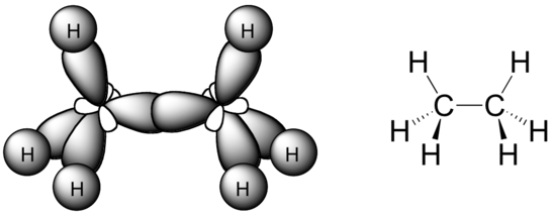
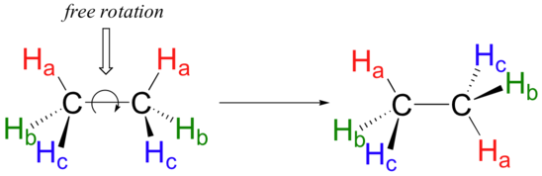
1.13: Ethane, Ethylene, and Acetylene

Bonding in Ethane

In the ethane molecule, the bonding picture according to valence orbital theory is very similar to that of methane. Both carbons are sp^3-hybridized, meaning that both have four bonds arranged with tetrahedral geometry. The carbon-carbon bond, with a bond length of 1.54 Å, is formed by overlap of one sp^3 orbital from each of the carbons, while the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1*s* orbitals of hydrogen atoms. All of these are sigma bonds.



Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on a hub, each one able to rotate freely with respect to the other.



In chapter 3 we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the 'conformation' of organic molecules.

The sp^3 bonding picture is also used to described the bonding in amines, including ammonia, the simplest amine. Just like the carbon atom in methane, the central nitrogen in ammonia is sp^3-hybridized. With nitrogen, however, there are five rather than four valence electrons to account for, meaning that three of the four hybrid orbitals are half-filled and available for bonding, while the fourth is fully occupied by a (non-bonding) pair of electrons.

C_2H_4, also known as ethylene or ethene, is a gaseous material created synthetically through steam cracking. In nature, it is released in trace amounts by plants to signal their fruits to ripen. Ethene consists of two sp^2-hybridized carbon atoms, which are sigma bonded to each other and to two hydrogen atoms each. The remaining unhybridized p orbitals on the carbon form a pi bond, which gives ethene its reactivity.

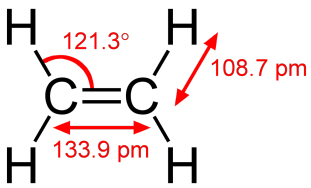
Bonding in Ethene

A key component of using Valence Bond Theory correctly is being able to use the Lewis dot diagram correctly. Ethene has a double bond between the carbons and single bonds between each hydrogen and carbon: each bond is represented by a pair of dots, which represent electrons. Each carbon requires a full octet and each hydrogen requires a pair of electrons. The correct Lewis structure for ethene is shown below:

For more information on how to use Lewis Dot Structures refer to http://chemwiki.ucdavis.edu/Wikitext...wis_Structures.

Valence Shell Electron Pair Repulsion (VSEPR) Theory is used to predict the bond angles and spatial positions of the carbon and hydrogen atoms of ethene and to determine the bond order of the carbon atoms (the number of bonds formed between them). Each carbon atom is of the general arrangement AX_3, where A is the central atom surrounded by three other atoms (denoted by X); compounds of this form adopt trigonal planar geometry, forming 120 degree bond angles. In order for the unhybridized p orbitals to

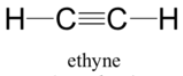
successfully overlap, the CH_2 must be coplanar: therefore, C_2H_4 is a planar molecule and each bond angle is about 120 degrees. The diagram below shows the bond lengths and hydrogen-carbon-carbon bond angles of ethene:



According to valence bond theory, two atoms form a covalent bond through the overlap of individual half-filled valence atomic orbitals, each containing one unpaired electron. In ethene, each hydrogen atom has one unpaired electron and each carbon is sp^2 hybridized with one electron each sp^2 orbital. The fourth electron is in the p orbital that will form the pi bond. The bond order for ethene is simply the number of bonds between each atom: the carbon-carbon bond has a bond order of two, and each carbon-hydrogen bond has a bond order of one. For more information see http://chemwiki.ucdavis.edu/Wikitexts/UCD_Chem_124A%3a_Kauzlarich/ChemWiki_Module_Topics/VSEPR

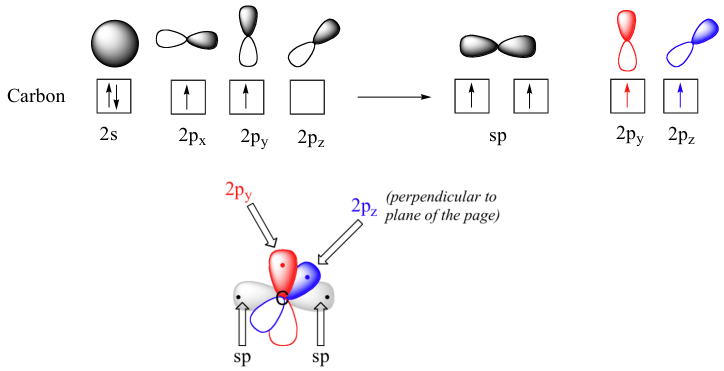
Bonding in acetylene

Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (common name acetylene), the simplest alkyne.

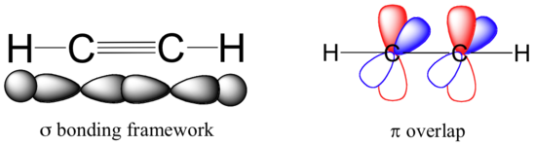


ethyne
(acetylene)

This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are **sp-hybridized**. In an sp-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two sp hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain unhybridized, and are oriented perpendicularly along the y and z axes, respectively.

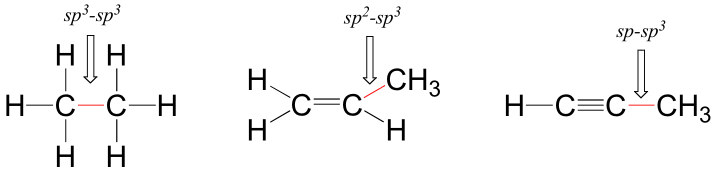


The C-C sigma bond, then, is formed by the overlap of one sp orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second sp orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).



σ bonding framework π overlap

The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than ‘normal’ single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.



A B C

In alkene B, however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in alkyne C the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + sp^3 overlap (as in alkyne C) are shorter and stronger than bonds involving sp^2 + sp^3 overlap (as in alkene B). Bonds involving sp^3-sp^3overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

Contributors

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