7.12.1: Biology- The Hydrophobic Effect and Properties of Small Polyatomic Molecules

The biological properties of molecules depends strongly on their polarity, because ***bond* polarity** and ***molecular* polarity** play a large part in "noncovalent attractions" between molecules. Noncovalent attractions which are responsible for the DNA double helix, and antibody-antigen bonding can be understood in terms of *Polar Covalent Bonds* alone, but sometimes the polarity of the whole molecule must be considered.

For example, the suitability of water for biogenesis depends on the polarity of the whole molecule, and often involves the critically important "hydrophobic effect". The polarity of the molecule leads to extensive "hydrogen bonding" between molecules:

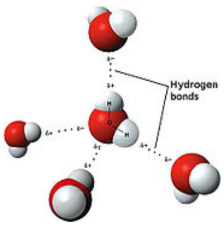


Figure 1:Hydrogen bonds between polar water molecules[1]

The hydrophobic effect accounts for the insolubility of nonpolar molecules, like CH_4. Note that nonpolar molecules may contain polar bonds!

Figure 2:Hydrophobic effect.

Figure 3: Magic Sand models hydrophobic effect [2]

The goal of this section is to differentiate between *bond polarity* and *molecular polarity*. To do that, we start with important biological, chemical, and physical properties of a few small molecules:

Physical Properties and Molecular Structure

First, look at the melting points and boiling points of substances in the table below. Surprisingly, they are not related in any way to the molecular weights. This makes sense if you remember that molecular weight is a nuclear property. Melting and boiling involve breaking bonds between molecules, so like all bonding, they involve electronic structure. They depend on the size of atoms and molecules, but by size we mean *volume*, not *mass*.

Second, notice that the small water molecule is exceptional. It has the largest dipole moment, and a boiling point that is over 100°C higher than molecules of similar size.

Molecules of very low boiling points have zero polarity, indicated by the molecular dipole moment in debyes[3]

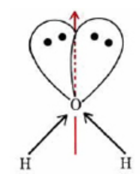
The molecular dipole moments determine all the biological properties mentioned above, so we must explain why water is so polar, and methane, CH_4, is a *nonpolar molecule*, even though it contains *polar bonds*.

Molecule	MW	MP°C	BP °C	dipole moment, D[4]	Significance
H_2	2	-259.14	-252.87	0	Used to reduce "bends"[5]
CH_4	16	-182.5	-161.6	0	methane, "hydrophobic effect"

NH_3	17	-77.73	-33.4	1.46	ammonia, very soluble
H_2O	18	0	100	1.84	liquid,
CO	28	-205	-191.5	0.12	toxic carbon monoxide
O_2	32	-218.79	-182.95	0	20% of air
CO_2	44	-78[6]	[7]	0	
SO_3	80	16.9	45	0	acid rain

H_2O

First, let's look at the water molecule. The O atom in H_2O is surrounded by four electron pairs, two bonded to H atoms and two lone pairs. Oxygen has a higher electronegativity (3.34) than hydrogen (2.2), so we have two dipole bond vectors pointing from H to O. There are also two lone pairs on O, enhancing its negative charge, so there is a resultant dipole.



The two "O" "H" bonds are represented by an arrow pointing from "H" towards "O". The two "H" are below "O" and are at an angle from one another. The two lone pairs are above "O" and represented by two pairs of dots. The resultant dipole is shown by a colored arrow pointing straight upwards from "O", right in the middle of the two lone pairs as well as the two "O" "H" bonds.

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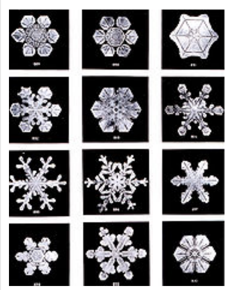

Figure 4 snowflake crystals.

The polarity of water leads to hydrogen bond networks in ice or snowflakes, which leads to destruction of plant tissue when water freezes. Snowflake crystals have shapes dictated by the angles between hydrogen bonded water molecules in Figure 1. Plants have several mechanisms to avoid ice damage. More important ramifications of water's polarity are mentioned later.

Vector Addition of Bond Dipoles

If water were linear, the dipole moment vectors of the two bonds would cancel each other by vector addition, as shown in Figure 5(a) below:

When more than one polar bond is present in the same molecule, the polarity of one bond may cancel that of another. Thus the presence of polar bonds in a polyatomic molecule does not *guarantee* that the molecule as a whole will have a dipole moment. In such a case it is necessary to treat each polar bond mathematically as a *vector* and represent it with an arrow. The *length* of such an arrow shows how large the bond dipole moment is, while the *direction* of the arrow is a line drawn from the positive to the negative end of the bond. Adding the individual bond dipole moments as vectors will give the overall molecular dipole moment.

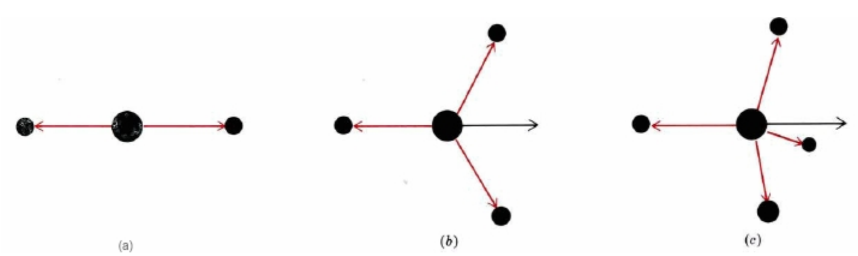

Figure 5: The simplest arrangements of equivalent bonds around a central atom which produce a resultant dipole moment of zero: (a) linear; (b) trigonal. The two right-hand bonds (black resultant) cancel the left-hand bond. (c) Tetrahedral. The three right-hand bonds (black resultant) cancel the left-hand bond.

Other arrangements of equivalent bonds that give zero dipole moment in this way are shown in Figure 5. The case of three equal bonds 120° apart, or a tetrahedral arrangement of equal bonds at 109° bond angles. Any combination of these arrangements will also be nonpolar. The molecule PF_5 for example, is nonpolar since the bonds are arranged in a trigonal bipyramid, as discussed in "The Shapes of Molecules." Since three of the five bonds constitute a trigonal arrangement, they will have no resultant dipole moment. The remaining two bonds have equal but opposite dipoles which will likewise cancel. If we replace any of the bonds shown in Figure 5 with a different bond, or with a lone pair, the vectors will no longer cancel and the molecule will have a resultant dipole moment.

CH_4

In methane, there are four C - H bonds, all slightly polar (the electronegativities of C and H are 2.55 and 2.20 respectively), but they are arranged so that the vectors cancel one another because methane is tetrahedral as shown in the Jmol model below. You may click the Magnetic Dipole check box to see the dipole in place on the model of methane.

Because methane is nonpolar, it does not dissolve in water. Other hydrocarbons and oils, like vegetable oil, can be made to dissolve by adding "amphiphilic" molecules (like soap), which have a polar ("hydrophilic", water loving) end that dissolves in water, and a nonpolar (hydrophobic, "water fearing") end that dissolves the oil. Amphiphilic molecules often make up cell walls, where the hydrophilic end of the molecule can face outward:

Figure 6 Lipid Bilayer.

SO_3

As another example of this vector addition, consider the SO_3 molecule. The dipole moments of the three S—O bonds are represented by the three arrows in Figure 6 below, at "1:00 o'clock", "5:00 o'clock", and "9:00 o'clock".

The sum of vectors at "2:00 o'clock" and "5:00 o'clock" may be obtained by the parallelogram law—lines parallel to the original vectors intersect at the tip of their resultant, a horizontal line ending at "3:00 o'clock". The resultant is exactly equal in length and exactly opposite in direction to the bond dipole at "9:00 o'clock". Therefore the net result is zero dipole moment.

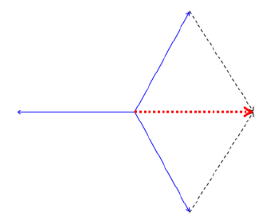

Figure 7: Parallelogram vector addition.

Note, however, that the melting point and boiling point of SO_3 are very high for a nonpolar substance. This is because it does not exist as a simple molecule in the solid state , but rather as a covalently bonded trimer (Figure 7), so covalent bonds need to be broken to melt or boil SO_3.

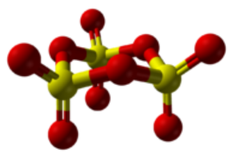

Figure 8: Solid form of sulfur trioxide [8]

NH_3

At first glance, you might expect NH_3 to have a zero molecular dipole moment, like SO_3. But in NH_3 or NF_3, the N atom is surrounded by four electron pairs in an approximately tetrahedral arrangement. Since all four pairs are not equivalent, the molecule is polar.

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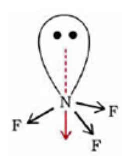

Above "N" is a pair of black dots. The three "F" below N form an overall tetrahedral shape. Each "N" "F" bond is represented by an arrow pointing from "N" to "F". The resultant arrow points straight downwards.

In NF_3, the dipole moment, though, is surprisingly small because the lone pair on N cancels much of the polarity of the N—F bonds, which place electron density on the more electronegative (4.0) F atoms.

Biomolecular Properties

Note that polar NH_3 is soluble in water, because each has charges which can attract one another, but nonpolar CH_4 is insoluble in water. The insolubility of CH_4 is due to the fact that it has no charges for water to attract, but also because water bonds to itself so well. A full explanation requires the concept of entropy, because it's a rearrangement of the liquid water structure, shown in the first figure, which prevents nonpolar molecules from dissolving. This is called the "hydrophobic effect", and it has a lot to do with formation of cell walls and other biological structures like the lipid bilayers shown above, as well as forcing proteins into specific conformations. The "structure creating" results of the hydrophobic effect can be seen with the "Magic Sand" model shown in the second Figure, and in several YouTube videos.

EXAMPLE 1 Which of the following molecules are polar? About how large a dipole moment would you expect for each? (a) CF_4; (b) CHF_3; (c) CH_3F; (d) CH_2F_2.;

Solution

a) VSEPR theory predicts a tetrahedral geometry for CF_4. Since all four bonds are the same, this molecule corresponds to Figure 2*c*. It has zero dipole moment.

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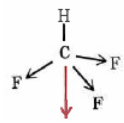

A central "C" has a H bond above it. The three "F" is below the "C" forming a tetrahedral. Each "C" "F" bond is represented by an arrow pointing downward to form a tetrahedral shape. The resultant dipole moment is shown in color and is opposite to the "C" H" bond and is longer than the "C" "H" bond.

b) For CHF_3, VSEPR theory again predicts a tetrahedral geometry. However, all the bonds are not the same, and so there must be a resultant dipole moment. The C—H bond is essentially nonpolar, but the three C—F bonds are very polar and negative on the F side. Thus the molecule should have quite a large dipole moment:

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The resultant dipole is shown in color.

c) This second jmol demonstrates the dipole when one hydrogen atom in methane is replaced by a highly electronegative fluorine. Fluorine pulls the electron strongly away from the carbon atom, creating a dipole moment pointing from carbon to fluorine.

d)The third jmol depicts the dipole moment when two hydrogen atoms in methane have been replaced by fluorine atoms. Each fluorine pulls the electrons in the carbon-fluorine bonds away from the carbon, creating a net dipole pointing between the two fluorine atoms.

References

1. Water [en.Wikipedia.org]
2. YouTube [www.youtube.com]
3. 1 debye = 1 D = 3.34 x 10⁻³⁰ C m.
4. 1 D (debye) = 3.34 x 10⁻³⁰ C m
5. en.Wikipedia.org/wiki/Decompression_sickness
6. sublimes
7. liquid only exists under pressure
8. en.Wikipedia.org/wiki/Sulfur_trioxide