# Chapter 9 The Shapes of Molecules

## CHEMICAL CONNECTIONS BOXED READING PROBLEMS

B9.1 Plan: Examine the Lewis structure, noting the number of regions of electron density around the carbon and nitrogen atoms in the two resonance structures. The molecular shape is determined by the number of electron regions. An electron region is any type of bond (single, double, or triple) and an unshared pair of electrons.

Solution:

Resonance structure on the left:

Carbon has three electron regions (two single bonds and one double bond); three electron regions are arranged in a trigonal planar arrangement. The molecular shape around the C atom is **trigonal** **planar**. Nitrogen has four electron regions (three single bonds and an unshared pair of electrons); the four electron regions are arranged tetrahedrally; since one corner of the tetrahedron is occupied by an unshared electron pair, the shape around N is **trigonal pyramidal**.

Resonance structure on the right:

This C atom also has three electrons regions (two single bond and one double bond) so the molecular shape is again **trigonal planar**. The N atom also has three electron regions (two single bonds and one double bond); the molecular shape is **trigonal planar**.

**END–OF–CHAPTER PROBLEMS**

9.2 The molecular shape and the electron-group arrangement are the same when there are no lone pairs on the central atom.

9.4 Plan: Examine a list of all possible structures, and choose the ones with four electron groups since the tetrahedral electron-group arrangement has four electron groups.

Solution:

Tetrahedral AX4

Trigonal pyramidal AX3E1

Bent or V shaped AX2E2

9.6 Plan: Begin with the basic structures and redraw them.

Solution:

a) A molecule that is V shaped has two bonds and generally has either one (AX2E1) or two (AX2E2) lone electron pairs.

b) A trigonal planar molecule follows the formula AX3 with three bonds and no lone electron pairs.

c) A trigonal bipyramidal molecule contains five bonding pairs (single bonds) and no lone pairs (AX5).

d) A T-shaped molecule has three bonding groups and two lone pairs (AX3E2).

e) A trigonal pyramidal molecule follows the formula AX3E1 with three bonding pairs and one lone pair.

f) A square pyramidal molecule shape follows the formula AX5E1 with five bonding pairs and one lone pair.



9.8 Plan: First, draw a Lewis structure, and then apply VSEPR.

Solution:

a) O3: The molecule has [3 x O(6e–)] = 18 valence electrons. Four electrons are used to place single bonds

between the oxygen atoms, leaving 18 – 4 = 14e– (seven pairs). Six pairs are required to give the end oxygen atoms an octet; the last pair is distributed to the central oxygen, leaving this atom two electrons short of an octet. Form a double bond from one of the end O atoms to the central O by changing a lone pair on the end O to a bonding pair on the central O. This gives the following Lewis structure:



There are three electron groups around the central O, one of which is a lone pair. This gives a **trigonal planar** electron-group arrangement (AX2E1), a **bent** molecular shape, and an ideal bond angle of **120°**.

b) H3O+: This ion has [3 x H(1e–)] + [1 x O(6e–)] – [1e– (due to + charge] = eight valence electrons. Six electrons are used to place a single bond between O and each H, leaving 8 – 6 = 2e– (one pair). Distribute this pair to the O atom, giving it an octet (the H atoms only get two electrons). This gives the following Lewis structure:



There are four electron groups around the O, one of which is a lone pair. This gives a **tetrahedral** electron-group arrangement (AX3E1), a **trigonal pyramidal** molecular shape, and an ideal bond angle of **109.5°**.

c) NF3: The molecule has [1 x N(5e–)] + [3 x F(7e–)] = 26 valence electrons. Six electrons are used to place a

single bond between N and each F, leaving 26 – 6 = 20 e– (ten pairs). These ten pairs are distributed to all of the F atoms and the N atoms to give each atom an octet. This gives the following Lewis structure:



There are four electron groups around the N, one of which is a lone pair. This gives a **tetrahedral** electron-group arrangement (AX3E1), a **trigonal pyramidal** molecular shape, and an ideal bond angle of **109.5°**.

9.10 Plan: First, draw a Lewis structure, and then apply VSEPR.

Solution:

(a) CO32–: This ion has [1 x C(4e–)] + [3 x O(6e–)] + [2e– (from charge)] = 24 valence electrons. Six electrons

are used to place single bonds between C and each O atom, leaving 24 – 6 = 18 e– (nine pairs). These nine pairs are used to complete the octets of the three O atoms, leaving C two electrons short of an octet. Form a double bond from one of the O atoms to C by changing a lone pair on an O to a bonding pair on C. This gives the following Lewis structure:



There are two additional resonance forms. There are three groups of electrons around the C, none of which are lone pairs. This gives a **trigonal planar** electron-group arrangement (AX3), a **trigonal planar** molecular shape, and an ideal bond angle of **120°**.

(b) SO2: This molecule has [1 x S(6e–)] + [2 x S(6e–)] = 18 valence electrons. Four electrons are used to place a single bond between S and each O atom, leaving 18 – 4 = 14e– (seven pairs). Six pairs are needed to complete the

octets of the O atoms, leaving a pair of electrons for S. S needs one more pair to complete its octet. Form a double bond from one of the end O atoms to the S by changing a lone pair on the O to a bonding pair on the S. This gives the following Lewis structure:



There are three groups of electrons around the C, one of which is a lone pair.

This gives a **trigonal planar** electron-group arrangement (AX2E1), a **bent (V-shaped)** molecular shape, and an ideal bond angle of **120°**.

(c) CF4: This molecule has [1 x C(4e–)] + [4 x F(7e–)] = 32 valence electrons. Eight electrons are used to place a single bond between C and each F, leaving 32 – 8 = 24 e– (twelve pairs). Use these twelve pairs to complete the octets of the F atoms (C already has an octet). This gives the following Lewis structure:



There are four groups of electrons around the C, none of which is a lone pair.

This gives a **tetrahedral** electron-group arrangement (AX4), a **tetrahedral** molecular shape, and an ideal bond

angle of **109.5°**.

9.12 Plan: Examine the structure shown, and then apply VSEPR.

Solution:

a) This structure shows three electron groups with three bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **trigonal planar**, the classification is **AX3**, with an ideal bond angle of **120°**.

b) This structure shows three electron groups with three bonds around the central atom.

The bonds are distorted down indicating the presence of a lone pair. The shape of the molecule is **trigonal**  **pyramidal** and the classification is **AX3E1**, with an ideal bond angle of **109.5°**.

c) This structure shows five electron groups with five bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **trigonal bipyramidal** and the classification is **AX5**, with ideal bond angles of **90°** and **120°**.

9.14 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures. Lone pairs on the central atom

generally result in a deviation of the ideal bond angle.

Solution:

a) The ClO2– ion has [1 x Cl(7e–)] + [2 x O(6e–)] + [1e– (from charge)] = 20 valence electrons. Four electrons are used to place a single bond between the Cl and each O, leaving 20 – 4 = 16 electrons (eight pairs). All eight pairs are used to complete the octets of the Cl and O atoms. There are two bonds (to the O atoms) and two lone pairs on the Cl for a total of four electron groups (AX2E2). The structure is based on a tetrahedral electron-group arrangement with an ideal bond angle of **109.5°**. The shape is **bent** (or V shaped). The presence of the lone pairs will cause the remaining angles to be **less than 109.5°**.

b) The PF5 molecule has [1 x P(5 e–)] + [5 x F(7 e–)] = 40 valence electrons. Ten electrons are used to place

single bonds between P and each F atom, leaving 40 – 10 = 30 e– (fifteen pairs). The fifteen pairs are used to

complete the octets of the F atoms. There are five bonds to the P and no lone pairs (AX5). The electron-group

arrangement and the shape is **trigonal bipyramidal**. The ideal bond angles are **90° and 120°**. The absence of lone pairs means the **angles are ideal**.

c) The SeF4 molecule has [1 x Se(6e–)] + [4 x F(7e–)] = 34 valence electrons. Eight electrons are used to place

single bonds between Se and each F atom, leaving 34 – 8 = 26e– (thirteen pairs). Twelve pairs are used to complete the octets of the F atoms which leaves one pair of electrons. This pair is placed on the central Se atom. There are four bonds to the Se which also has a lone pair (AX4E1). The structure is based on a trigonal bipyramidal structure with ideal angles of **90° and 120°**. The shape is **seesaw**. The presence of the lone pairs means the angles are **less than ideal**.

d) The KrF2 molecule has [1 x Kr(8e–)] + [2 x F(7e–)] = 22 valence electrons. Four electrons are used to place a

single bond between the Kr atom and each F atom, leaving 22 – 4 = 18 e– (nine pairs). Six pairs are used to complete the octets of the F atoms. The remaining three pairs of electrons are placed on the Kr atom. The Kr is the central atom. There are two bonds to the Kr and three lone pairs (AX2E3). The structure is based on a trigonal bipyramidal structure with ideal angles of 90° and 120°. The shape is **linear**. The placement of the F atoms makes their ideal bond angle to be 2 x 90° = **180°**. The placement of the lone pairs is such that they cancel each other’s repulsion, thus the actual **bond angle is ideal**.





a) b) c) d)

9.16 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures.

Solution:

a) CH3OH: This molecule has [1 x C(4e–)] + [4 x H(1e–)] + [1 x O(6e–)] = fourteen valence electrons. In the CH3OH molecule, both carbon and oxygen serve as central atoms. (H can never be central.) Use eight electrons to place a single bond between the C and the O atom and three of the H atoms and another two electrons to place a single bond between the O and the last H atom. This leaves 14 – 10 = 4 e– (two pairs). Use these two pairs to complete the octet of the O atom. C already has an octet and each H only gets two electrons. The carbon has four bonds and no lone pairs (AX4), so it is **tetrahedral** with **no deviation** (no lone pairs) from the ideal angle of 109.5°. The oxygen has two bonds and two lone pairs (AX2E2), so it is **V shaped** or **bent** with the angles **less than the ideal** angle of 109.5°.



b) N2O4: This molecule has [2 x N(5e–)] + [4 x O(6e–)] = 34 valence electrons. Use ten electrons to place a

single bond between the two N atoms and between each N and two of the O atoms. This leaves 34 – 10 = 24e–

(twelve pairs). Use the twelve pairs to complete the octets of the oxygen atoms. Neither N atom has an octet, however. Form a double bond from one O atom to one N atom by changing a lone pair on the O to a bonding pair on the N. Do this for the other N atom as well. In the N2O4 molecule, both nitrogen atoms serve as central atoms. This is the arrangement given in the problem. Both nitrogen atoms are equivalent with three groups and no lone pairs (AX3), so the arrangement is **trigonal planar** with **no deviation** (no lone pairs) from the ideal angle of 120°. The same results arise from the other resonance structures.



9.18 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures.

Solution:

a) CH3COOH has [2 x C(4e–)] + [4 x H(1e–)] + [2 x O(6e–)] = twenty-four valence electrons. Use fourteen electrons to place a single bond between all of the atoms. This leaves 24 – 14 = 10 e– (five pairs). Use these five pairs to complete the octets of the O atoms; the C atom bonded to the H atoms has an octet but the other C atom does not have a complete octet. Form a double bond from the O atom (not bonded to H) to the C by changing a lone pair on the O to a bonding pair on the C. In the CH3COOH molecule, the carbon atoms and the O with H attached serve as central atoms. The carbon bonded to the H atoms has four groups and no lone pairs (AX4), so it is **tetrahedral** with **no deviation** from the ideal angle of 109.5°. The carbon bonded to the O atoms has three groups and no lone pairs (AX3), so it is **trigonal planar** with **no deviation** from the ideal angle of 120°. The H bearing O has two bonds and two lone pairs (AX2E2), so the arrangement is **V shaped** or **bent** with an angle **less than the ideal** value of 109.5°.



b) H2O2 has [2 x H(1e–)] + [2 x O(6e–)] = fourteen valence electrons. Use six electrons to place single bonds between the O atoms and between each O atom and an H atom. This leaves 14 – 6 = 8 e– (four pairs). Use these four pairs to complete the octets of the O atoms. In the H2O2 molecule, both oxygen atoms serve as central atoms. Both O atoms have tw bonds and two2 lone pairs (AX2E2), so they are **V shaped** or **bent** with angles **less than the ideal** value of 109.5°.



9.20 Plan: First, draw a Lewis structure, and then apply VSEPR. The presence of lone pairs on the central atom

generally results in a smaller than ideal bond angle.

Solution:



120o 180o  109.5o < 109.5o << 109.5o

Bond angles: **OF2 < NF3 < CF4 < BF3 < BeF2**

BeF2 is an AX2 type molecule, so the angle is the ideal 180°. BF3 is an AX3 molecule, so the angle is the ideal 120°. CF4, NF3, and OF2 all have tetrahedral electron-group arrangements of the following types: AX4, AX3E1, and AX2E2, respectively. The ideal tetrahedral bond angle is 109.5°, which is present in CF4. The one lone pair in NF3 decreases the angle a little. The two lone pairs in OF2 decrease the angle even more.

9.22 Plan: The ideal bond angles depend on the electron-group arrangement. Deviations depend on lone pairs.

Solution:

a) The C and N have three groups, so they are **ideally 120°**, and the O has four groups, so **ideally the angle is 109.5°**. The N and O have lone pairs, so the **angles are less than ideal**.

b) All central atoms have four pairs, so ideally all the angles are **109.5°**. The lone pairs on the O **reduce** this value.

c) The B has three groups (no lone pairs) leading to an **ideal bond angle of 120°**. All the O atoms have four pairs **(ideally 109.5°)**, two of which are lone, and **reduce the angle**.

9.25 Plan: The Lewis structures are needed to predict the ideal bond angles.

Solution:

The P atoms have no lone pairs in any case so the angles are ideal.

PCl5: PCl4+: PCl6–:





The original PCl5 is AX5, so the shape is trigonal bipyramidal, and the angles are 120° and 90°.

The PCl4+ is AX4, so the shape is tetrahedral, and the angles are 109.5°.

The PCl6– is AX6, so the shape is octahedral, and the angles are 90°.

Half the PCl5 (trigonal bipyramidal, 120° and 90°) become tetrahedral PCl4+ (tetrahedral, 109.5°), and the other half become octahedral PCl6– (octahedral, 90°).

9.26 Molecules are polar if they have polar bonds that are not arranged to cancel each other. A polar bond is present any time there is a bond between elements with differing electronegativities.

9.29 Plan: To determine if a bond is polar, determine the electronegativity difference of the atoms participating in

the bond. The greater the electronegativity difference, the more polar the bond. To determine if a molecule is polar (has a dipole moment), it must have polar bonds, and a certain shape determined by VSEPR.

Solution:

a)Molecule Bond Electronegativities Electronegativity difference

SCl2 S–Cl S = 2.5 Cl = 3.0 3.0 – 2.5 = 0.5

F2 F–F F = 4.0 F = 4.0 4.0 – 4.0 = 0.0

CS2 C–S C = 2.5 S = 2.5 2.5 – 2.5 = 0.0

CF4 C–F C = 2.5 F = 4.0 4.0 – 2.5 = 1.5

BrCl Br–Cl Br = 2.8 Cl = 3.0 3.0 – 2.8 = 0.2

The polarities of the bonds increase in the order: F–F = C–S < Br–Cl < S–Cl < C–F. Thus, **CF4** has the most polar bonds.

b) The F2 and CS2 cannot be polar since they do not have polar bonds. CF4 is an AX4 molecule, so it is tetrahedral with the four polar C–F bonds arranged to cancel each other giving an overall nonpolar molecule. **BrCl has a dipole moment** since there are no other bonds to cancel the polar Br–Cl bond. **SCl2 has a dipole moment** (is polar) because it is a bent molecule, AX2E2, and the electron density in both S–Cl bonds is pulled towards the more electronegative chlorine atoms.



nonpolar polar

9.31 Plan: If only two atoms are involved, only an electronegativity difference is needed. The greater the difference in

electronegativity, the more polar the bond. If there are more than two atoms, the molecular geometry must be determined.

Solution:

a) All the bonds are polar covalent. The SO3 molecule is trigonal planar, AX3, so the bond dipoles cancel leading to a nonpolar molecule (no dipole moment). The SO2 molecule is bent, AX2E1, so the polar bonds result in

electron density being pulled towards one side of the molecule. **SO2 has a greater dipole moment** because it is the only one of the pair that is polar.



b) ICl and IF are polar, as are all diatomic molecules composed of atoms with differing electronegativities. The electronegativity difference for ICl (3.0 – 2.5 = 0.5) is less than that for IF (4.0 – 2.5 = 1.5). The greater difference means that **IF has a greater dipole moment**.

c) All the bonds are polar covalent. The SiF4 molecule is nonpolar (has no dipole moment) because the bonds are arranged tetrahedrally, AX4. SF4 is AX4E1, so it has a see-saw shape, where the bond dipoles do not cancel. **SF4**  **has the greater dipole moment**.



d) H2O and H2S have the same basic structure. They are both bent molecules, AX2E2, and as such, they are polar. The electronegativity difference in H2O (3.5 – 2.1 = 1.4) is greater than the electronegativity difference in

H2S (2.5 – 2.1 = 0.4) so **H2O has a greater dipole moment**.

9.33 Plan: Draw Lewis structures, and then apply VSEPR. A molecule has a dipole moment if polar bonds do not

cancel.

Solution:

C2H2Cl2 has [2 x C(4e–)] + [2 x H(1e–)] + [2 x Cl(7e–)] = 24 valence electrons. The two carbon atoms are bonded to each other. The H atoms and Cl atoms are bonded to the C atoms. Use ten electrons to place a single bond between all of the atoms. This leaves 24 – 10 = 14e– (seven pairs). Use these seven pairs to complete the octets of the Cl atoms and one of the C atoms; the other C atom does not have a complete octet. Form a double bond between the carbon atoms by changing the lone pair on one C atom to a bonding pair. There are three possible structures for the compound C2H2Cl2:



I II III

The presence of the double bond prevents rotation about the C=C bond, so the structures are “fixed.” The C–Cl bonds are more polar than the C–H bonds, so the key to predicting the polarity is the positioning of the C–Cl bonds. Structure I has the C–Cl bonds arranged so that they cancel leaving I as a nonpolar molecule. Both II and III have C–Cl bonds on the same side so the bonds work together making both molecules polar. Both I and II will react with H2 to give a compound with a Cl attached to each C (same product). Structure III will react with H2 to give a compound with two Cl atoms on one C and none on the other (different product). **Structure I must be X** as it is the only one that is nonpolar (has no dipole moment). **Structure II must be Z** because it is polar and gives the same product as compound X. This means that **Structure III must be the remaining compound, Y**. **Compound Y (III) has a dipole moment**.

9.37 Plan: Use the Lewis structures shown in the text. The equation for formal charge (FC) is FC = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

Solution:

a) Formal charges for Al2Cl6:

FCAl = 3 – [0 + ½(8)] = **–1**

FCCl, ends = 7 – [6 + ½(2)] = **0**

FCCl, bridging = 7 – [4 + ½(4)] = **+1**

(Check: Formal charges add to zero, the charge on the compound.)

Formal charges for I2Cl6:

FCI = 7 – [4 + ½(8)] = **–1**

FCCl, ends = 7 – [6 + ½(2)] = **0**

FCCl, bridging = 7 – [4 + ½(4)] = *+***1**

(Check: Formal charges add to zero, the charge on the compound.)

b) The aluminum atoms have no lone pairs and are AX4, so they are tetrahedral. The two tetrahedral Al atoms cannot give a planar structure. The iodine atoms in **I2Cl6** have two lone pairs each and are AX4E2 so they are square planar. Placing the square planar I atoms adjacent can give a planar molecule.

9.42 Plan: Draw the Lewis structures, and then use VSEPR to describe epoxypropane (propylene oxide).

Solution:

a)





In epoxypropane , the C atoms are all AX4. The C atoms do not have any unshared (lone) pairs. All of the ideal bond angles for the C atoms in epoxypropane are **109.5°** and the molecular shape around each carbon atom is **tetrahedral**.

b) In epoxypropane , the C that is not part of the three-membered ring should have an ideal angle. The atoms in the ring form an equilateral triangle. The angles in an equilateral triangle are 60°. The angles around the two carbon atoms in the rings are reduced from the ideal 109.5° to 60°.

9.45 Plan: The basic Lewis structure will be the same for all species. The Cl atoms are larger than the F atoms. All of

the molecules are of the type AX5 and have trigonal bipyramidal molecular shape. The equatorial positions are in

the plane of the triangle and the axial positions above and below the plane of the triangle. In this molecular shape, there is more room in the equatorial positions.

Solution:

a) The F atoms will occupy the smaller axial positions first so that the larger Cl atoms can occupy the equatorial

positions which are less crowded.

b) The molecule containing only F atoms is nonpolar (has no dipole moment), as all the polar bonds would cancel. The molecules with one F or one Cl would be polar since the P–F and P–Cl bonds are not equal in polarity and thus do not cancel each other. The presence of two axial F atoms means that their polarities will cancel (as would the three Cl atoms) giving a nonpolar molecule. The molecule with three F atoms is also polar.



Polar Nonpolar Polar Polar Nonpolar

No dipole moment No dipole moment



9.47 Plan: Pick the VSEPR structures for AY3 substances. Then determine which are polar.

Solution:

The molecular shapes that have a central atom bonded to three other atoms are trigonal planar, trigonal pyramidal,

and T shaped:



a) b) c)

three groups four groups five groups

(AX3) (AX3E1) (AX3E2)

trigonal planar trigonal pyramidal T shaped

Trigonal planar molecules, such as a), are nonpolar, so it cannot be AY3. Trigonal pyramidal molecules b) and T- shaped molecules c) are polar, so either could represent AY3.

9.50 Plan: Draw the Lewis structure of each compound. Atoms 180° apart are separated by the sum of the bond’s length. Atoms not at 180° apart must have their distances determined by geometrical relationships.

Solution:



a) C2H2 has [2 x C(4e–)] + [2 x H(1e–)] = 10 valence electrons to be used in the Lewis structure. Six of these electrons are used to bond the atoms with a single bond, leaving 10 – 6 = 4 electrons. Giving one carbon atom the four electrons to complete its octet results in the other carbon atom not having an octet. The two lone pairs from the carbon with an octet are changed to two bonding pairs for a triple bond between the two carbon atoms. The molecular shape is linear. The H atoms are separated by two carbon-hydrogen bonds (109 pm) and a carbon-carbon triple bond (121 pm).

Total separation = 2(109 pm) + 121 pm = **339 pm**

b) SF6 has [1 x S(6e–)] + [6 x F(7e–)] = 48 valence electrons to be used in the Lewis structure. Twelve of these electrons are used to bond the atoms with a single bond, leaving 48 – 12= 36 electrons. These thirty-six electrons are given to the fluorine atoms to complete their octets. The molecular shape is octahedral. The fluorine atoms on opposite sides of the S are separated by twice the sulfur-fluorine bond length (158 pm).

Total separation = 2(158 pm) = **316 pm**

Adjacent fluorines are at two corners of a right triangle, with the sulfur at the 90° angle. Two sides of the triangle are equal to the sulfur-fluorine bond length (158 pm). The separation of the fluorine atoms is at a distance equal to the hypotenuse of this triangle. This length of the hypotenuse may be found using the Pythagorean Theorem

(a2 + b2 = c2). In this case a = b = 158 pm. Thus, c2 = (158 pm)2 + (158 pm)2, and so c = 223.4457 pm = **223 pm**.

c) PF5 has [1 x P(5e–)] + [5 x F(7e–)] = 40 valence electrons to be used in the Lewis structure. Ten of these electrons are used to bond the atoms with a single bond, leaving 40 – 10= 30 electrons. These thirty electrons are given to the fluorine atoms to complete their octets. The molecular shape is trigonal bipyramidal. Adjacent equatorial fluorine atoms are at two corners of a triangle with an F-P-F bond angle of 120o. The length of the P-F bond is 156 pm. If the 120o bond angle is A, then the F-F bond distance is a and the P-F bond distances are b and c. The F-F bond distance can be found using the Law of Cosines: a2 = b2 + c2 – 2bc (cos A).

a2 = (156 pm)2 + (156 pm)2 – 2(156 pm)(156 pm)cos 120o. a = 270.1999 pm = **270 pm**.