

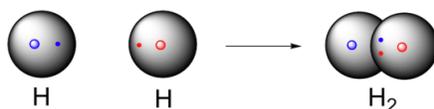
2.3: HYBRIDIZATION AND MOLECULAR SHAPES (REVIEW)

Learning Objectives

- predict the hybridization and geometry of atoms in a molecule - refer to section 2.3
- draw accurate 3-D representations of molecules with approximate bond angles

FORMATION OF SIGMA BONDS: THE H₂ MOLECULE

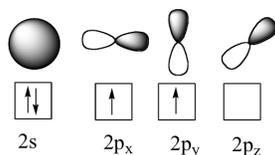
The simplest case to consider is the hydrogen molecule, H₂. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1s orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals.



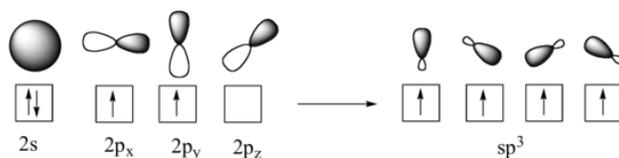
These two electrons are now attracted to the positive charge of *both* of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

BONDING IN METHANE

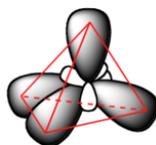
Now let's turn to methane, the simplest organic molecule. Recall the valence electron configuration of the central carbon:



This picture, however, is problematic. How does the carbon form four bonds if it has only two half-filled *p* orbitals available for bonding? A hint comes from the experimental observation that the four C-H bonds in methane are arranged with tetrahedral geometry about the central carbon, and that each bond has the same length and strength. In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2s and three 2p orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named **sp³ orbitals** because they are formed from mixing one s and three p orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp³ orbital.



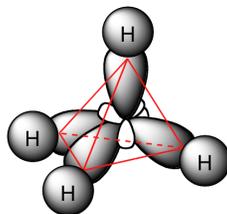
The sp³ hybrid orbitals, like the *p* orbitals of which they are partially composed, are oblong in shape, and have two lobes of opposite sign. Unlike the *p* orbitals, however, the two lobes are of very different size. The larger lobes of the sp³ hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5°.



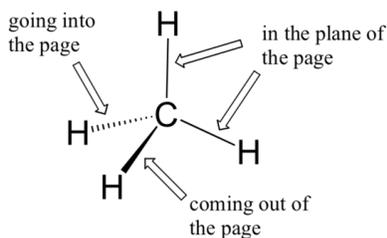
This geometric arrangement makes perfect sense if you consider that it is precisely this angle that allows the four orbitals (and the electrons in them) to be as far apart from each other as possible. This is simply a restatement of the Valence Shell Electron Pair Repulsion (VSEPR) theory that you learned in General Chemistry: electron pairs (in orbitals) will arrange themselves in such a way as to remain as far apart as possible, due to negative-negative electrostatic repulsion.

Each C-H bond in methane, then, can be described as an overlap between a half-filled 1s orbital in a hydrogen atom and the larger lobe of one of the four half-filled sp³ hybrid orbitals in the central carbon. The length of the carbon-hydrogen bonds in methane is 1.09 Å (1.09 x

10^{-10} m).



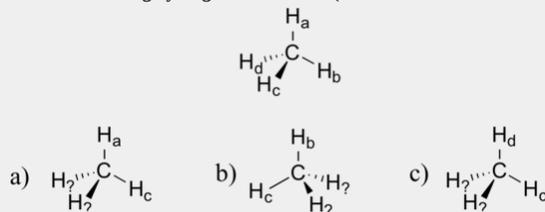
While previously we drew a Lewis structure of methane in two dimensions using lines to denote each covalent bond, we can now draw a more accurate structure in three dimensions, showing the tetrahedral bonding geometry. To do this on a two-dimensional page, though, we need to introduce a new drawing convention: the solid / dashed wedge system. In this convention, a solid wedge simply represents a bond that is meant to be pictured emerging from the plane of the page. A dashed wedge represents a bond that is meant to be pictured pointing into, or behind, the plane of the page. Normal lines imply bonds that lie in the plane of the page.



This system takes a little bit of getting used to, but with practice your eye will learn to immediately 'see' the third dimension being depicted.

Example

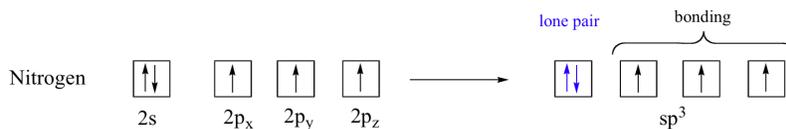
Imagine that you could distinguish between the four hydrogens in a methane molecule, and labeled them H_a through H_d . In the images below, the *exact same* methane molecule is rotated and flipped in various positions. Draw the missing hydrogen atom labels. (It will be much easier to do this if you make a model.)



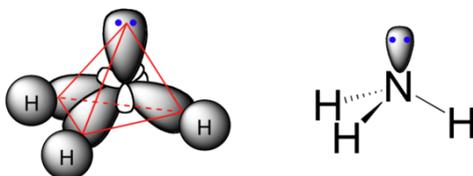
Exercise

Describe, with a picture and with words, the bonding in chloroform, $CHCl_3$.

[Solutions](#)

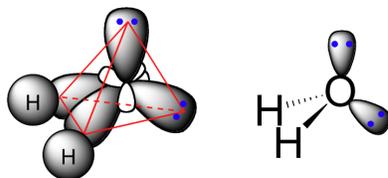
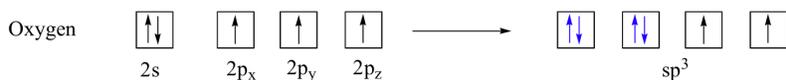


The bonding arrangement here is also tetrahedral: the three N-H bonds of ammonia can be pictured as forming the base of a trigonal pyramid, with the fourth orbital, containing the lone pair, forming the top of the pyramid.



Recall from your study of VSEPR theory in General Chemistry that the lone pair, with its slightly greater repulsive effect, 'pushes' the three N-H bonds away from the top of the pyramid, meaning that the H-N-H bond angles are slightly less than tetrahedral, at 107.3° rather than 109.5° .

VSEPR theory also predicts, accurately, that a water molecule is 'bent' at an angle of approximately 104.5° . It would seem logical, then, to describe the bonding in water as occurring through the overlap of sp^3 -hybrid orbitals on oxygen with $1s$ orbitals on the two hydrogen atoms. In this model, the two nonbonding lone pairs on oxygen would be located in sp^3 orbitals.



Some experimental evidence, however, suggests that the bonding orbitals on the oxygen are actually unhybridized $2p$ orbitals rather than sp^3 hybrids. Although this would seem to imply that the H-O-H bond angle should be 90° (remember that p orbitals are oriented perpendicular to one another), it appears that electrostatic repulsion has the effect of distorting this p -orbital angle to 104.5° . Both the hybrid orbital and the nonhybrid orbital models present reasonable explanations for the observed bonding arrangement in water, so we will not concern ourselves any further with the distinction.

Exercise

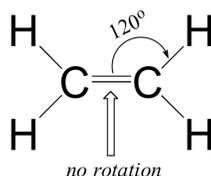
Draw, in the same style as the figures above, an orbital picture for the bonding in methylamine.

[Solution](#)

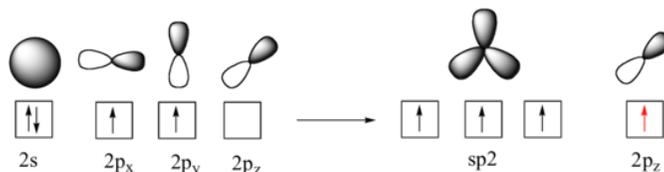
FORMATION OF π BONDS - sp^2 AND sp HYBRIDIZATION

The valence bond theory, along with the hybrid orbital concept, does a very good job of describing double-bonded compounds such as ethene. Three experimentally observable characteristics of the ethene molecule need to be accounted for by a bonding model:

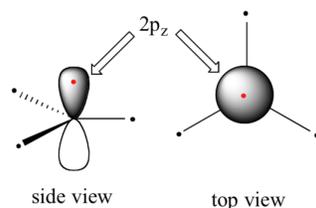
1. Ethene is a planar (flat) molecule.
2. Bond angles in ethene are approximately 120° , and the carbon-carbon bond length is 1.34 \AA , significantly shorter than the 1.54 \AA single carbon-carbon bond in ethane.
3. There is a significant barrier to rotation about the carbon-carbon double bond.



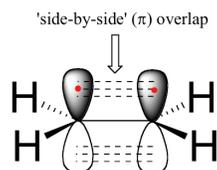
Clearly, these characteristics are not consistent with an sp^3 hybrid bonding picture for the two carbon atoms. Instead, the bonding in ethene is described by a model involving the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the $2s$, $2p_x$ and $2p_y$ orbitals – combine to form three sp^2 hybrids, leaving the $2p_z$ orbital unhybridized.



The three sp^2 hybrids are arranged with trigonal planar geometry, pointing to the three corners of an equilateral triangle, with angles of 120° between them. The unhybridized $2p_z$ orbital is *perpendicular* to this plane (in the next several figures, sp^2 orbitals and the sigma bonds to which they contribute are represented by lines and wedges; only the $2p_z$ orbitals are shown in the 'space-filling' mode).

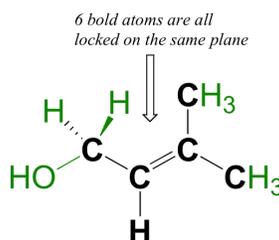


The carbon-carbon double bond in ethene consists of one σ bond, formed by the overlap of two sp^2 orbitals, and a second bond, called a π (**pi**) **bond**, which is formed by the *side-by-side* overlap of the two unhybridized $2p_z$ orbitals from each carbon.



spacefilling image of bonding in ethene

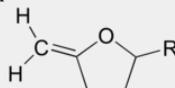
The pi bond does *not* have symmetrical symmetry. Because they are the result of side-by-side overlap (rather than end-to-end overlap like a sigma bond), *pi bonds are not free to rotate*. If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane. This argument extends to larger alkene groups: in each case, the six atoms of the group form a single plane.



Conversely, σ bonds such as the carbon-carbon single bond in ethane (CH_3CH_3) exhibit free rotation, and can assume many different conformations, or shapes - this is one of the main subjects of Chapter 3.

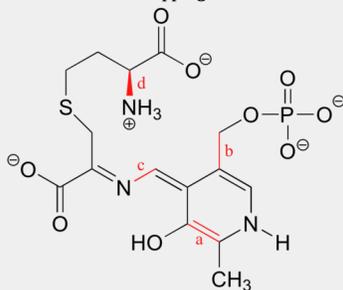
Exercise

Circle the six atoms in the molecule below that are 'locked' into the same plane.



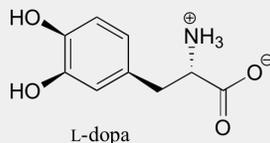
Exercise

What kinds of orbitals are overlapping in bonds a-d indicated below?



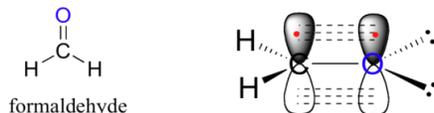
Exercise

What is wrong with the way the following structure is drawn?



Solutions

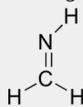
A similar picture can be drawn for the bonding in carbonyl groups, such as formaldehyde. In this molecule, the carbon is sp^2 -hybridized, and we will assume that the oxygen atom is also sp^2 hybridized. The carbon has three sigma bonds: two are formed by overlap between two of its sp^2 orbitals with the $1s$ orbital from each of the hydrogens, and the third sigma bond is formed by overlap between the remaining carbon sp^2 orbital and an sp^2 orbital on the oxygen. The two lone pairs on oxygen occupy its other two sp^2 orbitals.



The pi bond is formed by side-by-side overlap of the unhybridized $2p_z$ orbitals on the carbon and the oxygen. Just like in alkenes, the $2p_z$ orbitals that form the pi bond are perpendicular to the plane formed by the sigma bonds.

Exercise

Describe and draw the bonding picture for the imine group shown below. Use the drawing of formaldehyde above as your guide.



Solution

CONTRIBUTORS AND ATTRIBUTIONS

- **Organic Chemistry With a Biological Emphasis** by **Tim Soderberg** (University of Minnesota, Morris)

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