, $SeF_4$, $IF_5$, $XeO_3$, $BF_2Cl$, $SnCl_2$

**3.45** **a.** The H–O bond of methanol is more polar than the H–S bond of methyl mercaptan. As a result, hydrogen bonding holds the molecules together and requires more energy for vaporization. The larger molecular weight of methyl mercaptan has a similar effect, but the hydrogen bonding in methanol has a stronger influence.

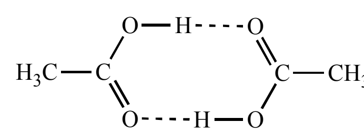
**b.** CO and $N_2$ have nearly identical molecular weights, but the polarity of CO leads to dipole-dipole attractions that help hold CO molecules together in the solid and liquid states.

**c.** The *ortho* isomer of hydroxybenzoic acid can form *intra*molecularhydrogen bonds, while the *meta* and *para* isomers tend to form dimers and larger aggregates in their hydrogen bonding. As a result of their better ability to form hydrogen bonds between molecules (*inter*molecular hydrogen bonds), the *meta* and *para* isomers have higher melting points (*ortho*, 159°; *meta*, 201.3°; *para*, 214-5°).

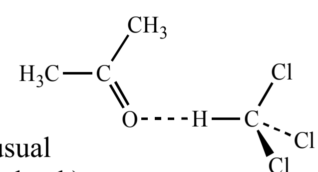



**d.** The London (dispersion) forces between atoms increase with the number of electrons, so the noble gases with larger *Z* have larger interatomic forces and higher boiling points.

**e.** Acetic acid can form hydrogen-bonded dimers in the gas phase, so the total number of particles in the gas is half the number expected by using the ideal gas law.



**f.** Acetone has a negative carbonyl oxygen; chloroform has a positive hydrogen, due to the electronegative character of the chlorines. As a result, there is a stronger attraction between the different kinds of molecules than between molecules of the same kind, and a resulting lower vapor pressure. (This is an unusual case of hydrogen bonding, with no H–N, H–O, or H–F bond involved.)



**g.** CO has about 76 kJ contribution to its bond energy because of the electronegativity difference between C and O; attraction between the slightly positive and negative ends strengthens the bonding. Although this is not a complete explanation, it covers most of difference between CO and $N_2$. In spite of its high bond energy, $N_2$ is thought by some to have some repulsion in its sigma bonding because of the short bond distance.

**3.46** **a**. The trend in these angles is counter-intuitive on the basis of electronegativity arguments. Electronegativity decreases as P > As > Sb, and the C—group 15 atom—C angle is expected to decrease as P > As > Sb on the basis of less *bp*-*bp* repulsion at the group 15 atom as P > As > Sb. Both $As(CF_3)_3$ and $Sb(CF_3)_3$ are expected to exhibit more acute C—group 15 atom—C angles relative to $P(CF_3)_3$.

**b**. On the basis of the argument above, the C—Sb—C angle of $Sb(CF_3)_3$ should be reinvestigated. This angle is predicted to be smaller than the newly determined C—As—C angle of $As(CF_3)_3$.