

- e.  $\text{S}_2\text{O}_8^{2-}$  has  $\text{SO}_2$  units with an angle of about  $30^\circ$  between their planes, in an eclipsed conformation.



- f.  $\text{N}_2\text{H}_4$  has a trigonal pyramidal shape at each N, and a *gauche* conformation. There is one lone pair on each N.

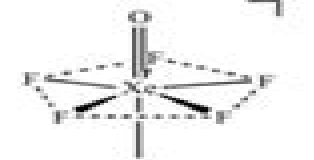


- g.  $\text{ClOF}_2^-$  is a distorted trigonal pyramid with one lone pair and double bond character in the Cl—O bond.



- h.  $\text{CS}_2$ , like  $\text{CO}_2$ , is linear with double bonds.  $\text{S}=\text{C}=\text{S}$

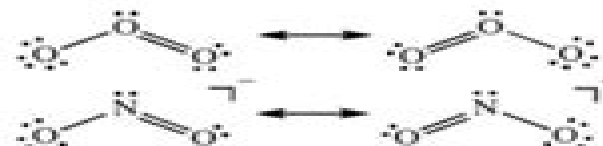
- i. The structure of  $\text{XeOF}_5^-$  is based on a pentagonal bipyramid, with a lone pair and the oxygen atom in axial positions. See K. O. Christie et al., *Inorg. Chem.*, **1995**, *34*, 1868 for evidence in support of this structure.



**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  $\text{Cl} > \text{Br} > \text{I}$  of the central atom also allows the electrons to be pulled farther out, reducing the *bp-bp* repulsion.

- 3.12** a.  $\text{AsH}_3$  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:  $\text{AsH}_3 = 91.8^\circ$ ,  $\text{PH}_3 = 93.8^\circ$ ,  $\text{NH}_3 = 106.6^\circ$ .
- b. Cl is larger than F, and F is more electronegative and should pull the electrons farther from the S, so the  $\text{F—S—F}$  angle should be smaller in  $\text{OSF}_2$ . This is consistent with the experimental data: the  $\text{F—S—F}$  angle in  $\text{OSF}_2$  is  $92.3^\circ$  and the  $\text{Cl—S—Cl}$  angle in  $\text{OSCl}_2$  is  $96.2^\circ$ .

- c.  $\text{NO}_2^-$  has rather variable angles ( $115^\circ$  and  $132^\circ$ ) in different salts. The sodium salt ( $115.4^\circ$ ) has a slightly smaller angle than  $\text{O}_3$  ( $116.8^\circ$ ). The N—O electronegativity difference should pull electrons away from N, reducing the *bp-bp* repulsion and the angle.



- d.  $\text{BrO}_3^-$  ( $104^\circ$ ) has a slightly smaller angle than  $\text{ClO}_3^-$  ( $107^\circ$ ), 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.  $\text{N}_3^-$  is linear, with two double bonds.  $\text{O}_3$  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.

# Miessler Tarr 4th Edition Solutions Manual

**Judd E. Hollander**



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