

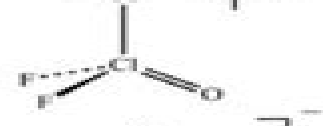
- e. $\text{S}_2\text{O}_8^{2-}$ has SO_2 units with an angle of about 30° between their planes, in an eclipsed conformation.



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

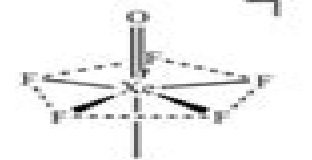


- g. ClOF_2^- is a distorted trigonal pyramid with one lone pair and double bond character in the Cl—O bond.



- h. CS_2 , like CO_2 , is linear with double bonds. $\text{S}=\text{C}=\text{S}$

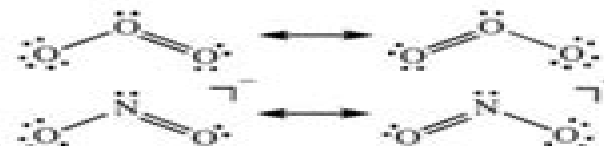
- i. The structure of XeOF_5^- is based on a pentagonal bipyramid, with a lone pair and the oxygen atom in axial positions. See K. O. Christie et al., *Inorg. Chem.*, **1995**, *34*, 1868 for evidence in support of this structure.



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. 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 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.

Miessler Tarr 4th Edition Solutions Manual

Daniel D. Anderson



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