SOLUTIONS MANUAL FOR
PERSPECTIVES ON
STRUCTURE AND MECHANISM
IN ORGANIC CHEMISTRY

Second Edition

Felix A. Carroll
Davidson College
SOLUTIONS MANUAL FOR
PERSPECTIVES ON
STRUCTURE AND MECHANISM
IN ORGANIC CHEMISTRY
SOLUTIONS MANUAL FOR
PERSPECTIVES ON
STRUCTURE AND MECHANISM
IN ORGANIC CHEMISTRY
Second Edition

Felix A. Carroll
Davidson College
# Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 1</td>
<td>Fundamental Concepts of Organic Chemistry</td>
<td>1</td>
</tr>
<tr>
<td>Chapter 2</td>
<td>Stereochemistry</td>
<td>11</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>Conformational Analysis and Molecular Mechanics</td>
<td>27</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Applications of Molecular Orbital Theory and Valence Bond Theory</td>
<td>35</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Reactive Intermediates</td>
<td>53</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>Methods of Studying Organic Reactions</td>
<td>63</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>Acid and Base Catalysis of Organic Reactions</td>
<td>69</td>
</tr>
<tr>
<td>Chapter 8</td>
<td>Substitution Reactions</td>
<td>79</td>
</tr>
<tr>
<td>Chapter 9</td>
<td>Addition Reactions</td>
<td>91</td>
</tr>
<tr>
<td>Chapter 10</td>
<td>Elimination Reactions</td>
<td>101</td>
</tr>
<tr>
<td>Chapter 11</td>
<td>Pericyclic Reactions</td>
<td>111</td>
</tr>
<tr>
<td>Chapter 12</td>
<td>Photochemistry</td>
<td>127</td>
</tr>
</tbody>
</table>
CHAPTER 1

Fundamental Concepts of Organic Chemistry

1.1. An answer to this question should be stated in terms of macroscopic phenomena, and a historical exposition provides a rationale for the basis of contemporary chemistry. Reference to any of several monographs on the history of chemistry can be used to summarize the ideas and observations that led to contemporary chemistry theory.\(^1\),\(^2\),\(^3\)

   a. In this example, atomic force microscopy was used.
   b. The eye sees a macroscopic image on a computer monitor or printed image. The human eye does not see atoms.

1.3. a. The alternative geometries and their elimination on the basis of number of isomers are as follows:
   i. square planar — There would be two isomers of CH\(_2\)Cl\(_2\), one “cis,” in which the Cl–C–Cl bond angle is 90°, and one “trans,” in which the Cl–C–Cl bond angle is 180°.
   ii. square pyramid — Similarly, there would be two isomers of CH\(_3\)Cl\(_2\).

---

\(^1\) Asimov, I. *A Short History of Chemistry*; Anchor Books: Garden City, NY, 1965.

Felix A. Carroll.
b. In all answers, a substituent is presumed to replace a hydrogen atom in the parent structure of the candidate structure.\(^4\)

i. If benzene had the structure we now call fulvene, there should be three different derivatives with the formula \(\text{C}_6\text{H}_5\text{Cl}\).

ii. If benzene had the structure we now call Dewar benzene, there would be two and only two isomers with the formula \(\text{C}_6\text{H}_5\text{Cl}\).

iii. If benzene had the structure we now call benzvalene, there would be three possible isomers with the formula \(\text{C}_6\text{H}_5\text{Cl}\).

iv. If benzene had the structure we now call prismane, there would be only one isomer with the formula \(\text{C}_6\text{H}_5\text{Cl}\), but there would be four isomers with the formula \(\text{C}_6\text{H}_4\text{Cl}_2\) (two of them existing as a pair of enantiomers).

v. If benzene had the structure we now call [3]radialene, there would be one and only one isomer with the formula \(\text{C}_6\text{H}_5\text{Cl}\), but there would be four possible isomers with the formula \(\text{C}_6\text{H}_4\text{Cl}_2\) (shown below).

\[
\begin{array}{ccc}
\text{Cl} & \text{Cl} & \text{Cl} \\
\text{H} & \text{Cl} & \text{H} \\
\text{H} & \text{Cl} & \text{H} \\
\text{H} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{H} \\
\end{array}
\quad
\begin{array}{ccc}
\text{H} & \text{Cl} & \text{Cl} \\
\text{H} & \text{Cl} & \text{Cl} \\
\text{H} & \text{Cl} & \text{Cl} \\
\text{H} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{H} \\
\end{array}
\quad
\begin{array}{ccc}
\text{Cl} & \text{Cl} & \text{Cl} \\
\text{H} & \text{Cl} & \text{H} \\
\text{H} & \text{Cl} & \text{H} \\
\text{H} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{H} \\
\end{array}
\]

vi. There are also acyclic structures with the formula \(\text{C}_6\text{H}_6\), such as 2,4-hexadiyne, and they may be analyzed similarly. For example, if benzene were 2,4-hexadiyne, then there would be one and only one \(\text{C}_6\text{H}_5\text{Cl}\), but there would be only two structures with the formula \(\text{C}_6\text{H}_4\text{Cl}_2\).

c. One can never know that something that has not been tested is like something else to which it seems similar. However, it seems unproductive to dwell on this possibility until there is an experimental result that could be rationalized on the basis of a structure for chloromethane that is different from the tetrahedral structure of methane. The spectroscopic results for chloromethane are consistent with a tetrahedral geometry.

1.4. The data and equations are given in Bondi, J. J. Phys. Chem. 1964, 68, 441. For \(n\)-pentane, the volume is given by

\[V_W = 2 \times 13.67 + 3 \times 10.23 = 58.03 \text{ cm}^3 \text{ mol}^{-1}\]

and the area is given by

\[A_W = 3 \times 1.35 + 2 \times 2.12 = 8.29 \times 10^9 \text{ cm}^2 / \text{mol}\]

These results agree with those given by the general formulas for \( n \)-alkanes:

\[
V_W = 6.88 + 10.23N_C = 6.88 + 10.23 \times 5 = 58.03 \text{ cm}^3 \text{ mol}^{-1}
\]

\[
A_W = 1.54 + 1.35N_C = 1.54 + 1.35 \times 5 = 8.29 \times 10^9 \text{ cm}^2 \text{ mol}^{-1}
\]

For isopentane,

\[
V_W = 3 \times 13.67 + 10.23 + 6.78 = 58.02 \text{ cm}^3 \text{ mol}^{-1}
\]

\[
A_W = 3 \times 2.12 + 1.35 + 0.57 = 8.28 \times 10^9 \text{ cm}^2 \text{ mol}^{-1}
\]

For neopentane,

\[
V_W = 4 \times 13.67 + 3.33 = 58.01 \text{ cm}^3 \text{ mol}^{-1}
\]

\[
A_W = 4 \times 2.12 + 0 = 8.48 \times 10^9 \text{ cm}^2 \text{ mol}^{-1}
\]

Note that these equations do not consider effects of crowding. A semi-empirical calculation suggests that molecular area decreases along the series \( n \)-pentane, isopentane, and neopentane.


\[
81.81 + 29.01 = 110.82 \text{ kcal/mol}
\]


The difference in heats of hydrogenation indicates that quadricyclane is less stable than norbornadiene by 24 kcal/mol, so this is the potential energy storage density for the photochemical reaction.


\[
\begin{align*}
\text{C}_8\text{H}_{12}\text{O}_2(s) &\rightarrow \text{C}_8\text{H}_{12}\text{O}_2(g) & \Delta H_f &= 23.71 \text{ kcal/mol} \\
8 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) &\rightarrow \text{C}_8\text{H}_{12}\text{O}_2(s) + 10 \text{O}_2(g) & -\Delta H_e &= 1042.90 \text{ kcal/mol} \\
8 \text{C(graphite)} + 8 \text{O}_2(g) &\rightarrow 8 \text{CO}_2(g) & \Delta H_f = 8(-94.05) &= -752.4 \text{ kcal/mol} \\
6 \text{H}_2(g) + 3 \text{O}_2(g) &\rightarrow 6 \text{H}_2\text{O}(l) & \Delta H_f = 6(-68.32) &= -409.92 \text{ kcal/mol} \\
8 \text{C(graphite)} + 6 \text{H}_2(g) + \text{O}_2(g) &\rightarrow \text{C}_8\text{H}_{12}\text{O}_2(g) & \Delta H_f &= -95.71 \text{ kcal/mol}
\end{align*}
\]


\[
\Delta H_f(\text{phenylethyne}) = \Delta H_f(\text{phenylethane}) - \Delta H_f(\text{phenylethyne}) \\
= 7.15 - (-66.12) = 73.27 \text{ kcal/mol}
\]


\[ \Delta H_f (\text{cis-3-methyl-2-pentene}) = \Delta H_f (2\text{-ethyl-1-butene}) - \Delta \Delta H_f \]
\[ = -10.66 - (-1.65) = -9.01 \text{ kcal/mol} \]


\[
\begin{align*}
\text{cis-1, 3, 5-hexadiene + 3 H}_2 & \rightarrow n\text{-hexane} & \Delta H = -81.0 \text{ kcal/mol} \\
n\text{-hexane} & \rightarrow 1, 5\text{-hexadiene + 2 H}_2 & \Delta H = +60.3 \text{ kcal/mol} \\
\text{cis-1, 3, 5-hexadiene + H}_2 & \rightarrow 1, 5\text{-hexadiene} & \Delta H_f = -20.7 \text{ kcal/mol} \\
\text{trans-1, 3, 5-hexadiene + 3 H}_2 & \rightarrow n\text{-hexane} & \Delta H = -80.0 \text{ kcal/mol} \\
n\text{-hexane} & \rightarrow 1, 5\text{-hexadiene + 2 H}_2 & \Delta H = +60.3 \text{ kcal/mol} \\
\text{trans-1, 3, 5-hexadiene + H}_2 & \rightarrow 1, 5\text{-hexadiene} & \Delta H_f = -19.7 \text{ kcal/mol}
\end{align*}
\]

1.12. a. Using equation 1.9:

\[ \Delta H_f = 6(-146) + 16(-124.2) + 11(6.64) + 26(9.29) \\
+ 5(10.2) + 7(231.3) + 16(52.1) \\
= -44.92 \text{ kcal/mol} \]

b. Using equation 1.12:

\[ \Delta H_f = -17.89 + 6(-2.15) + 5(-2.83) + 0(-7.74) \\
+ 0(-13.49) = -44.94 \text{ kcal/mol} \]


a. The gas phase dipole moments for CH$_3$–F, CH$_3$–Cl, CH$_3$–Br, and CH$_3$–I are 1.81, 1.87, 1.80 and 1.64 $\text{D}$, respectively. Using the bond length data in Table 1.1 and rewriting equation 1.18 leads to the following partial charges on F, Cl, Br, and I, respectively: $-0.27, -0.22, -0.19, -0.16$.

b. The dipole moments do not show a monotonic trend along the series because a dipole moment is a product of two terms. In series of methyl halides, one term (the partial charge) goes down and the other term (bond length) goes up. The product of these two terms is a maximum at the second member of the series.
Note that the assumption that only the carbon and halogen atoms are charged is an oversimplification. An Extended Hückel calculation indicates that the three methyl hydrogen atoms bear some charge also.

1.14. Because Pauling electronegativities are computed from the properties of atoms in molecules, they generally cannot be computed for the inert gases. However, krypton and xenon fluorides are known, and electronegativities of krypton and xenon have been reported by Meek, T. L., J. Chem. Educ. 1995, 72, 17.

1.15. Using equation 1.41,

\[ 1 + \lambda_c^2 \cos \theta_{CC} = 0 \]

leads to a value of 2.62 for \( \lambda_c^2 \). Therefore the hybridization of carbon orbitals used for carbon-carbon bonds is \( sp^{2.62} \). Now using the relation

\[ 2 \left[ \frac{1}{1 + 2.62} \right] + 2 \left[ \frac{1}{1 + \lambda_H^2} \right] = 1 \]

leads to a value of 3.47 for the carbon orbitals used for the carbon-hydrogen bonds.


a. As the bond angle increases, the C–C bond length decreases. Conversely, as the bond angle decreases, the C–C bond length increases.

b. The larger \( \alpha \), the greater the contribution of \( p \) character to the orbital of \( C_2 \) used for the \( C_2-C_3 \) bond. This means greater \( s \) character in the orbital of \( C_2 \) used for the \( C_1-C_2 \) bond, which results in a shorter \( C_1-C_2 \) bond. The same result can be rationalized using the VSEPR approach. As the angle \( \alpha \) increases, there is less repulsion in the electrons comprising the \( C_1-C_2 \) bond with the electrons in the \( C_2-C_3 \) bond. This allows the electrons in the \( C_1-C_2 \) bond to move closer to \( C_2 \), thus decreasing the bond length.


a. ethyne, ethene, cyclopropane, cyclobutane, ethane.

b. 1,3-butadiyne, 1-butene-3-yne, 1,3-butadiene, propene, 2-methylpropene, 2-methylpropane, ethane.

1.18. a. According to the bent bond formulation, the electrons in the bent bonds are pulled in toward the other olefinic carbon atom, so the electrons in these bonds repel the electrons in the carbon-hydrogen bonds less than they would in propane. Therefore the H–C–H bond angle opens to a larger value.
b. The electrons in formaldehyde should be pulled even more strongly away from the carbon atom than is the case in ethene. Therefore, the repulsion of electrons in either of these bonds with the electrons in either carbon-hydrogen bond is even less than that in ethene, so the H–C–H bond angle in formaldehyde should be even greater than that of ethene.

1.19. Based on an H–C–H angle of 116.2° for ethene, Robinson, E. A.; Gillespie, R. J. *J. Chem. Educ.* 1980, 57, 329 (appendix, p. 333) report \( sp^{2.26} \) or 30.6% \( s \) character for the carbon-hydrogen bond. Using 117° for the H–C–H angle\(^5\) leads to \( sp^{2.20} \), or 31.2% \( s \) character. For formaldehyde, using an H–C–H angle of 125.8°\(^6\) similarly leads to 36.9% \( s \) character for the carbon orbital used for carbon-hydrogen bonding.

1.20. a. The formula is given by Newton, M. D.; Schulman, J. M.; Manus, M. M. *J. Am. Chem. Soc.* 1974, 96, 17. Set equation 1.46: \( J = 5.7 \times (\% s) - 18 \) Hz. Then \( 500/(1 + \lambda^2) = 5.7 \times (\% s) - 18 \). Then let \( \% s = 100/(1 + \lambda^2) \) and solve for \( \lambda^2 \). It turns out to be just under 3. Thus the equation is approximately correct for orbitals that are roughly \( sp^{3} \)-hybridized, but it is not exact for other orbitals.

b. The equation is

\[
r_{C-H} = 1.1597 - (4.17 \times 10^{-4})(500)/(1 + \lambda^2)
\]

so

\[
r_{C-H} = 1.1597 - 0.209/(1 + \lambda^2)
\]

This equation is equivalent to

\[
r_{C-H} = 1.1597 - 2.09 \times 10^{-3}(\rho_{C-H})
\]

where \( \rho_{C-H} \) is percent \( s \) character, which is defined as \( 100/(1 + \lambda^2) \). This is the form of the equation given by Muller, N.; Pritchard, D. E. *J. Chem. Phys.* 1959, 31, 1471.

1.21. a. Here are calculations based on literature values for H–C–H bond angles and assuming that all molecules have planar carbon skeletons. (That is necessarily true only for cyclopropane.) Note that the values calculated depend on the choice of literature values for the bond angles.


Each carbon has 2 C–H bonds and 2 C–C bonds. Therefore for a C–C bond of cyclopropane, the fractional s character is \(0.5 \times (1 - 2 \times (0.319)) = 0.181\). Similarly,

<table>
<thead>
<tr>
<th></th>
<th>cyclopropane (^7)</th>
<th>cyclobutane (^8)</th>
<th>cyclopentane (^9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–C–H</td>
<td>118°</td>
<td>114°</td>
<td>109.5°</td>
</tr>
</tbody>
</table>
| Using the formula \(1 + \lambda_i^2 \cos \theta = 0\),
| \(\lambda_i^2\)   | 2.13                 | 2.459            | 2.996             |
| Fraction s in C–H| 0.319                | 0.289            | 0.25              |
| Fraction p in C–H| 0.681                | 0.711            | 0.75              |

\(\lambda_i^2\) values for cyclobutane and cyclopentane are different from those of cyclopropane, indicating different bond angles.

If the molecules are planar, then cyclopropane has \((102.77 - 60) / 2 = 21.4°\) of angle strain at each carbon. Similarly, cyclobutane has 7.75° of strain, and cyclopentane has no strain.\(^{10}\) As will be discussed in Chapter 3, cyclobutane and cyclopentane are not flat. The large fraction of p character in the cyclopropane carbon–carbon sigma bonds suggests that they might react (at least to some extent) like \(\pi\) bonds, which is partially true. Note that the interorbital bond angle of cyclopropane is 102.77°, whereas the internuclear bond angle is required to be 60°. Thus the cyclopropane bonds are bent or banana bonds.\(^{11}\)

b. The acidity values can be correlated with s character by combining equations 1.46 and 1.48 to show a relationship between kinetic acidity and s character, and the results shown in Table 1.14 are consistent with such a relationship. By using the VSEPR concept, the very bent carbon–carbon bonds of cyclopropane (and to a lesser extent, cyclobutane) allow the electrons in the carbon-hydrogen bonds to be pulled closer to the carbon nucleus. That not only increases the H–C–H bond angle, but it also stabilizes a carbanion resulting from proton removal, so the acidity of a compound with more bent bonds is greater than that of a compound with less bent bonds.

1.22. a. The predicted value, 110°, is very close to the value of 109.9° in Table 1.1.

b. As shown in the plot below, the error is indeed smallest for H–C–X bond angles near 109.5° and becomes appreciable for bond angles 5° or 10° different from the normal tetrahedral value.

---

\(^{7}\) Reference 5 (b), p. M98s.


\(^{9}\) Reference 5 (a), p. M 185.

\(^{10}\) This result for cyclopentane is based on the H–C–H bond angle reported in the literature. If the five carbon atoms of cyclopentane form a perfect pentagon, then the C–C–C bond angles are all 108°, so there is a slight amount of angle strain.

\(^{11}\) Note also that cyclopropane has been described in terms of Walsh orbitals, which are based on \(p\) orbitals.