

## Dipoles

In a previous lecture we examined how atoms hybridize when forming bonds. In this lecture we address the question: How do we know that hybridization theory is correct?

**Electronegativity**

One of the most important attributes of an atom is its electronegativity (symbolized by the Greek letter chi  $\chi$ ), which is defined as that atom's ability to attract electrons. The American physicist and chemist Robert Mullikan (Nobel Prize, 1966) proposed that electronegativity  $\chi$  be calculated by the formula

$$\chi = (0.00197) \times (\text{IP} - \text{EA}) + 0.19$$

where IP is an atom's first ionization potential and EA is that atom's electron affinity, both in units of kilojoule per mole;  $\chi$  has no units.

A large value of IP means that an atom gives up an electron reluctantly: it is good at holding on to the electrons it has. A negative value of EA means that an atom captures an electron readily. Thus, the most electronegative atoms should have a large value of IP and a negative value of EA; conversely, the least electronegative atoms should have a small value of IP and a positive value of EA.

Problem Calculate the Mullikan electronegativity of fluorine (IP = 1681 kJ/mol, EA = -333 kJ/mol) and of carbon (IP = 1086 kJ/mol, EA = -121 kJ/mol).

Answer For fluorine  $\chi = 4.16$ ; for carbon  $\chi = 2.57$ . Fluorine is much more electronegative than carbon. This result could have been anticipated given that fluorine has both a larger value of IP and a more negative value of EA.

There are two fairly reliable periodic-table trends in electronegativity: electronegativity increases from left to right across a row and increases up a column. An important exception to these general trends is that the electronegativity of hydrogen ( $\chi = 2.20$ ) is intermediate between that of boron ( $\chi = 2.04$ ) and carbon ( $\chi = 2.55$ ) even though hydrogen appears far to the left on

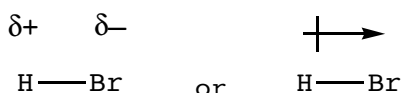
most periodic tables. We should also note that, among the elements most important to organic chemistry, N, O, F, S, Cl, Br and I are more electronegative than carbon.

### Bond dipoles

Because electronegativity is the ability to attract electrons, whenever two atoms of different electronegativity are bonded together, electrons flow from the less electronegative to the more electronegative atom. In ionic bonds the flow of electrons is extreme: we characterize ionic bonds as the complete transfer of electrons from a metal to a non-metal. The flow of electrons from the less to the more electronegative atom also takes place in covalent bonds between non-metals, albeit to a lesser extent than in ionic bonds because the electronegativity differences between two non-metals tend to be less than the electronegativity differences between metals and non-metals.

Let's consider a covalent bond between atoms of different electronegativity. In HBr, for example, Br ( $\chi_{\text{Br}} = 2.96$ ) withdraws electrons from H ( $\chi_{\text{H}} = 2.20$ ). The electrons in the H-Br bond tend to gang up near the more electronegative Br atom: thus, the Br end of the H-Br bond has an excess of negative charge whereas the H end has a deficit of negative charge (or, put another way, an excess of positive charge).

An unsymmetrical distribution of electrons in a bond is called a bond dipole. A bond that has a bond dipole is called a polar bond. A bond dipole can be denoted in several ways. The first method is to write the symbol  $\delta+$  (delta plus), which indicates a partial positive charge, over the less electronegative atom and to write the symbol  $\delta-$  (delta minus), which indicates a partial negative charge, over the more electronegative atom. The second method is to draw an arrow pointing in the direction in which electrons flow, that is, from the less electronegative to the more electronegative atom. The arrow is crossed near the less electronegative atom as a sort of shorthand notation for a positive sign. Applied to HBr, the bond dipole is symbolized as follows:



The second method of representing a bond dipole is particularly useful because it indicates that a bond dipole is a vector. You may recall that a vector has direction (i.e., it points somewhere) and magnitude (i.e., it has a

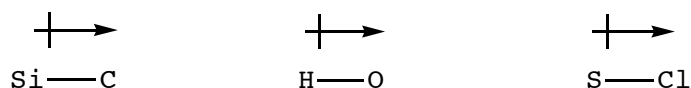
definite length). A bond dipole vector points toward the more electronegative atom and its magnitude depends in a complicated way on both the electronegativity difference between the two atoms involved in the bond and the length of that bond. However, as illustrated by the data table below which presents the magnitude of the bond dipole in units of debye (D), the magnitude of the bond dipole vector is reasonably well correlated to electronegativity differences alone.

Bond	Electronegativity difference*	Bond length [m]	Bond dipole [D]
<i>Bonds to carbon</i>			
C-F	1.43	$1.39 \times 10^{-10}$	2.48
C-O	0.89	$1.43 \times 10^{-10}$	1.19
C-Cl	0.61	$1.78 \times 10^{-10}$	0.79
C-N	0.49	$1.47 \times 10^{-10}$	0.45
C-Br	0.41	$1.94 \times 10^{-10}$	0.45
C-H	0.35	$1.09 \times 10^{-10}$	0.19
C-I	0.11	$2.14 \times 10^{-10}$	0.07
C-S	0.03	$1.79 \times 10^{-10}$	0.01
<i>Bonds to hydrogen</i>			
H-O	1.24	$0.97 \times 10^{-10}$	1.39
H-N	0.84	$1.00 \times 10^{-10}$	0.76
H-S	0.38	$1.32 \times 10^{-10}$	0.27
H-C	0.35	$1.09 \times 10^{-10}$	0.19

\* Value given is the absolute value without regard for algebraic sign.

Problem Using the crossed arrow notation, indicate the direction of the bond dipole of these bonds: (a) C-Si; (b) O-H; (c) S-Cl.

Answer



Problem Rank the following bonds in order of the magnitude of their bond dipole: H-O, Cl-Cl, H-F. Explain the reasoning behind your ranking.

Answer Cl-Cl < H-O < H-F. The Cl-Cl bond features two atoms of equal electronegativity and thus has no bond dipole. Deciding whether the H-O or H-F bond is more polar could be tricky because the magnitude of the bond dipole depends both on electronegativity difference and bond length. Luckily, O and F reside on the same row of the periodic table: their covalent radii are similar and so the H-O bond ( $0.97 \times 10^{-10}$  m) has about the same length as the H-F bond ( $1.09 \times 10^{-10}$  m). We can confidently assume that electronegativity differences are in control: the H-F bond (2.70 D) is indeed more polar than the H-O bond (1.39 D).

### Dipole moments

Most organic molecules have many bonds and many bond dipoles. The vector sum of all the bond dipoles in a molecule is called the dipole moment and is symbolized by  $\mu$  (the Greek letter mu). The unit of the dipole moment is the debye (D). If a molecule has a dipole moment equal to zero, that molecule is said to be non-polar. If a molecule has a non-zero dipole moment, that molecule is said to be polar. We will see that measured values of  $\mu$  lend support to the correctness of hybridization theory.

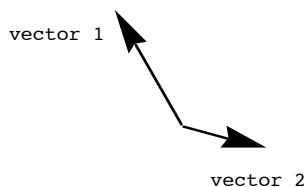
### Adding vectors

Because the dipole moment  $\mu$  is a vector sum, it might be wise to first review how to add vectors. A vector has an origin (a starting point) and a terminus (an end point) whose location is identified by the tip of an arrow. Let's call the two vectors we wish to add "vector 1" and "vector 2".



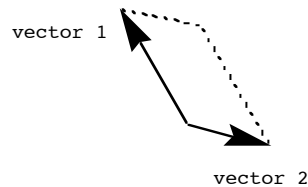
- Step # 1

Without changing their magnitudes or the direction in which the vectors point, place the origins of both vectors together.



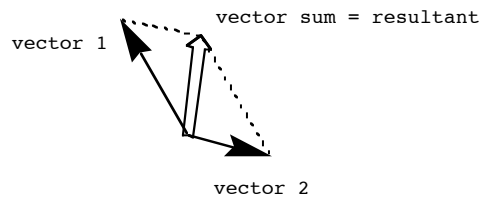
- Step # 2

Beginning at the terminus of vector 1, draw a line parallel to and of the same length as vector 2. Then, beginning at the terminus of vector 2, draw a line parallel to and of the same length as vector 1. You should be looking at a four-sided figure called a parallelogram, which may look like a diamond, a rectangle, or a square:



- Step # 3

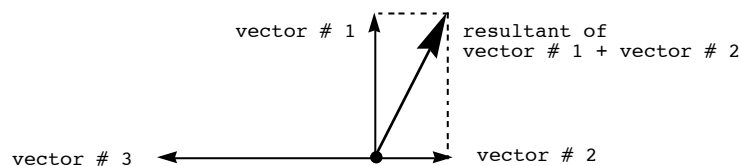
The vector sum, called the resultant, is the vector that bisects the parallelogram as shown in the figure below.



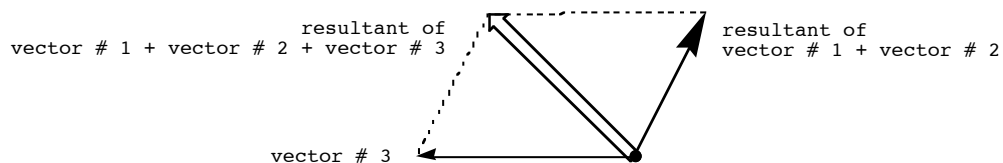
Vector addition, just like the addition of any two numbers, is commutative and associative, that is, when we add three or more vectors, we first add any two vectors, then add the third to the resultant of the first two, then add the fourth to the resultant of the first three, and so on.

Problem Vector # 1 has a magnitude of 2 units and points in the positive y direction. Vector # 2 has a magnitude of 1 unit and points in the positive x direction. Vector # 3 has a magnitude of 3 units and points in the negative x direction. Determine the magnitude and direction of the resultant.

Answer We first add vector # 1 and vector # 2:

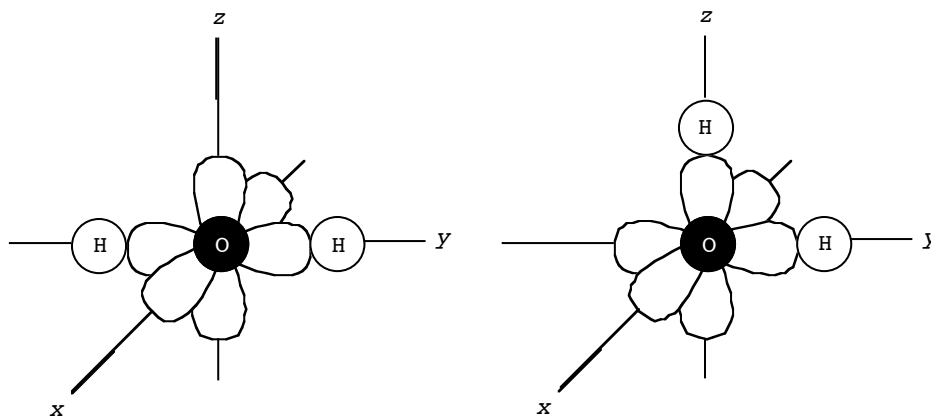


Then add vector # 3 to the resultant of vector # 1 + vector # 2:

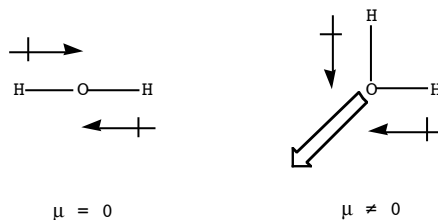


### Dipole moments and hybridization

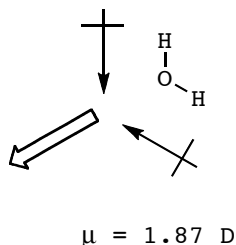
Let's now apply vector addition to a molecule in order to determine whether hybridization theory correctly predicts whether that molecule has a dipole moment. Consider  $\text{H}_2\text{O}$ . What if hybridization theory were wrong and oxygen formed bonds to hydrogen using its pure 2p AOs? If that were the case, depending on which 2p AOs oxygen used to form bonds, there would be two isomeric forms of water, a linear form having a hydrogen–oxygen–hydrogen bond angle ( $\angle\text{HOH}$ ) of  $180^\circ$  and a bent form having  $\angle\text{HOH} = 90^\circ$ :



From its location on the periodic table, it is evident that O is more electronegative than H: thus, both H–O bonds have a bond dipole that points away from H and toward O. When we add the two bond dipole vectors, we would conclude that linear  $\text{H}_2\text{O}$  would be a non-polar molecule (i.e.,  $\mu = 0$ ) because the two bond dipoles precisely cancel, whereas bent  $\text{H}_2\text{O}$  would be a polar molecule (i.e.,  $\mu \neq 0$ ):

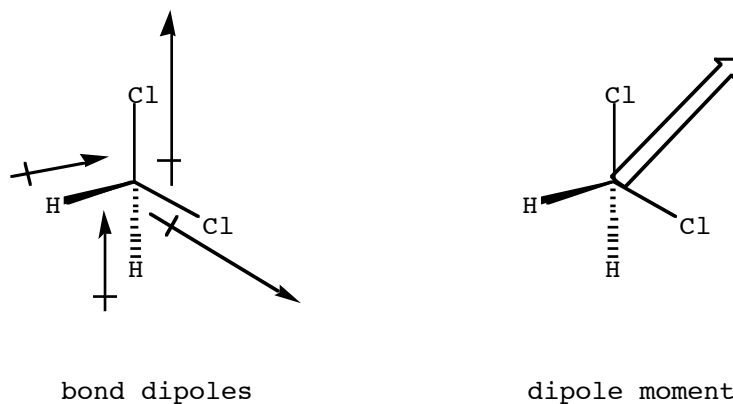


Of course, this is total fantasy! Water does not exist in polar and non-polar forms because oxygen does not use pure 2p AOs when forming bonds to hydrogen. All water molecules are polar ( $\mu = 1.87 \text{ D}$ ) because all water molecules have the bent shape predicted by  $sp^3$  hybridization:



Problem Is methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) polar or non-polar?

Answer  $\text{CH}_2\text{Cl}_2$  is polar ( $\mu = 1.6 \text{ D}$ ) because all  $\text{CH}_2\text{Cl}_2$  molecules have the tetrahedral shape predicted by  $sp^3$  hybridization:

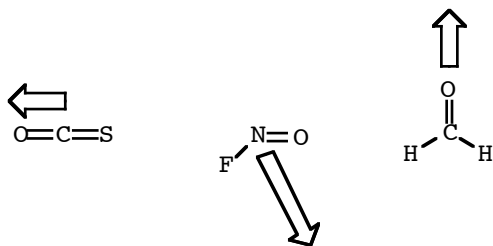


The dipole moment lies in the plane formed by the chlorine and carbon atoms and bisects the chlorine-carbon-chlorine bond angle.

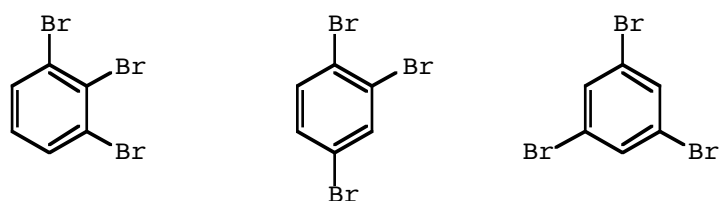
Problem Circle the molecules that are polar. For those molecules you circled, indicate the direction of the dipole moment using the symbol  $\Rightarrow$ .

- (a)  $\text{CO}_2$  (carbon dioxide, C is the central atom)
- (b)  $\text{COS}$  (carbon oxysulfide, C is the central atom)
- (c)  $\text{BH}_3$  (borane, B is the central atom)
- (d)  $\text{FNO}$  (nitrosyl fluoride, N is the central atom)
- (e)  $\text{CH}_2\text{O}$  (formaldehyde, C is the central atom)

Answer The polar molecules are (b), (d) and (e).

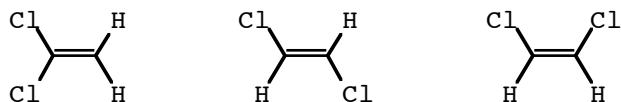


Problem Which of the following  $\text{C}_6\text{H}_3\text{Br}_3$  isomers is non-polar?



Answer The  $\text{C}_6\text{H}_3\text{Br}_3$  isomer on the right.

Problem Which of the following  $\text{C}_2\text{H}_2\text{Cl}_2$  isomers is non-polar?



Answer The  $\text{C}_2\text{H}_2\text{Cl}_2$  isomer in the middle.