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]

1.2. See, for example, Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G. *Science* **2009**, *325*, 1110.

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_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.

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[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 replace a hydrogen atom in the parent structure of the candidate structure.[4]

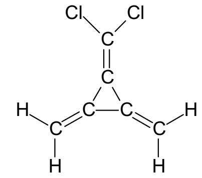
  i. If benzene had the structure we now call fulvene, there should be three different derivatives with the formula C_6H_5Cl.

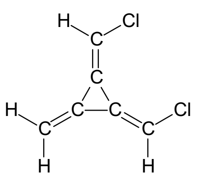
  ii. If benzene had the structure we now call Dewar benzene, there would be two and only two isomers with the formula C_6H_5Cl.

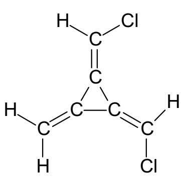
  iii. If benzene had the structure we now call benzvalene, there would be three possible isomers with the formula C_6H_5Cl.

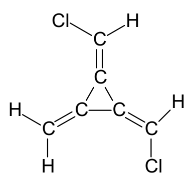
  iv. If benzene had the structure we now call prismane, there would be only one isomer with the formula C_6H_5Cl, but there would be four isomers with the formula $C_6H_4Cl_2$ (two of them existing as a pair of enantiomers).

  v. If benzene had the structure we now call [3]radialene, there would be one and only one isomer with the formula C_6H_5Cl, but there would be four possible isomers with the formula $C_6H_4Cl_2$ (shown below).









  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 would 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 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

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

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

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.

1.5. Kiyobayashi, T.; Nagano, Y.; Sakiyama, M.; Yamamoto, K.; Cheng, P.-C.; Scott, L. T. *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.; Doering, W. v. E.; Coburn, Jr., J. F.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315. Also see Hautala, R. R.; King, R. B.; Kutal, C. in *Solar Energy: Chemical Conversion and Storage*; Hautala, R. R.; King, R. B.; Kutal, C., eds.; 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.; Heatley, F.; Fletcher, D.; Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Monte M. J. S.; Fang, J. *J. Phys. Chem.* **1993**, *97*, 243.

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

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.; Foces-Foces, C.; Notario, R.; Verevkin, S. P.; Liebman, J. F. *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.; Notario, R.; Chickos, J. S.; Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2007**, *111*, 11084.

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

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

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

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

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

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

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

b. Using equation 1.12:

$$\begin{aligned}\Delta H_f &= -17.89 + 6(-2.15) + 5(-2.83) + 0(-7.74)\\ &\quad + 0(-13.49) = -44.94\ \text{kcal/mol}\end{aligned}$$

1.13. See Smyth, C. P. in *Physical Methods of Chemistry*, Vol. 1, Part 4; Weissberger, A.; Rossiter, B. W., eds.; 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 1.18 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 λ_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.

1.16. Mastryukov, V. S.; Schaefer III, H. F.; 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 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 in 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 bonds are a function of the hybridization of carbon.

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 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

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

so

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

This equation is equivalent to

$$r_{\mathrm{C-H}} = 1.1597 - 2.09 \times 10^{-3}\,(\rho_{\mathrm{C-H}})$$

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 values calculated depend on the choice of literature values for the bond angles.

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[5] (a) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Bowen, H. J. M.; Donohue, J.; Jenkin, D. G.; Kennard, O.; Wheatley, P. J.; Whiffen, D. H., comps.; 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.

	cyclopropane[7]	cyclobutane[8]	cyclopentane[9]
<H–C–H	118°	114°	109.5°
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

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,

Fraction *s* in C–C	0.181	0.211	0.25
Fraction *p* in C–C	0.819	0.789	0.75
$\lambda_j^2 =$	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 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 π bonds, which is partially true. Note that the inter*orbital* bond angle of cyclopropane is 102.77°, whereas the inter*nuclear* 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.

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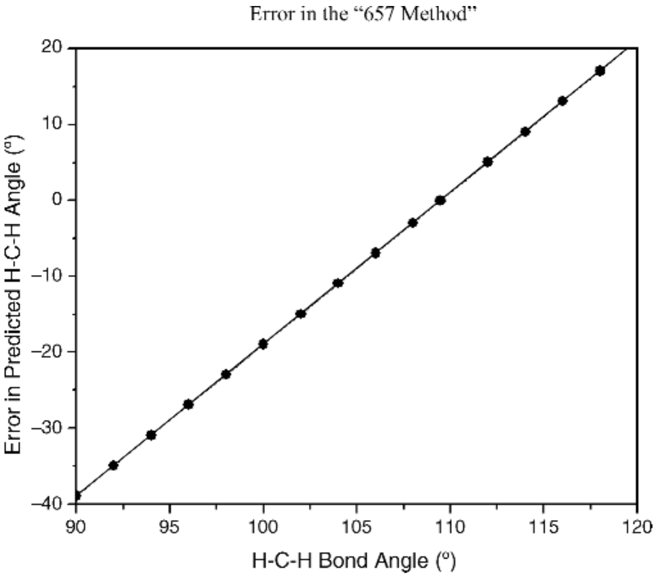
[7] Reference 5 (b), p. M98s.

[8] Reference 5 (a), p. M 168.

[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.



1.23. An excellent correlation is obtained for ethane, ethene, and ethyne. The gas phase acidity estimated for cyclopropane, 408.3 kcal/mol, is close to the experimental value, 410.7 kcal/mol. See Bartmess, J. E. *NIST Webbook, NIST Standard Reference Database Number 69*, Mallard, W. G.; Linstrom, P. J., eds., National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov). See also Fattahi, A.; McCarthy, R. E.; Ahmad, M. R.; Kass, S. R. *J. Am. Chem. Soc.* **2003**, *125*, 11746.

1.24. See 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. There is no literature reference for this problem. If hybridization does not exist, then a quantification of hybridization is only a convenient artifice. Even though λ cannot be observed directly, it is a useful concept because it provides a more satisfying conceptual basis for correlating coupling constants, acidities and bond angles with each other than would a purely empirical correlation of any two of these observables.

1.26. There is no literature reference for this problem, nor is there a single right answer. One response is that the concept of hybridization provides a useful conceptual model for understanding the bonding of carbon compounds without the need for carrying out molecular orbital calculations in which hybridized orbitals are not assumed. Therefore hybridized orbitals are useful, but only if it is remembered that they are only a mental convenience and not a physical attribute of atoms.

1.27. The answer to this question depends on the orientation of the answerer. Organic chemists use pictorial representations because they work with structures that are often larger and more complex than those that can be described in purely mathematical terms—at least those mathematical expressions that are immediately meaningful to organic chemist. Although organic chemistry may become more mathematical as the role of computation becomes ever more important, it is likely that the results of a mathematical analysis will continue to be presented in a largely pictorial form for the organic chemist.

1.28. Coulson has stated the basic paradox of chemistry. We live in a "macroscopic" world, but we explain that world in terms of unseen particles and unseen forces. To the chemist, atoms, bonds, and molecules are real and can be demonstrated. However, Coulson's reminder that these concepts are intangible reinforces the view that chemistry is based on models that are subject to revision if better models become available.

1.29. Hoffmann is entirely correct in saying that psychology plays an important role in the acceptance of theories. However, scientists who truly understand the limits of human knowledge may be less tempted to make decisions on the basis of a strong conviction of causality than are nonscientists.

1.30. Weisberg's comments are consistent with the primary argument of Chapter 1 only if there are multiple, complementary models for the question at hand. If there is only one model for a particular situation, then the relationship between precision and generality is less certain.