Chapter 9
Alkynes
9.1 Sources of Alkynes
Industrial preparation of acetylene is by dehydrogenation of ethylene.

\[
\text{CH}_3\text{CH}_3 \xrightarrow{800^\circ C} \text{H}_2\text{C}≡\text{CH}_2 + \text{H}_2
\]

\[
\text{H}_2\text{C}≡\text{CH}_2 \xrightarrow{1150^\circ C} \text{HC}≡\text{CH} + \text{H}_2
\]

cost of energy makes acetylene a more expensive industrial chemical than ethylene.
9.2
Nomenclature
Acetylene and ethyne are both acceptable IUPAC names for HC≡CH

Higher alkynes are named in much the same way as alkenes except using an -yne suffix instead of -ene.

- \( \text{HC≡CCH}_3 \) Propyne
- \( \text{HC≡CCH}_2\text{CH}_3 \) 1-Butyne
- \( (\text{CH}_3)_3\text{CC≡CCH}_3 \) 4,4-Dimethyl-2-pentyne
9.3 Physical Properties of Alkynes

The physical properties of alkynes are similar to those of alkanes and alkenes.
9.4 Structure and Bonding in Alkynes: 
$sp$ Hybridization
Structure

linear geometry for acetylene

120 pm

H –––– C≡C –––– H

106 pm  106 pm

121 pm

CH₃ –––– C≡C –––– H

146 pm  106 pm
Cyclononyne is the smallest cycloalkyne stable enough to be stored at room temperature for a reasonable length of time.

Cyclooctyne polymerizes on standing.
Mix together (hybridize) the 2s orbital and one of the three 2p orbitals.
Mix together (hybridize) the 2s orbital and one of the three 2p orbitals

Each carbon has two half-filled \( sp \) orbitals available to form \( \sigma \) bonds.
Each carbon is connected to a hydrogen by a $\sigma$ bond. The two carbons are connected to each other by a $\sigma$ bond and two $\pi$ bonds.

**Figure 9.2 (a)**
One of the two $\pi$ bonds in acetylene is shown here. The second $\pi$ bond is at right angles to the first.

Figure 9.2 (b)
This is the second of the two \( \pi \) bonds in acetylene.

\[ \pi \text{ Bonds in Acetylene} \]
The region of highest negative charge lies above and below the molecular plane in ethylene.

The region of highest negative charge encircles the molecule around its center in acetylene.
Table 9.1
Comparison of Ethane, Ethylene, and Acetylene

<table>
<thead>
<tr>
<th></th>
<th>Ethane</th>
<th>Ethylene</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C distance</td>
<td>153 pm</td>
<td>134 pm</td>
<td>120 pm</td>
</tr>
<tr>
<td>C—H distance</td>
<td>111 pm</td>
<td>110 pm</td>
<td>106 pm</td>
</tr>
<tr>
<td>H—C—C angles</td>
<td>111.0°</td>
<td>121.4°</td>
<td>180°</td>
</tr>
<tr>
<td>C—C BDE</td>
<td>368 kJ/mol</td>
<td>611 kJ/mol</td>
<td>820 kJ/mol</td>
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<tr>
<td>C—H BDE</td>
<td>410 kJ/mol</td>
<td>452 kJ/mol</td>
<td>536 kJ/mol</td>
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<tr>
<td>hybridization of C</td>
<td>sp&lt;sup&gt;3&lt;/sup&gt;</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;</td>
<td>sp</td>
</tr>
<tr>
<td>% s character</td>
<td>25%</td>
<td>33%</td>
<td>50%</td>
</tr>
<tr>
<td>pK&lt;sub&gt;a&lt;/sub&gt;</td>
<td>62</td>
<td>45</td>
<td>26</td>
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