

## 1.3: Hybridization of orbitals and 3D structures of simple organic compounds

### Learning Objectives

- Understand  $sp^3$ ,  $sp^2$ , and  $sp$  hybridization of C, N, O, and halogens in organic compounds.
- Understand bond angles and geometries in simple molecules having  $sp^3$ ,  $sp^2$ , and  $sp$  hybridization of C, N, O.
- Read an electrostatic potential map of a simple organic molecule and recognize the partially charged regions and the lone pairs.
- Understand free rotation around single and triple bonds but not around double bonds.

### Prelude to the hybridization of atomic orbitals

Electron configuration of C atom is:  $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$ , where  $1s$  is the core-shell and  $2s$  and  $2p$  are in the valence shell. Since two unpaired electrons are in the valence shell in  $2p_x^1, 2p_y^1$  orbitals, it implies that C should have two bonds in its compound. In reality, C has four bonds, e.g., there are four C–H covalent bonds in methane ( $CH_4$ ). It can be explained by assuming that one electron is promoted from  $2s$  to  $2p$  orbital of C, resulting in the electron configuration of  $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^0$ , which allows four bonds. The rationale is that making two additional bonds releases more energy than more than compensates the energy consumed in promoting an electron from  $2s$  to  $2p$  orbital.

The molecular formula of methane is ( $CH_4$ ), which shows the elemental composition but does not show bonds. The Lewis

structure of methane is  $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$  which shows covalent bonds as lines but does not show the actual geometry of the molecule. The

geometry of the methane molecule is tetrahedral. C is at the center of the tetrahedron, and four H atoms at the corners of the tetrahedron as illustrated in Figure 1.3.1 a and b. The four bonds are equal and at  $109.5^\circ$  from each other.

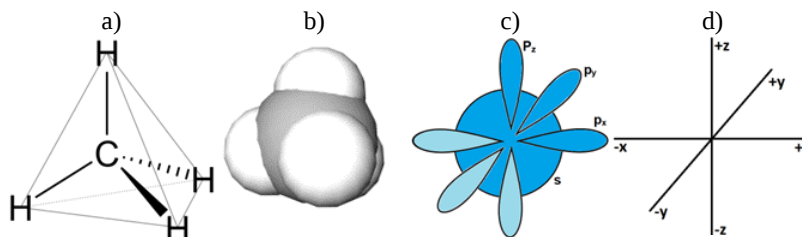


Figure 1.3.1: a) Illustration of tetrahedral geometry of  $CH_4$ , b) model of methane molecule where white spheres on the periphery are H and gray sphere in the center is C, c) illustration of valence orbitals of C atom, i.e., ( $2s, 2p_x, 2p_y$ , and  $2p_z$ ), and d) 3D-coordinate axis for reference (Copyright; a) Hbf878, CC0, via Wikimedia Commons, b), c, and d) Public domain)

The geometry of the methane molecule, shown in Figure 1.3.1 a and b, disagrees with the geometry of valence orbitals of C illustrated in Figure 1.3.1 c. The  $s$  orbital is a spherical shape with a single phase shown by a single shade, while  $p$  orbitals have two lobes of opposite phases along the axis indicated by two different shades. The three  $p$  orbitals are perpendicular to each other, each lying along one of the three axes:  $p_x$  along the  $x$ -axis,  $p_y$  along the  $y$ -axis, and  $p_z$  along the  $z$ -axis. Suppose the valence  $s$  and the three  $p$  orbitals of C were involved in the bonding. In that case, there should have been three bonds from the  $p$  orbitals perpendicular to each other and one bond from the  $s$  orbital different from the other three at any angle around the C nucleus. This difference between the actual and the expected geometry of  $CH_4$  molecule is explained by the orbital hybridization concept.

According to the **orbital hybridization** concept, atomic orbitals can combine and produce an equal number of hybrid orbitals of energy and orientation different from the constituent orbitals. The  $s$  and all three, any two, or any one of the  $p$  valence orbitals of C can mix and produce four  $sp^3$ , three  $sp^2$ , or two  $sp$  hybrid orbitals.

The geometry around C atoms in organic molecules agrees with the geometry of the hybrid orbitals, as described in the following sections.

## sp<sup>3</sup> Hybridization of C

### sp<sup>3</sup> Hybridization process

The s-orbital has a spherical shape and has a single phase as illustrated in 1.3.2 a. Each p orbital has two lobes lying on a straight line with the nucleus at the center. The two lobes have opposite phases, represented by shades as illustrated in 1.3.2 a. The term phase is about the wave nature of electrons. Waves have crests and troughs that are opposite phases.

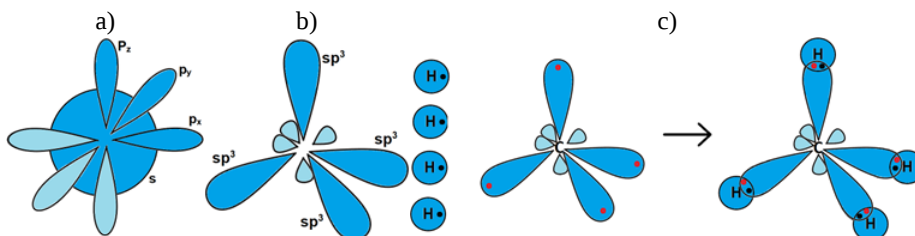


Figure 1.3.2: a) An s and three p valence orbitals before hybridization, b) a set of four equal sp<sup>3</sup> hybrid orbitals formed from the s and the three p orbitals, c) illustration of four covalent bonds formed by the overlap of one sp<sup>3</sup> orbital of C and one s orbital of H each, called  $\sigma_{sp^3-s}$  bond, resulting in CH<sub>4</sub> molecule. Each orbital contributes one electron to the bond, represented by a red dot in the case of sp<sup>3</sup> and a black dot in the case of s orbital for illustration (Copyright; Public domain).

When one s and three p orbitals mix, a set of four equal hybrid orbitals, called sp<sup>3</sup> orbitals, is formed as illustrated in 1.3.2 b. An sp<sup>3</sup> orbital has two lobes of opposite phases, a more prominent lobe and a smaller lobe, lying along a straight line with the nucleus between the two lobes. Each sp<sup>3</sup> orbital has one-fourth of s and three-fourths of p orbital character. The sp<sup>3</sup> orbitals are arranged in a tetrahedral geometry around the nucleus, as illustrated in Figure 1.3.2 b. In the case of C, the four valence electrons distribute one each in the four sp<sup>3</sup> hybrid orbitals.

### Formation of methane (CH<sub>4</sub>) molecule

Each of the four sp<sup>3</sup> orbitals of C overlaps with one 1s orbital of H, making a set of four covalent bonds as illustrated in Figure 1.3.2 c. The bond formed by a head-on overlap of atomic orbitals is called a sigma-bond ( $\sigma$ -bond), which in the present case is called  $\sigma_{sp^3-s}$  bond. The result is a CH<sub>4</sub> molecule with all bonds equal in a tetrahedral geometry around C, which agrees with the observed geometry, as illustrated in Figure 1.3.1: a. All bonds are equal of 108.70 pm bond length and 109.5° bond angles in a CH<sub>4</sub> molecule. Figure 1.3.3 presents an interactive model of CH<sub>4</sub> molecule for lea

### Formation of ethane (CH<sub>3</sub>CH<sub>3</sub>) molecule

Carbon can form a chain of carbons by making covalent bonds between carbon atoms. For example, a C overlaps a bigger lobe of one of its sp<sup>3</sup> hybrid orbitals with the bigger lobe of the sp<sup>3</sup> orbital of the second carbon along the axis of the sp<sup>3</sup> orbitals to make a  $\sigma_{sp^3-sp^3}$  bond as illustrated in Figure 1.3.4 a. The remaining sp<sup>3</sup> orbitals on each C make  $\sigma_{sp^3-s}$  bond by overlapping with s orbital of H resulting in an ethane C<sub>2</sub>H<sub>6</sub> molecule.

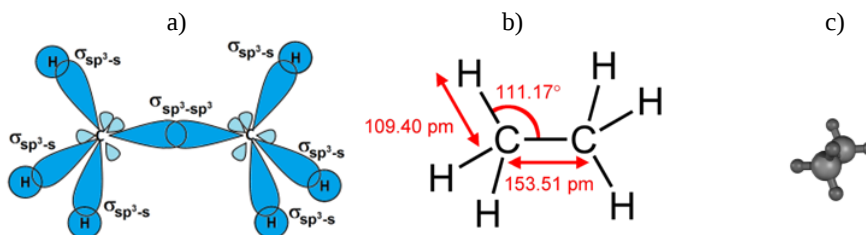


Figure 1.3.4: a) illustration of covalent bonds in a CH<sub>3</sub>CH<sub>3</sub> molecule, b) structure showing bond lengths and angles in a CH<sub>3</sub>CH<sub>3</sub> molecule, and c) Model of CH<sub>3</sub>CH<sub>3</sub> molecule showing views from different angles and also showing rotation around  $\sigma_{sp^3-sp^3}$  bond in a CH<sub>3</sub>CH<sub>3</sub> molecule. Note that the bond angles are not precisely equal to but very close to the predicted 109.5°, (Copyright; a) Public domain, b) Benjah-bmm27, Public domain, via Wikimedia Commons, and c) <mailto:ralf@ark.in-berlin.de>, CC BY 2.5 via Wikimedia Commons)

Rotation around a single bond is possible under ambient conditions. Rotation around a C—H bond does not change the shape or orientation of any atom in the molecule. However, rotation around C—C in CH<sub>3</sub>CH<sub>3</sub> molecule results in different orientations of H atoms on one C relative to the H atoms on the other C, as illustrated in Figure 1.3.4 c. The structures with different orientations of atoms in the same molecule, as a result of rotation around a single bond, are called **conformers** of each other.

## sp<sup>2</sup> Hybridization of C

### sp<sup>2</sup> Hybridization process

One s and two p orbitals in a valence shell can mix and produce a set of three equal hybrid orbitals, called sp<sup>2</sup> orbitals, as illustrated in Figure 1.3.5. An sp<sup>2</sup> orbital has one-third s-orbital and two-third p-orbital character. An sp<sup>2</sup> orbital comprises two lobes, a more prominent lobe and a smaller lobe of opposite polarity along a straight line with the nucleus between the two lobes, as in the case of the sp<sup>3</sup> orbital. The three sp<sup>2</sup> are in a plane at 120° from each other, i.e., a trigonal planer geometry with the nucleus in the middle. One p orbital left out from the hybridization lies perpendicular to the plane of the three sp<sup>2</sup> orbitals.

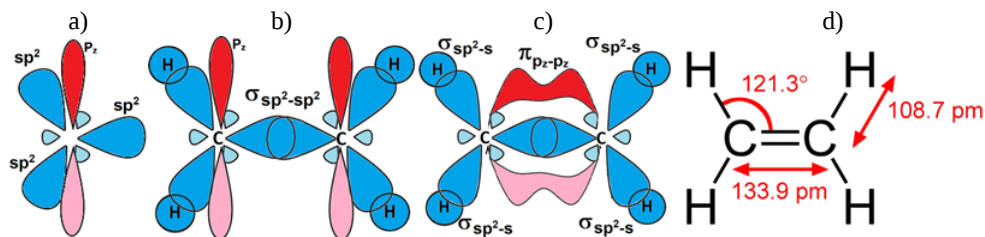


Figure 1.3.5: Cartoons of a) a set of three equal sp<sup>2</sup> hybrid orbitals in a trigonal planer geometry, formed from the mixing of one s and the two p orbitals along with the un-hybridized p perpendicular to the plane, b) a  $\sigma_{sp^2-sp^2}$  bond formation between two sp<sup>2</sup> hybridized C atoms along with four  $\sigma_{sp^2-s}$  bond formation between sp<sup>2</sup> hybridized C and H atoms, c) a  $\pi$ -bond formation between two parallel p orbitals on adjacent C atoms, and d) structure showing bond lengths and angles in a CH<sub>2</sub>CH<sub>2</sub> molecule, (Copyright; a), b, and c) Public domain, d) Benjah-bmm27, Public domain, via Wikimedia Commons)

### Formation of ethene (H<sub>2</sub>C=CH<sub>2</sub>) molecule

A C can form multiple bonds with a C or a heteroatom. For example, a C overlaps a bigger lobe of one of its sp<sup>2</sup> hybrid orbitals with the bigger lobe of the sp<sup>2</sup> orbital of the second carbon along the axis of the sp<sup>2</sup> orbital to make a  $\sigma_{sp^2-sp^2}$  bond as illustrated in Figure 1.3.5b. The remaining sp<sup>2</sup> orbitals on each C make  $\sigma_{sp^2-s}$  bond by overlapping with s orbital of H. Two p orbitals on adjacent carbons orient themselves parallel and overlap sideways, forming a pi-bond ( $\pi$ -bond). This results in the ethene molecule illustrated in Figure 1.3.5c.

The  $\pi$ -bond is weaker than a  $\sigma$ -bond because the sideways overlap of two parallel p-orbitals making a  $\pi$ -bond is less than the head-on overlap of orbitals making a  $\sigma$ -bond. Therefore, a  $\pi$ -bond is formed only when a  $\sigma$ -bond can not be created. A single bond is always a  $\sigma$ -bond. A  $\pi$ -bond and a  $\sigma$ -bond together, i.e., C=C is called a double bond. A double bond is stronger than a single bond. The  $\pi$ -bond becomes more weak if the p-orbitals constituting it are not parallel because the overlap is less between nonparallel p-orbitals than between parallel p-orbitals. There is no overlap between p-orbitals perpendicular to each other, i.e., there is no  $\pi$ -bond when p-orbitals are at 90° (perpendicular). Therefore, rotation around a double does not happen until the  $\pi$ -bond is broken. There is no free rotation around C=C bond.

Geometry around each carbon in the ethene molecule is trigonal planar and bond angles close to the predicted value of 120°, as illustrated in Figure 1.3.5d. All six atoms in the ethene (CH<sub>2</sub>CH<sub>2</sub>) molecule are in the same plane and are locked in this geometry due to no free rotation around the C=C bond.

## sp Hybridization of C

### sp Hybridization process

One s, and one p orbitals in a valence shell can mix and produce a set of two equal hybrid orbitals, called sp orbitals, as illustrated in Figure 1.3.6a. An sp-orbital has 50% s-orbital and 50% p-orbital character. Like sp<sup>3</sup> and sp<sup>2</sup> orbitals, an sp orbital comprises two lobes, a more prominent lobe and a smaller lobe of opposite polarity along a straight line with the nucleus between the two lobes. The two sp orbitals are in a line at 180° from each other, i.e., a linear geometry with the nucleus in the middle. Two p orbitals left out from the hybridization lie perpendicular to the axis of the sp orbitals and perpendicular to each other, as illustrated in Figure 1.3.6a.

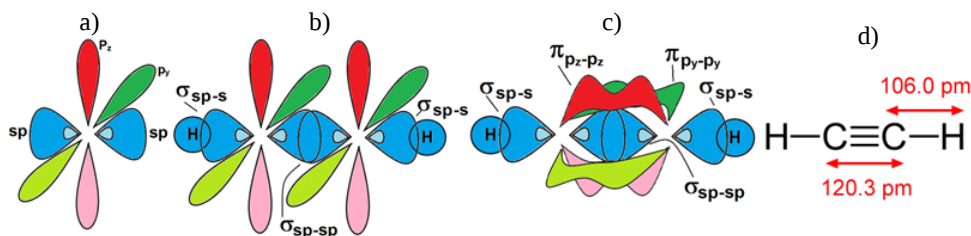


Figure 1.3.6: Cartoons of a) a set of two equal  $sp$  hybrid orbitals in a linear geometry, along with the two un-hybridized  $p$ -orbitals perpendicular to each other, b) a  $\sigma_{sp-sp}$  bond formation between two  $sp$  orbitals on  $C$  atoms along with two  $\sigma_{sp-s}$  bond formation between  $sp$  hybridized  $C$  orbital and  $s$ -orbital of  $H$  atoms, c) two  $\pi$ -bond formation between parallel  $p$  orbitals on adjacent  $C$  atoms, and d) structure showing bond lengths and angles in a  $CHCH$  molecule, (Copyright; a), b, and c) Public domain, d) Benjah-bmm27, Public domain, via Wikimedia Commons)

### Formation of ethyne ( $HC\equiv CH$ ) molecule

An  $sp$ -hybridized  $C$  overlaps a more prominent lobe of one of its  $sp$  orbitals with the bigger lobe of  $sp$  orbital of the second carbon along the axis of the  $sp$  orbitals to make a  $\sigma_{sp-sp}$  bond as illustrated in Figure 1.3.6b. The remaining  $sp$  orbitals on each  $C$  make  $\sigma_{sp-s}$  bond by overlapping with  $s$  orbital of  $H$ . One  $p$  orbitals on a  $C$  orient itself parallel to one  $p$ -orbital on the other and overlap sideways, forming a  $\pi$ -bond. The other two  $p$  orbitals are also parallel to each other and overlap sideways to form the second  $\pi$ -bond as illustrated in Figure 1.3.6c. This results in an ethyne molecule with a triple ( $C\equiv C$ ) bond, i.e., a  $\sigma$ -bond and two  $\pi$ -bonds between the two  $C$  atoms, as illustrated in Figure 1.3.6d.

A triple-bond is stronger than a double-bond, and a double-bond is stronger than a single-bond. Unlike a double bond, rotation around a triple bond happens because as the  $\pi$ -bond starts breaking due to  $p$ -orbitals going away from parallel orientation, a new  $\pi$ -bond starts making with the alternate  $p$ -orbital on the neighboring  $C$ . This fact becomes apparent by comparing the  $\pi$ -bond electron clouds in the cases of a double bond of ethene and a triple bond of ethyne illustrated in Figure 1.3.7. However, the rotation around a triple-bond means less as its geometry is linear.

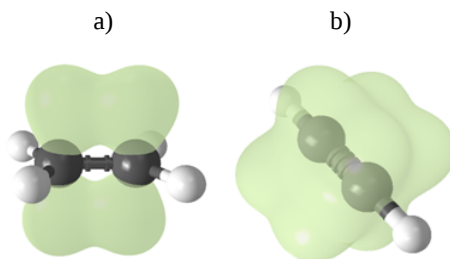


Figure 1.3.7: a) illustration of electron-cloud of a  $\pi$ -bond above and below the axis of the nuclei in ethene  $H_2C=CH_2$  molecule, and b) the electron-cloud of two  $\pi$ -bonds around the axis of the nuclei in ethyne  $HC\equiv CH$  molecule, (Copyright; Jiří Janoušek, Public domain, via Wikimedia Commons)

### Hybridization of N, O, and halogens

Heteroatoms like  $N$ ,  $O$ , and halogen atoms (represented as:  $X$ ) can also mix all or some of their valence shell  $s$  and  $p$  orbitals to have  $sp^3$ ,  $sp^2$ , or  $sp$  hybridization like  $C$ . The differences are the following.

#### Number of covalent bonds and lone pairs in compounds

Table 1 shows the number of covalent bonds and the number of lone pairs on atoms of elements commonly found in organic compounds.  $C$  has four valence electrons that distribute one each in the hybrid orbitals and the remaining  $p$  orbitals. Lewis symbols of elements represent valence electrons around the symbol of the element. For example, Lewis symbol of  $C$  is  $\cdot\dot{C}\cdot$  that shows four unpaired electrons in the valence shell. Each unpaired valence electron can make one covalent bond. So,  $C$  makes four covalent bonds in organic compounds.

$H$  has one valence electron, represented as  $\dot{H}$  that shows one unpaired electron that makes one bond and no lone pair on  $H$  in their compounds.

$N$  has five valence electrons represented in Lewis symbol as  $\cdot\ddot{N}\cdot$  that shows three unpaired electrons and one electron pair. The unpaired electrons make one bond each while the paired electrons remain as a lone pair on  $N$  in its compounds.

O has six valence electrons represented in Lewis symbol as  $\cdot\ddot{\text{O}}\cdot$  that shows two unpaired electrons and two electron pairs. The unpaired electrons make one bond each while the paired electrons remain as two lone pairs on O in its compounds.

Halogen X (where X can be F, Cl, Br, or I) has seven valence electrons. For example, Cl represented as  $\cdot\ddot{\text{Cl}}\cdot$  that shows one unpaired electron that makes one bond while the paired electrons remain as three lone pairs on X in their compounds.

Table 1: Number of covalent bonds and lone pairs of electrons around elements commonly found in organic compounds.

Atom (Lewis symbol)	Number of Covalent bonds	Number of lone pairs
$\cdot\ddot{\text{C}}\cdot$	4	0
$\cdot\text{H}$	1	0
$\cdot\ddot{\text{N}}\cdot$	3	1
$\cdot\ddot{\text{O}}\cdot$	2	2
Halogen $\cdot\ddot{\text{X}}\cdot$ (where X can be F, Cl, Br, or I)	1	3

## Geometry around the central atom

### $sp^3$ Hybridization

An  $sp^3$  hybridized C makes four  $\sigma$ -bonds in a tetrahedral geometry around C where bonds are around  $109^\circ$  from each other, as illustrated Figure 1.3.8a for the case of methane ( $\text{CH}_4$ ). The electrostatic potential map of methane is also shown.

An electrostatic potential map shows electron cloud in colors: green means neutral or nonpolar region, red means  $\delta^-$  region, blue means  $\delta^+$  region, yellow is between neutral and  $\delta^-$  and light blue is between neutral and  $\delta^+$ .

Methane is nonpolar, shown by green in the electrostatic potential map.

The  $sp^3$  orbitals of N have tetrahedral geometry where three orbitals make  $\sigma$ -bonds while a lone pair occupies the fourth. The three peripheral atoms are at the base forming a triangle while N is raised from the middle of the triangle resulting in a trigonal-pyramidal geometry, as illustrated in Figure 1.3.8b for  $\text{NH}_3$  molecule. The trigonal-pyramidal geometry is a modified form of tetrahedral geometry where the fourth corner of the tetrahedron is missing due to being occupied by a lone pair. The bond angles are close to  $109^\circ$  as predicted by the tetrahedral geometry. The molecule is not symmetric with polar bonds, so, it is polar, which is evident from its electrostatic potential map. The red region is due to the polarity of N–H bonds and also due to the lone pair region showing red because it is in an  $sp^3$ -orbital which, unlike a p-orbital, is not symmetric with most of the electron located in the more prominent lobe on one side of the nucleus.

The  $sp^3$  orbitals of O have tetrahedral geometry where two orbitals make  $\sigma$ -bonds while lone pairs occupy the other two. The two corners of a tetrahedron which are peripheral atoms and the O in the middle of the tetrahedron shape, results in a bent shape with the other two corners of the tetrahedron missing due to being occupied by lone pairs as illustrated in Figure 1.3.8c for  $\text{H}_2\text{O}$  molecule. The bent shape is a modified form of tetrahedral geometry where two corners of the tetrahedron are missing due to being occupied by lone pairs. The bond angle is close to  $109^\circ$  as predicted by the tetrahedral geometry. The electrostatic potential map reflects the polarity of two O–H bonds and the two lone pairs in  $sp^3$ -orbitals.

The  $sp^3$  orbitals of halogen atoms have tetrahedral geometry where one orbital makes a  $\sigma$ -bond while lone pairs occupy the other three. One bond can make only a linear geometry as illustrated in Figure 1.3.8d for HCl molecule. The other three corners of the tetrahedron are missing due to being occupied by lone pairs. The electrostatic potential map reflects the polarity of the bond and the three lone pairs in  $sp^3$ -orbitals.

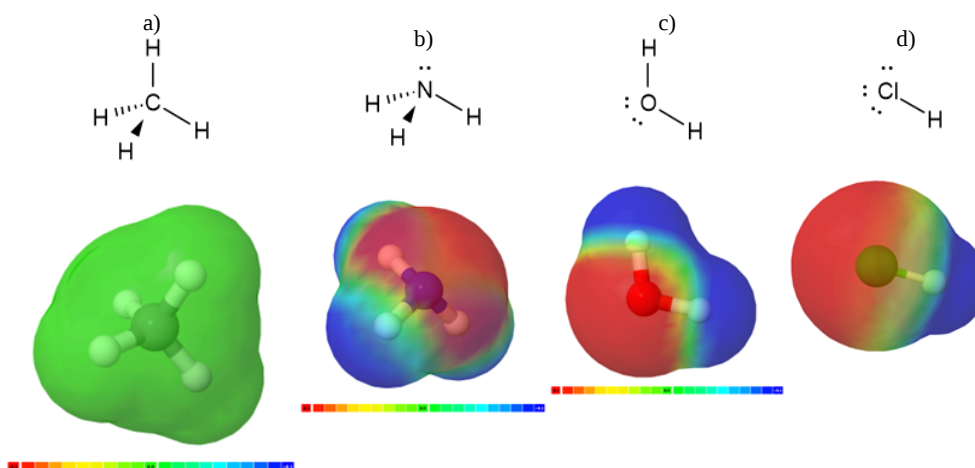


Figure 1.3.8: Structure of a) methane ( $\text{CH}_4$ ) molecule, b) ammonia ( $\text{NH}_3$ ) molecule, c.) water ( $\text{H}_2\text{O}$ ) molecule, and d) hydrochloric acid ( $\text{HCl}$ ) molecule, (Copyright; Public domain)

### $\text{sp}^2$ Hybridization

An  $\text{sp}^2$  hybridized C makes three  $\sigma$ -bonds using its  $\text{sp}^2$  orbitals in a trigonal planer geometry around C and a  $\pi$ -bond using its p-orbital. The  $\sigma$ -bonds are around  $120^\circ$  from each other, as illustrated in Figure 1.3.9a for ethene ( $\text{H}_2\text{C}=\text{CH}_2$ ) molecule. The electrostatic potential map of  $\text{H}_2\text{C}=\text{CH}_2$  in Figure 1.3.9a shows red region around the axis of the  $\text{C}=\text{C}$  bond which is due to the  $\pi$ -bondin electrons placed above and below the  $\sigma$ -bond. Further the H's are bluish compared to those in  $\text{CH}_4$  molecule indicating that the  $\text{C}-\text{H}$  is slightly polar with  $\delta+$  charge on the H.

The  $\text{sp}^2$  orbitals of N have trigonal planer geometry where two of the  $\text{sp}^2$  orbitals make  $\sigma$ -bonds, and the lone pair occupies the third  $\text{sp}^2$  orbital. The p-orbital makes a  $\pi$ -bond. The geometry around an  $\text{sp}^2$  hybridized N is bent with a bond angle around  $120^\circ$  as the trigonal planer geometry predicted. The bent geometry of  $\text{sp}^2$  hybridized N is illustrated in Figure 1.3.9b for methanimine ( $\text{H}_2\text{C}=\text{NH}$ ) molecule. The electrostatic potential map reflects the bond polarity and the lone pair of electrons in one  $\text{sp}^2$ -orbital as a red region.

The  $\text{sp}^2$  orbitals of O have trigonal planer geometry where one  $\text{sp}^2$  orbital makes a  $\sigma$ -bond, and a lone pair occupies the other two  $\text{sp}^2$  orbitals. The p-orbital makes a  $\pi$ -bond. An  $\text{sp}^2$ -hybridized O has a linear geometry around O atom, as illustrated in Figure 1.3.9c for formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ) molecule. The electrostatic potential map reflects the bond polarity and the lone pair of electrons in two  $\text{sp}^2$ -orbitals as a red region.

The  $\text{sp}^2$  or hybridization of halogens is not observed except in a few cases, e.g., when one of the lone pairs is involved in resonance which will be described in a later section.

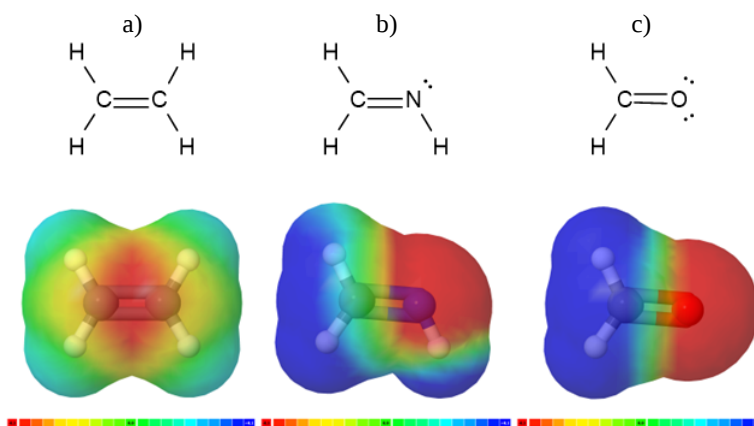


Figure 1.3.9: Structure of a) ethene ( $\text{CH}_2\text{CH}_2$ ) molecule, b) methanimine ( $\text{CH}_2\text{NH}$ ) molecule, and c.) formaldehyde ( $\text{CH}_2\text{O}$ ) molecule, (Copyright; Public domain)

### sp Hybridization

An sp hybridized C makes two  $\sigma$ -bonds using its sp-orbitals that are at  $180^\circ$  from each other, i.e., in a linear geometry. The remaining two p-orbitals make two  $\pi$ -bonds perpendicular to each other and around the sigma bond resulting in a linear geometry around the sp hybridized carbon, as illustrated in Figure 1.3.10a for ethyne ( $\text{HC}\equiv\text{CH}$ ) molecule. Electrostatic map shows red region around the  $\text{C}\equiv\text{C}$  bond axis which is due to  $\pi$ -electrons and it also shows that the C-H bond in ethyne is polar with  $\delta^+$  charge on H

The sp orbitals of N have linear geometry. One of the sp orbitals makes a  $\sigma$ -bond, and the other is occupied by a lone pair, and the two p-orbital make two  $\pi$ -bonds resulting in a triple bond. The geometry around an sp hybridized N is linear, as illustrated in Figure 1.3.10b for hydrogen cyanide ( $\text{HCN}$ ) molecule. The electrostatic potential map reflects the bond polarity and shows the red region where the lone pair of electrons are located in an sp-orbital of nitrogen.

The sp hybridization of O is rare in organic compounds, but it does exist, e.g., in carbon monoxide molecule ( $\text{CO}$ ) molecule. It involves formal charges on the atoms, which will be described in a later section.

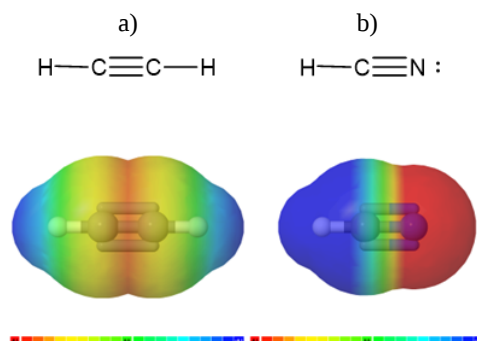


Figure 1.3.10: Structure of a) ethyne ( $\text{CHCH}$ ) molecule, and b) hydrogen cyanide ( $\text{HCN}$ ) molecule, (Copyright; Public domain)

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