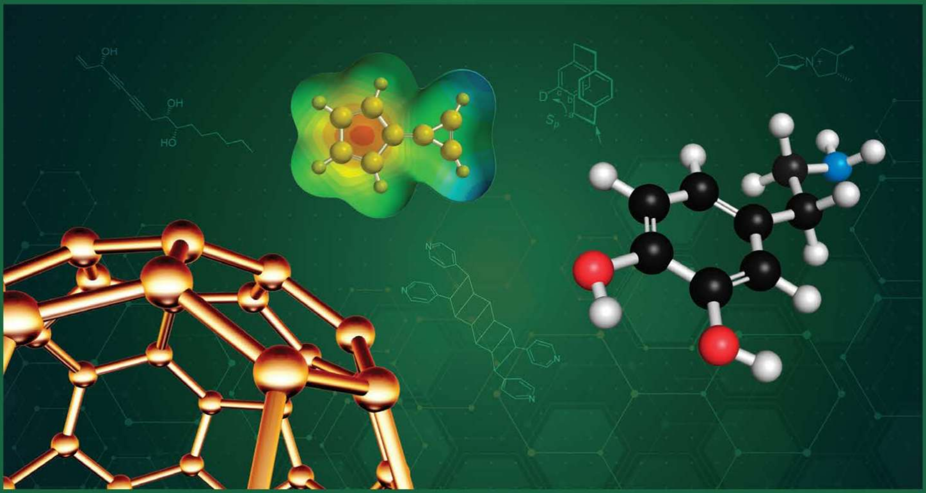
THIRD EDITION

SOLUTIONS MANUAL FOR PERSPECTIVES ON STRUCTURE AND MECHANISM IN ORGANIC CHEMISTRY

FELIX A. CARROLL



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Third Edition

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CHAPTER 1

Fundamental Models of Organic Chemistry

1.1. An answer to this question should be stated in terms of macroscopic phenomena. A historical exposition provides a rationale for the basis of contemporary chemistry, and 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]

1.2. See, for example, figure 2D in Tieu, P.; Yan, X.; Xu, M.; et al. *Small* **2021**, *17*, 2006482.

a. Transmission electron microscopy was used in this study.
b. The eye sees a macroscopic image on a computer screen or on a printed page.

For another example, see the image of kekulene reported by Pozo, I.; Majzik, Z.; Pavliček, N.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 15488.

1.3. **a.** Two alternative geometries and their elimination on the basis of number of isomers are:
- **i.** Square planar. There would be two isomers of CH_2Cl_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_2Cl_2 with the chlorines in the square base plus another isomer with one chlorine at the apex of the pyramid.

---

[1] Asimov, I. *A Short History of Chemistry*; Anchor Books: Garden City, NY, 1965.

[2] Ihde, A. J. *The Development of Modern Chemistry*; Harper & Row: New York, 1964.

[3] See, for example, Butterfield, H. *The Origins of Modern Science*, 1300-1800, Revised Edition; The Free Press: New York, 1965.

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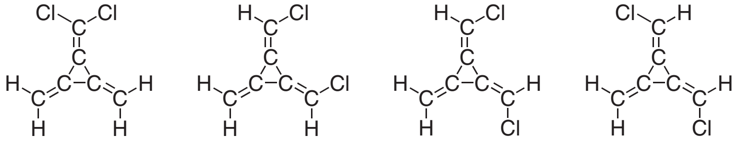
b. In all answers, a substituent is presumed to occupy a position previously occupied by a hydrogen atom in the parent structure.[4]

- **i.** If benzene had the structure we now call fulvene, there should be three different derivatives with the formula C_6H_5Cl.
- **ii.** If benzene had the structure we now call Dewar benzene, there would be two and only two isomers with the formula C_6H_5Cl.
- **iii.** If benzene had the structure we now call benzvalene, there would be three possible isomers with the formula C_6H_5Cl.
- **iv.** If benzene had the structure we now call prismane, there would be only one isomer with the formula C_6H_5Cl, but there would be four isomers (including a pair of enantiomers) with the formula $C_6H_4Cl_2$.
- **v.** If benzene had the structure we now call [3]radialene, there would be one and only one isomer with the formula C_6H_5Cl, but there would be four possible isomers (shown below) with the formula $C_6H_4Cl_2$.



- **vi.** There are also acyclic structures with the formula C_6H_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 C_6H_5Cl, but there could be only two structures with the formula $C_6H_4Cl_2$.

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 with 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,

$$V_W = 2 \times 13.67 + 3 \times 10.23 = 58.03\ \text{cm}^3/\text{mol}$$

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

These results agree with those given by the general formulas for *n*-alkanes:

$$V_W = 6.88 + 10.23\text{N}_C = 6.88 + 10.23 \times 5 = 58.03\ \text{cm}^3/\text{mol}$$

$$A_W = 1.54 + 1.35\text{N}_C = 1.54 + 1.35 \times 5 = 8.29 \times 10^9\ \text{cm}^2/\text{mol}$$

---

[4] For a discussion of the number of isomers of benzene, see Reinecke, M. G. *J. Chem. Educ.* **1992**, 69, 859 and references therein.

For isopentane,

$$V_W = 3\times 13.67 + 10.23 + 6.78 = 58.02\ \text{cm}^3/\text{mol}$$

$$A_W = 3\times 2.12 + 1.35 + 0.57 = 8.28\times 10^9\ \text{cm}^2/\text{mol}$$

For neopentane,

$$V_W = 4\times 13.67 + 3.33 = 58.01\ \text{cm}^3/\text{mol}$$

$$A_W = 4\times 2.12 + 0 = 8.48\times 10^9\ \text{cm}^2/\text{mol}$$

1.5. Kiyobayashi, T.; Nagano, Y.; Sakiyama, M.; et al. *J. Am. Chem. Soc.* **1995**, *117*, 3270.

$$81.81 + 29.01 = 110.82\ \text{kcal/mol.}$$

1.6. Turner, R. B.; Goebel, P.; Mallon, B. J.; et al. *J. Am. Chem. Soc.* **1968**, *90*, 4315. Also see Hautala, R. R.; King, R. B.; Kutal, C. in Hautala, R. R.; King, R. B.; Kutal, C., Eds. *Solar Energy: Chemical Conversion and Storage*; Humana Press: Clifton, NJ, 1979; p. 333. 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.

1.7. Pilcher, G.; Parchment, O. G.; Hillier, I. H.; et al. *J. Phys. Chem.* **1993**, *97*, 243.

$$\begin{array}{ll}
C_8H_{12}O_{2\,(s)} \rightarrow C_8H_{12}O_{2\,(g)} & \Delta H_s = \quad 23.71\,\text{kcal/mol} \\
8CO_{2\,(g)} + 6H_2O_{\,(l)} \rightarrow C_8H_{12}O_{2\,(s)} + 10O_{2(g)} & -\Delta H_c = 1042.90\,\text{kcal/mol} \\
8C_{(\text{graphite})} + 8O_{2\,(g)} \rightarrow 8CO_{2\,(g)} & \Delta H_f = 8(-94.05) = -752.4\ \text{kcal/mol} \\
\underline{6H_{2\,(g)} + 3O_{2\,(g)} \rightarrow 6H_2O_{\,(l)}} & \underline{\Delta H_f = 6(-68.32) = -409.92\,\text{kcal/mol}} \\
8C_{(\text{graphite})} + 6H_{2(g)} + O_{2\,(g)} \rightarrow C_8H_{12}O_{2\,(g)} & \Delta H_f = -95.71\,\text{kcal/mol}
\end{array}$$

1.8. See Davis, H. E.; Allinger, N. L.; Rogers, D. W. *J. Org. Chem.* **1985**, *50*, 3601.

$$\begin{aligned}\Delta H_f(\text{phenylethyne}) &= \Delta H_f(\text{phenylethane}) - \Delta H_r(\text{phenylethyne}) \\ &= 7.15 - (-66.12) = 73.27\ \text{kcal/mol}\end{aligned}$$

1.9. **a.** −632.6 ± 2.2 kJ/mol. Roux, M. V.; Temprado, M.; Jiménez, P.; et al. *J. Phys. Chem. A* **2006**, *110*, 12477.

b. 2-acetylthiophene is 4.7 kJ/mol more stable than 3-acetylthiophene in the gas phase. Roux, M. V.; Temprado, M.; Jiménez, P.; et al. *J. Phys. Chem. A* **2007**, *111*, 11084.

1.10. Wiberg, K. B.; Hao, S. *J. Org. Chem.* **1991**, *56*, 5108.

$$\begin{aligned}\Delta H_r(\textit{cis}\text{-3-methyl-2-pentene}) &= \Delta H_r(\text{2-ethyl-1-butene}) - \Delta\Delta H_f \\ &= -10.66 - (-1.65) = -9.01\ \text{kcal/mol}\end{aligned}$$

1.11. Fang, W.; Rogers, D. W. *J. Org. Chem.* **1992**, *57*, 2294.

$$\begin{array}{ll}
cis\text{-1,3,5-hexatriene} + 3\mathrm{H_2} \rightarrow n\text{-hexane} & \Delta H = -81.0\,\mathrm{kcal/mol} \\
n\text{-hexane} \rightarrow \text{1,5-hexadiene} + 2\mathrm{H_2} & \Delta H = +60.3\,\mathrm{kcal/mol} \\
\hline
cis\text{-1,3,5-hexatriene} + \mathrm{H_2} \rightarrow \text{1,5-hexadiene} & \Delta H_\mathrm{r} = -20.7\,\mathrm{kcal/mol}
\end{array}$$

$$\begin{array}{ll}
trans\text{-1,3,5-hexatriene} + 3\mathrm{H_2} \rightarrow n\text{-hexane} & \Delta H = -80.0\,\mathrm{kcal/mol} \\
n\text{-hexane} \rightarrow \text{1,5-hexadiene} + 2\mathrm{H_2} & \Delta H = +60.3\,\mathrm{kcal/mol} \\
\hline
trans\text{-1,3,5-hexatriene} + \mathrm{H_2} \rightarrow \text{1,5-hexadiene} & \Delta H_\mathrm{r} = -19.7\,\mathrm{kcal/mol}
\end{array}$$

1.12. **a.** Using equation 1.9:

$$\begin{aligned}
\Delta H_\mathrm{f} &= 6(-146) + 16(-124.2) + 11(6.64) + 26(9.29) \\
&\quad +5(10.2) + 7(231.3) + 16(52.1) \\
&= -44.92\,\mathrm{kcal/mol}
\end{aligned}$$

b. Using equation 1.12:

$$\begin{aligned}
\Delta H_\mathrm{f} &= -17.89 + 6(-2.15) + 5(-2.83) + 0(-7.74) + 0(-13.49) \\
&= -44.94\,\mathrm{kcal/mol}
\end{aligned}$$

1.13. See Smyth, C. P. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. 1, Part 4; Wiley-Interscience: New York, 1972; pp. 397–429.

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 D, respectively. Using the bond length data in Table 1.1 and rewriting equation 1.23 lead 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 the 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 (X = Cl). Note that the assumption that only the carbon and halogen atoms are charged is an over-simplification. An Extended Hückel calculation indicates that the three methyl hydrogen atoms also bear some charge.

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 were reported by Meek, T. L. *J. Chem. Educ.* **1995**, *72*, 17.

1.15. Using equation 1.47 leads to a value of 2.62 for λ_C^2. Therefore, the hybridization of carbon orbitals used for carbon–carbon bonds is $sp^{2.62}$. The relationship

$$2\left[\frac{1}{1+2.62}\right] + 2\left[\frac{1}{1+\lambda_\mathrm{H}^2}\right] = 1$$

then gives a λ_C^2 value of 3.47 for the carbon orbitals used for the carbon–hydrogen bonds.

1.16. Mastryukov, V. S.; Schaefer, H. F., III.; Boggs, J. E. *Acc. Chem. Res.* **1994**, *27*, 242. Also see the discussion in Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.

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 the α, the greater the contribution of p character to the orbital of C2 used for the C2–C3 bond. This means greater s character in the orbital of C2 used for the C1–C2 bond, which results in a shorter C1–C2 bond. The same result can be rationalized using the VSEPR approach. As the angle α increases, there is less repulsion of the electrons comprising the C1–C2 bond with the electrons in the C2–C3 bond. This allows the electrons in the C1–C2 bond to move closer to C2, thus decreasing the bond length.

1.17. Maksić, Z. B.; Randić, M. *J. Am. Chem. Soc.* **1970**, *92*, 424. The bond lengths are a function of the hybridization of the carbon atoms.

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 C–C 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 C–O bond with electrons in a C–H bond is even less than the repulsion of electrons in the C–C bonds with electrons in a C–H bond in ethene. Therefore, the H–C–H bond angle in formaldehyde should be greater than that in 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) reported $sp^{2.26}$ or 30.6% s character for the C–H 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° similarly leads to 36.9% s character for the carbon orbital used for carbon–hydrogen bonding.[6]

1.20. a. The formula is given by Newton, M. D.; Schulman, J. M.; Manus, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 17. Rewrite equation 1.52 as $J = 5.7 \times (\%\, s) - 18.4\,\text{Hz}$. Then $500/(1+\lambda^2) = 5.7 \times (\%\, s) - 18.4$. Now let $\%\, s = 100/(1+\lambda^2)$ and solve for λ^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

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

---

[5] (a) Bowen, H. J. M.; Donohue, J.; Jenkin, D. G.; et al., comps. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 11; Chemical Society (London): Burlington House, W.1, London, 1958. (b) Supplement, 1965, p. M 78s.

[6] Reference 5(b), p. M 109.

so

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

This equation is equivalent to

$$r_{\mathrm{C-H}} = 1.1597 - 2.09\times10^{-3}(\rho_{\mathrm{C-H}})$$

where $\rho_{\mathrm{C-H}}$ 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 calculated values depend on the choice of literature values for the bond angles.

	Cyclopropane[a]	Cyclobutane[b]	Cyclopentane[c]
∠H–C–H	118°	114°	109.5°
Using the formula $1+\lambda_i^2\cos\theta=0$,			
λ_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

[a] Reference 5(b), p. M98s.
[b] Reference 5(a), p. M 168.
[c] Reference 5(a), p. M 185.

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 $0.5\times(1-2\times0.319)=0.181$.

Similarly,

	Cyclopropane	Cyclobutane	Cyclopentane
Fraction *s* in C–C:	0.181	0.211	0.25
Fraction *p* in C–C:	0.819	0.789	0.75
λ_j^2:	4.525	3.74	3.00
C–C–C interorbital angle:	102.77°	105.5°	109.47°

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 angle strain, and cyclopentane has no angle strain.[7] As will be discussed in Chapter 4, cyclobutane and cyclopentane are not flat. The large fraction of *p* character in the cyclopropane carbon–carbon sigma bonds suggests that they might react to some extent like π bonds, which is the case. Note that the interorbital bond angle of cyclopropane is 102.77°, whereas the inter*nuclear* bond angle is required to be 60°. Thus, the cyclopropane bonds can be considered bent bonds.[8]

---

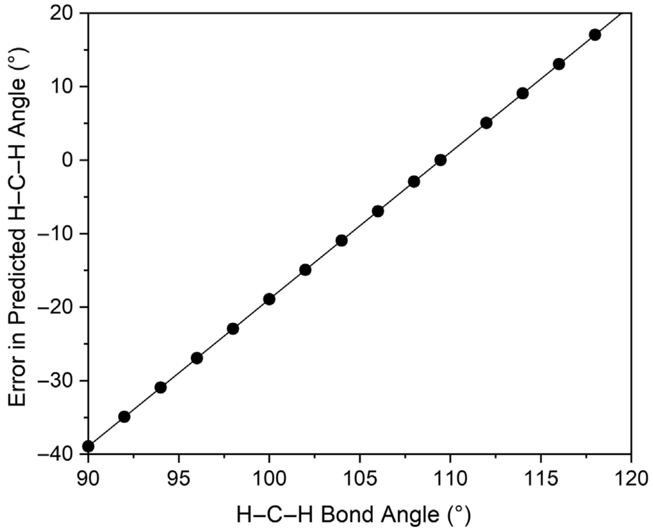
[7] This result for cyclopentane is based on the H–C–H bond angle reported in the literature. If the five carbon atoms of cyclopentane form a perfect pentagon, then the C–C–C bond angles are all 108°, so there is a slight amount of angle strain.

[8] Note also that cyclopropane has been described in terms of Walsh orbitals, which are based on *p* orbitals.

b. The acidity values can be correlated with *s* character by combining equations 1.52 and 1.53 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.

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 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.



1.23. Plotting the data for ethane, ethene, and ethyne gives a linear ($R^2 = 0.999$) correlation:

$$\Delta H^{\circ}_{\text{acid}}\left(\text{kcal} / \text{mol}\right) = 461.9 - 53.96\, J_{^{13}\text{C-H}}$$

The gas phase acidity thus calculated for cyclopropane, 407.9 kcal/mol, is close to the experimental value, 410.7 kcal/mol. See Bartmess, J. E. in Mallard, W. G.; Linstrom, P. J., Eds. *NIST Webbook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov). See also Fattahi, A.; McCarthy, R. E.; Ahmad, M. R.; et al. *J. Am. Chem. Soc.* **2003**, *125*, 11746.

1.24. Kass S. R.; Chou, P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899. $1 + \lambda^2 = 500/202$, so $\lambda^2 = 1.475$. Therefore, the percent *s* character is $100/2.475 = 40.4\%$. This is less than the 50% *s* character in acetylene C–H bonds, so acetylene should be more acidic.

1.25. If hybridization does not exist, then a quantification of hybridization is an artifice. Even though λ cannot be observed directly, however, it provides a more satisfying basis for correlating coupling constants, acidities, and bond angles with each other than would a purely empirical correlation of any two of these observables.