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\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

ethylene
(substitutive name: ethene)

Because compounds containing double or triple bonds have fewer hydrogens than the corresponding alkanes, they are classified as unsaturated hydrocarbons, in contrast to alkanes, which are classified as saturated hydrocarbons.

This chapter covers the structure, bonding, nomenclature, and physical properties of alkenes. Then, using a few alkene reactions, some of the physical principles are discussed that are important in understanding the reactivities of organic compounds in general.

4.1 STRUCTURE AND BONDING IN ALKENES

The double-bond geometry of ethylene is typical of that found in other alkenes. Ethylene follows the rules for predicting molecular geometry (Sec. 1.3B), which require each carbon of ethylene to have trigonal planar geometry; that is, all the atoms surrounding each carbon lie in the same plane with bond angles approximating 120°. The experimentally determined structure of ethylene agrees with these expectations and shows further that ethylene is a planar molecule. For alkenes in general, the carbons of a double bond and the atoms directly attached to them all lie in the same plane.

Models of ethylene are shown in Fig. 4.1, and a comparison of the geometries of ethylene and propene with those of ethane and propane is given in Fig. 4.2. Notice that the carbon–carbon
4.1 STRUCTURE AND BONDING IN ALKENES

Double bonds of ethylene and propene (1.33 Å) are shorter than the carbon–carbon single bonds of ethane and propane (1.54 Å). This illustrates the relationship of bond length and bond order (Sec. 1.3B): double bonds are shorter than single bonds between the same atoms.

Another feature of alkene structure is apparent from a comparison of the structures of propene and propane in Fig. 4.2. Notice that the carbon–carbon single bond in propene, moreover, is somewhat shorter than the carbon–carbon bonds of propane.

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Another feature of alkene structure is apparent from a comparison of the structures of propene and propane in Fig. 4.2. Notice that the carbon–carbon single bond of propene (1.50 Å) is shorter than the carbon–carbon single bonds of propane (1.54 Å). The shortening of all these bonds is a consequence of the particular way that carbon atoms are hybridized in alkenes.

A. Carbon Hybridization in Alkenes

The carbons of an alkene double bond are hybridized differently from those of an alkane. In this hybridization (Fig. 4.3, p. 124), the carbon 2s orbital is mixed, or hybridized, with only two of the three available 2p orbitals. In Fig. 4.3, we have arbitrarily chosen to hybridize the 2px and 2py orbitals. Thus, the 2pz orbital is unaffected by the hybridization. Because three orbitals are mixed, the result is three hybrid orbitals and a “leftover” 2pz orbital. Each hybrid orbital has one
part $s$ character and two parts $p$ character. These hybrid orbitals are called $sp^2$ (pronounced “$s$-$p$-two”) orbitals, and the carbon is said to be $sp^2$-hybridized. Thus, an $sp^2$ orbital has 33% $s$ character (in contrast to an $sp^3$ orbital, which has 25% $s$ character). A perspective drawing of an $sp^2$ orbital is shown in Fig. 4.4a, and a commonly used stylized representation of an $sp^2$-hybridized carbon atom is shown in Fig. 4.4b. If you compare Fig. 4.4a with Fig. 1.16a (p. 40), you can see that the shape of an individual $sp^2$ orbital is much like that of an $sp^3$ orbital. The difference between these two types of hybrid orbitals is that the electron density within an $sp^2$ orbital is concentrated slightly closer to the nucleus. The reason for this difference is the larger amount of $s$ character in an $sp^2$ orbital. Electron density in a carbon 2$s$ orbital is concentrated a little closer to the nucleus than electron density in a carbon 2$p$ orbital. The more $s$ character a hybrid orbital has, then, the more “$s$-like” its electrons are, and the closer its electrons are to the nucleus.

Because the 2$p_x$ and 2$p_y$ orbitals are used for hybridization, and because the 2$s$ orbital is spherical (that is, without direction), the axes of the three $sp^2$ orbitals lie in the $xy$-plane (see
they are oriented at the maximum angular separation of 120°. Because the “leftover” (unhybridized) 2p orbital is a 2pz orbital, its axis is the z-axis, which is perpendicular to the plane containing the axes of the sp2 orbitals. Conceptually, ethylene can be formed in the hybrid orbital model by the bonding of two sp2-hybridized carbon atoms and four hydrogen atoms (Fig. 4.5). An sp2 orbital on one carbon containing one electron overlaps with an sp2 orbital on another to form a two-electron sp2–sp2 C–C σ bond. Each of the two remaining sp2 orbitals, each containing one electron, overlaps with a hydrogen 1s orbital, also containing one electron, to form a two-electron sp2–1s C–H σ bond. These orbitals account for the four carbon–hydrogen bonds and one of the two carbon–carbon bonds of ethylene, which together comprise the sigma-bond framework of ethylene. (We have not yet accounted for the 2p orbital on each carbon.) Notice carefully that the trigonal planar geometry of each carbon of ethylene is a direct consequence of the way its sp2 orbitals are directed in space. Once again, we see that hybridization and molecular geometry are related. (Sec. 1.9). Whenever a main-group atom has trigonal planar geometry, its hybridization is sp2.

Whenever such an atom has tetrahedral geometry, its hybridization is sp3.

B. The π (Pi) Bond

The two 2pz orbitals not used in σ-bond formation (dashed lines in Fig. 4.5) overlap side-to-side to form the second bond of the double bond. In the hybrid orbital picture, each 2pz orbital contributes one electron to make an electron-pair bond. A bond formed by the side-to-side overlap of p orbitals is called a π bond. (The symbol π, or pi, is used because π is the Greek equivalent of the letter p and because the π bond originates from the overlap of p orbitals.) To visualize electron distribution in a π bond, we’ll use molecular orbital (MO) theory (Sec. 1.8). MO theory provides a richer description of the π bond, and it also forms the basis for understanding of ultraviolet spectroscopy (an important tool for molecular analysis; see Sec. 15.2) as well as a class of reactions called pericyclic reactions (Chapter 27). Notice that we are treating the σ-bond framework with hybrid orbital theory and the π bond with MO theory. This is justified in MO theory because the π MOs are, to a good approximation, independent of the other MOs of an alkene molecule. This is another relatively rare situation (as in dihydrogen, H2; Sec. 1.8B) in which molecular orbitals are associated with a particular bond that we can draw in a Lewis structure.

The interaction of two 2pz orbitals of ethylene by a side-to-side overlap is shown in an orbital interaction diagram (Fig. 4.6, p. 126). Because two atomic orbitals are used, two molecular orbitals are formed. These are formed by additive and subtractive combinations of the 2pz.
orbitals. Remember that subtracting orbitals is the same as reversing the peaks and troughs of one orbital and then adding.

The bonding molecular orbital that results from additive overlap of the two carbon 2p orbitals is called a \( \pi \) molecular orbital. This molecular orbital, like the \( p \) orbitals from which it is formed, has a nodal plane (shown in Fig. 4.6); this plane coincides with the plane of the ethylene molecule. The antibonding molecular orbital, which results from subtractive overlap of the two carbon 2p orbitals, is called a \( \pi^* \) molecular orbital. It has two nodes. One of these nodes is the plane of the molecule, and the other is a plane between the two carbons, perpendicular to the plane of the molecule. The bonding (\( \pi \)) molecular orbital lies at lower energy than the isolated 2p orbitals, whereas the antibonding (\( \pi^* \)) molecular orbital lies at higher en-
4.1 STRUCTURE AND BONDING IN ALKENES

ergy. By the aufbau principle, the two 2p electrons (one from each carbon, with opposite spin) occupy the molecular orbital of lower energy—the π molecular orbital. The antibonding molecular orbital is unoccupied.

The filled π molecular orbital is the π bond. Unlike a σ bond, a π bond is not cylindrically symmetrical about the line connecting the two nuclei. The π bond has electron density both above and below the plane of the ethylene molecule, with a wave peak on one side of the molecule, a wave trough on the other, and a node in the plane of the molecule. This electron distribution is particularly evident from an EPM of ethylene, which shows the local negative charge associated with electron density above and below the molecule.

![EPM of ethylene](image)

It is important to understand that the π bond is one bond with two lobes, just as a 2p orbital is one orbital with two lobes. In this bonding picture, then, there are two types of carbon–carbon bonds: a σ bond, with most of its electron density relatively concentrated between the carbon atoms, and a π bond, with most of its electron density concentrated above and below the plane of the ethylene molecule.

This bonding picture shows why ethylene is planar. If the two CH₂ groups were twisted away from coplanarity, the 2p orbitals could not overlap to form the π bond. Thus, the overlap of the 2p orbitals and consequently the very existence of the π bond require the planarity of the ethylene molecule.

An important aspect of the π electrons is their relative energy. As Fig. 4.3 suggests, the 2p_z electrons (which become the π electrons of ethylene) have higher energy than the electrons in the hybrid orbitals. Thus, π electrons generally have higher energy than σ electrons, just as p electrons have higher energy than s electrons. A consequence of this higher energy is that π electrons are more easily removed than σ electrons. In fact, we’ll find that electrophiles react preferentially with the π electrons in an alkene because those electrons are most easily donated. Most of the important reactions of alkenes involve the electrons of the π bond, and many of these reactions involve the reaction of electrophiles with the π electrons.

The π bond is also a weaker bond than typical carbon–carbon σ bonds because π overlap, which is “side-to-side,” is inherently less effective than σ overlap, which is “head-to-head.” It takes about 243 kJ mol⁻¹ (58 kcal mol⁻¹) of energy to break a carbon–carbon π bond, whereas it takes a much greater energy—about 377 kJ mol⁻¹ (90 kcal mol⁻¹)—to break the carbon–carbon σ bond of ethane.

Return to the structure of propene in Fig. 4.2, and notice that the carbon–carbon bond to the —CH₃ group is shorter by about 0.04 Å than the carbon–carbon bonds of ethane or propane. This small but real difference is general: single bonds to an sp²-hybridized carbon are somewhat shorter than single bonds to an sp³-hybridized carbon. The carbon–carbon single bond of propene, for example, is derived from the overlap of a carbon sp³ orbital of the —CH₃ group with a carbon sp² orbital of the alkene carbon. A carbon–carbon bond of propane is derived from the overlap of two carbon sp³ orbitals. Because the electron density of an sp² orbital is somewhat closer to the nucleus than the electron density of an sp³ orbital, a bond involving an sp² orbital, such as the one in propene, is shorter than one involving only sp³ orbitals, such as
the one in propane. In other words, within bonds of a given bond order, bonds with more s character are shorter.

\[
\begin{align*}
\text{H}_3\text{C} & \text{CH}_2 \\
\text{H}_3\text{C} & \text{CH}_3
\end{align*}
\]

\text{sp}^3-\text{sp}^2 \text{ single bond (shorter)} \quad \text{sp}^3-\text{sp}^3 \text{ single bond (longer)}

\section*{C. Double-Bond Stereoisomers}

The bonding in alkenes has other interesting consequences, which are illustrated by the four-carbon alkenes, the butenes. The butenes exist in isomeric forms. First, in the butenes with unbranched carbon chains, the double bond may be located either at the end or in the middle of the carbon chain.

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{CH} - \text{CH}_2 - \text{CH}_3 \\
\text{H}_2\text{C} & \equiv \text{CH} - \text{CH} - \text{CH}_3
\end{align*}
\]

1-butene \quad 2-butene

Isomeric alkenes, such as these, that differ in the position of their double bonds are further examples of constitutional isomers (Sec. 2.4A).

The structure of 2-butene illustrates another important type of isomerism. There are two separable, distinct 2-butenes. One has a boiling point of 3.7 °C; the other has a boiling point of 0.88 °C. In the compound with the higher boiling point, called cis-2-butene or (Z)-2-butene, the methyl groups are on the same side of the double bond. In the other 2-butene, called trans-2-butene, or (E)-2-butene, the methyl groups are on opposite sides of the double bond.

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{CH} \quad \text{CH}_3 \\
\text{H}_3\text{C} & \equiv \text{CH} \quad \text{CH}_3
\end{align*}
\]

\text{cis-2-butene (Z)-2-butene} \quad \text{trans-2-butene (E)-2-butene}

These isomers have identical atomic connectivities (CH₃ connected to CH, CH doubly bonded to CH, CH connected to CH₃). Despite their identical connectivities, the two compounds differ in the way their constituent atoms are arranged in space. Compounds with identical connectivities that differ in the spatial arrangement of their atoms are called stereoisomers. Hence, cis- and trans-2-butene are stereoisomers. (The (E) and (Z) notation has been adopted by the IUPAC as a general way of naming cis and trans isomers. This notation is discussed in Sec. 4.2B.)

The interconversion of cis- and trans-2-butene requires a 180° internal rotation about the double bond—that is, a rotation of one carbon while holding the other carbon stationary.

\[
\begin{align*}
\text{cis-2-butene} & \quad \text{trans-2-butene} \\
\text{(interconversion does not occur at ordinary temperatures)}
\end{align*}
\]

Because cis- and trans-2-butene do not interconvert, even at relatively high temperatures, it follows that this internal rotation must be very slow. For such an internal rotation to occur, the 2p orbitals on each carbon must be twisted away from coplanarity; that is, the \( \pi \) bond must be
broken. (Fig. 4.7). Because bonding is energetically favorable, lack of it is energetically costly. It takes more energy to break the π bond than is available under normal conditions; thus, the π bond in alkenes remains intact, and internal rotation about the double bond does not occur. In contrast, internal rotation about the carbon–carbon single bonds of ethane or butane can occur rapidly (Sec. 2.3) because no chemical bond is broken in the process.

Cis- and trans-2-butene are examples of double-bond stereoisomers. Double-bond stereoisomers (also called cis–trans stereoisomers or E,Z-stereoisomers) are defined as compounds related by an internal rotation of 180° about the double bond. (We can always imagine such a rotation even though it does not occur at ordinary temperatures.) Another equivalent definition is that double-bond stereoisomers are different compounds related by interchange of the two groups at either carbon of a double bond.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} = \text{C} \quad \text{H} \\
& \quad \text{CH}_3 \quad \text{interchange colored groups} \quad \text{CH}_3 \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

(4.2)

When an alkene can exist as double-bond stereoisomers, both carbons of the double bond are stereocenters. Interchanging two groups at a stereocenter gives stereoisomers. (Other terms that mean the same thing are stereogenic atom and stereogenic center.)

Because the exchange of the two groups at either carbon of the double bond gives stereoisomers, each of these carbons is a stereocenter.
You’ll learn in Chapter 6 that double-bond stereoisomers are not the only type of stereoisomer. In every set of stereoisomers we’ll be able to identify one or more stereocenters.

**Study Problem 4.1**

Tell whether each of the following molecules has a double-bond stereoisomer. If so, identify its stereocenters.

![Molecules A and B](image)

**Solution** Apply the definition of double-bond stereoisomers as illustrated in Eq. 4.2. That is, interchange the positions of the two groups at either carbon of the double bond. This process will give one of two results: either the resulting molecule will be identical to the original—that is, superimposable on the original atom-for-atom—or it will be different. If it’s different, it can only be a stereoisomer, because its connectivity is the same.

In molecule A, interchanging the two groups at either carbon of the double bond gives different molecules. In the original, the methyl groups are *trans*; after the interchange, the methyl groups are *cis*. Hence, A has a double-bond stereoisomer:

![Interchange colored groups](image)

(You should verify that exchanging the two groups at the other carbon of the double bond gives the same result.) The two carbons of the double bond are both stereocenters.

In the case of structure B, interchanging the two groups at either carbon of the double bond gives back an identical molecule.

![Interchange colored groups](image)

You may have found that the structure you obtained from interchanging the two groups doesn’t look identical to the one on the left, but it is. You can demonstrate their identity by flipping either structure 180° about a horizontal axis (green dashed line)—in other words, by turning it over, as shown in Eq. 4.4. But if you have difficulty seeing this, you must build molecular models of both structures and convince yourself that the two can be superimposed atom-for-atom. There is no substitute for model building when it comes to the spatial aspects of organic chemistry! After a little work with models on issues like this, you will develop the ability to see these relationships without models. Study Guide Link 4.1 offers more insights about how to achieve facility in relating alkene structures.

Because interchanging two groups in Eq. 4.4 does not give stereoisomers, this alkene contains no stereocenters.

**STUDY GUIDE LINK 4.1**

Different Ways to Draw the Same Structure
4.2 NOMENCLATURE OF ALKENES

A. IUPAC Substitutive Nomenclature

The IUPAC substitutive nomenclature of alkenes is derived by modifying alkane nomenclature in a simple way. An unbranched alkene is named by replacing the \textit{ane} suffix in the name of the corresponding alkane with the ending \textit{ene} and specifying the location of the double bond with a number. The carbons are numbered from one end of the chain to the other so that the double bond receives the lowest number. The carbons of the double bond are numbered consecutively.

\[ \text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

name = \text{hexane} + \text{ene} = \text{hexene}

The IUPAC recognizes an exception to this rule for the name of the simplest alkene, \( \text{H}_2\text{C} = \text{CH}_2 \), which is usually called ethylene rather than ethene. (\textit{Chemical Abstracts} (Sec. 2.4D, p. 66), however, uses the substitutive name ethene.)

The names of alkenes with branched chains are, like those of alkanes, derived from their \textit{principal chains}. In an alkene, the principal chain is defined as \textit{the carbon chain containing the greatest number of double bonds}, even if this is not the longest chain. If more than one candidate for the principal chain have equal numbers of double bonds, the principal chain is the longest of these. The principal chain is numbered from the end that results in the lowest numbers for the carbons of the double bonds.

When the alkene contains an alkyl substituent, the position of the double bond, not the position of the branch, determines the numbering of the chain. This is the main difference in the nomenclature of alkenes and alkanes. However, the position of the double bond is cited in the name \textit{after} the name of the alkyl group. Study Problem 4.2 shows how these principles are implemented.

**Study Problem 4.2**

Name the following compound using IUPAC substitutive nomenclature.

\[ \text{H}_2\text{C} = \text{C} - \text{CH}_2\text{CH}_2\text{CH}_3 \]

\[ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]