

## Chem C1403 Lecture 6. Lewis structures and the geometry of molecules with a central atom.

- (1) Covalent bonding: sharing of electron pairs by atoms
- (2) Rules for writing valid Lewis structures
- (3) Multiple bonding
- (3) Formal charges within Lewis structures
- (4) Isomers
- (5) Limitations of Lewis structures: resonance structures and violations of the octet rule (odd electron, hypovalent and hypervalent molecules).

## Beyond Lewis structures: the geometry of molecules

- (1) Shapes of simple molecules with "central" atoms.
- (2) Configuration: the position of atoms in space about a central atom. The VSEPR theory of configuration.
- (3) Steric number rules.
- (4) The five favored electronic geometries of configurations
- (5) Connecting molecular geometries to electronic geometries by VSEPRs
- (6) Polar covalent bonds: using molecular geometries to deduce the dipole moments of molecules

## Writing acceptable Lewis structures

- (1) From composition to acceptable Lewis structures
- (2) Same composition, different constitution = **isomers** = different molecules
- (3) Same constitution, different Lewis structure = **resonance structures** = one molecule different electronic representations
- (4) Comparing stabilities of isomers and resonance structures through computation of **formal charge** for Lewis structures

**Important:** Lewis structures indicate the way bonds connect the atoms of a molecule, but *they do not show the three-dimensional molecular geometry.*

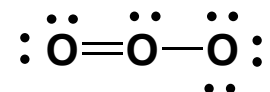
*A strategy for writing Lewis structures (others are possible).*

- (1) Compute the number of valence electrons from the composition. Add one more electron for each negative charge in the composition. Subtract one electron for each positive charge in the composition.
- (2) All acceptable Lewis structures must have the correct composition of atoms and charge.
- (3) An atomic constitution must be assumed or given.
- (4) Start to build up the electronic constitution (Lewis structure) by giving the outer atoms a duet (H) or octet (C, N, O, F).
- (5) Share electrons until an acceptable Lewis structure is achieved.

## Example: ozone, $O_3$

- (1) Compute the number of valence electrons from the composition. Add one more electron for each negative charge in the composition. Subtract one electron for each positive charge in the composition:  $VE = 3 \times 6 = 18$
- (2) All acceptable Lewis structures must have the correct composition of atoms and charge:  $Net\ charge = 0$
- (3) An atomic constitution must be assumed or given:  $O-O-O$
- (4) Start to build up the electronic constitution (Lewis structure) by giving the outer atoms a duet (H) or octet (C, N, O, F), then adding any remaining electron pairs to the internal atoms:  
$$\begin{array}{ccc} \text{:}\ddot{O}\text{---}O\text{---}\ddot{O}\text{:} & & \text{:}\ddot{O}\text{---}\ddot{O}\text{---}\ddot{O}\text{:} \\ \text{..} & & \text{..} \\ \text{VE} = 16 & & \text{VE} = 18 \end{array}$$
- (5) Share electrons until an acceptable Lewis structure is achieved:

Acceptable Lewis structure for  $O_3$ :



## Formal charge (FC) in Lewis structures

Comparison of the **formal number** of valence electrons about an atom in the Lewis structure of a molecule and comparison of FN with the number of **valence electrons (VE)** in the neutral atom.

Computation of FC:

$$FC = VE (\text{neutral atom}) - LE (\text{atom in molecule}) - 1/2BE (\text{atom in molecule})$$

where

VE = the number of valence electrons in the neutral atom

LE = the number of lone pair electrons on the atom in the molecule

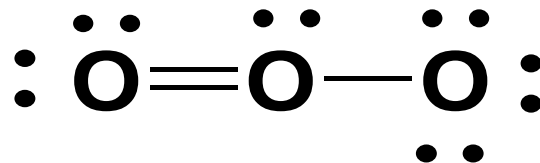
BE = the number of bonding electrons on the atom in the molecule

Example of formal charge computation: ozone,  $O_3$

VE (atom)	=	6	6	6
1/2 BE (molecule)	=	-2	-3	-1
LE (molecule)	=	-4	-2	-6

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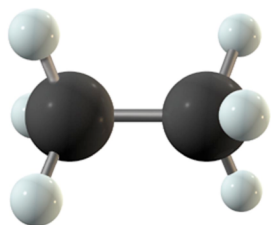
FC	=	0	+1	-1
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Note: New charge for molecule = 0, sum of formal charges must = 0.

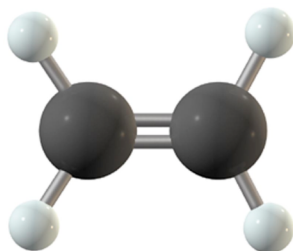
## Multiple bonding in Lewis structures

Two atoms can share one pair of electrons (single bond) 2 pairs of electrons (double bond) or 3 pairs of electrons (triple bonds)



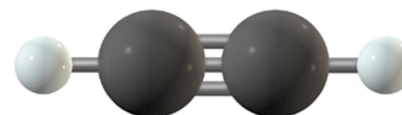
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$C_2H_6$  (ethane)



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$C_2H_4$  (ethylene)



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$C_2H_2$  (acetylene)

TABLE 3-3

Average Bond Lengths

C—C	1.54	N—N	1.45	C—H	1.10	O—O	1.48
C=C	1.34	N=N	1.25	N—H	1.01	O=O	1.21
C≡C	1.20	N≡N	1.10	O—H	0.96		
C—O	1.43	N—O	1.43	C—N	1.47		
C=O	1.20	N=O	1.18	C≡N	1.16		

All values are in units of  $10^{-10}$  m.

Rule: More bonds, shorter bonds: triple bond shorter than double bond; double bond shorter than single bond.



**Isomers: Same composition, two different constitutional Lewis structures**

HCN = atomic compositional structure

HCN possesses 10 VE = Lewis compositional structures

Two possible Lewis constitutional structures:

H-C-N or H-N-C

Both need to have 10 VE in their Lewis structure

**Problem: Try to achieve an acceptable Lewis structure (duet and octet rule followed) for both.**

HCN = atomic compositional structure

HCN: 10 VE = Lewis compositional structures

Two possible Lewis constitutional structures

H-C-N or H-N-C

Any acceptable Lewis structure for HCN needs to *show* 10 VE

Try to achieve an acceptable Lewis structure (duet and octet rules obeyed) for all isomeric structures.

Two acceptable Lewis structures. Which is better?

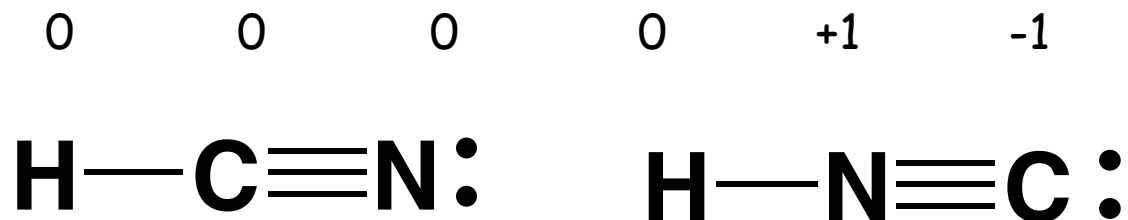


Use formal charges to decide on the stability of isomeric Lewis structures

	<b>H—C≡N:</b>			<b>H—N≡C:</b>		
VE (atom)	1	4	5	1	5	4
1/2 BE (molecule)	-1	-4	-3	-1	-4	-3
UE (molecule)	0	0	-2	0	0	-2
<hr/>						
FC on atom	0	0	0	0	+1	-1
	<b>H—C≡N:</b>			<b>H—N≡C:</b>		

Important: the net charge of composition HCN = 0, so the sum of the formal charges in any acceptable Lewis structure must be = 0 also.

Which is more stable?



Rule:

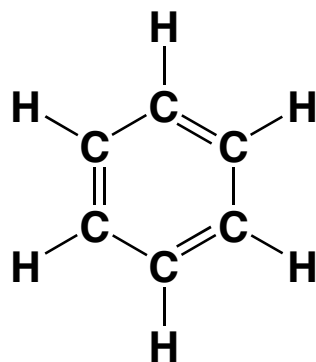
For two isomeric acceptable Lewis structures, the one with the least separation of formal charges is more stable.

Therefore,  $\mathbf{H-C\equiv N:}$  is the more stable isomer of the pair.

The same atomic composition can correspond to many  
Lewis acceptable structures

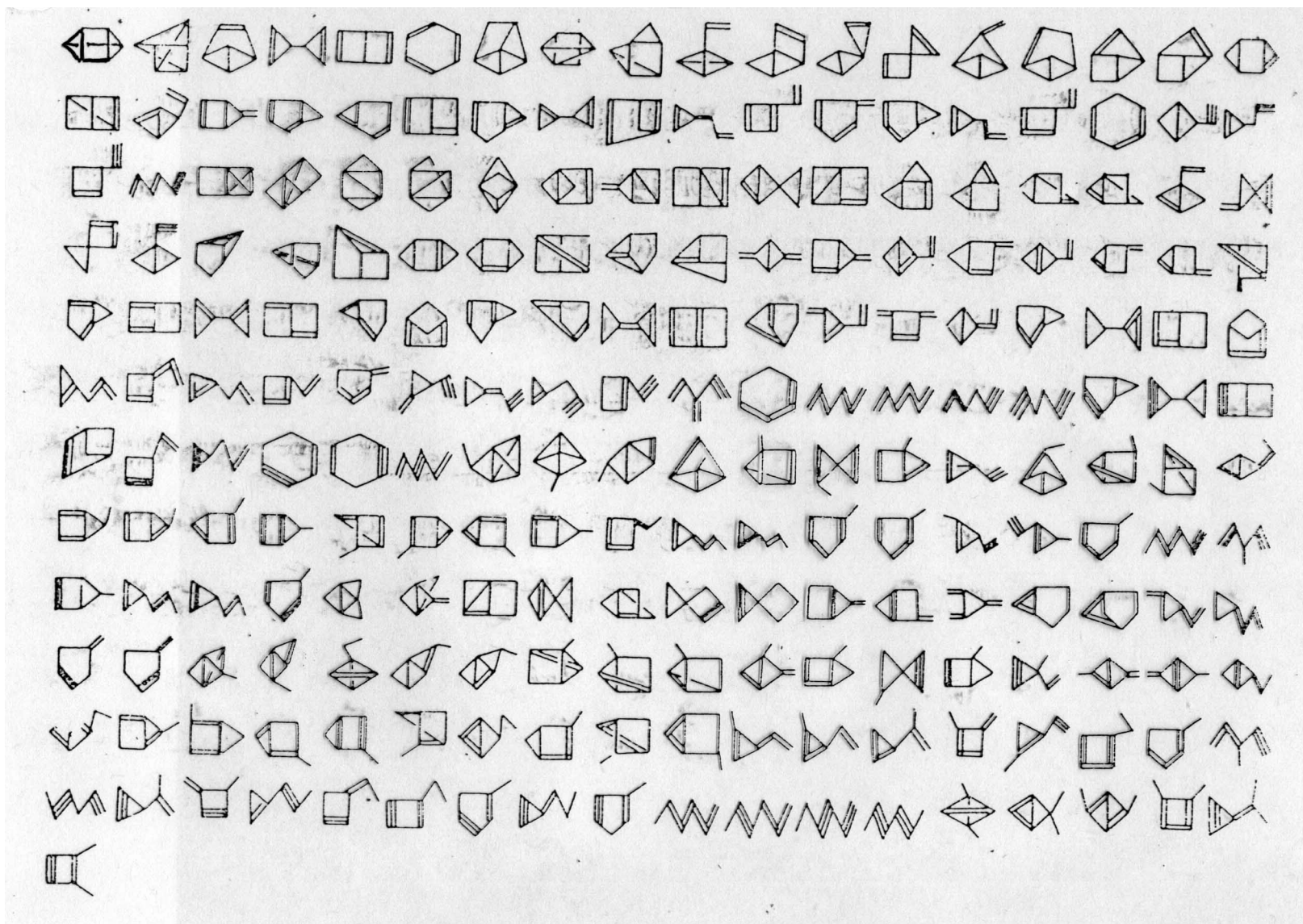
Example:  $C_6H_6$

This is the atomic composition of the famous organic  
molecule, benzene



How many other isomers (acceptable Lewis  
structures) of  $C_6H_6$  are possible?

# Isomers of the composition $C_6H_6$



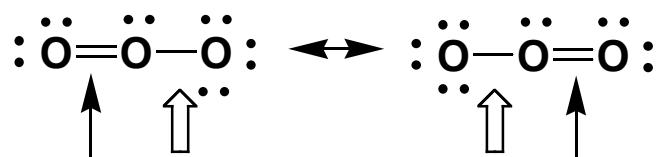
Resonance structures: two or more Lewis electronic structures for the same atomic composition

Example: ozone: atomic composition =  $O_3$

Atomic constitution:



Electronic constitution:



Neither Lewis structure is an accurate representation of the actual molecule: an equal mixture of the two structures is required:

Both O-O bonds of  $O_3$  are equal in length.

### *3.7 The Geometry (Shape) of Molecules: Valence Shell Electron Pair Repulsion (VSEPR) Theory*

- (1) Computing the number of bonds and pairs of non-bonding electrons on a central atom of a molecule
- (2) Predicting the shape of the disposition of atoms in space about a central atom of a molecule from (1)
- (3) Dealing with dipole moments, polar bonds, non-polar bonds
- (4) Dealing with polar and non-polar molecules with polar bonds



## The Valence shell electron pair repulsion (VSEPR) theory of the configuration (shape) of simple molecules

Lewis structures show how atoms are connected, not the angles or lengths of bonds in 3D.

VSEPR allows the translation of a Lewis structure into a configuration about a central atom by following the rules of VSEPR theory.

## VSEPR Theory

- (1) Electron pairs repel each other and try to remain as far apart from one another as possible.
- (2) The positions of atoms in space (molecular geometry or configuration about a central atom) is determined by the relative positions that electron pairs achieve after taking repulsions into account.
- (3) The arrangement of pairs about a central atom depends on the number of pairs that exist about the atom.

# The 5 basic electronic arrangements about a central atom:

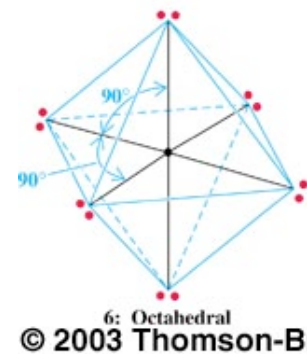
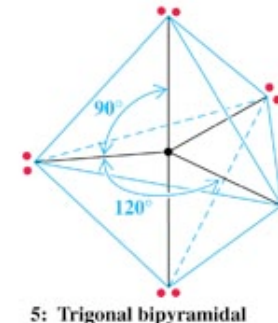
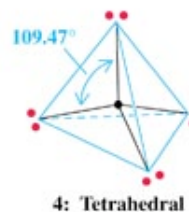
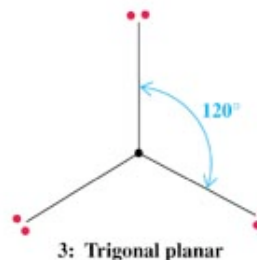
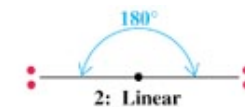
(1) Linear

(2) Trigonal planar

(3) Tetrahedral

(4) Trigonal bipyramidal

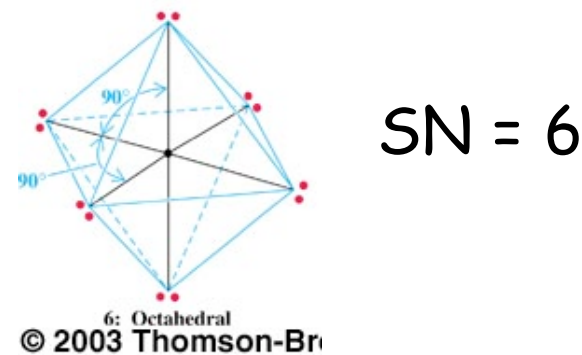
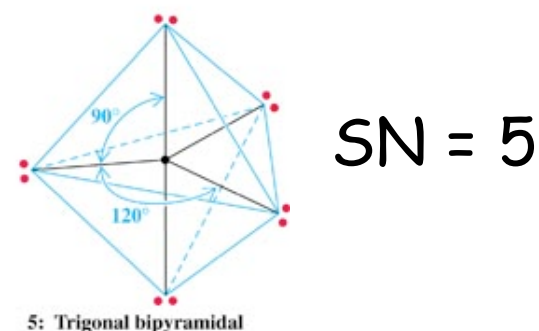
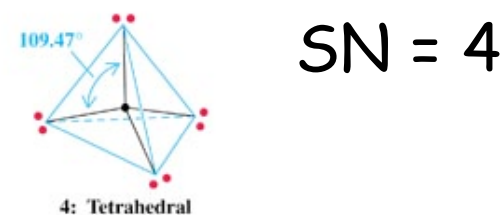
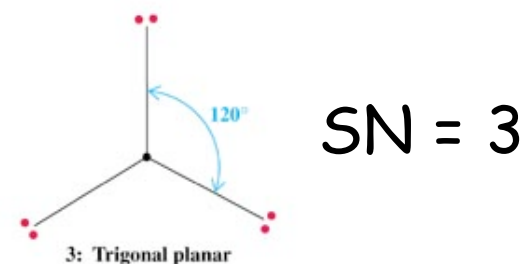
(5) Octahedral



# Determination of molecular geometry from a Lewis structure and its *steric number*

- (1) Consider all of the valence electrons about a central atom in a Lewis structure whose geometry is to be determined.
- (2) Compute the "steric number" (SN) of the central atom from the formula:  

$$\text{SN} = (\text{number of } \textit{atoms} \text{ bonded to the central atom}) + \text{the number of lone (non-bonded) } \textit{electron pairs} \text{ on the central atom.}$$
- (4) Use the Figure (3-17 in text) to the right to determine the *idealized electronic* arrangement from the steric number.

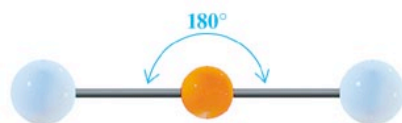


- (5) After the electronic arrangement about the central atom has been determined, place the atoms available in the Lewis structure at the vertices of the geometric figures in Figure 3-17.
- (6) For the trigonal bipyramidal and octahedral geometries, when more than one choice exists for placing the atoms at the vertices, use the  $90^\circ$  rules:
- (7) Minimize the number of lone pair-lone pair repulsions first, then minimize the number of lone pair-bonding pair repulsions.

See text Section 3-7 for examples. See homework problems 57-70 for more examples.

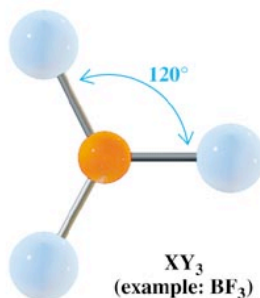
The five basic *molecular geometries* for the five basic electronic geometries about a central atom.

SN +2



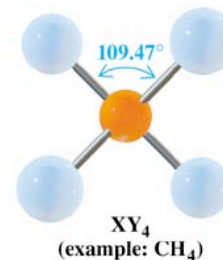
$XY_2$   
(example:  $CO_2$ )

SN = 3



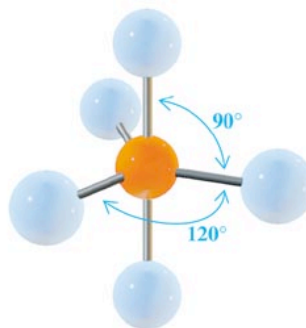
$XY_3$   
(example:  $BF_3$ )

SN = 4



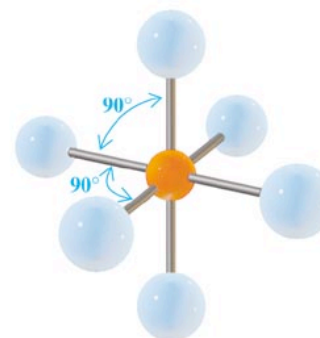
$XY_4$   
(example:  $CH_4$ )

SN = 5



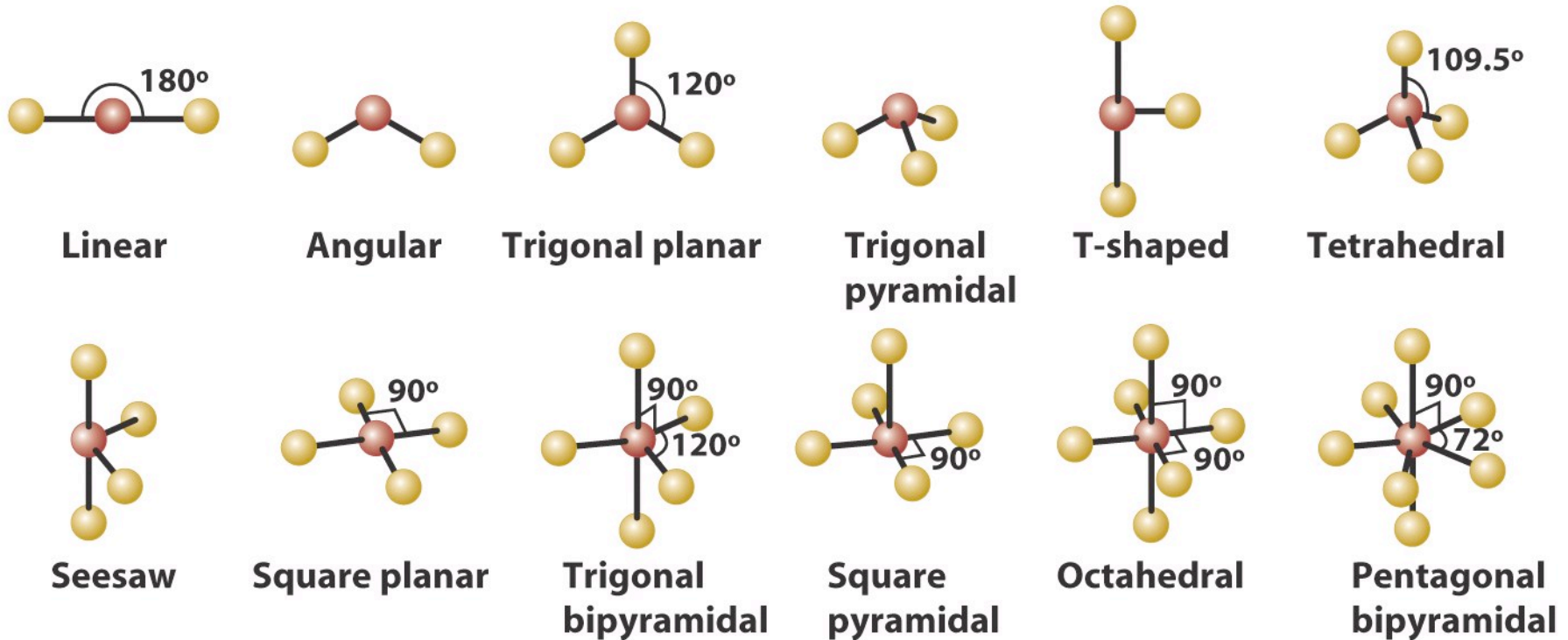
$XY_5$   
(example:  $PCl_5$ )

SN = 6



$XY_6$   
(example:  $SF_6$ )

Some geometries (configurations) of simple molecules possessing a "central atom" surrounded by a single kind of second atom. The names of the geometries are given under the structures.

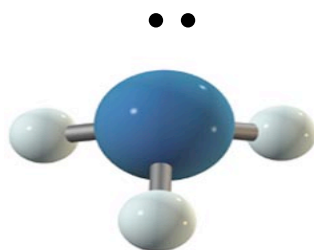
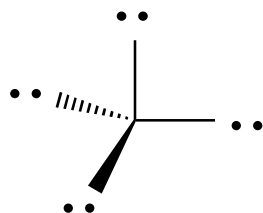


Important: the term "**molecular geometry**" refers to the positions of the atoms in space about the central atom. Any lone pairs that are on the central atom are not considered in describing the final geometry.

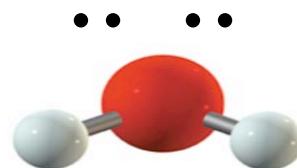
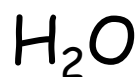
Thus, the SAME electronic geometry (same steric number) may correspond to more than one molecular geometry.

Examples. All have steric number = 4 but different molecular geometries:  $\text{H}_2\text{O}$  (bent),  $\text{NH}_3$  (pyramidal) and  $\text{CH}_4$  all are correlated with the same idealized **tetrahedral electronic geometry**.

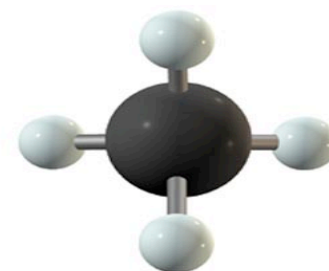
Tetrahedral  
Electronic  
Geometry SN = 4



(a)



(b)

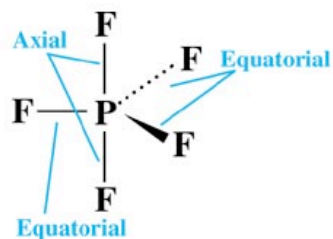


(c)

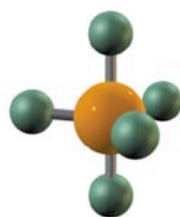


Another example of one steric number, one electronic geometry, but more than one molecular geometry: For steric number = 5 (trigonal bipyramid) there are a number of molecular geometries depending on the number of atoms forming bonds with the central atom.

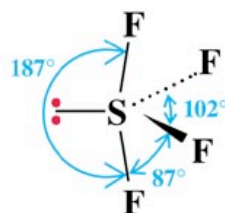
Examples:  $\text{PF}_5$ ,  $\text{SF}_4$  (two isomers shown),  $\text{ClF}_3$ ,  $\text{XeF}_2$



(a)  $\text{PF}_5$



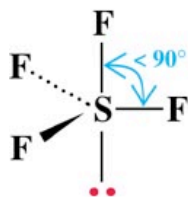
Trigonal bipyramid



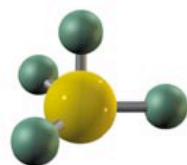
(b)  $\text{SF}_4$



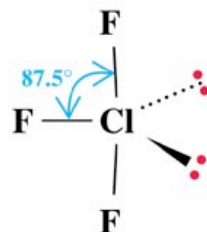
Seesaw  
(low-energy, favored)



(c)  $\text{SF}_4$



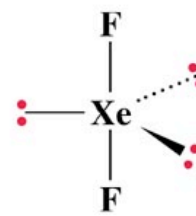
Distorted pyramid  
(high-energy, not favored)



(d)  $\text{ClF}_3$



Distorted T



(e)  $\text{XeF}_2$



Linear

Bond polarity: A difference in the sharing of electrons by a pair of atoms. The more electronegative atom pulls electrons more toward it to create an electric dipole with a negative end closer to the more electronegative atom.

Although bonds may be polar in a molecule, the dipole moments associated with the polar bonds may cancel, leading to a non-polar molecule with polar bonds.

