

## 8: Alkenes and Alkynes

- *Alkenes*
- *Alkynes*
- *Spectrometric Features of C=C and C≡C Bonds*

### Preview

**Alkenes** are hydrocarbons with C=C bonds and **alkynes** are hydrocarbons with C≡C bonds. Since C=C bonds have  $sp^2$  hybridized C, atoms or groups directly attached to a C=C bond lie in a plane and are separated by approximately  $120^\circ$  bond angles. A molecule cannot freely rotate about its C=C bond. As a result, some *alkenes* have stereoisomers, in addition to structural isomers, with different relative stabilities. *Alkenes* can also have other functional groups.

Atoms or groups directly bonded to a C-C bond lie in a straight line since C-C bonds have  $sp$  hybridized C. This makes it difficult to place a C-C bond in rings of cyclic molecules. The nomenclature of *alkynes* is analogous to that of *alkenes*. C=C and C-C bonds impart characteristic features to NMR and IR spectra of their compounds that aid in their structural identification.

### 8.1 Alkenes

**Alkenes** and **cycloalkenes** are *hydrocarbons* with one C=C bond. They are also commonly referred to as **olefins**.

#### Unbranched Alkenes (8.1A)

*Unbranched alkenes* are analogous to *unbranched alkanes*. Since the C=C can be located in different positions in unbranched alkenes with four or more C's, they have *structural isomers*.

**Ethene.** The simplest alkene **ethene** ( $H_2C=CH_2$ ) is *planar* with H-C-H and H-C-C bond angles that are close to  $120^\circ$ .

Figure 8.2

These  $120^\circ$  bond angles and the planar geometry are consistent with  $sp^2$  hybridization for each of ethene's C atoms (Chapter 1). Each C uses its three  $sp^2$

atomic orbitals to form the two C-H bonds and one of the C-C bonds as we illustrate here.

Figures 8.49 and 8.50

In addition to the ( $sp^2$ - $sp^2$ ) C-C bond just shown, the other C-C bond in C=C is ( $2p$ - $2p$ ) that results from sideways overlap of the  $2p$  orbitals on each  $sp^2$  C.

**Propene.** We show **propene** ( $CH_3CH=CH_2$ ), the next higher mass alkene, in two different views.

Figure 8.5

The  $CH_3$  group causes bond angles to deviate slightly from the bond angles in *ethene* because of its larger steric size compared to H. While the C=C bond and its directly attached atoms lie in a plane,  $CH_3$  has a normal *tetrahedral* geometry.

Figure 8.6

Rotation about C-C single bonds is usually a low energy process (Chapter 2), so *propene* has different *conformations* due to rotation about the  $H_3C$ -CH bond. The most stable one is (A) where the  $C_a$ -H bond is staggered between two C-H bonds of  $CH_3$ . Conformation (B), where the C=C bond is staggered between C-H bonds of  $CH_3$ , has a higher energy than (A) so it is less stable than (A).

**1-Butene and 2-Butene.** The next higher molecular mass alkenes after *ethene* and *propene* are the two different  $C_4$  *structural isomers* **1-butene** and **2-butene**.

Figure 8.7

The number prefix in each of these names (1- or 2-) corresponds to the lower C number of the two C's of each C=C bond. Alkenes are numbered so that the C=C bond is in the longest continuous carbon chain and has the lowest possible C number.

**Other Alkenes and Cycloalkenes.** We name other unbranched *alkenes* in the same manner that we just named *1-butene* and *2-butene*. We always indicate the position of the double bond in *acyclic alkenes* using a number that precedes the name of the parent alkene, but unbranched *cycloalkenes* (Figure 8.7a) do not require these number designations since one C of the C=C is always C1.

Figure 8.7a

We describe the nomenclature of branched and *substituted* alkenes and cycloalkenes later in this chapter.

**Alkene Stereoisomers** (8.1B)

Some unbranched alkenes can exist as two different *stereoisomers*. An example is *2-butene* ( $\text{CH}_3\text{CH}=\text{CHCH}_3$ ).

**(E)-2-Butene and (Z)-2-Butene.** Atoms directly attached to a C=C bond must lie in a plane, so the *terminal*  $\text{CH}_3$  groups (C1 and C4) of *2-butene* can be on the same or opposite sides of the C=C bond (Figure 8.8).

Figure 8.8

These two *stereoisomers* of *2-butene* do not interconvert at normal temperatures so they are different molecules with different properties and different names. Interconversion requires C=C rotation that breaks the (2p-2p) bond and this process requires a large energy input (about 270 kJ/mol).

Figure 8.8a

The two  $\text{CH}_3$  groups of **(Z)-2-butene** are on the same side of the C=C, while its *stereoisomer* with two  $\text{CH}_3$  groups on opposite sides of the C=C is **(E)-2-butene** (Figure 8.8). *E* is the first letter of the German word "*entgegen*" that means "opposite", while *Z* is the first letter of the German word "*zusammen*" that means "together".

**Other E and Z Alkenes.** Alkenes have *E* and *Z* *stereoisomers* whenever the two atoms and/or groups on each C of the C=C are different from each other. This is the case for (*E*) and (*Z*)-*2-butene* (Figure 8.9).

Figure 8.9

The two groups on  $\text{C}_a$  ( $\text{CH}_3$  and H) are different from each other, and so are the two groups ( $\text{CH}_3$  and H) on  $\text{C}_b$ . It does not matter that both  $\text{C}_a$  and  $\text{C}_b$  have identical pairs of groups ( $\text{CH}_3$  and H) because we separately consider  $\text{C}_a$  and  $\text{C}_b$ . We show other examples of alkenes with *E* and *Z* *stereoisomers* in Figure 8.10.

Figure 8.10

We will name these alkenes after we learn the *E/Z* assignment rules in the next section.

***E,Z* Assignment Rules.** The rules for assigning the *E* and *Z* designations are based on those that we used in Chapter 4 to assign the *R* and *S* designations to carbon stereocenters. We give *priority numbers* 1 and 2 to the two atoms and/or groups bonded to each C of the C=C using the *R,S* *priority assignment rules* (Chapter

4). This results in two different general possibilities for all alkenes with *E*, *Z* isomers.

Figure 8.11

The isomer with the same priority numbers on the same side of the C=C is the *Z* ("together") isomer, while the isomer with the same priority numbers on opposite sides of the C=C is the *E* ("opposite") isomer. We show once again the examples from Figure 8.10 that have *E*,*Z*-isomers and include their priority assignments.

Figure 8.11a

***E* and *Z* Stereoisomers are Diastereomers.** We learned in Chapter 4 that two stereoisomers of a compound may either be *enantiomers* or *diastereomers*.

*Enantiomers* are always mirror images (that are non-superimposable), so *E* and *Z* stereoisomers are *diastereomers* because they are not mirror images.

Figure 8.12

*E* and *Z* stereoisomers are generally not *chiral compounds* because each alkene stereoisomer usually has a plane of symmetry defined by the double bond and its attached atoms as we show here.

Figures 8.13 and 8.14

Alkenes that are chiral most often have this property because they additionally have one or more chiral tetrahedral C's that are chiral.

***cis* and *trans* Isomers.** Organic chemists generally refer to (*E*)-2-butene as *trans*-2-butene, and (*Z*)-2-butene as *cis*-2-butene (Figure 8.15).

Figure 8.15

We introduced the terms *cis* ("on the same side") and *trans* ("across") in Chapter 1 to name disubstituted cycloalkanes. They have the same meaning with respect to the CH<sub>3</sub> (or H) groups on the C=C of 2-butene as we illustrate in Figure 8.15.

Before *E*,*Z* nomenclature was introduced in 1968, organic chemists exclusively used the terms *cis* and *trans* to designate alkene stereoisomers, and these terms remain an integral part of organic chemistry vocabulary. For example, when two groups are on the same side of a C=C we say they are "*cis*" to each other, while we say that groups on opposite sides of a C=C are "*trans*". This use of *cis* and *trans* is convenient and unambiguous, but this is often not true of their use in specific chemical names. We can unambiguously assign *cis* and *trans* to *E* and *Z* stereoisomers of 2-butene, but this is not true for many alkenes as we show in Figure 8.16 [next page].

## Figure 8.16

For example we can assign the alkene stereoisomer in Figure 8.16 as *Z* using the *E/Z* assignment rules above, but it is not clear whether we should call it *cis* or *trans*. As a result, *E* and *Z* have replaced *cis* and *trans* in systematic nomenclature.

**More than One C=C in a Molecule** (8.1C)

Hydrocarbons can have more than one C=C bond.

**Polyenes.** Polyenes have two or more C=C bonds in the same continuous chain (Figure 8.19).

## Figure 8.19

We use prefixes such as *di*, *tri*, *tetra*, *penta*, *hexa*, *etc.* to indicate the number of double bonds in the *polyene* and we indicate the positions of these C=C bonds with prefix numbers that we choose so that the first C=C bond has the lowest possible C number (Figure 8.20).

## Figure 8.20

If this provides two equal choices, the next C=C bonds are numbered until a difference is found.

Similarly, in *cyclic polyenes*, we choose one C=C as C1-C2 so that subsequent C=C bonds have the lowest C numbers. Where appropriate, we can designate each individual C=C bond of a *polyene* as ***E*** or ***Z*** as we previously described for *alkenes*.

**Allenes.** Compounds where two C=C bonds share a common carbon are called **allenes**.

## Figure 8.20a

We systematically name *allenes* in the same way as *polyenes* (Figure 8.19). We discuss them in more detail later in this chapter after we introduce *alkynes*. *Allenes* can sometimes isomerize to *alkynes* and their chemical properties are more like those of *alkynes* than those of *polyenes* in which each C=C is separated by at least one C-C single bond.

**Nomenclature of Substituted Alkenes** (8.1C)

We name *substituted alkenes* as derivatives of their *parent unsubstituted alkenes*.

**Alkyl and Halogen Substituted Alkenes.** We designate the position of an *alkyl group*, or *halogen atom* on an alkene, with the number of the carbon to which it is bonded based on the numbering of the parent alkene. When we find that either end of the parent alkene can be C1 based on the location of the C=C, we choose C1 so that the first halogen or alkyl substituent has the lowest number (Figure 8.17).

Figure 8.17

**Alkyl and Halogen Substituted Cycloalkenes.** Although we do not use a number to designate the C=C position in an unsubstituted cycloalkene with a number, we need a number to define the position of a halogen atom or alkyl group with respect to the C=C in a substituted cycloalkene. To accomplish this, we assign the C's of C=C as C1 and C2 so that the alkyl group or halogen atom substituent closest to the C=C has the lowest possible number as we show in Figure 8.18.

Figure 8.18

**Alkyl and Halogen Substituted Polyenes.** In order to name substituted polyenes, we select the parent hydrocarbon that has the maximum number of double bonds. As a result, the parent hydrocarbon may have a shorter chain length than the longest chain with a C=C (Figure 8.22).

Figure 8.22

Once we identify the chain with the greatest number of C=C bonds, we number it so that the first C=C bond (or subsequent C=C bonds) has the lowest possible C numbers. When there are two equivalent alternative names for a structure such as those in Figure 8.33, we choose the numbering that gives the lowest number to the first group or atom substituted on the parent chain.

Figure 8.33 [*Note: There are no Figures 8.23 through 8.32*]

**Alkenes With OH or NH<sub>2</sub> Groups.** Alkenes with OH or NH<sub>2</sub> groups have different types of systematic names than alkyl or halogen substituted alkenes and polyenes. Whenever possible, we name them as **alkenols** (OH group) and **alkenamines** (NH<sub>2</sub> group) using nomenclature analogous to that we described in Chapter 3 for *alcohols (alkanols)* and *amines (alkanamines)*.

For *alkenols*, we first identify the chain that contains OH and the most C=C bonds. We number the chain so that the OH group has the lowest possible number. When there is more than one way to number a chain that gives the same lowest number to

C-OH, we choose the numbering sequence that causes the first (or a subsequent) C=C to have the lowest number (Figure 8.34).

Figure 8.34

We name *alkenamines* in the same way as *alkenols* (Figure 8.35).

Figure 8.35

***CH<sub>2</sub>=CH-OH and CH<sub>2</sub>=CH-NH<sub>2</sub>***. Compounds with OH or NH<sub>2</sub> directly bonded to a C=C bond are unstable and isomerize to their more stable isomers with C=O or C=N groups (Figure 8.35a).

Figure 8.35a

In the resulting equilibria shown above, the *alkenol* and *alkenamine* forms (those with the C=C) are present to only a very small extent. Nonetheless, these minor forms are important in a variety of organic reactions that we describe later. We mentioned the stable compounds with C=O and C=NH groups in Chapter 1 and we describe them later in the text.

***Common Names of Substituted and Unsubstituted Alkenes.*** Organic chemists frequently use *common names* for the simple substituted and unsubstituted alkenes such as those we show in Table 8.1.

**Table 8.1. Common Names of Unsubstituted and Substituted Alkenes.**

<u>Structure</u>	<u>Common Name</u>	<u>Systematic Name</u>
CH <sub>2</sub> =CH <sub>2</sub>	ethylene	ethene
CH <sub>3</sub> -CH=CH <sub>2</sub>	propylene	propene
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	isobutylene	2-methylpropene
CH <sub>2</sub> =C=CH <sub>2</sub>	allene	propadiene
CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CH <sub>2</sub>	isoprene	2-methyl-1,3-butadiene
CH <sub>2</sub> =CH-Cl	vinyl chloride*	chloroethene
CH <sub>2</sub> =CH-CH <sub>2</sub> -Cl	allyl chloride*	3-chloropropene
CH <sub>2</sub> =CH-CH <sub>2</sub> -OH	allyl alcohol	2-propenol
CH <sub>2</sub> =CH-CH <sub>2</sub> -NH <sub>2</sub>	allyl amine	2-propenamine

\* We can replace *chloride* (Cl) by *fluoride* (F), *bromide* (Br), or *iodide* (I).

The terms **vinyl** and **allyl** (Table 8.1) are *common names* for the **1-ethenyl** and **2-propenyl** groups (Figure 8.36)[next page].

Figure 8.36

They also appear in the common names of other compounds (besides those in Table 8.1) with the general structure  $\text{CH}_2=\text{CH}-\text{Y}$  and  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Y}$ .

### Alkene Stability (8.1D)

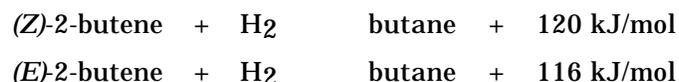
The relative stability of *alkene isomers* depends on whether they are *E* or *Z*, and the location of the C=C bond in the hydrocarbon chain.

**Relative Stability of Isomeric *E* and *Z* Alkenes.** There is an unfavorable steric interaction between two alkyl groups *cis* to each other on a C=C bond (as in (*Z*)-2-butene) that causes the molecule to be less stable (have higher energy) than the isomer where those alkyl groups are *trans* to each other (as in (*E*)-2-butene)

Figure 8.37

Organic chemists have determined the relative stabilities of isomers such as (*E*) and (*Z*)-2-butene by measuring and comparing the heat change in their reactions with molecular hydrogen ( $\text{H}_2$ ).

Figure 8.38



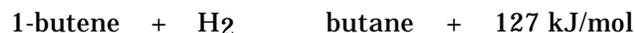
Since these **hydrogenation reactions** of (*E*) and (*Z*)-2-butene both give *butane* as the reaction product, the difference between their measured heat changes reflects their comparative *thermodynamic stabilities*.

These reactions release heat, so both (*Z*) and (*E*)-2-butene have higher energies than *butane* (along with  $\text{H}_2$ ) so we say that the reactions are *exothermic*. *Hydrogenation* of a mole of (*Z*)-2-butene produces 4 kJ/mol more heat than hydrogenation of a mole of (*E*)-2-butene ( $120 \text{ kJ} - 116 \text{ kJ} = 4 \text{ kJ}$ ), so (*Z*)-2-butene is 4 kJ/mol higher in energy than (*E*)-2-butene. Alternatively we can say that (*Z*)-2-butene is 4 kJ/mol less stable than its *E* isomer. We illustrate these relationships using an energy diagram.

Figure 8.39

**C=C Substitution and Alkene Stability.** The *stability* or *relative energy* of an alkene also depends on the position of the C=C bond in a carbon chain. For example, hydrogenation of *1-butene* that also gives *butane* releases more heat than hydrogenation of either (*E*) or (*Z*)-2-butene [Figure next page]

Figure 8.40

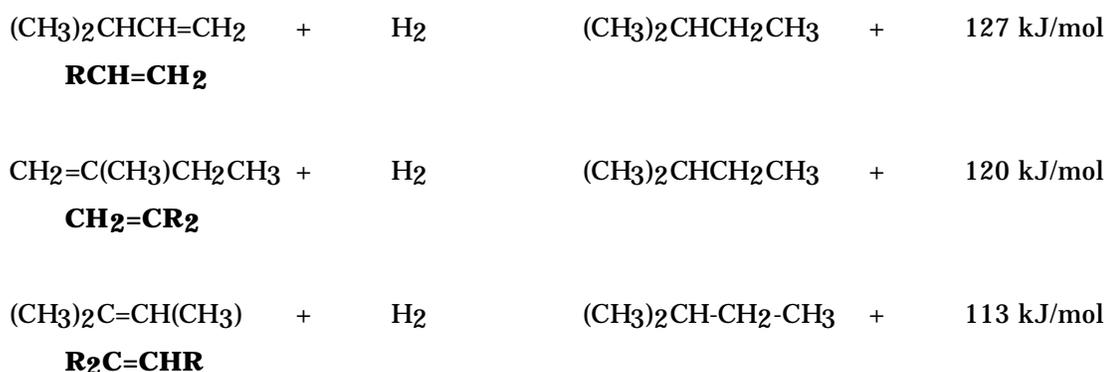


This means that *1-butene* is less stable (has a higher energy) than either (*Z*) or (*E*)-*2-butene* as we illustrate here.

Figure 8.40a

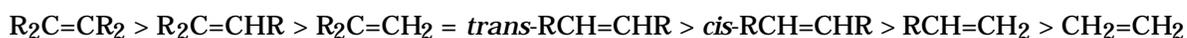
1-Butene has the general formula  $\text{RCH}=\text{CH}_2$  while both isomeric (*E*) and (*Z*)-*2-butene* have the general formula  $\text{RCH}=\text{CHR}$ . We usually find that an increase in the number of R groups on a  $\text{C}=\text{C}$  increases the stability of an alkene (Figure 8.40a and Figure 8.41).

Figure 8.41



*Hydrogenation* of each of the alkenes in Figure 8.41 gives the same alkane ( $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ ), so their heats of hydrogenation reflect the relative stabilities of the three alkenes. The alkene with one R group on the  $\text{C}=\text{C}$  is less stable (has a higher heat of hydrogenation) than that with two R groups on the  $\text{C}=\text{C}$ , while that with three R groups on  $\text{C}=\text{C}$  is the most stable (has the smallest heat of hydrogenation).

These and other similar results indicate that the general stability order for isomeric alkenes is:



We explain this order by proposing that electron density from  $\text{C}-\text{H}$  bonds in alkyl substituents (R) delocalizes into the  $\text{C}=\text{C}$  bond as we show in Figure 8.59c.

Figure 8.59c

We refer to this *electron density donation* from a  $\sigma$  bond to a  $\pi$  bond as *hyperconjugation* in the same way we referred to electron density donation from alkyl groups to carbocations as hyperconjugation in Chapter 7.

**Stability of Cycloalkenes.** *Cycloalkenes* can have as few as three C atoms, however both *cyclopropene* (C3) and *cyclobutene* (C4) are highly strained molecules.

Figure 8.43

These two highly strained cycloalkenes are planar and their internal ring bond angles are much smaller than normal. In contrast, *cyclopentene* with significantly larger bond angles, and *cyclohexene* with almost normal bond angles, are both relatively strain-free.

The ring constrains the C=C bond to be exclusively *Z* (*cis*) for *cyclopropene* through *cycloheptene*. However, there are *E* as well as *Z* isomers of *cyclooctene* and higher cycloalkenes.

Figure 8.43a

While the *Z* isomer (*cis* isomer) of *cyclooctene* is more stable than its *E* isomer (*trans* isomer) by about 38 kJ/mol, this energy difference decreases to about 12 kJ/mol for (*E*)- and (*Z*)-*cyclononene* and continues to decrease with increasing ring size. (*E*)-cycloalkenes (*trans* cycloalkenes) become more stable than (*Z*)-cycloalkenes (*cis* cycloalkenes) when there are more than 11 C's in the ring.

## 8.2 Alkynes

Hydrocarbons with a C-C bond are systematically named **alkynes** and commonly referred to as **acetylenes**. For reasons that you will see later, we also describe *allenes* ( $R_2C=C=CR_2$ ) in this section.

### **Unbranched Alkynes** (8.2A)

Unbranched *alkynes* have *structural isomers* because the C-C can be at different locations in the carbon skeleton. However we will see below that they do not have *stereoisomers* associated with the C-C bond.

**Nomenclature.** We show unbranched *alkynes* with five or fewer C's in Table 8.2 [next page] along with their systematic names and common names where appropriate.

**Table 8.2. Some Simple Alkynes**

<u>Structure</u>	<u>Systematic</u>	<u>Common</u>
HC CH	ethyne	acetylene
CH <sub>3</sub> -C CH	propyne	methylacetylene
CH <sub>3</sub> CH <sub>2</sub> -C CH	1-butyne	
CH <sub>3</sub> -C C-CH <sub>3</sub>	2-butyne	dimethylacetylene
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -C CH	1-pentyne	
CH <sub>3</sub> CH <sub>2</sub> -C C-CH <sub>3</sub>	2-pentyne	

Chemists usually refer to **ethyne** by its common name *acetylene*. We mentioned above that *acetylene* is also used as the common name for the whole *class* of *alkynes*.

**Alkyne Structure.** Alkynes (*acetylenes*) have a **linear geometry** at the C C triple bond. In acyclic compounds, the bond angles between the triple bond and bonded atoms or groups are exactly 180° as we show in Figure 8.44.

Figure 8.44

This linear geometry results from the directional character of the *sp hybrid* atomic orbitals of the C's in a C C (Chapter 1). The H-C bonds in *ethyne* use (1s-sp) molecular orbitals, while one of the C-C bonds is (sp-sp). The other two bonds in the C C group of ethyne (and all other alkynes) are (2p-2p) bonds resulting from sideways overlap of the two *2p* orbitals on each of the *sp hybridized* C's of the C C.

In **propyne**, the CH<sub>3</sub>-C bond is (sp<sup>3</sup>-sp). Tetrahedral carbons in alkynes, such as those in the CH<sub>3</sub> groups in *propyne* or *2-butyne*, and the CH<sub>3</sub> or CH<sub>2</sub> groups in *1-butyne* or *2-pentyne*, have normal tetrahedral bond angles and C-C rotation as we show using *propyne* as our example.

Figure 8.44a

With only one group or atom attached to each carbon of the C C bond, and 180° C-C C bond angles, alkynes have no *cis/trans* (*E/Z*) stereoisomers.

**Polyynes.** More than one C C bond can be in the same molecule and the nomenclature rules for these **polyynes** are analogous to those for *polyenes*. When a double and triple bond are in the same continuous chain, we name the molecule an **alkene-yne** and give double bonds preference over triple bonds in choosing C1.

Figure 8.45

Substitution of alkyl groups, halogen atoms, OH or NH<sub>2</sub> groups on alkynes, polyynes, or ene-yne gives compounds that are systematically named analogously to OH and NH<sub>2</sub> substituted alkenes.

### **Alkyne Stability (8.2B)**

Alkyl groups bonded to the C-C bond stabilize *alkynes* in the same way that they stabilize *alkenes*. For example, *2-butyne* (with the general structure R-C≡C-R) is more stable than its structural isomer *1-butyne* (with the general structure R-C≡C-H) as we see by comparing their heats of hydrogenation.

Figure 8.44b

1-butyne	+	2H <sub>2</sub>	butane	+	292 kJ/mol
2-butyne	+	2H <sub>2</sub>	butane	+	272 kJ/mol

The favored linear geometry of the C-C-C grouping of alkynes restricts the presence of a C-C bond in rings to cycloalkynes that are relatively large.

**Cyclononyne** (C<sub>9</sub>) is relatively strain free, while **cyclooctyne** (C<sub>8</sub>) is strained but has been isolated. In contrast, **cyclohexyne** (C<sub>6</sub>) and **cycloheptyne** (C<sub>7</sub>) are very unstable compounds that only exist at very low temperatures for short periods of time.

### **C-H and C-C Bond Lengths (8.2C)**

Now that we have described and compared the bonding in *alkanes* (Chapter 2), *alkenes*, *alkynes*, and *allenes*, we compare and contrast their C-H and C-C bond lengths.

**Alkanes, Alkenes, and Alkynes.** We compare calculated bond lengths in *ethene*, and *ethyne*, with those in *ethane* in Table 8.3.

**Table 8.3. Approximate C-H and C-C Bond Lengths**

<u>Compound</u>	<u>C Hybridization</u>	<u>C-H (Å)</u>	<u>C-C (Å)</u>
ethane	sp <sup>3</sup>	1.09	1.53
ethene	sp <sup>2</sup>	1.08	1.32
ethyne	sp	1.06	1.18

Each C-H bond uses a molecular orbital made up of an overlapping  $1s$  atomic orbital on H and an  $sp^3$ ,  $sp^2$ , or  $sp$  atomic orbital on C (Chapter 1). The decrease in C-H bond length as C hybridization changes from  $sp^3$  to  $sp^2$  to  $sp$  reflects the decrease in the "length" of the hybrid C atomic orbital used in the C-H bonding MO.

This C atomic orbital "length" is determined by the relative amounts of  $2s$  and  $2p$  character in the hybrid AO (Table 8.3a)

**Table 8.3a. Relative Amounts of  $2s$  and  $2p$  Character in Hybrid Atomic Orbitals**

<u>Atomic Orbital</u>	<u>% -2s Character</u>	<u>% -2p Character</u>
$sp^3$	25	75
$sp^2$	33	67
$sp$	50	50

The amount of  $2p$  character in the hybrid AO determines how "extended" the hybrid AO is from the C nucleus. You can see that %- $2p$  character in these hybrid carbon AO's decreases in the order  $sp^3 > sp^2 > sp$ . As a result, the C-H bond lengths resulting from overlap of those AO's with the  $1s$  AO on H decreases in the same order (Table 8.3).

The analogous decrease in C-C bond lengths with a change in C hybridization from  $sp^3$  to  $sp^2$  to  $sp$  is more pronounced than the decrease in C-H bond length, and results from two effects. The first is the change in "size" of the C AO's that we have just described to explain C-H bond lengths, while the second is a consequence of ( $2p$ - $2p$ ) bonds between the two C's.

Effective sideways overlap of two  $2p$  orbitals to form a ( $2p$ - $2p$ ) bond requires that C-C bond lengths be shorter than those associated with just a bond considered by itself. For example, the length of the C-C bond ( ( $sp^2$ - $sp^2$ )) for the twisted form of ethene, where the  $2p$  orbitals are perpendicular to each other and cannot overlap (Figure 8.59a), is longer (1.39 Å) than that in planar ethene (1.32 Å) that has both a ( $sp^2$ - $sp^2$ ) bond and a fully developed ( $2p$ - $2p$ ) bond.

Figure 8.59a

**Acidity of C≡C-H Hydrogens** (8.2D)

The strong base sodium amide (NaNH<sub>2</sub>) removes C≡C-H protons of 1-alkynes, but does not comparably react with C-H's bonded to C=C or to C-C bonds.



This is reflected in the relative pK<sub>a</sub> values of these various types of C-H protons.

Hydrocarbon	R <sub>3</sub> C-H	R <sub>2</sub> C=CRH	R-C≡C-H
pK <sub>a</sub> Value	50	44	25

We explain this relatively high C≡C-H acidity by the relatively large amount (50%) of 2s character (Table 8.3a) in a C≡C-H bond that is made up of a C sp hybrid orbital. That relatively large s character makes an sp hybrid C more electronegative than sp<sup>2</sup> or sp<sup>3</sup> C's, and hence more able to stabilize the negative charge resulting from removal of a proton by a base.

Acetylide ions resulting from loss of a C≡C-H proton are nucleophiles and react with a variety of substrates such as those described at the end of Chapter 7 in nucleophilic substitution reactions such as the type shown here.



We will see further examples of them serving as nucleophiles in later chapters.

**Allenenes** (8.2E)

We include *allenenes* (R<sub>2</sub>C=C=CR<sub>2</sub>) in this *alkyne* section because the central C of the allene C=C=C group is *sp* hybridized like the C's in C≡C bonds. Some *allenenes* also isomerize to *alkynes*.

Figure 8.57

**Nomenclature.** The systematic name of the simplest *allene* (C<sub>3</sub>) is **propadiene**, however it is almost always called **allene** which is its common name. The next higher molecular mass allene is *1,2-butadiene* (H<sub>2</sub>C=C=CH-CH<sub>3</sub>), followed by *1,2-pentadiene* (H<sub>2</sub>C=C=CH-CH<sub>2</sub>CH<sub>3</sub>) and its structural isomer *2,3-pentadiene* (CH<sub>3</sub>-CH=C=CH-CH<sub>3</sub>).

**A Nomenclature Aside.** Remember that the common name of *alkynes* is *acetylenes* and *acetylene* is also the common name of the simplest alkyne. You can see that the same is true for the class of compounds commonly referred to as *allenenes*.

**Structure and Bonding.** Since the two C=C bonds in *allenes* share a common C we say that they have **cumulated** double bonds. The  $sp$  hybridization of the central C of C=C=C is consistent with the  $180^\circ$  C-C-C bond angle of the *allene* group.

Figure 8.58

Each C=C has one ( $sp^2$ - $sp$ ) bond and one ( $2p$ - $2p$ ) bond, and all four of the C-H bonds in the specific compound named *allene* ( $H_2C=C=CH_2$ ) are ( $sp^2$ - $1s$ ). The four H atoms of *allene* lie in two different planes that are perpendicular to each other since each of the two *cumulated* C=C bonds uses a different  $2p$  orbital on the central  $sp$  C atom.

Figure 8.59

**Bond Lengths.** C-H bond lengths in *allene* ( $H_2C=C=CH_2$ ) are almost the same as those in *ethene* ( $H_2C=CH_2$ ) since they are ( $1s$ - $sp^2$ ) in both compounds.

Figure 8.59b

In contrast, the C-C bond lengths for the compound *allene* have values between those of *ethene* and *ethyne*. Each C-C bond in *allene* uses a ( $sp^2$ - $sp$ ) MO that causes the C-C separation to fall between the ( $sp^2$ - $sp^2$ ) bond in *ethene* and the ( $sp$ - $sp$ ) bond in *ethyne*.

### 8.3 Spectrometric Features of C=C and C≡C Bonds

C=C and C≡C bonds impart unique spectrometric characteristics to their molecules. We present the most important of these for *NMR* and *IR* spectrometry in this section. You should review the sections on *NMR* and *IR* in Chapter 5 before or as you read this section.

#### **$^{13}C$ NMR Spectrometry (8.3A)**

The  $^{13}C$  chemical shift values (  $\delta$  values) for the C atoms in C=C and C≡C bonds are larger than those for tetrahedral C atoms substituted only with H or alkyl groups. This downfield shift (Chapter 5) is much greater for C=C bonds than for C≡C bonds.

**C=C Bonds.** The  $^{13}C$  chemical shift values (  $\delta$  values) of C=C carbons substituted only by H or alkyl groups range from 110 to 150. The  $^{13}C$  value for terminal C=C carbons (the C of a =CH<sub>2</sub> group) is at the lower end of this range while internal C=C carbons (those with alkyl substitution) have larger  $\delta$  values (Figure 8.61)[next page].

**Figure 8.61**

In contrast, a C=C group has only a small effect on  $^{13}\text{C}$  chemical shifts of attached C's as we see by comparing  $^{13}\text{C}$  values for a similar alkane and alkene (Figure 8.62).

**Figure 8.62**

The C=C carbons show the expected large values, but the corresponding tetrahedral C's have almost identical values in each molecule.

Groups other than alkyl groups substituted on or near a C=C, show a variety of effects on  $^{13}\text{C}$  values of the C=C carbons (Figure 8.63) that depend on whether the C=C is internal or terminal.

**Figure 8.63**

**C=O Bonds.** The value for the C in C=O bonds is much greater than values for C's of any C=C. Typically the chemical shift values for C's in C=O are between 160 and 200 depending on the rest of the chemical structure. We describe compounds containing the C=O group beginning in Chapter 11 and present additional information about their NMR spectrometric characteristics there.

**C≡C Bonds.** The  $^{13}\text{C}$  values for C-C carbons are shifted downfield like those of C=C, but the magnitude of the shift is much smaller as we see in a comparison of  $^{13}\text{C}$  shifts for C's in 1-butyne and 1-butene (Figure 8.64).

**Figure 8.64**

The chemical shift value of a terminal C in a C-C is less than that of an internal C as we observed for C=C's.

We can see that the effect of a C-C on neighboring alkyl groups is greater than that of a C=C by comparing  $^{13}\text{C}$  values for all of the C's in *2-hexyne*, (*E*)-*2-hexene*, and *hexane* (Figure 8.65).

**Figure 8.65**

The  $^{13}\text{C}$  values of C1 and C4 in 2-hexyne are significantly smaller than the  $^{13}\text{C}$  values for the analogous C's in either of the other two compounds.

**Allenes.** The  $^{13}\text{C}$  values for the C's in the C=C=C group of *allenes* are unusual as we illustrate here for *3-methyl-1,2-butadiene*.

**Figure 8.66**

While the central C atom has a very large  $^{13}\text{C}$  value ( 207), the end C's have much smaller values ( 73 and 94). These comparative values are typical for those of the analogous C's in other allenes.

### **$^1\text{H}$ NMR Spectrometry (8.3B)**

The  $^1\text{H}$  values of H's attached to C=C are much larger than those for H's attached to tetrahedral C with only H or alkyl substitution. However, the values for H-C C protons are much smaller and fall within the chemical shift range of H's on alkyl substituted tetrahedral C.

**C=C-H  $^1\text{H}$   $\delta$  Values.** H's attached to C=C have  $^1\text{H}$  values ranging from approximately 4.7 to 6 (Figure 8.67).

Figure 8.67

Since these values are much longer than those for most other C-H hydrogens,  $^1\text{H}$  NMR is very useful for identifying H-C=C protons in organic molecules. A C=C bond also increases  $^1\text{H}$  chemical shift values of C-H's on directly attached tetrahedral C's by about 0.7 as you can see here in the comparison of  $^1\text{H}$  values for *pentane* and (*Z*) and (*E*)-2-pentene.

Figure 8.68

These spectra (Figure 8.68a) clearly show the distinctive location of C=C-H  $^1\text{H}$  NMR signals.

Figure 8.68a

**$^1\text{H}$  Spin-Splitting in Alkenes.** The splitting patterns that arise due to spin splitting between H's attached to the same C=C, and to alkyl groups directly attached to the C=C, are also very useful for spectral identifications. They can help identify whether a substituted C=C is *E* or *Z* and confirm the relative relationships of groups substituted on the C=C.

We see in Figure 8.69 that the magnitude of the spin-spin splitting ( $J_{ab}$  (Hz)) between two H's attached to the same C=C varies greatly depending on their relative positions.

Figure 8.69

In each case,  $\text{H}_a$  splits  $\text{H}_b$  into a doublet and *vice-versa*, but the magnitude of the splitting ( $J_{ab}$ ) is greatest when the H's are *trans*, less when they are *cis*, and very small when they are on the same carbon.

In addition to these splittings, a C=C bond permits **long range splitting** to occur between certain H's even when they are not on the same or adjacent C's as we show in the examples in Figure 8.70.

Figure 8.70

The magnitude of the splitting between two non-equivalent H's on a cycloalkene ring varies greatly with the size of the ring (Figure 8.71).

Figure 8.71

**Alkynes.** A C-C bond has a much smaller effect on the  $^1\text{H}$  value of an attached H than a C=C bond (Figure 8.72).

Figure 8.72

H's on alkynes exhibit long range splitting similar to that observed for alkenes (Figure 8.73).

Figure 8.73

**Origin of the C≡C Effect on  $^1\text{H}$   $\delta$  Values.** The small effect of a C-C on the values of a C-C-H proton is the result of two large effects simultaneously operating in opposite directions. The first effect by itself, seen in the case of the C=CH<sub>2</sub> protons, would cause C-CH protons to have much larger values (a large downfield shift) compared to those attached to tetrahedral C's. However, the 4 electrons of a C-C independently interact with the applied magnetic field to setup a magnetic field in the opposite direction to that of the applied magnetic field leading to a predicted upfield shift. The result is that the large downfield shift due to the first effect is canceled out by the correspondingly large upfield shift due to the "ring current" effect (second effect) leads to observed chemical shift values for C-C-H hydrogens of about 2. We will discuss this in more detail when we introduce "aromatic" compounds such as benzene (C<sub>6</sub>H<sub>6</sub>) in Chapter 12.

### **Infrared Spectrometry (8.3C)**

C=C and C-C bonds give characteristic peaks in infrared (IR) spectra. These IR signals are due to bond stretching and are located between 1640 and 1670 cm<sup>-1</sup> for C=C bonds, and 2100 and 2260 cm<sup>-1</sup> for C-C bonds. The energy required to stretch carbon-carbon bonds has the order C-C > C=C > C-C. The spectral chart in Figure 8.74 shows the IR spectral positions of these peaks and their relative energy values as well as those for several other types of chemical bonds.

Figure 8.74

The relative energies for stretching apart two bonded atoms depends not only on whether they are bonded by a single, double, or triple bond, but also on the specific atoms bonded together. The energy required to stretch a single bond between a heavy and a light atom such as in a C-H, N-H, or O-H bond is actually greater than the stretching energies of triple bonds (Figure 8.74).

There are relatively few other IR absorptions in either the C=C or C C stretching regions, so IR peaks in these regions are very diagnostic for double or triple bonds in the molecule being analyzed. IR peaks in these regions can also be due to C=O, C=N, or C N bonds. We discuss the relative positions of the IR signals for different types of double and triple bonds later in the text after we introduce compounds containing C=O, C=N, and C N bonds.

### ***UV-Vis Spectrometry*** (8.3D)

C=C and C C bonds give absorption signals in *UV-Vis* spectra only if the compound contains several of these bonds in an arrangement where they alternate with single bonds (are "conjugated"). For this reason we include our discussion of the *UV-Vis* characteristics of multiple bonds in Chapter 10 where we describe such "conjugated" polyenes and polyynes.

***UV-Vis Spectrometry.*** Individual C=C and C C bonds do not give *UV-Vis* spectra (Chapter 5). C=C and C C bonds give absorption signals in *UV-Vis* spectra only if the compound contains several of these bonds in an arrangement where they alternate with single bonds (are "conjugated").

Figure 8.60a Some Conjugated Polyenes and Polyynes that Absorb UV Radiation

$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	$\lambda_{\text{max}} = 217 \text{ nm}$ ( $\epsilon = 21,000$ )
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	$\lambda_{\text{max}} = 253 \text{ nm}$ ( $\epsilon = 50,000$ )
$\text{CH}_3-\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}-\text{CH}_3$	$\lambda_{\text{max}} = 207 \text{ nm}$ ( $\epsilon = 135,000$ )

For this reason we include our discussion of the *UV-Vis* characteristics of multiple bonds in Chapter 10 where we describe such "conjugated" polyenes and polyynes. These "conjugated" *polyenes* (or *polyynes*) also have special chemical and physical properties that set them apart from alkenes (or polyenes) and alkynes (or polyynes) with isolated (non-conjugated) multiple bonds.

## Chapter Review

### Alkenes

(1) Alkenes are hydrocarbons with a C=C bond ( $R_2C=CR_2$ ). (2) The C's in the C=C bond are  $sp^2$  hybridized and the R groups in  $R_2C=CR_2$  lie in a plane with R-C=C bond angles of approximately  $120^\circ$ . (3) A high rotational barrier (about 270 kJ/mol) restricts rotation about C=C ( $2p-2p$ ) bonds. (4) Alkene systematic names use the prefixes *eth-*, *prop-*, *but-*, *etc.* to indicate the length of the longest carbon chain containing the C=C and the C=C position is assigned the lowest possible carbon number. (5) Alkenes with the general structure  $R_aR_bC=CR_xR_y$  have two stereoisomers labeled *E* or *Z* if  $R_a \neq R_b$ , and  $R_x \neq R_y$ . (6) We assign *E* and *Z* using *R* and *S* priority rules for the  $R_a/R_b$  pair and the  $R_x/R_y$  pair. (7) In  $R_aR_bC=CR_xR_y$ ,  $R_a$  and  $R_x$  are *cis* to each other if they are on the same side of the C=C, and *trans* to each other if they are on opposite sides of the C=C. (8) Polyenes are alkenes with two or more C=C bonds separated by at least one C-C bond. (9) Branched alkenes are named as "alkylalkenes", alkenes with halogen atoms (X) are named as "*haloalkenes*", while those with OH or NH<sub>2</sub> groups are named as *alkenols* or *alkenamines* analogously to *alkanols* and *alkanamines*. (10) *cis*-alkenes with the general structure RCH=CHR' are generally more thermodynamically stable than their *trans* isomers. (11) Alkene stability increases with increasing alkyl substitution on the C=C. (12) Cyclopropene and cyclobutene are very strained due to distortion of the normal R-C=C-R bond angles, while cyclopentene is only slightly strained and cyclohexene is relatively strain free.

### Alkynes

(1) Alkynes are hydrocarbons with a C-C bond (RC-CR). (2) The C's in the C-C bond are  $sp$  hybridized and the R groups in RC-CR lie along a straight line with R-C-C bond angles of  $180^\circ$ . (3) Systematic names of unbranched *alkynes* (RC-CR') are analogous to those of unbranched *alkenes* and use the same prefixes *eth-*, *prop-*, *but-*, *pent-*, followed by the ending *-yne*. (4) Numbers (eg. *1-butyne* or *2-butyne*) show the position of the C-C in the unbranched C chain. (5) *Alkynes* do not have *E/Z* (or *cis/trans*) stereoisomers. (6) Branched alkynes are named as "alkylalkynes", and halogen substituted alkynes are named as "haloalkynes". (7) Alkyne stability increases with increasing alkyl substitution on the C-C. (8) Cycloalkynes smaller than C<sub>9</sub> are highly strained compounds due to distortion of the normal  $180^\circ$  R-C-C-R bond angles. (9) Bond lengths between two C's depend on the hybridization of the C leading to a bond length order of C-C > C=C > C-C. (10) C-H bond lengths similarly have the order  $C(sp^3)-H > C(sp^2)-H > C(sp)-H$ . (11) C-C-H protons are much more acidic than other C-H protons. due to the relatively large amount of s character in C-H bonds to  $sp$  hybridized C. (12) Allenes are 1,2-dienes ( $R_2C=C=CR_2$ ) whose central C of C=C=C is  $sp$  hybridized. (13) Allenes readily isomerize to alkynes.

***Spectrometric Features of C=C and C≡C Bonds***

(1) C=C atoms have  $^{13}\text{C}$  chemical shift values from 110 to 150 that are affected by attached substituents, but a C=C bond does not significantly affect the  $^{13}\text{C}$  chemical shift of attached C atoms. (2) C C atoms have  $^{13}\text{C}$  chemical shifts from 65 to 90, and in contrast with alkenes they cause the  $^{13}\text{C}$  value of an attached C to shift to smaller values. (3)  $^1\text{H}$  values for H-C=C are very large ( 5 and 6.5) and C=C bonds also increase chemical shifts for adjacent C-H atoms. (4) The magnitudes of spin-spin splitting between H's attached to a double bond, and to groups directly attached to the double bond, aid in structure identification. (5)  $^1\text{H}$  chemical shift values of approximately 2 for H-C C are much smaller than those of alkenes. (6) IR stretching frequencies of 1640 to 1670  $\text{cm}^{-1}$  for C=C and 2100 to 2260  $\text{cm}^{-1}$  for C C fall in relatively unique regions of an IR spectrum. (7) Individual C=C or C C bonds do not give signals in normal UV-Vis spectra.