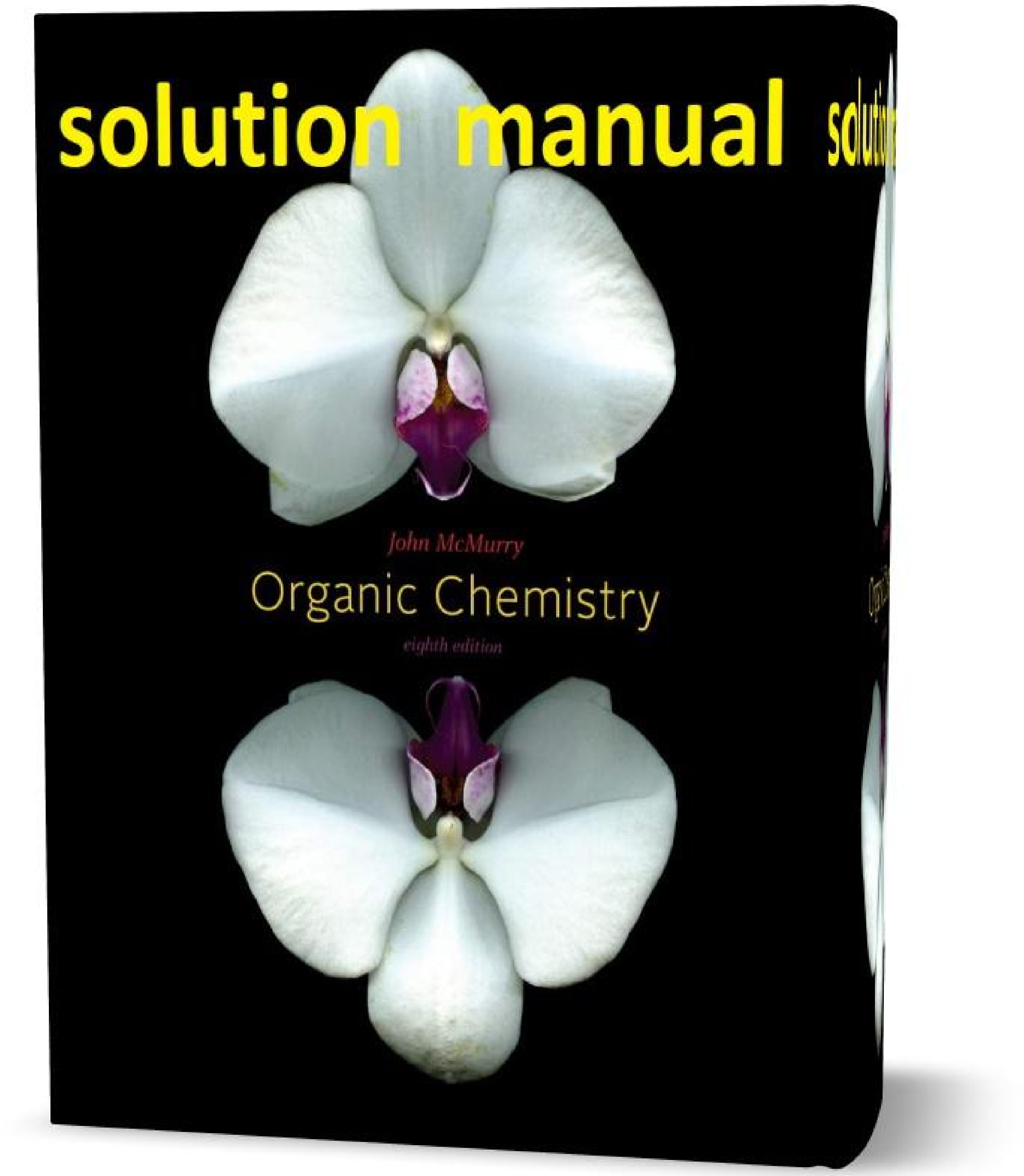
solution manual
John McMurry
Organic Chemistry
eighth edition

Study Guide and Student Solutions Manual

Organic Chemistry

EIGHTH EDITION

John McMurry

Prepared by

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Preface

What enters your mind when you hear the words "organic chemistry?" Some of you may think, "the chemistry of life," or "the chemistry of carbon." Other responses might include "pre-med, "pressure," "difficult," or "memorization." Although formally the study of the compounds of carbon, the discipline of organic chemistry encompasses many skills that are common to other areas of study. Organic chemistry is as much a liberal art as a science, and mastery of the concepts and techniques of organic chemistry can lead to improved competence in other fields.

As you work on the problems that accompany the text, you will bring to the task many problem-solving techniques. For example, planning an organic synthesis requires the skills of a chess player; you must plan your moves while looking several steps ahead, and you must keep your plan flexible. Structure-determination problems are like detective problems, in which many clues must be assembled to yield the most likely solution. Naming organic compounds is similar to the systematic naming of biological specimens; in both cases, a set of rules must be learned and then applied to the specimen or compound under study.

The problems in the text fall into two categories: drill and complex. Drill problems, which appear throughout the text and at the end of each chapter, test your knowledge of one fact or technique at a time. You may need to rely on memorization to solve these problems, which you should work on first. More complicated problems require you to recall facts from several parts of the text and then use one or more of the problem-solving techniques mentioned above. As each major type of problem—synthesis, nomenclature, or structure determination—is introduced in the text, a solution is extensively worked out in this *Solutions Manual*.

Here are several suggestions that may help you with problem solving:

1. The text is organized into chapters that describe individual functional groups. As you study each functional group, *make sure that you understand the structure and reactivity of that group*. In case your memory of a specific reaction fails you, you can rely on your general knowledge of functional groups for help.

2. *Use molecular models*. It is difficult to visualize the three-dimensional structure of an organic molecule when looking at a two-dimensional drawing. Models will help you to appreciate the structural aspects of organic chemistry and are indispensable tools for understanding stereochemistry.

3. Every effort has been made to make this *Solutions Manual* as clear, attractive, and error-free as possible. Nevertheless, you should *use the Solutions Manual in moderation*. The principal use of this book should be to check answers to problems you have already worked out. The *Solutions Manual* should not be used as a substitute for effort; at times, struggling with a problem is the only way to teach yourself.

4. *Look through the appendices at the end of the Solutions Manual*. Some of these appendices contain tables that may help you in working problems; others present information related to the history of organic chemistry.

Although the *Solutions Manual* is written to accompany *Organic Chemistry,* it contains several unique features. Each chapter of the *Solutions Manual* begins with an outline of the text that can be used for a concise review of the text material and can also serve as a reference. After every few chapters a Review Unit has been inserted. In most cases, the chapters covered in the Review Units are related to each other, and the units are planned to appear at approximately the place in the textbook where a test might be given. Each unit lists the vocabulary for the chapters covered, the skills needed to solve problems, and several important points that might need reinforcing or that restate material in the text from a slightly different point of view. Finally, the small self-test that has been included allows you to test yourself on the material from more than one chapter.

I have tried to include many types of study aids in this *Solutions Manual*. Nevertheless, this book can only serve as an adjunct to the larger and more complete textbook. If *Organic Chemistry* is the guidebook to your study of organic chemistry, then the *Solutions Manual* is the roadmap that shows you how to find what you need.

Acknowledgments I would like to thank my husband, John McMurry, for offering me the opportunity to write this book many years ago and for supporting my efforts while this edition was being prepared. Although many people at Brooks/Cole Publishing company have given me encouragement during this project, special thanks are due to Elizabeth Woods. I also would like to acknowledge the contribution of Bette Kreuz, whose comments, suggestions and incredibly thorough accuracy checks was indispensable.

Chapter 1 – Structure and Bonding

Chapter Outline

I. Atomic Structure (Sections 1.1–1.3).
  A. Introduction to atomic structure (Section 1.1).
    1. An atom consists of a dense, positively charged nucleus surrounded by negatively charged electrons.
      a. The nucleus is made up of positively charged protons and uncharged neutrons.
      b. The nucleus contains most of the mass of the atom.
      c. Electrons move about the nucleus at a distance of about 2×10^{-10} m (200 pm).
    2. The atomic number (*Z*) gives the number of protons in the nucleus.
    3. The mass number (*A*) gives the total number of protons and neutrons.
    4. All atoms of a given element have the same value of *Z*.
      a. Atoms of a given element can have different values of *A*.
      b. Atoms of the same element with different values of *A* are called isotopes.
  B. Orbitals (Section 1.2).
    1. The distribution of electrons in an atom can be described by a wave equation.
      a. The solution to a wave equation is an orbital, represented by Ψ.
      b. Ψ^2 predicts the volume of space in which an electron is likely to be found.
    2. There are four different kinds of orbitals (*s*, *p*, *d*, *f*).
      a. The *s* orbitals are spherical.
      b. The *p* orbitals are dumbbell-shaped.
      c. Four of the five *d* orbitals are cloverleaf-shaped.
    3. An atom's electrons are organized into electron shells.
      a. The shells differ in the numbers and kinds of orbitals they contain.
      b. Electrons in different orbitals have different energies.
      c. Each orbital can hold up to a maximum of two electrons.
    4. The two lowest-energy electrons are in the 1*s* orbital.
      a. The 2*s* orbital is the next higher in energy.
      b. The next three orbitals are $2p_x$, $2p_y$ and $2p_z$, which have the same energy.
        i. Each *p* orbital has a region of zero density, called a node.
      c. The lobes of a *p* orbital have opposite algebraic signs.
  C. Electron Configuration (Section 1.3).
    1. The ground-state electron configuration of an atom is a listing of the orbitals occupied by the electrons of the atom in the lowest energy configuration.
    2. Rules for predicting the ground-state electron configuration of an atom:
      a. Orbitals with the lowest energy levels are filled first.
        i. The order of filling is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*.
      b. Only two electrons can occupy each orbital, and they must be of opposite spin.
      c. If two or more orbitals have the same energy, one electron occupies each until all are half-full (Hund's rule). Only then does a second electron occupy one of the orbitals.
        i. All of the electrons in half-filled shells have the same spin.
II. Chemical Bonding Theory (Sections 1.4–1.5).
  A. Development of chemical bonding theory (Section 1.4).
    1. Kekulé and Couper proposed that carbon has four "affinity units"; carbon is tetravalent.
    2. Kekulé suggested that carbon can form rings and chains.

3. Van't Hoff and Le Bel proposed that the 4 atoms to which carbon forms bonds sit at the corners of a regular tetrahedron.
4. In a drawing of a tetrahedral carbon, a wedged line represents a bond pointing toward the viewer, a dashed line points behind the plane of the page, and a solid line lies in the plane of the page..

B. Covalent bonds.
1. Atoms bond together because the resulting compound is more stable than the individual atoms.
   a. Atoms tend to achieve the electron configuration of the nearest noble gas.
   b. Atoms in groups 1A, 2A and 7A either lose electrons or gain electrons to form ionic compounds.
   c. Atoms in the middle of the periodic table share electrons by forming covalent bonds.
   d. The neutral collection of atoms held together by covalent bonds is a molecule.
2. Covalent bonds can be represented two ways.
   a. In electron-dot structures, bonds are represented as pairs of dots.
   b. In line-bond structures, bonds are represented as lines drawn between two bonded atoms.
3. The number of covalent bonds formed by an atom depends on the number of electrons it has and on the number it needs to achieve an octet.
4. Valence electrons not used for bonding are called lone-pair (nonbonding) electrons.
   a. Lone-pair electrons are often represented as dots.

C. Valence bond theory (Section 1.5).
1. Covalent bonds are formed by the overlap of two atomic orbitals, each of which contains one electron. The two electrons have opposite spins.
2. Bonds formed by the head-on overlap of two atomic orbitals are cylindrically symmetrical and are called σ bonds.
3. Bond strength is the measure of the amount of energy needed to break a bond.
4. Bond length is the optimum distance between nuclei.
5. Every bond has a characteristic bond length and bond strength.

III. Hybridization (Sections 1.6–1.10).

A. sp^3 Orbitals (Sections 1.6, 1.7).
1. Structure of methane (Section 1.6).
   a. When carbon forms 4 bonds with hydrogen, one 2*s* orbital and three 2*p* orbitals combine to form four equivalent atomic orbitals (sp^3 hybrid orbitals).
   b. These orbitals are tetrahedrally oriented.
   c. Because these orbitals are unsymmetrical, they can form stronger bonds than unhybridized orbitals can.
   d. These bonds have a specific geometry and a bond angle of 109.5°.
2. Structure of ethane (Section 1.7).
   a. Ethane has the same type of hybridization as occurs in methane.
   b. The C–C bond is formed by overlap of two sp^3 orbitals.
   c. Bond lengths, strengths and angles are very close to those of methane.

B. sp^2 Orbitals (Section 1.8).
1. If one carbon 2*s* orbital combines with two carbon 2*p* orbitals, three hybrid sp^2 orbitals are formed, and one *p* orbital remains unchanged.
2. The three sp^2 orbitals lie in a plane at angles of 120°, and the unhybridized *p* orbital is perpendicular to them.
3. Two different types of bonds form between two carbons.
   a. A σ bond forms from the overlap of two sp^2 orbitals.
   b. A π bond forms by sideways overlap of two *p* orbitals.
   c. This combination is known as a carbon–carbon double bond.

4. Ethylene is composed of a carbon–carbon double bond and four σ bonds formed between the remaining four sp^2 orbitals of carbon and the 1*s* orbitals of hydrogen.
    a. The double bond of ethylene is both shorter and stronger than the C–C bond of ethane.

C. *sp* Orbitals (Section 1.10).
1. If one carbon 2*s* orbital combines with one carbon 2*p* orbital, two hybrid *sp* orbitals are formed, and two *p* orbitals are unchanged.
2. The two *sp* orbitals are 180° apart, and the two *p* orbitals are perpendicular to them and to each other.
3. Two different types of bonds form.
    a. A σ bond forms from the overlap of two *sp* orbitals.
    b. Two π bonds form by sideways overlap of four unhybridized *p* orbitals.
    c. This combination is known as a carbon–carbon triple bond.
4. Acetylene is composed of a carbon–carbon triple bond and two σ bonds formed between the remaining two *sp* orbitals of carbon and the 1*s* orbitals of hydrogen.
    a. The triple bond of acetylene is the strongest carbon–carbon bond.

D. Hybridization of nitrogen and oxygen (Section 1.10).
1. Covalent bonds between other elements can be described by using hybrid orbitals.
2. Both the nitrogen atom in ammonia and the oxygen atom in water form sp^3 hybrid orbitals.
    a. The lone-pair electrons in these compounds occupy sp^3 orbitals.
3. The bond angles between hydrogen and the central atom is often less than 109° because the lone-pair electrons take up more room than the σ bond.
4. Because of their positions in the third row, phosphorus and sulfur can form more than the typical number of covalent bonds.

IV. Molecular orbital theory (Section 1.11).

A. Molecular orbitals arise from a mathematical combination of atomic orbitals and belong to the entire molecule.
1. Two 1*s* orbitals can combine in two different ways.
    a. The additive combination is a bonding MO and is lower in energy than the two hydrogen 1*s* atomic orbitals.
    b. The subtractive combination is an antibonding MO and is higher in energy than the two hydrogen 1*s* atomic orbitals.
2. Two *p* orbitals in ethylene can combine to form two π MOs.
    a. The bonding MO has no node; the antibonding MO has one node.
3. A node is a region between nuclei where electrons aren't found.
    a. If a node occurs between two nuclei, the nuclei repel each other.

V. Chemical structures (Section 1.12).

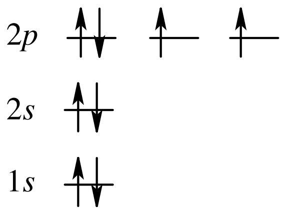
A. Drawing chemical structures.
1. Condensed structures don't show C–H bonds and don't show the bonds between CH_3, CH_2 and CH units.
2. Skeletal structures are simpler still.
    a. Carbon atoms aren't usually shown.
    b. Hydrogen atoms bonded to carbon aren't usually shown.
    c. Other atoms (O, N, Cl, etc.) are shown.

Solutions to Problems

1.1 (a) To find the ground-state electron configuration of an element, first locate its atomic number. For oxygen, the atomic number is 8; oxygen thus has 8 protons and 8 electrons. Next, assign the electrons to the proper energy levels, starting with the lowest level. Fill each level *completely* before assigning electrons to a higher energy level.

Notice that the 2*p* electrons are in different orbitals. According to *Hund's rule*, we must place one electron into each orbital of the same energy level until all orbitals are half-filled.

Oxygen

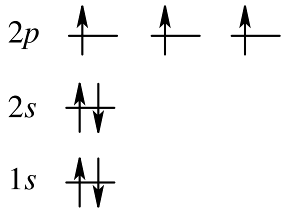


Remember that only two electrons can occupy the same orbital, and that they must be of opposite spin.

A different way to represent the ground-state electron configuration is to simply write down the occupied orbitals and to indicate the number of electrons in each orbital. For example, the electron configuration for oxygen is $1s^2\ 2s^2\ 2p^4$.

(b) Nitrogen, with an atomic number of 7, has 7 electrons. Assigning these to energy levels:

Nitrogen



The more concise way to represent ground-state electron configuration for nitrogen: $1s^2\ 2s^2\ 2p^3$

(c) Sulfur has 16 electrons.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Sulfur