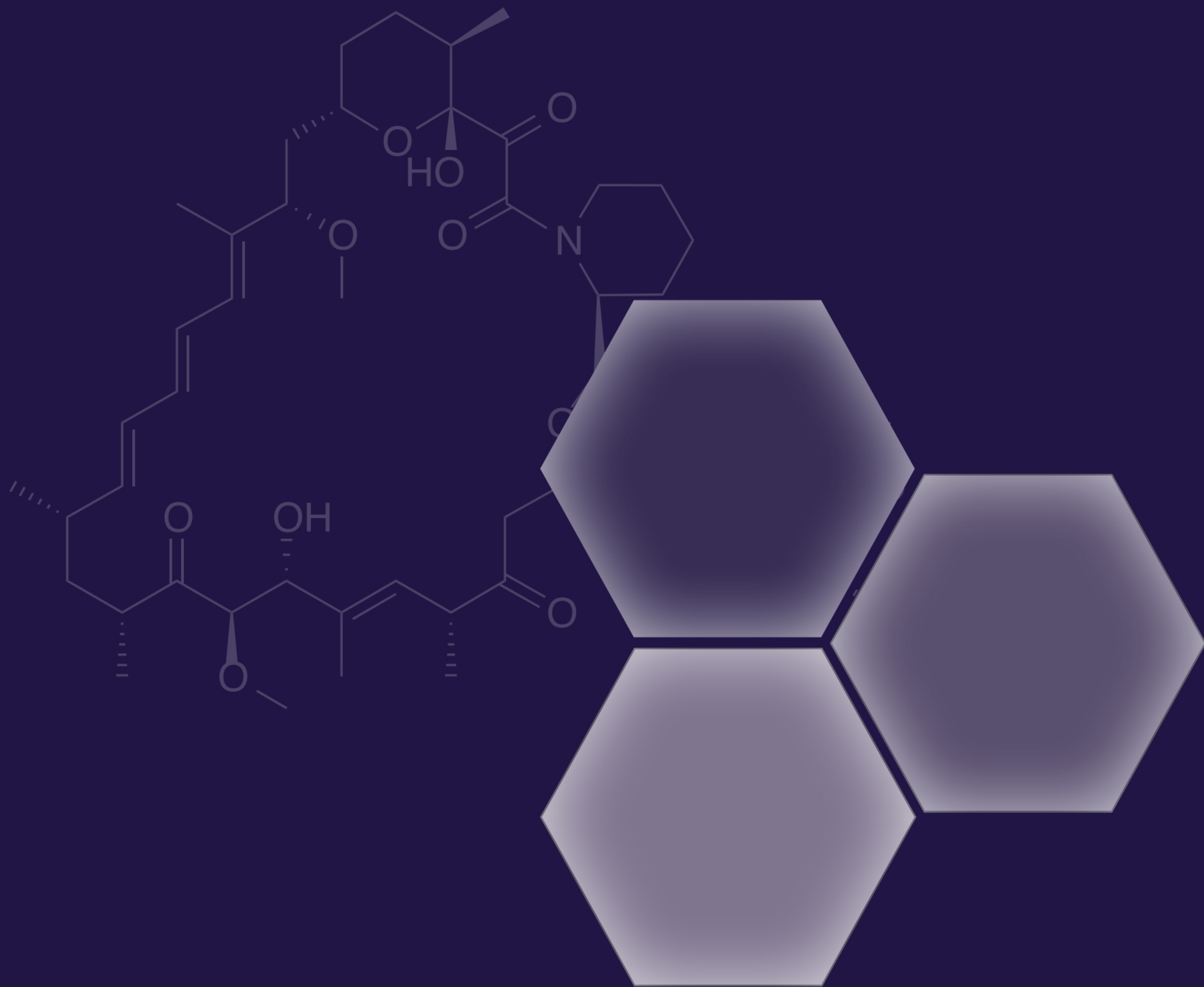


Study Guide and Solutions Manual to Accompany

T.W. Graham Solomons • Craig B. Fryhle • Scott A. Snyder



ORGANIC CHEMISTRY

TWELFTH EDITION

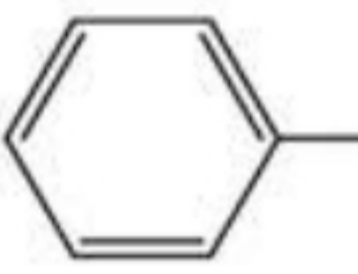
WILEY

Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT (δ , ppm)
1° Alkyl, RCH ₃	0.8–1.2
2° Alkyl, RCH ₂ R	1.2–1.5
3° Alkyl, R ₃ CH	1.4–1.8
Allylic, R ₂ C=C(CH ₃)R	1.6–1.9
Ketone, RC(=O)CH ₃	2.1–2.6
Benzylic, ArCH ₂	2.2–2.6
Acetylenic, RC≡CH	2.5–3.1
Ether, ROCH ₂ R	3.3–3.9
Alcohol, HOCH ₂ R	3.3–4.0
Alkyl iodide, RCH ₂ I	3.1–3.3
Alkyl bromide, RCH ₂ Br	3.4–3.6
Alkyl chloride, RCH ₂ Cl	3.6–3.8
Vinyl, R ₂ C=CH ₂	4.6–5.0
Vinyl, R ₂ C=CHR	5.2–5.7
Aromatic, ArH	6.0–8.5
Aldehyde, RCHO	9.5–10.5
Alcohol hydroxyl, ROH	0.5–6.0 ^a
Amino, RNH ₂	1.0–5.0 ^a
Phenolic, ArOH	4.5–7.7 ^a
Carboxylic, RCOOH	10–13 ^a

^aThe chemical shifts of these exchangeable protons vary in different solvents and with temperature and concentration.

Approximate carbon-13 chemical shifts

TYPE OF CARBON ATOM	CHEMICAL SHIFT (δ , ppm)
1° Alkyl, RCH ₃	0–40
2° Alkyl, RCH ₂ R	10–50
3° Alkyl, RCHR ₂	15–50
Alkyl halide or amine, —C—X (X = Cl, Br, or N—)	10–65
Alcohol or ether, —C—O	50–90
Alkyne, —C≡	60–90
Alkene, C=C	100–170
Aryl, 	100–170
Nitriles, —C≡N	120–130
Amides, —C(=O)—N—	150–180
Carboxylic acids, esters, —C(=O)—O	160–185
Aldehydes, ketones, —C(=O)—	182–215

STUDY GUIDE
AND
SOLUTIONS MANUAL
TO ACCOMPANY
**ORGANIC
CHEMISTRY**
TWELFTH EDITION

T. W. GRAHAM SOLOMONS

University of South Florida

CRAIG B. FRYHLE

Pacific Lutheran University

SCOTT A. SNYDER

University of Chicago

ROBERT G. JOHNSON

Xavier University

JON ANTILLA

University of South Florida

WILEY

ACKNOWLEDGMENTS

We are grateful to those people who have made many helpful suggestions for various editions of this study guide. These individuals include: George R. Jurch, George R. Wenzinger, and J. E. Fernandez at the University of South Florida; Darell Berlin, Oklahoma State University; John Mangravite, West Chester State College; J. G. Traynham, Louisiana State University; Desmond M. S. Wheeler, University of Nebraska; Chris Callam, The Ohio State University; Sean Hickey, University of New Orleans; and Neal Tonks, College of Charleston.

We are especially grateful to R.G. (Bob) Johnson (Xavier University) for his dedication and many contributions to this Study Guide over the years.

T. W. Graham Solomons; Craig B. Fryhle; Scott A. Snyder; Jon Antilla

Cover Image Structure image from the RCSB PDB (www.rcsb.org) of 1FKB (Van Duyne, G. D., Standaert, R. F., Schreiber, S. L., Clardy, J. C. (1992) Atomic Structure of the Ramapmycin Human Immunophilin Fkbp-12 Complex, *J. Amer. Chem. Soc.* 1991, **113**, 7433.) created with JSMol.

This book was set in 10/12 Times Roman by Aptara Noida, UP.

Copyright © 2016, 2014, 2011, 2008 John Wiley & Sons, Inc. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, website at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030-5774, (201) 748-6011, fax (201) 748-6008, website <http://www.wiley.com/go/permissions>.

Evaluation copies are provided to qualified academics and professionals for review purposes only, for use in their courses during the next academic year. These copies are licensed and may not be sold or transferred to a third party. Upon completion of the review period, please return the evaluation copy to Wiley. Return instructions and a free of charge return shipping label are available at www.wiley.com/go/returnlabel. Outside of the United States, please contact your local representative.

ISBN 978-1-119-07732-9

Binder-Ready version ISBN 978-1-119-07733-6

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

CONTENTS

To the Student vi

INTRODUCTION

“Solving the Puzzle” or “Structure Is Everything (Almost)” vii

CHAPTER 1

THE BASICS: BONDING AND MOLECULAR STRUCTURE 1

Solutions to Problems 1

Quiz 15

CHAPTER 2

FAMILIES OF CARBON COMPOUNDS: FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY 18

Solutions to Problems 18

Quiz 31

CHAPTER 3

ACIDS AND BASES: AN INTRODUCTION TO ORGANIC REACTIONS AND THEIR MECHANISMS 34

Solutions to Problems 34

Quiz 46

CHAPTER 4

NOMENCLATURE AND CONFORMATIONS OF ALKANES AND CYCLOALKANES 48

Solutions to Problems 48

Quiz 64

CHAPTER 5

STEREOCHEMISTRY: CHIRAL MOLECULES 67

Solutions to Problems 67

Quiz 84

CHAPTER 6

NUCLEOPHILIC REACTIONS: PROPERTIES AND SUBSTITUTION REACTIONS OF ALKYL HALIDES 87

Solutions to Problems 87

Quiz 102

CHAPTER 7

ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS. ELIMINATION REACTIONS OF ALKYL HALIDES 104

Solutions to Problems 104

Quiz 131

CHAPTER 8

ALKENES AND ALKYNES II: ADDITION REACTIONS 134

Solutions to Problems 134

Quiz 158

CHAPTER 9

NUCLEAR MAGNETIC RESONANCE AND MASS SPECTROMETRY: TOOLS FOR STRUCTURE DETERMINATION 161

Solutions to Problems 161

Quiz 182

CHAPTER 10

RADICAL REACTIONS 184

Solutions to Problems 184

Quiz 204

CHAPTER 11

ALCOHOLS AND ETHERS: SYNTHESIS AND REACTIONS 207

Solutions to Problems 207

Quiz 233

CHAPTER 12

ALCOHOLS FROM CARBONYL COMPOUNDS: OXIDATION-REDUCTION AND ORGANOMETALLIC COMPOUNDS 235

Solutions to Problems 235

Quiz 262

ANSWERS TO FIRST REVIEW PROBLEM SET 268

(First Review Problem Set is available only in *WileyPlus*, www.wileyplus.com)

CHAPTER 13

CONJUGATED UNSATURATED SYSTEMS 289

Solutions to Problems 289

Quiz 311

SUMMARY OF REACTIONS BY TYPE, CHAPTERS 1–13 313

METHODS FOR FUNCTIONAL GROUP PREPARATION, CHAPTERS 1–13 317

CHAPTER 14

AROMATIC COMPOUNDS 320

Solutions to Problems 320

Quiz 334

CHAPTER 15

REACTIONS OF AROMATIC COMPOUNDS 336

Solutions to Problems 336

Quiz 372

CHAPTER 16

ALDEHYDES AND KETONES. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP 374

Solutions to Problems 374

Quiz 406

CHAPTER 17

CARBOXYLIC ACIDS AND THEIR DERIVATIVES: NUCLEOPHILIC ADDITION-ELIMINATION AT THE ACYL CARBON 409

Solutions to Problems 409

Quiz 441

CHAPTER 18

REACTIONS AT THE α CARBON OF CARBONYL COMPOUNDS: ENOLS AND ENOLATES 445

Solutions to Problems 445

Quiz 473

CHAPTER 19

CONDENSATION AND CONJUGATE ADDITION REACTIONS OF CARBONYL COMPOUNDS: MORE CHEMISTRY OF ENOLATES 476

Solutions to Problems 476

Quiz 516

**CHAPTER 20
AMINES 521**

Solutions to Problems 524

Quiz 560

**CHAPTER 21
TRANSITION METAL COMPLEXES:
PROMOTERS OF KEY BOND-FORMING
REACTIONS 563**

Solutions to Problems 563

Quiz 573

**ANSWERS TO SECOND REVIEW PROBLEM
SET 575**(Second Review Problem Set is available only
in *WileyPlus*, www.wileyplus.com)**CHAPTER 22
CARBOHYDRATES 594**

Solutions to Problems 595

Quiz 620

**CHAPTER 23
LIPIDS 624**

Solutions to Problems 624

Quiz 636

**CHAPTER 24
AMINO ACIDS AND PROTEINS 639**

Solutions to Problems 639

Quiz 654

**CHAPTER 25
NUCLEIC ACIDS AND PROTEIN
SYNTHESIS 655**

Solutions to Problems 655

Special Topics are available only in *WileyPlus*,
www.wileyplus.com. Solutions to problems in
the Special Topics are found on the following
pages:**Special Topic A
¹³C NMR Spectroscopy 663****Special Topic B
NMR Theory and Instrumentation 664****Special Topic C
Chain-Growth Polymers 665****Special Topic D
Electrocyclic and Cycloaddition
Reactions 666****Special Topic E
Step-Growth Polymers 671****Special Topic F
Thiols, Sulfur Ylides, and Disulfides 677****Special Topic G
Thiol Esters and Lipid Biosynthesis 679****Special Topic H
Alkaloids 680****APPENDIX A
EMPIRICAL AND MOLECULAR
FORMULAS 685**

Problems 687

Additional Problems 688

Solutions to Problems of Appendix A 689

**APPENDIX B
ANSWERS TO QUIZZES 693****APPENDIX C
MOLECULAR MODEL SET EXERCISES 707**

To the Student

Contrary to what you may have heard, organic chemistry does not have to be a difficult course. It will be a rigorous course, and it will offer a challenge. But you will learn more in it than in almost any course you will take—and what you learn will have a special relevance to life and the world around you. However, because organic chemistry can be approached in a logical and systematic way, you will find that with the right study habits, mastering organic chemistry can be a deeply satisfying experience. Here, then, are some suggestions about how to study:

- 1. Keep up with your work from day to day—never let yourself get behind.** Organic chemistry is a course in which one idea almost always builds on another that has gone before. It is essential, therefore, that you keep up with, or better yet, be a little ahead of your instructor. Ideally, you should try to stay one day ahead of your instructor's lectures in your own class preparations. The lecture, then, will be much more helpful because you will already have some understanding of the assigned material. Your time in class will clarify and expand ideas that are already familiar ones.
- 2. Study material in small units, and be sure that you understand each new section before you go on to the next.** Again, because of the cumulative nature of organic chemistry, your studying will be much more effective if you take each new idea as it comes and try to understand it completely before you move on to the next concept.
- 3. Work all of the in-chapter and assigned problems.** One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained. You should also carefully study the Solved Problems. If you understand a Solved Problem and can work the related in-chapter problem, then you should go on; if you cannot, then you should go back and study the preceding material again. Work all of the problems assigned by your instructor from the end of the chapter, as well. Do all of your problems in a notebook and bring this book with you when you go to see your instructor for extra help.
- 4. Write when you study.** Write the reactions, mechanisms, structures, and so on, over and over again. Organic chemistry is best assimilated through the fingertips by writing, and not through the eyes by simply looking, or by highlighting material in the text, or by referring to flash cards. There is a good reason for this. Organic structures, mechanisms, and reactions are complex. If you simply examine them, you may think you understand them thoroughly, but that will be a misperception. The reaction mechanism may make sense to you in a certain way, but you need a deeper understanding than this. You need to know the material so thoroughly that you can explain it to someone else. This level of understanding comes to most of us (those of us without photographic memories) through writing. Only by writing the reaction mechanisms do we pay sufficient attention to their details, such as which atoms are connected to which atoms, which bonds break in a reaction and which bonds form, and the three-dimensional aspects of the structures. When we write reactions and mechanisms, connections are made in our brains that provide the long-term memory needed for success in organic chemistry. We virtually guarantee that your grade in the course will be directly proportional to the number of pages of paper that you fill with your own writing in studying during the term.
- 5. Learn by teaching and explaining.** Study with your student peers and practice explaining concepts and mechanisms to each other. Use the *Learning Group Problems* and other exercises your instructor may assign as vehicles for teaching and learning interactively with your peers.
- 6. Use the answers to the problems in the *Study Guide* in the proper way.** Refer to the answers only in two circumstances: (1) When you have finished a problem, use the Study Guide to check your answer. (2) When, after making a real effort to solve the problem, you find that you are completely stuck, then look at the answer for a clue and go back to work out the problem on your own. The value of a problem is in solving it. If you simply read the problem and look up the answer, you will deprive yourself of an important way to learn.
- 7. Use molecular models when you study.** Because of the three-dimensional nature of most organic molecules, molecular models can be an invaluable aid to your understanding of them. When you need to see the three-dimensional aspect of a particular topic, use the Molecular Visions™ model set that may have been packaged with your textbook, or buy a set of models separately. An appendix to the *Study Guide* that accompanies this text provides a set of highly useful molecular model exercises.
- 8. Make use of the rich online teaching resources in *WileyPLUS*** including ORION's adaptive learning system.

INTRODUCTION

“Solving the Puzzle” or “Structure Is Everything (Almost)”

As you begin your study of organic chemistry it may seem like a puzzling subject. In fact, in many ways organic chemistry is like a puzzle—a jigsaw puzzle. But it is a jigsaw puzzle with useful pieces, and a puzzle with fewer pieces than perhaps you first thought. In order to put a jigsaw puzzle together you must consider the shape of the pieces and how one piece fits together with another. In other words, solving a jigsaw puzzle is about **structure**. In organic chemistry, molecules are the pieces of the puzzle. Much of organic chemistry, indeed life itself, depends upon the fit of one molecular puzzle piece with another. For example, when an antibody of our immune system acts upon a foreign substance, it is the puzzle-piece-like fit of the antibody with the invading molecule that allows “capture” of the foreign substance. When we smell the sweet scent of a rose, some of the neural impulses are initiated by the fit of a molecule called geraniol in an olfactory receptor site in our nose. When an adhesive binds two surfaces together, it does so by billions of interactions between the molecules of the two materials. Chemistry is truly a captivating subject.

As you make the transition from your study of general to organic chemistry, it is important that you solidify those concepts that will help you understand the structure of organic molecules. A number of concepts are discussed below using several examples. We also suggest that you consider the examples and the explanations given, and refer to information from your general chemistry studies when you need more elaborate information. There are also occasional references below to sections in your text, Solomons, Fryhle, and Snyder *Organic Chemistry*, because some of what follows foreshadows what you will learn in the course.

SOME FUNDAMENTAL PRINCIPLES WE NEED TO CONSIDER

What do we need to know to understand the structure of organic molecules? First, we need to know where electrons are located around a given atom. To understand this we need to recall from general chemistry the ideas of **electron configuration** and **valence shell electron orbitals**, especially in the case of atoms such as carbon, hydrogen, oxygen, and nitrogen. We also need to use **Lewis valence shell electron structures**. These concepts are useful because the shape of a molecule is defined by its constituent atoms, and the placement of the atoms follows from the location of the electrons that bond the atoms. Once we have a Lewis structure for a molecule, we can consider **orbital hybridization** and **valence shell electron pair repulsion (VSEPR) theory** in order to generate a three-dimensional image of the molecule.

Secondly, in order to understand why specific organic molecular puzzle pieces fit together we need to consider the attractive and repulsive forces between them. To understand this we need to know how electronic charge is distributed in a molecule. We must use tools such as **formal charge** and **electronegativity**. That is, we need to know which parts of a molecule are relatively positive and which are relatively negative—in other words, their **polarity**. Associations between molecules strongly depend on both shape and the complementarity of their electrostatic charges (polarity).

When it comes to organic chemistry it will be much easier for you to understand why organic molecules have certain properties and react the way they do if you have an appreciation for the structure of the molecules involved. Structure is, in fact, almost everything, in that whenever we

want to know why or how something works we look ever more deeply into its structure. This is true whether we are considering a toaster, jet engine, or an organic reaction. If you can visualize the shape of the puzzle pieces in organic chemistry (molecules), you will see more easily how they fit together (react).

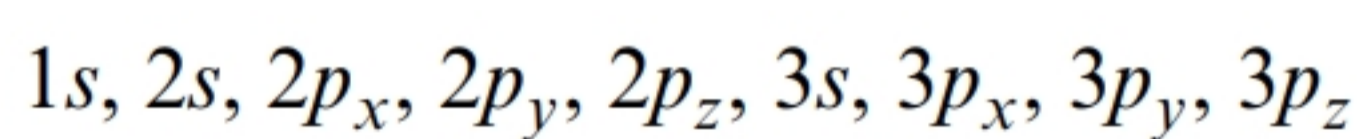
SOME EXAMPLES

In order to review some of the concepts that will help us understand the structure of organic molecules, let's consider three very important molecules—water, methane, and methanol (methyl alcohol). These three are small and relatively simple molecules that have certain similarities among them, yet distinct differences that can be understood on the basis of their structures. Water is a liquid with a moderately high boiling point that does not dissolve organic compounds well. Methanol is also a liquid, with a lower boiling point than water, but one that dissolves many organic compounds easily. Methane is a gas, having a boiling point well below room temperature. Water and methanol will dissolve in each other, that is, they are miscible. We shall study the structures of water, methanol, and methane because the principles we learn with these compounds can be extended to much larger molecules.

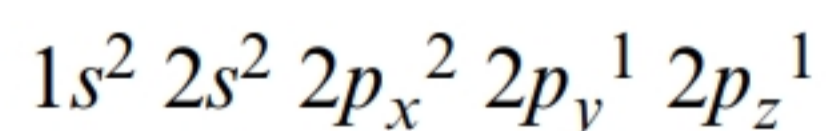
Water

HOH

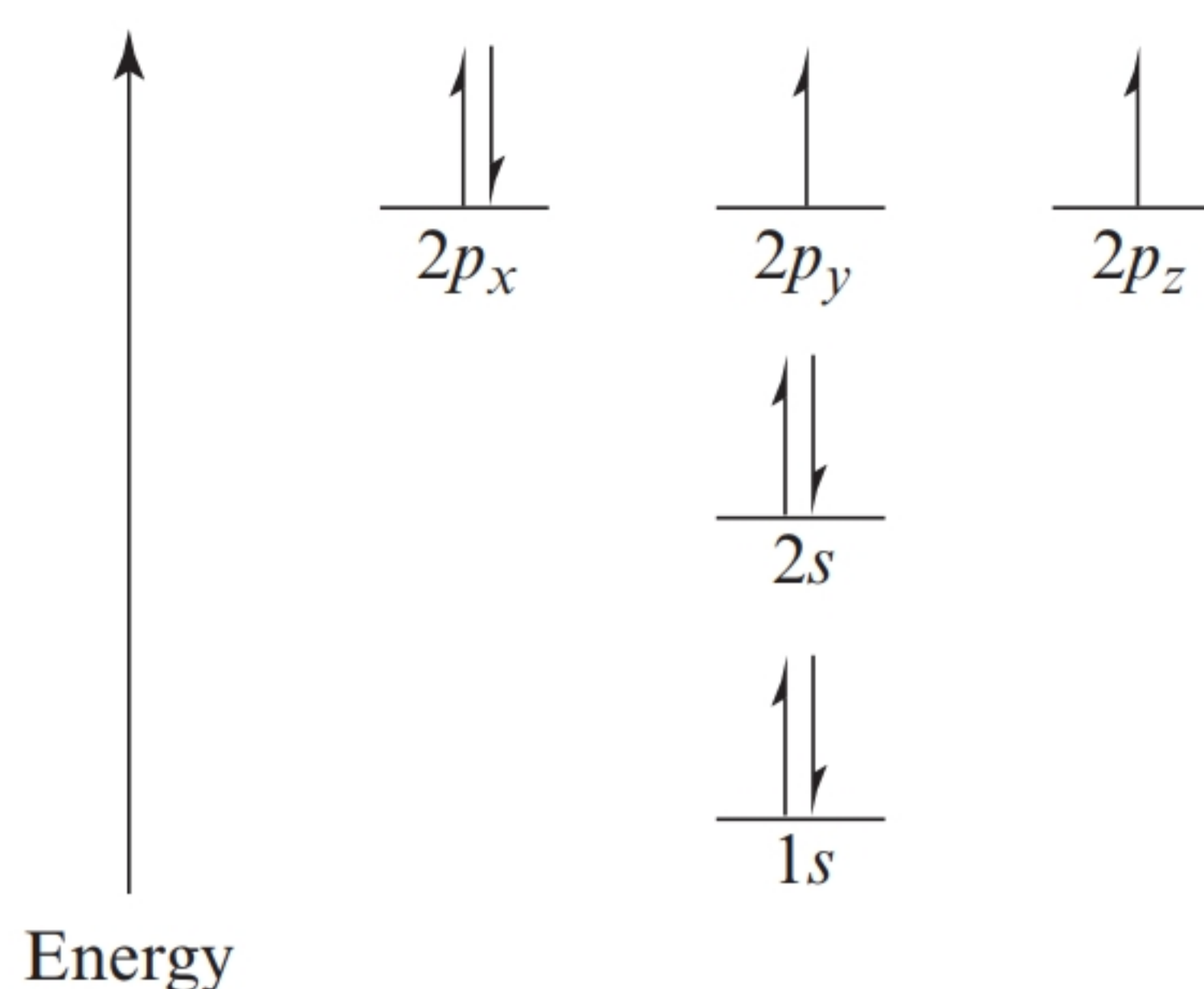
Let's consider the structure of water, beginning with the central oxygen atom. Recall that the atomic number (the number of protons) for oxygen is eight. Therefore, an oxygen atom also has eight electrons. (An ion may have more or less electrons than the atomic number for the element, depending on the charge of the ion.) Only the valence (outermost) shell electrons are involved in bonding. Oxygen has six valence electrons—that is, six electrons in the second principal shell. (Recall that the number of valence electrons is apparent from the group number of the element in the periodic table, and the row number for the element is the principal shell number for its valence electrons.) Now, let's consider the electron configuration for oxygen. The sequence of atomic orbitals for the first three shells of any atom is shown below. Oxygen uses only the first two shells in its lowest energy state.



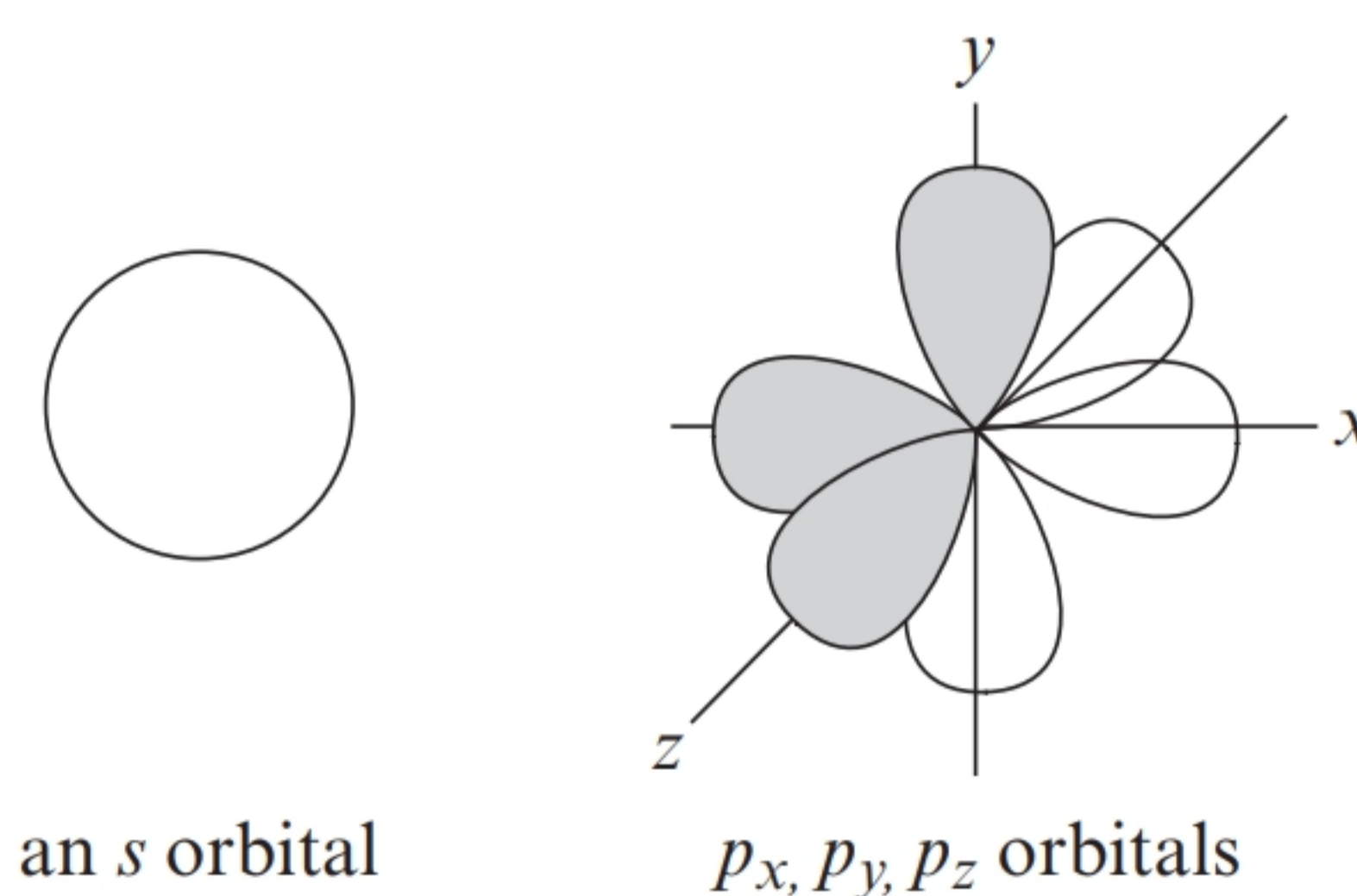
The p orbitals of any given principal shell (second, third, etc.) are of equal energy. Recall also that each orbital can hold a maximum of two electrons and that each equal energy orbital must accept one electron before a second can reside there (Hund's rule). So, for oxygen we place two electrons in the $1s$ orbital, two in the $2s$ orbital, and one in each of the $2p$ orbitals, for a subtotal of seven electrons. The final eighth electron is paired with another in one of the $2p$ orbitals. The ground state configuration for the eight electrons of oxygen is, therefore



where the superscript numbers indicate how many electrons are in each orbital. In terms of relative energy of these orbitals, the following diagram can be drawn. Note that the three $2p$ orbitals are depicted at the same relative energy level.



Now, let's consider the shape of these orbitals. The shape of an **s orbital** is that of a sphere with the nucleus at the center. The shape of each **p orbital** is approximately that of a dumbbell or lobe-shaped object, with the nucleus directly between the two lobes. There is one pair of lobes for each of the three p orbitals (p_x , p_y , p_z) and they are aligned along the x , y , and z coordinate axes, with the nucleus at the origin. Note that this implies that the three p orbitals are at 90° angles to each other.



Now, when oxygen is bonded to two hydrogens, bonding is accomplished by the sharing of an electron from each of the hydrogens with an unpaired electron from the oxygen. This type of bond, involving the sharing of electrons between atoms, is called a **covalent bond**. The formation of covalent bonds between the oxygen atom and the two hydrogen atoms is advantageous because each atom achieves a full valence shell by the sharing of these electrons. For the oxygen in a water molecule, this amounts to satisfying the octet rule.

A **Lewis structure** for the water molecule (which shows only the valence shell electrons) is depicted in the following structure. There are two nonbonding pairs of electrons around the oxygen as well as two bonding pairs.

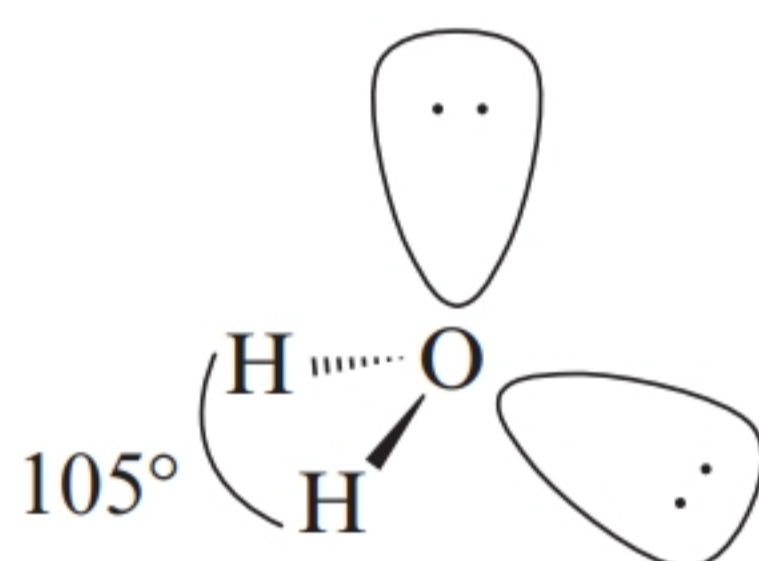


In the left-hand structure the six valence electrons contributed by the oxygen are shown as dots, while those from the hydrogens are shown as x's. This is done strictly for bookkeeping purposes. All electrons are, of course, identical. The right-hand structure uses the convention that a bonding pair of electrons can be shown by a single line between the bonded atoms.

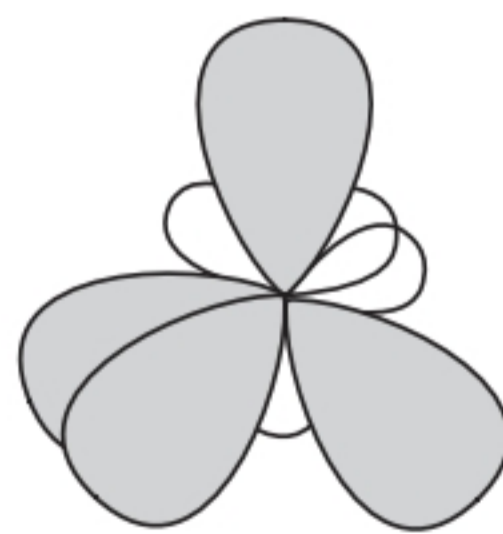
This structural model for water is only a *first approximation*, however. While it is a proper Lewis structure for water, it is not an entirely correct three-dimensional structure. It might appear that the angle between the hydrogen atoms (or between any two pairs of electrons in a water molecule) would be 90° , but this is not what the true angles are in a water molecule. The angle between the two hydrogens is in fact about 105° , and the nonbonding electron pairs are in a different plane than the hydrogen atoms. The reason for this arrangement is that groups of bonding and nonbonding electrons tend to repel each other due to the negative charge of the electrons. Thus, the ideal angles between bonding and nonbonding groups of electrons are those angles that allow maximum separation in three-dimensional space. This principle and the theory built around it are called the **valence shell electron pair repulsion (VSEPR) theory**.

VSEPR theory predicts that the ideal separation between four groups of electrons around an atom is 109.5° , the so-called **tetrahedral angle**. At an angle of 109.5° all four electron groups are separated equally from each other, being oriented toward the corners of a regular tetrahedron. The exact tetrahedral angle of 109.5° is found in structures where the four groups of electrons and bonded groups are identical.

In water, there are two different types of electron groups—pairs bonding the hydrogens with the oxygen and nonbonding pairs. Nonbonding electron pairs repel each other with greater force than bonding pairs, so the separation between them is greater. Consequently, the angle between the pairs bonding the hydrogens to the oxygen in a water molecule is compressed slightly from 109.5° , being actually about 105° . As we shall see shortly, the angle between the four groups of bonding electrons in methane (CH_4) is the ideal tetrahedral angle of 109.5° . This is because the four groups of electrons and bound atoms are identical in a methane molecule.



Orbital hybridization is the reason that 109.5° is the ideal tetrahedral angle. As noted earlier, an s orbital is spherical, and each p orbital is shaped like two symmetrical lobes aligned along the x , y , and z coordinate axes. Orbital hybridization involves taking a weighted average of the valence electron orbitals of the atom, resulting in the same number of new hybridized orbitals. With four groups of valence electrons, as in the structure of water, one s orbital and three p orbitals from the second principal shell in oxygen are hybridized (the $2s$ and $2p_x$, $2p_y$, and $2p_z$ orbitals). The result is four new hybrid orbitals of equal energy designated as sp^3 orbitals (instead of the original three p orbitals and one s orbital). Each of the four sp^3 orbitals has roughly 25% s character and 75% p character. The geometric result is that the major lobes of the four sp^3 orbitals are oriented toward the corners of a tetrahedron with an angle of 109.5° between them.



sp^3 hybrid orbitals
(109.5° angle between lobes)

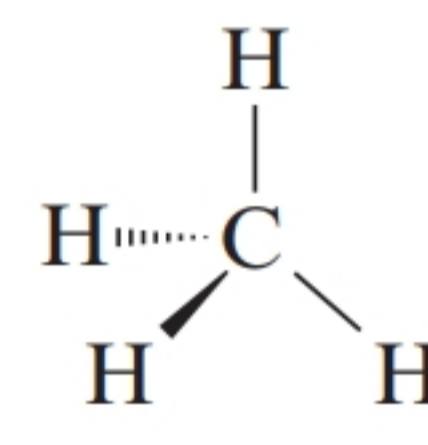
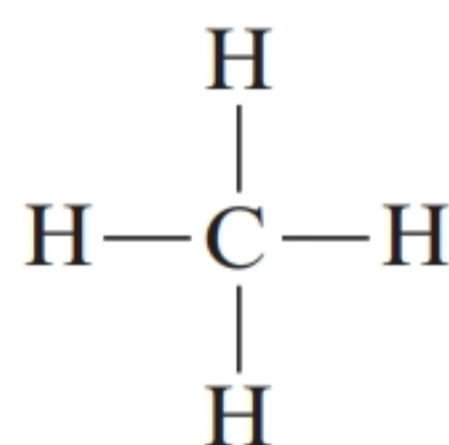
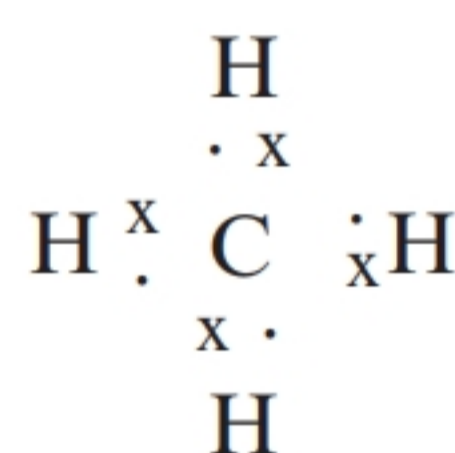
In the case of the oxygen in a water molecule, where two of the four sp^3 orbitals are occupied by nonbonding pairs, the angle of separation between them is larger than 109.5° due to additional electrostatic repulsion of the nonbonding pairs. Consequently, the angle between the bonding electrons is slightly smaller, about 105° .

More detail about orbital hybridization than provided above is given in Sections 1.9–1.15 of *Organic Chemistry*. With that greater detail it will be apparent from consideration of orbital hybridization that for three groups of valence electrons the ideal separation is 120° (trigonal planar), and for two groups of valence electrons the ideal separation is 180° (linear). VSEPR theory allows us to come to essentially the same conclusion as by the mathematical hybridization of orbitals, and it will serve us for the moment in predicting the three-dimensional shape of molecules.

Methane

CH_4

Now let's consider the structure of methane (CH_4). In methane there is a central carbon atom bearing four bonded hydrogens. Carbon has six electrons in total, with four of them being valence electrons. (Carbon is in Group IVA in the periodic table.) In methane each valence electron is shared with an electron from a hydrogen atom to form four covalent bonds. This information allows us to draw a Lewis structure for methane (see below). With four groups of valence electrons the VSEPR theory allows us to predict that the three-dimensional shape of a methane molecule should be tetrahedral, with an angle of 109.5° between each of the bonded hydrogens. This is indeed the case. Orbital hybridization arguments can also be used to show that there are four equivalent sp^3 hybrid orbitals around the carbon atom, separated by an angle of 109.5° .



All H-C-H angles are 109.5°

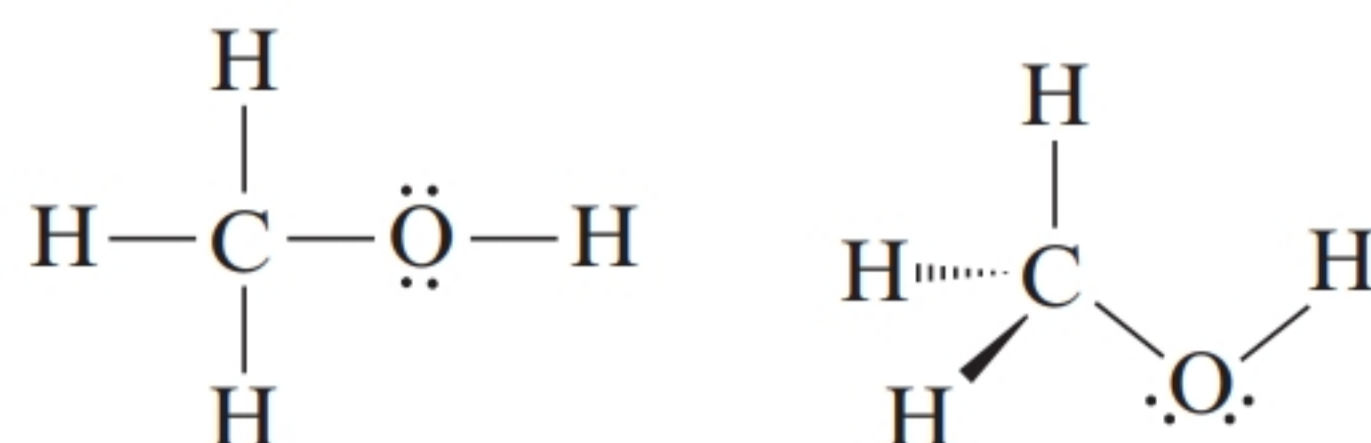
The structure at the far right above uses the dash-wedge notation to indicate three dimensions. A solid wedge indicates that a bond projects out of the paper toward the reader. A dashed bond indicates that it projects behind the paper away from the viewer. Ordinary lines represent bonds in the plane of the paper. The dash-wedge notation is an important and widely used tool for depicting the three-dimensional structure of molecules.

Methanol

CH_3OH

Now let's consider a molecule that incorporates structural aspects of both water and methane. Methanol (CH_3OH), or methyl alcohol, is such a molecule. In methanol, a central carbon atom has three hydrogens and an O–H group bonded to it. Three of the four valence electrons of the carbon atom are shared with a valence electron from the hydrogen atoms, forming three C–H bonds. The fourth valence electron of the carbon is shared with a valence electron from the oxygen atom, forming a C–O bond. The carbon atom now has an octet of valence electrons through the formation of four covalent bonds. The angles between these four covalent bonds is very near the ideal tetrahedral angle of 109.5° , allowing maximum separation between them. (The valence orbitals of the carbon are sp^3 hybridized.) At the oxygen atom, the situation is very

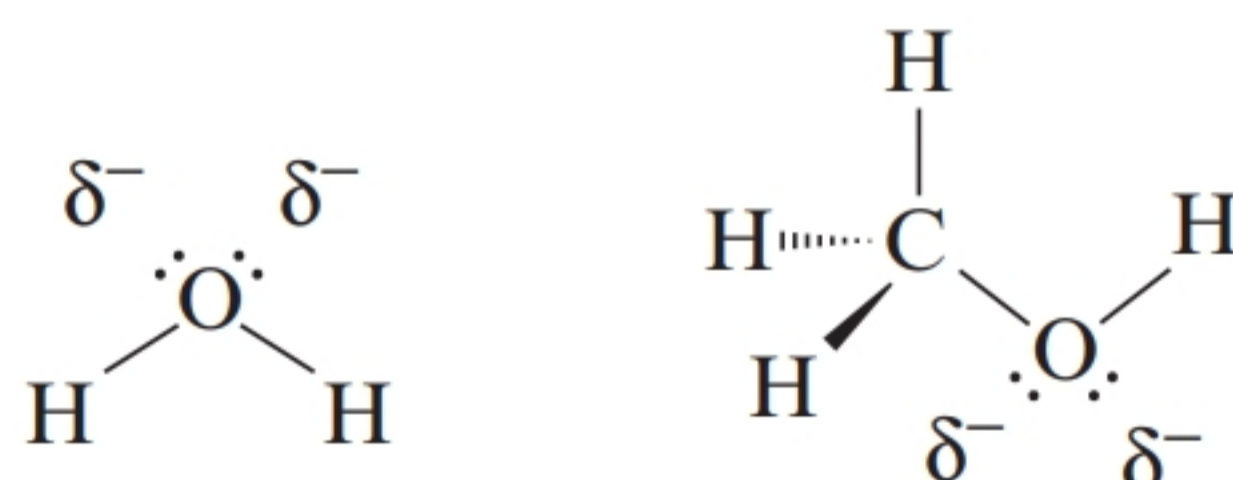
similar to that in water. The oxygen uses its two unpaired valence electrons to form covalent bonds. One valence electron is used in the bond with the carbon atom, and the other is paired with an electron from the hydrogen to form the O–H bond. The remaining valence electrons of the oxygen are present as two nonbonding pairs, just as in water. The angles separating the four groups of electrons around the oxygen are thus near the ideal angle of 109.5° , but reduced slightly in the C–O–H angle due to repulsion by the two nonbonding pairs on the oxygen. (The valence orbitals of the oxygen are also sp^3 hybridized since there are four groups of valence electrons.) A Lewis structure for methanol is shown below, along with a three-dimensional perspective drawing.



THE "CHARACTER" OF THE PUZZLE PIECES

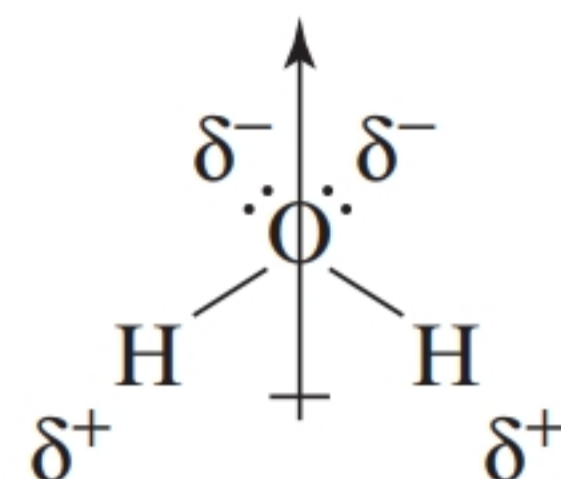
With a mental image of the three-dimensional structures of water, methane, and methanol, we can ask how the structure of each, as a "puzzle piece," influences the interaction of each molecule with identical and different molecules. In order to answer this question we have to move one step beyond the three-dimensional shape of these molecules. We need to consider not only the location of the electron groups (bonding and nonbonding) but also the distribution of electronic charge in the molecules.

First, we note that nonbonding electrons represent a locus of negative charge, more so than electrons involved in bonding. Thus, water would be expected to have some partial negative charge localized in the region of the nonbonding electron pairs of the oxygen. The same would be true for a methanol molecule. The lower case Greek δ (delta) means "partial."

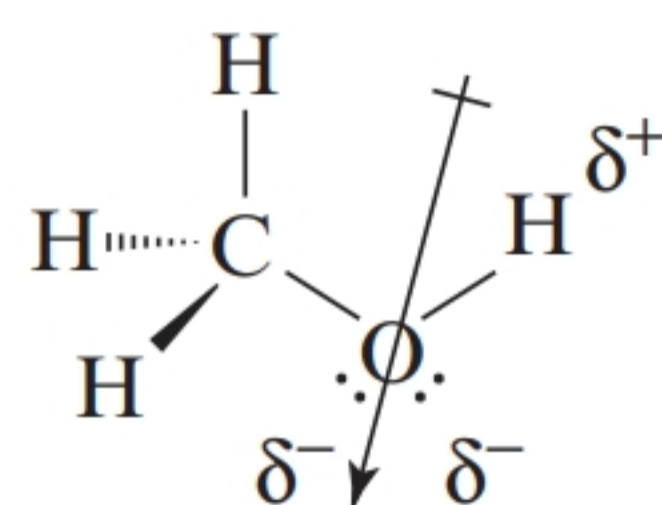


Secondly, the phenomenon of electronegativity influences the distribution of electrons, and hence the charge in a molecule, especially with respect to electrons in covalent bonds. **Electronegativity** is the propensity of an element to draw electrons toward it in a covalent bond. The trend among elements is that of increasing electronegativity toward the upper right corner of the periodic table. (Fluorine is the most electronegative element.) By observing the relative locations of carbon, oxygen, and hydrogen in the periodic table, we can see that oxygen is the most electronegative of these three elements. Carbon is more electronegative than hydrogen, although only slightly. Oxygen is significantly more electronegative than hydrogen. Thus, there is substantial separation of charge in a water molecule, due not only to the nonbonding electron pairs on the oxygen but also to the greater electronegativity of the oxygen with respect to the hydrogens. The oxygen tends to draw electron density toward itself in the bonds with the hydrogens, leaving the hydrogens partially positive. The resulting separation of charge is called **polarity**. The oxygen–hydrogen bonds are called **polar covalent bonds** due to this separation of

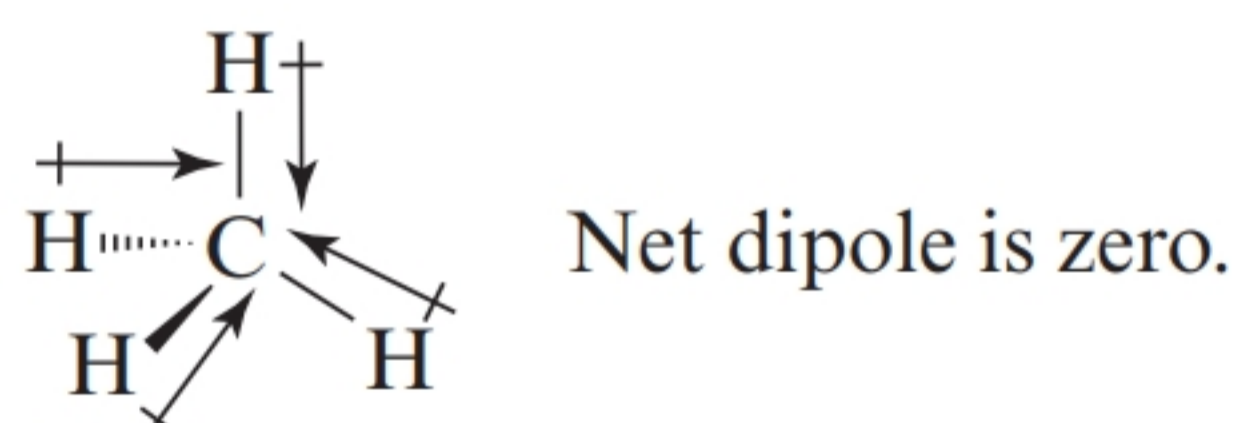
charge. If one considers the net effect of the two nonbonding electron pairs in a water molecule as being a region of negative charge, and the hydrogens as being a region of relative positive charge, it is clear that a water molecule has substantial separation of charge, or polarity.



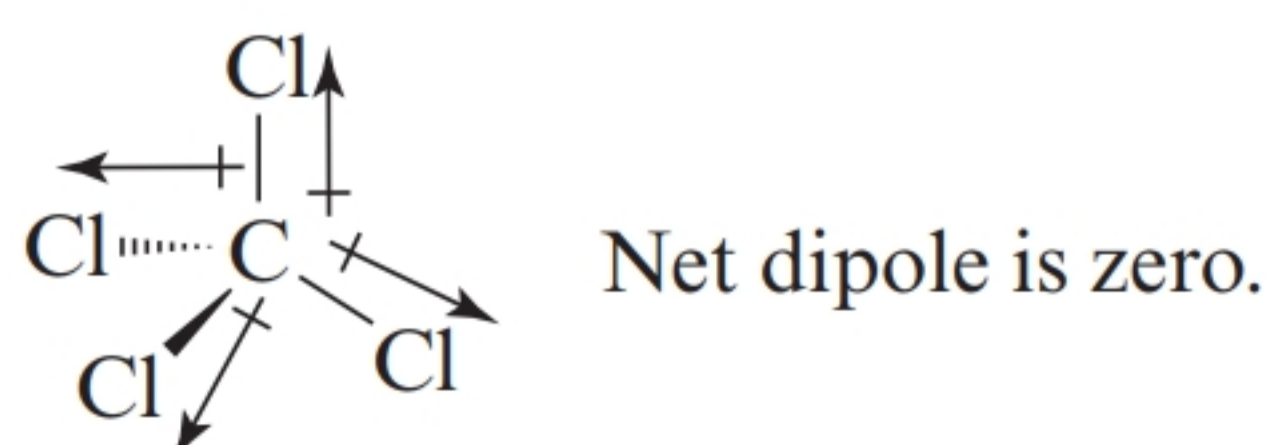
An analysis of polarity for a methanol molecule would proceed similarly to that for water. Methanol, however, is less polar than water because only one O–H bond is present. Nevertheless, the region of the molecule around the two nonbonding electron pairs of the oxygen is relatively negative, and the region near the hydrogen is relatively positive. The electronegativity difference between the oxygen and the carbon is not as large as that between oxygen and hydrogen, however, so there is less polarity associated with the C–O bond. Since there is even less difference in electronegativity between hydrogen and carbon in the three C–H bonds, these bonds contribute essentially no polarity to the molecule. The net effect for methanol is to make it a polar molecule, but less so than water due to the nonpolar character of the CH₃ region of the molecule.



Now let's consider methane. Methane is a nonpolar molecule. This is evident first because there are no nonbonding electron pairs, and secondly because there is relatively little electronegativity difference between the hydrogens and the central carbon. Furthermore, what little electronegativity difference there is between the hydrogens and the central carbon atom is negated by the symmetrical distribution of the C–H bonds in the tetrahedral shape of methane. The slight polarity of each C–H bond is canceled by the symmetrical orientation of the four C–H bonds. If considered as vectors, the vector sum of the four slightly polar covalent bonds oriented at 109.5° to each other would be zero.



The same analysis would hold true for a molecule with identical bonded groups, but groups having electronegativity significantly different from carbon, so long as there were symmetrical distribution of the bonded groups. Tetrachloromethane (carbon tetrachloride) is such a molecule. It has no net polarity.

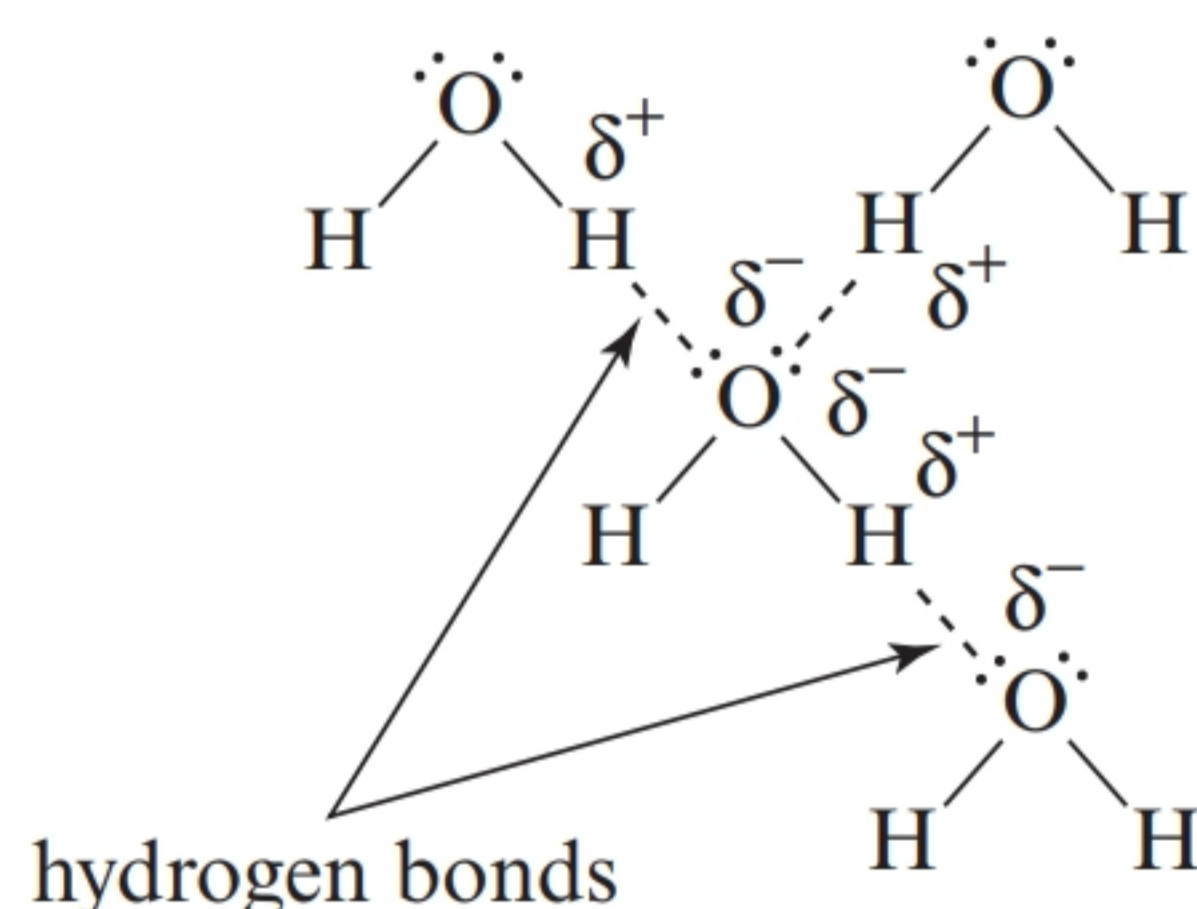


INTERACTIONS OF THE PUZZLE PIECES

Now that you have an appreciation for the polarity and shape of these molecules it is possible to see how molecules might interact with each other. The presence of polarity in a molecule bestows upon it attractive or repulsive forces in relation to other molecules. The negative part of one molecule is attracted to the positive region of another. Conversely, if there is little polarity in a molecule, the attractive forces it can exert are very small [though not completely nonexistent, due to dispersion forces (Section 2.13B in *Organic Chemistry*)]. Such effects are called **intermolecular forces** (forces between molecules), and strongly depend on the polarity of a molecule or certain bonds within it (especially O—H, N—H, and other bonds between hydrogen and more electronegative atoms with nonbonding pairs). Intermolecular forces have profound effects on physical properties such as **boiling point**, **solubility**, and **reactivity**. An important manifestation of these properties is that the ability to isolate a pure compound after a reaction often depends on differences in boiling point, solubility, and sometimes reactivity among the compounds present.

Boiling Point

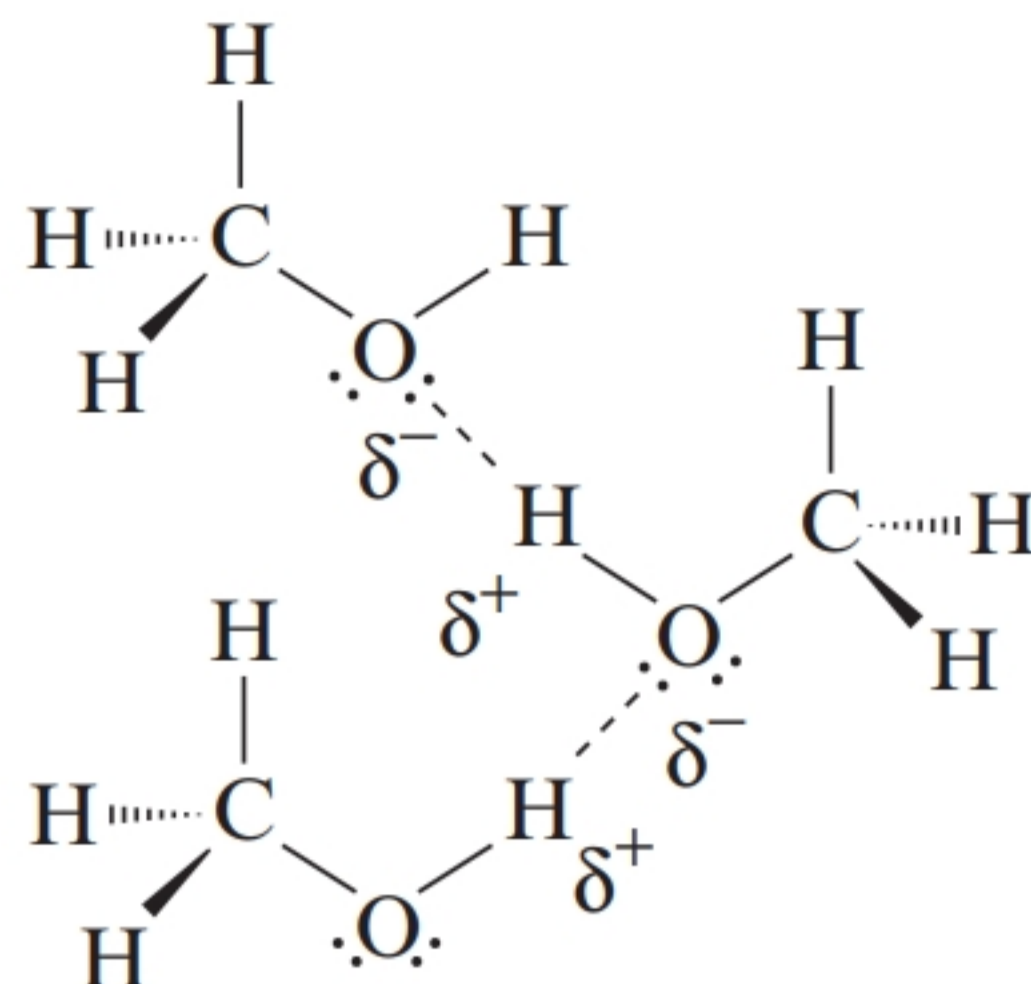
An intuitive understanding of boiling points will serve you well when working in the laboratory. The polarity of water molecules leads to relatively strong intermolecular attraction between water molecules. One result is the moderately high boiling point of water (100 °C, as compared to 65 °C for methanol and -162 °C for methane, which we will discuss shortly). Water has the highest boiling point of these three example molecules because it will strongly associate with itself by attraction of the partially positive hydrogens of one molecule (from the electronegativity difference between the O and H) to the negatively charged region in another water molecule (where the nonbonding pairs are located).



The specific attraction between a partially positive hydrogen atom attached to a heteroatom (an atom with both nonbonding and bonding valence electrons, e.g., oxygen or nitrogen) and the nonbonding electrons of another heteroatom is called **hydrogen bonding**. It is a form of **dipole-dipole attraction** due to the polar nature of the hydrogen–heteroatom bond. A given water molecule can associate by hydrogen bonding with several other water molecules, as shown above. Each water molecule has two hydrogens that can associate with the non-bonding pairs of other water molecules, and two nonbonding pairs that can associate with the hydrogens of other water molecules. Thus, several hydrogen bonds are possible for each water molecule. It takes a significant amount of energy (provided by heat, for example) to give the molecules enough kinetic energy (motion) for them to overcome the polarity-induced attractive forces between them and escape into the vapor phase (evaporation or boiling).

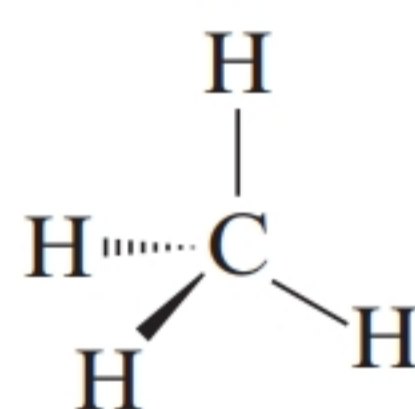
Methanol, on the other hand, has a lower boiling point (65 °C) than water, in large part due to the decreased hydrogen bonding ability of methanol in comparison with water. Each

methanol molecule has only one hydrogen atom that can participate in a hydrogen bond with the nonbonding electron pairs of another methanol molecule (as compared with two for each water molecule). The result is reduced intermolecular attraction between methanol molecules and a lower boiling point since less energy is required to overcome the lesser intermolecular attractive forces.



The CH_3 group of methanol does not participate in dipole–dipole attractions between molecules because there is not sufficient polarity in any of its bonds to lead to significant partial positive or negative charges. This is due to the small electronegativity difference between the carbon and hydrogen in each of the C–H bonds.

Now, on to methane. Methane has no hydrogens that are eligible for hydrogen bonding, since none is attached to a heteroatom such as oxygen. Due to the small difference in electronegativity between carbon and hydrogen there are no bonds with any significant polarity. Furthermore, what slight polarity there is in each C–H bond is canceled due to the tetrahedral symmetry of the molecule. [The minute attraction that is present between methane molecules is due to dispersion forces, but these are negligible in comparison to dipole–dipole interactions that exist when significant differences in electronegativity are present in molecules such as water and methanol.] Thus, because there is only a very weak attractive force between methane molecules, the boiling point of methane is very low (-162°C) and it is a gas at ambient temperature and pressure.



Solubility

An appreciation for trends in solubility is very useful in gaining a general understanding of many practical aspects of chemistry. The ability of molecules to dissolve other molecules or solutes is strongly affected by polarity. The polarity of water is frequently exploited during the isolation of an organic reaction product because water will not dissolve most organic compounds but will dissolve salts, many inorganic materials, and other polar byproducts that may be present in a reaction mixture.

As to our example molecules, water and methanol are miscible with each other because each is polar and can interact with the other by dipole–dipole hydrogen bonding interactions. Since methane is a gas under ordinary conditions, for the purposes of this discussion let's consider a close relative of methane—hexane. Hexane (C_6H_{14}) is a liquid having only carbon—carbon and carbon—hydrogen bonds. It belongs to the same chemical family as methane. Hexane is *not*

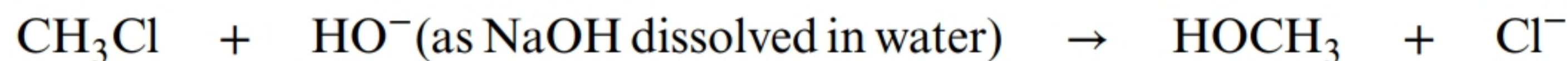
soluble in water due to the essential absence of polarity in its bonds. Hexane is slightly soluble in methanol due to the compatibility of the nonpolar CH_3 region of methanol with hexane. The old saying “like dissolves like” definitely holds true. This can be extended to solutes, as well. Very polar substances, such as ionic compounds, are usually freely soluble in water. The high polarity of salts generally prevents most of them from being soluble in methanol, however. And, of course, there is absolutely no solubility of ionic substances in hexane. On the other hand, very nonpolar substances, such as oils, would be soluble in hexane.

Thus, the structure of each of these molecules we’ve used for examples (water, methanol, and methane) has a profound effect on their respective physical properties. The presence of non-bonding electron pairs and polar covalent bonds in water and methanol versus the complete absence of these features in the structure of methane imparts markedly different physical properties to these three compounds. Water, a small molecule with strong intermolecular forces, is a moderately high boiling liquid. Methane, a small molecule with only very weak intermolecular forces, is a gas. Methanol, a molecule combining structural aspects of both water and methane, is a relatively low boiling liquid, having sufficient intermolecular forces to keep the molecules associated as a liquid, but not so strong that mild heat can’t disrupt their association.

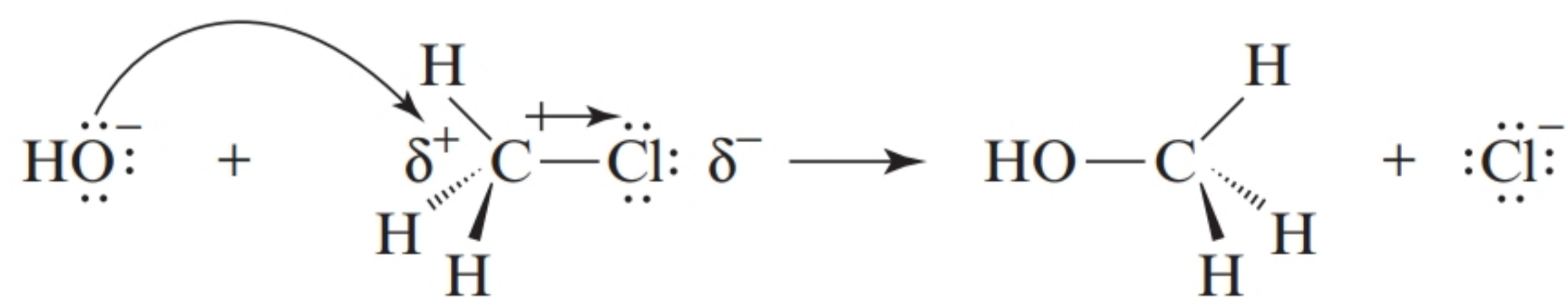
Reactivity

While the practical importance of the physical properties of organic compounds may only be starting to become apparent, one strong influence of polarity is on the **reactivity** of molecules. It is often possible to understand the basis for a given reaction in organic chemistry by considering the relative polarity of molecules and the propensity, or lack thereof, for them to interact with each other.

Let us consider one example of reactivity that can be understood at the initial level by considering structure and polarity. When chloromethane (CH_3Cl) is exposed to hydroxide ions (HO^-) in water a reaction occurs that produces methanol. This reaction is shown below.



This reaction is called a substitution reaction, and it is of a general type that you will spend considerable time studying in organic chemistry. The reason this reaction occurs readily can be understood by considering the principles of structure and polarity that we have been discussing. The hydroxide ion has a negative charge associated with it, and thus should be attracted to a species that has positive charge. Now recall our discussion of electronegativity and polar covalent bonds, and apply these ideas to the structure of chloromethane. The chlorine atom is significantly more electronegative than carbon (note its position in the periodic table). Thus, the covalent bond between the carbon and the chlorine is polarized such that there is partial negative charge on the chlorine and partial positive charge on the carbon. This provides the positive site that attracts the hydroxide anion!



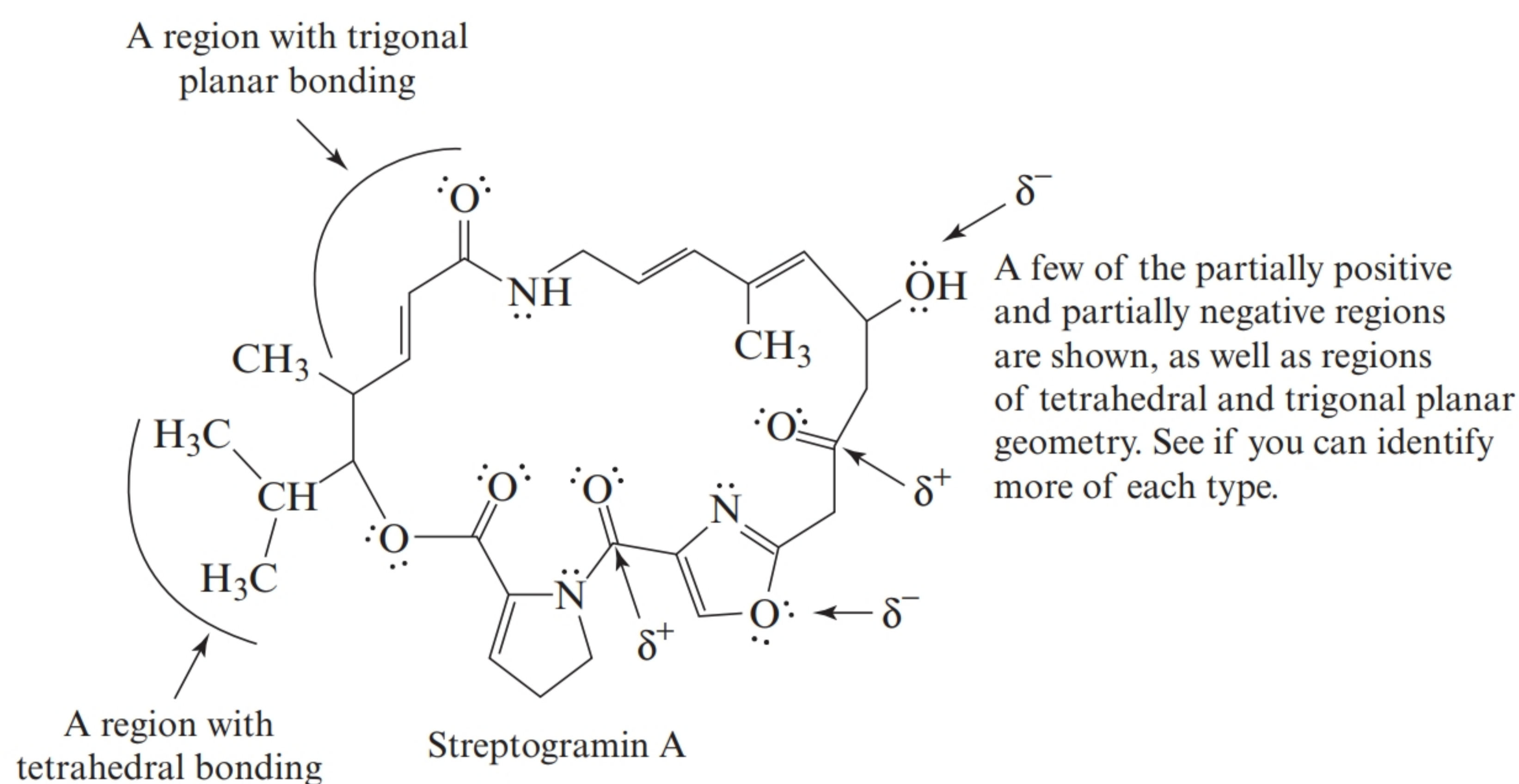
The intimate details of this reaction will be studied in Chapter 6 of your text. Suffice it to say for the moment that the hydroxide ion attacks the carbon atom using one of its nonbonding electron pairs to form a bond with the carbon. At the same time, the chlorine atom is pushed away from the carbon and takes with it the pair of electrons that used to bond it to the carbon.

The result is substitution of OH for Cl at the carbon atom and the synthesis of methanol. By calculating **formal charges** (Section 1.5 in the text) one can show that the oxygen of the hydroxide anion goes from having a formal negative charge in hydroxide to zero formal charge in the methanol molecule. Similarly, the chlorine atom goes from having zero formal charge in chloromethane to a formal negative charge as a chloride ion after the reaction. *The fact that the reaction takes place at all rests largely upon the complementary polarity of the interacting species. This is a pervasive theme in organic chemistry.*

Acid-base reactions are also very important in organic chemistry. Many organic reactions involve at least one step in the overall process that is fundamentally an acid-base reaction. Both Brønsted-Lowry acid-base reactions (those involving proton donors and acceptors) and Lewis acid-base reactions (those involving electron pair acceptors and donors, respectively) are important. In fact, the reaction above can be classified as a Lewis acid-base reaction in that the hydroxide ion acts as a Lewis base to attack the partially positive carbon as a Lewis acid. It is strongly recommended that you review concepts you have learned previously regarding acid-base reactions. Chapter 3 in *Organic Chemistry* will help in this regard, but it is advisable that you begin some early review about acids and bases based on your previous studies. Acid-base chemistry is widely applicable to understanding organic reactions.

JOINING THE PIECES

Finally, while what we have said above has largely been in reference to three specific compounds, water, methanol, and methane, the principles involved find exceptionally broad application in understanding the structure, and hence reactivity, of organic molecules in general. You will find it constantly useful in your study of organic chemistry to consider the electronic structure of the molecules with which you are presented, the shape caused by the distribution of electrons in a molecule, the ensuing polarity, and the resulting potential for that molecule's reactivity. What we have said about these very small molecules of water, methanol, and methane can be extended to consideration of molecules with 10 to 100 times as many atoms. You would simply apply these principles to small sections of the larger molecule one part at a time. The following structure of Streptogramin A provides an example.



A natural antibacterial compound that blocks protein synthesis at the 70S ribosomes of Gram-positive bacteria.

We have not said much about how overall shape influences the ability of one molecule to interact with another, in the sense that a key fits in a lock or a hand fits in a glove. This type of consideration is also extremely important, and will follow with relative ease if you have worked hard to understand the general principles of structure outlined here and expanded upon in the early chapters of *Organic Chemistry*. An example would be the following. Streptogramin A, shown above, interacts in a hand-in-glove fashion with the 70S ribosome in bacteria to inhibit binding of transfer RNA at the ribosome. The result of this interaction is the prevention of protein synthesis in the bacterium, which thus accounts for the antibacterial effect of Streptogramin A. Other examples of hand-in-glove interactions include the olfactory response to geraniol mentioned earlier, and the action of enzymes to speed up the rate of reactions in biochemical systems.

FINISHING THE PUZZLE

In conclusion, if you pay attention to learning aspects of structure during this initial period of “getting your feet wet” in organic chemistry, much of the three-dimensional aspects of molecules will become second nature to you. You will immediately recognize when a molecule is tetrahedral, trigonal planar, or linear in one region or another. You will see the potential for interaction between a given section of a molecule and that of another molecule based on their shape and polarity, and you will understand why many reactions take place. Ultimately, you will find that there is much less to memorize in organic chemistry than you first thought. You will learn how to put the pieces of the organic puzzle together, and see that structure is indeed almost everything, just applied in different situations!

1

THE BASICS: BONDING AND MOLECULAR STRUCTURE

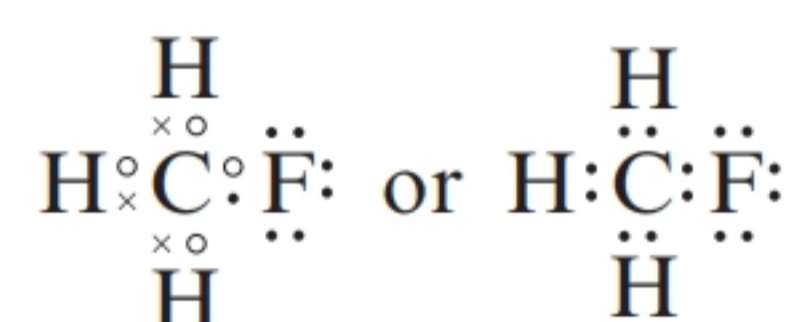
SOLUTIONS TO PROBLEMS

Another Approach to Writing Lewis Structures

When we write Lewis structures using this method, we assemble the molecule or ion from the constituent atoms showing only the valence electrons (i.e., the electrons of the outermost shell). By having the atoms share electrons, we try to give each atom the electronic structure of a noble gas. For example, we give hydrogen atoms two electrons because this gives them the structure of helium. We give carbon, nitrogen, oxygen, and fluorine atoms eight electrons because this gives them the electronic structure of neon. The number of valence electrons of an atom can be obtained from the periodic table because it is equal to the group number of the atom. Carbon, for example, is in Group IVA and has four valence electrons; fluorine, in Group VIIA, has seven; hydrogen, in Group IA, has one. As an illustration, let us write the Lewis structure for CH_3F . In the example below, we will at first show a hydrogen's electron as x, carbon's electrons as o's, and fluorine's electrons as dots.

Example A

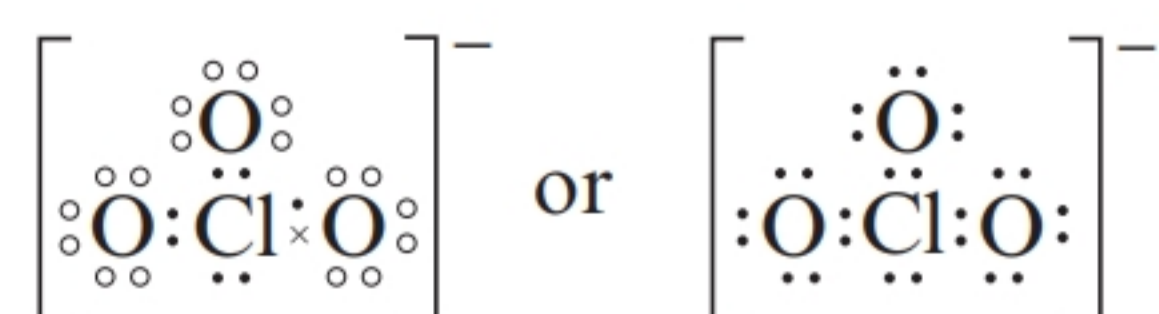
3H^{\times} , $^{\circ}\text{C}^{\circ}$, and $\cdot\ddot{\text{F}}\cdot$ are assembled as



If the structure is an ion, we add or subtract electrons to give it the proper charge. As an example, consider the chlorate ion, ClO_3^- .

Example B

$\cdot\ddot{\text{Cl}}\cdot$, and $^{\circ}\ddot{\text{O}}^{\circ}$ and an extra electron \times are assembled as



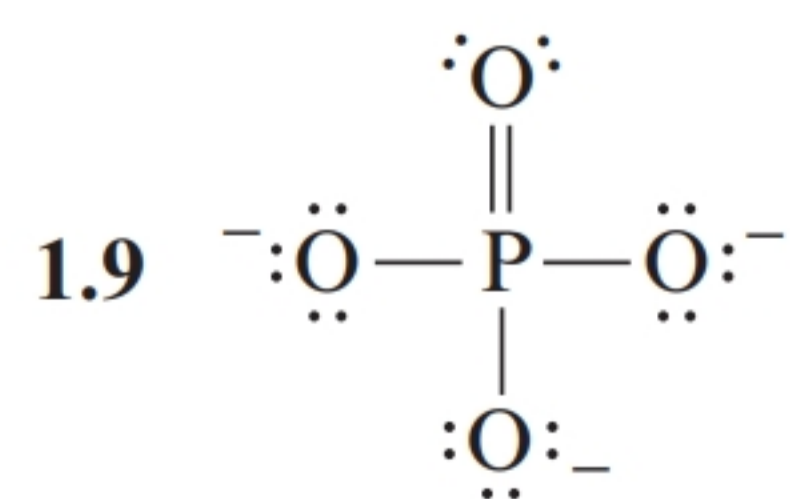
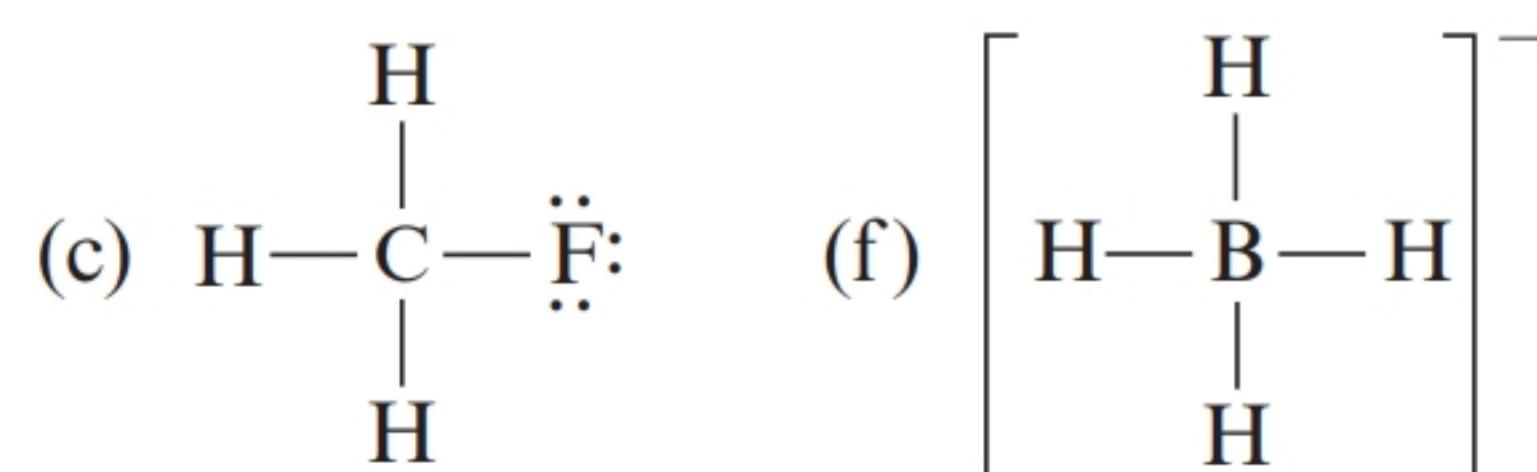
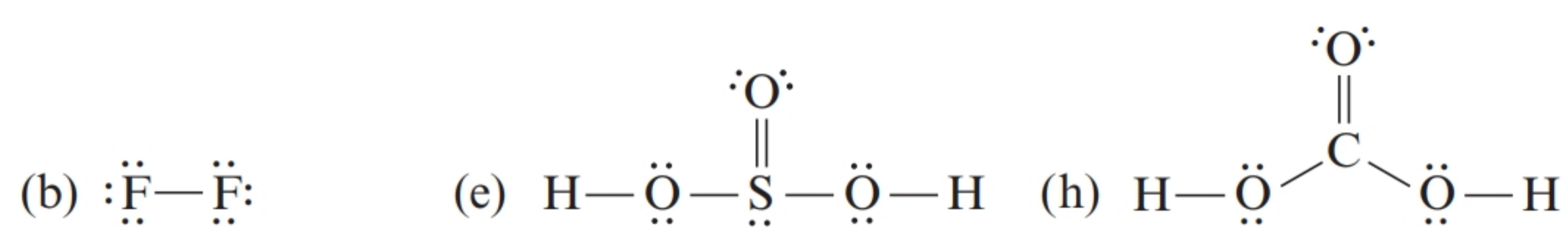
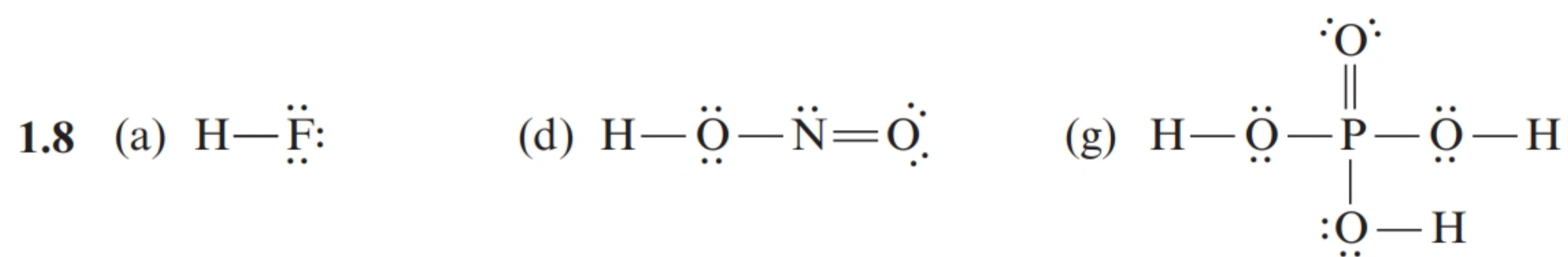
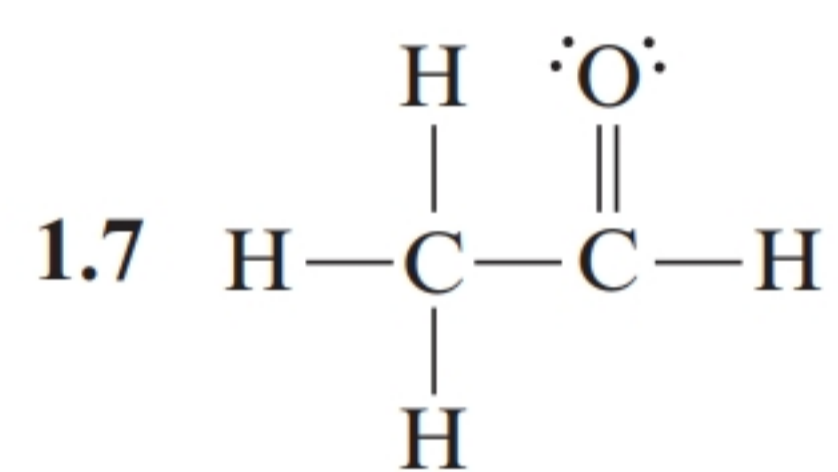
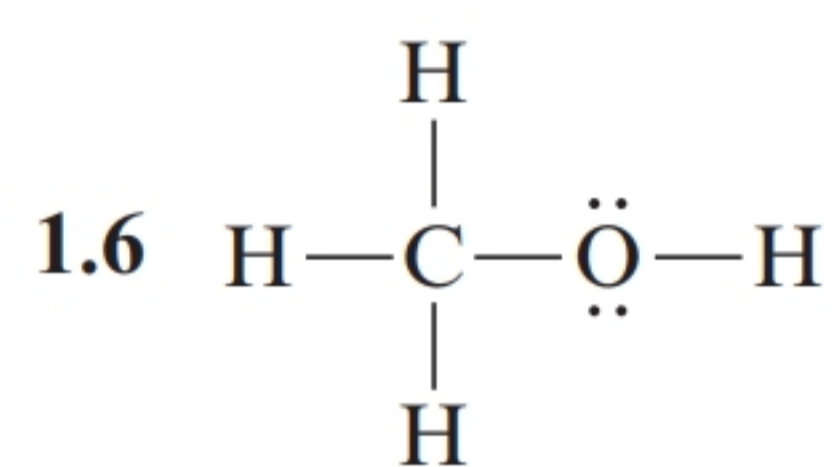
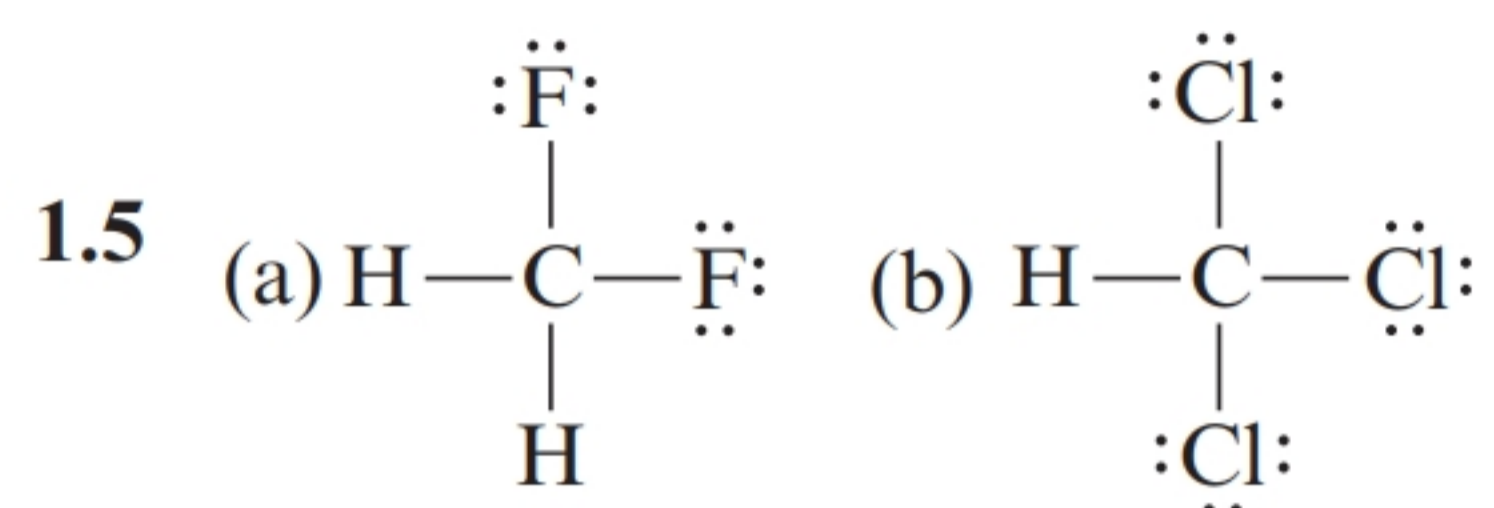
2 THE BASICS: BONDING AND MOLECULAR STRUCTURE

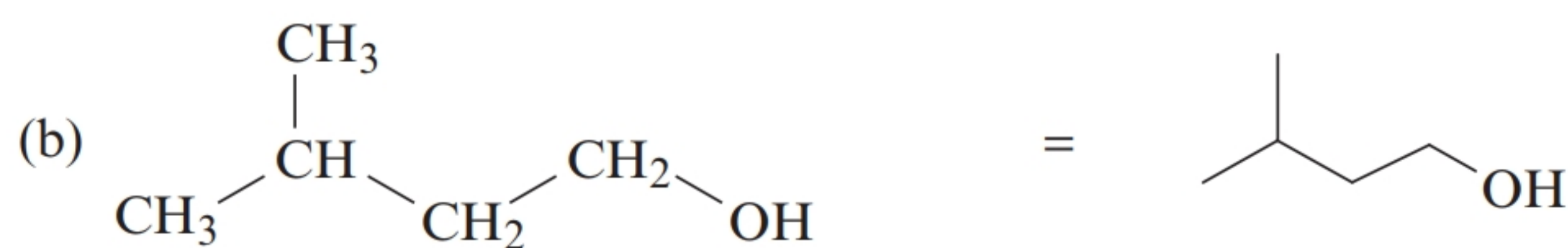
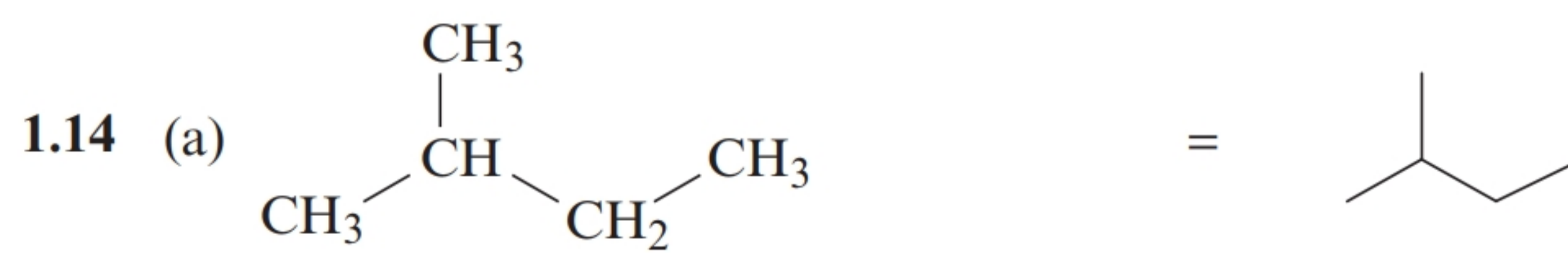
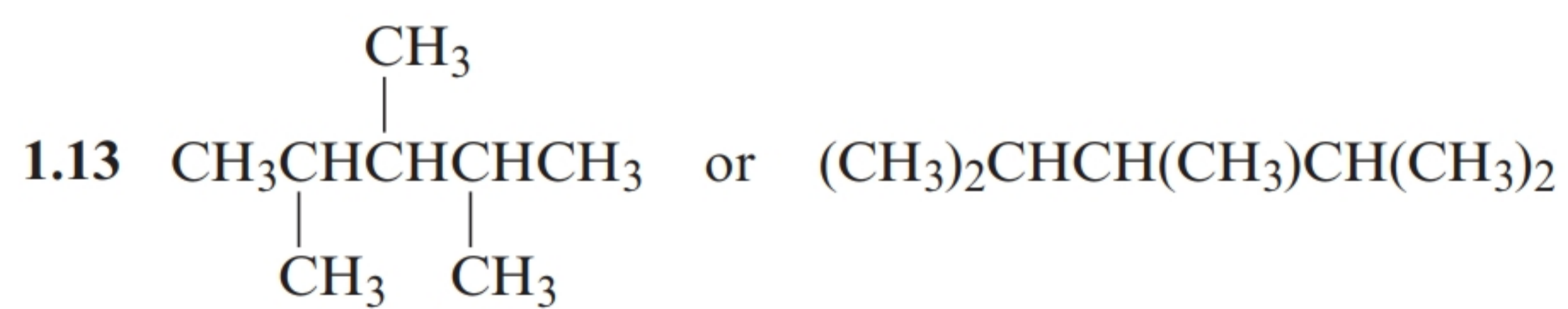
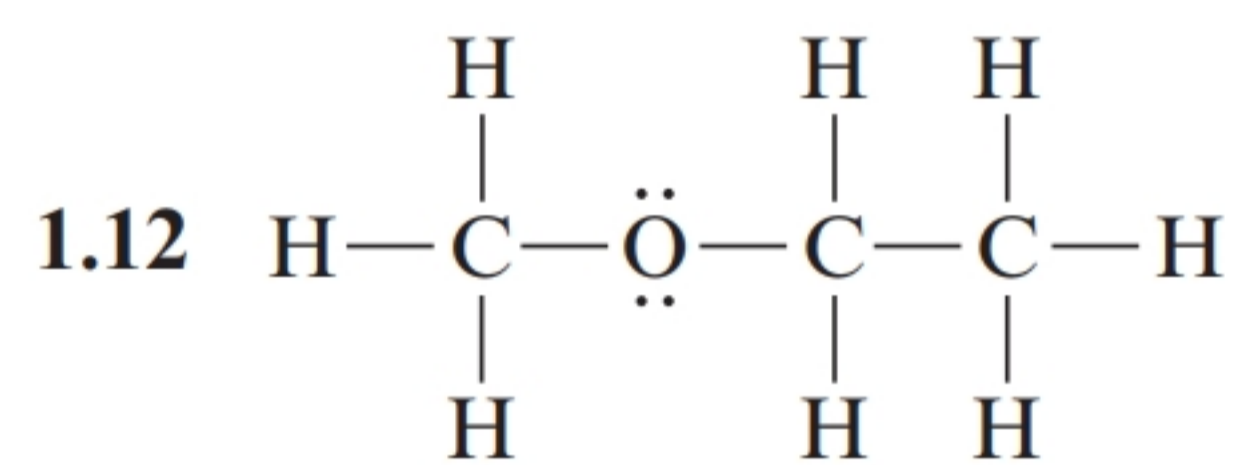
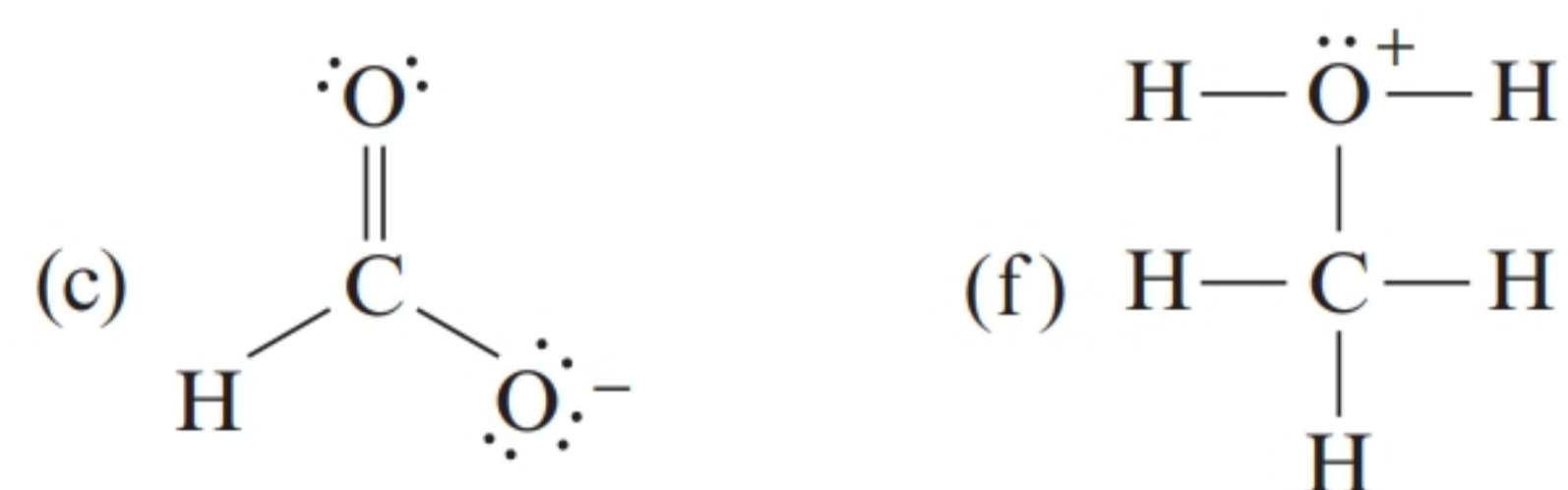
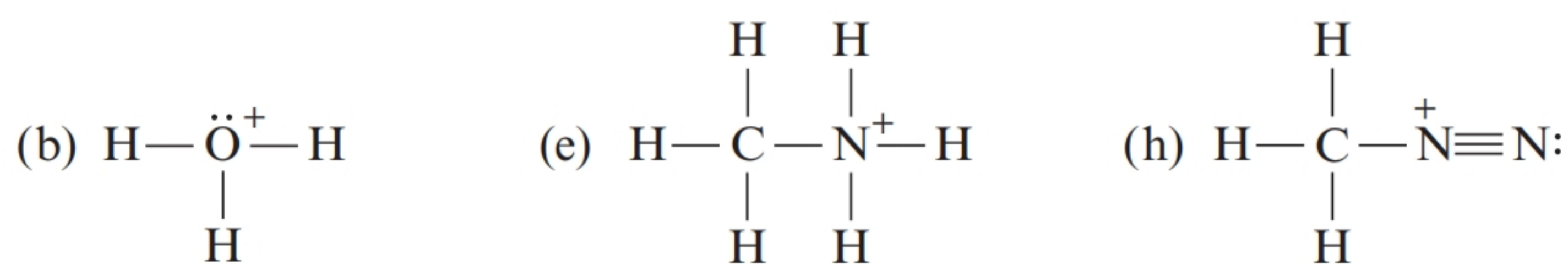
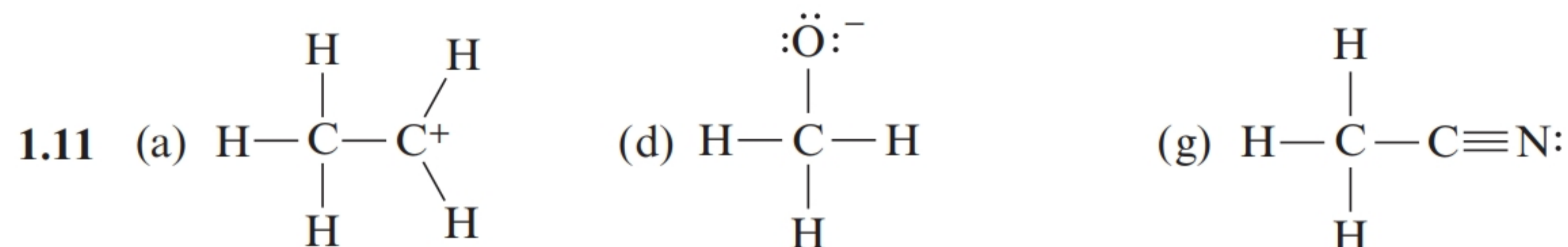
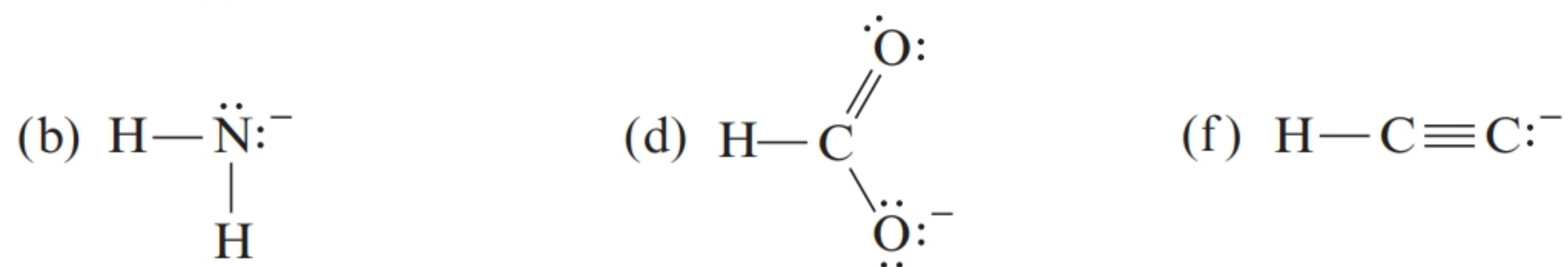
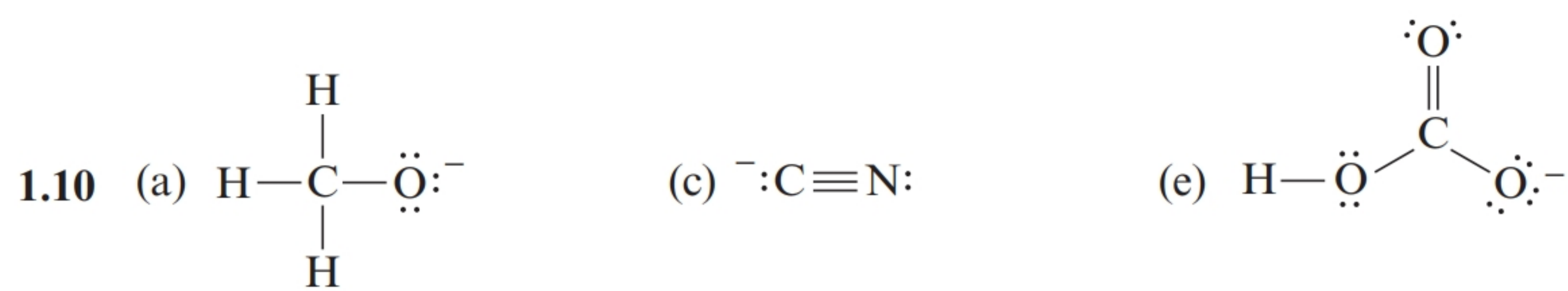
1.1 ^{14}N , 7 protons and 7 neutrons; ^{15}N , 7 protons and 8 neutrons

1.2 (a) one (b) seven (c) four (d) three (e) eight (f) five

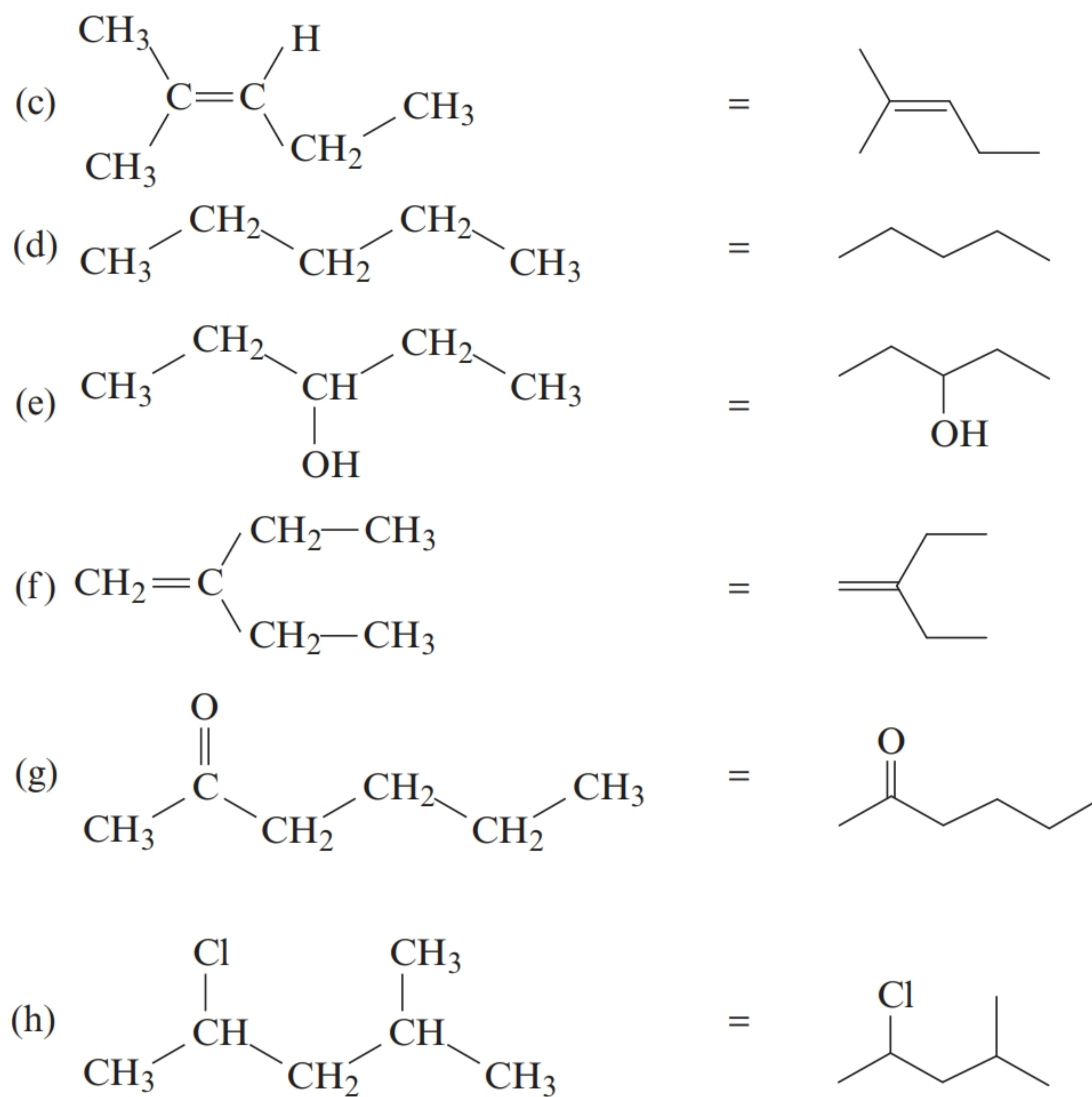
1.3 (a) O (b) N (c) Cl (d) S

1.4 (a) ionic (b) covalent (c) covalent (d) covalent

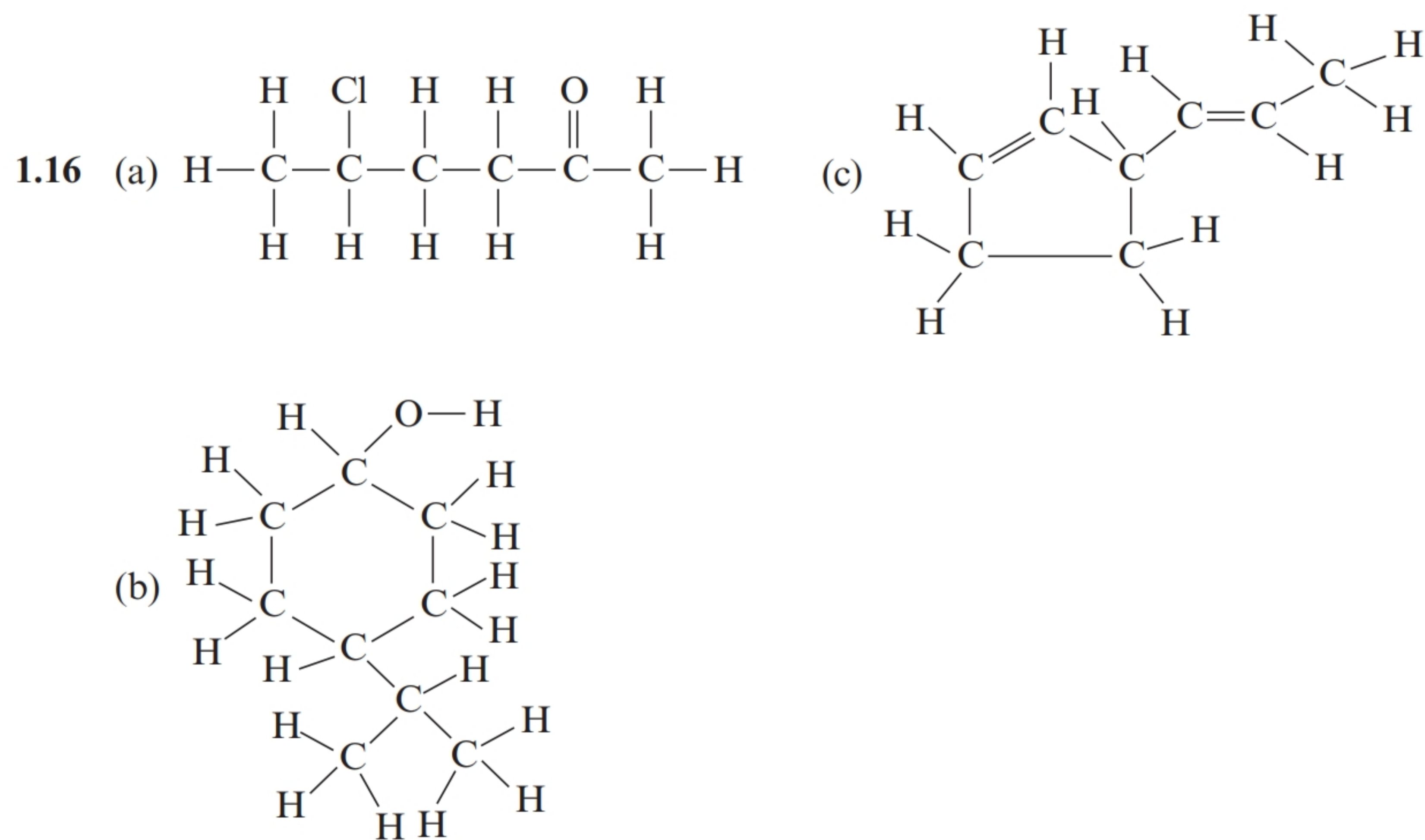


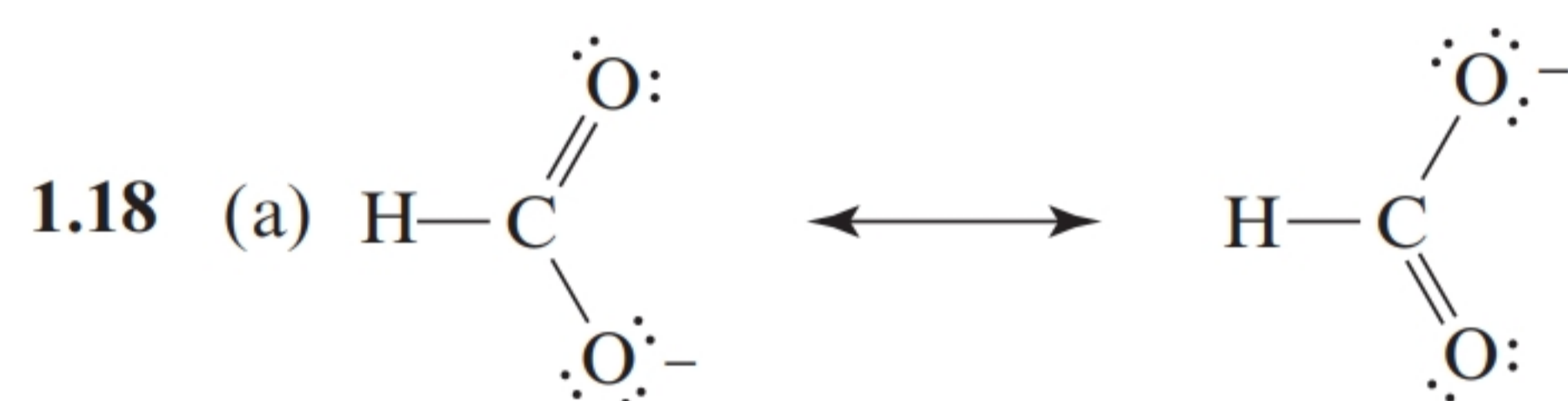
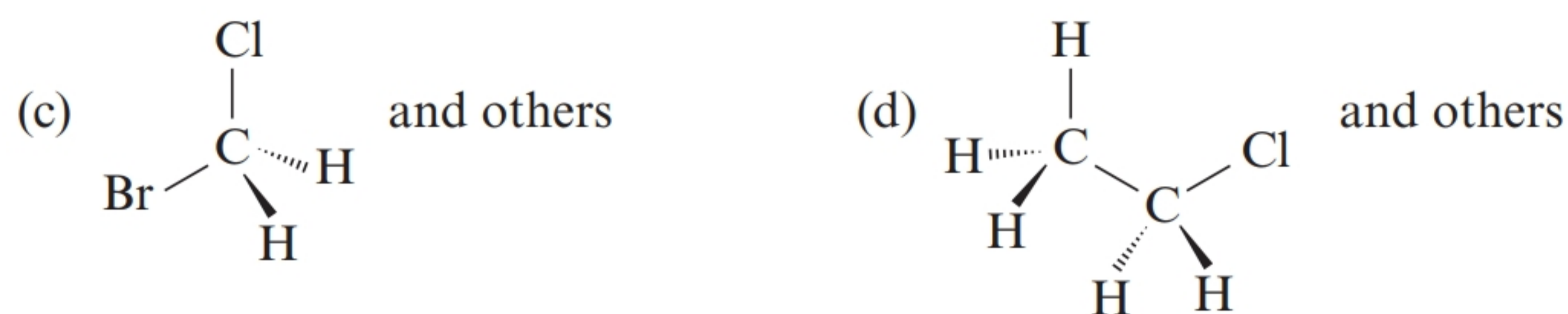
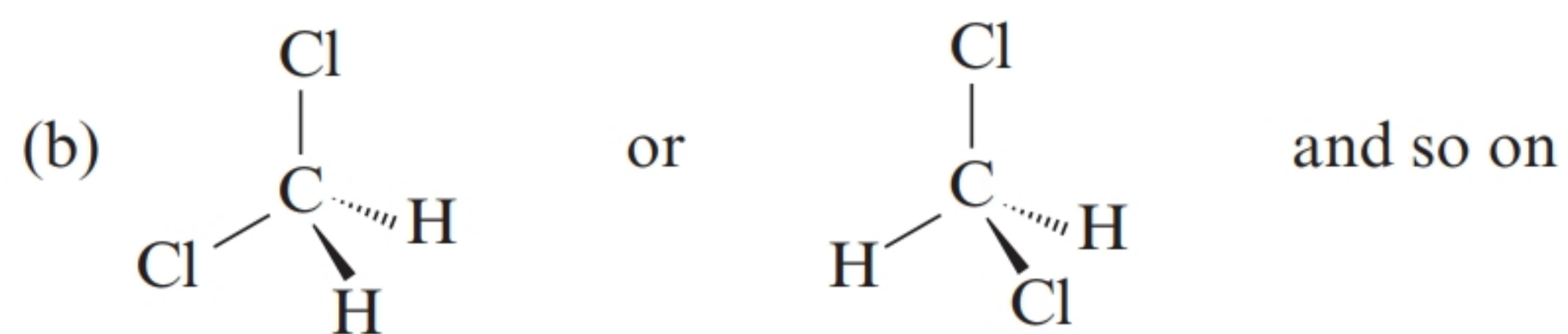
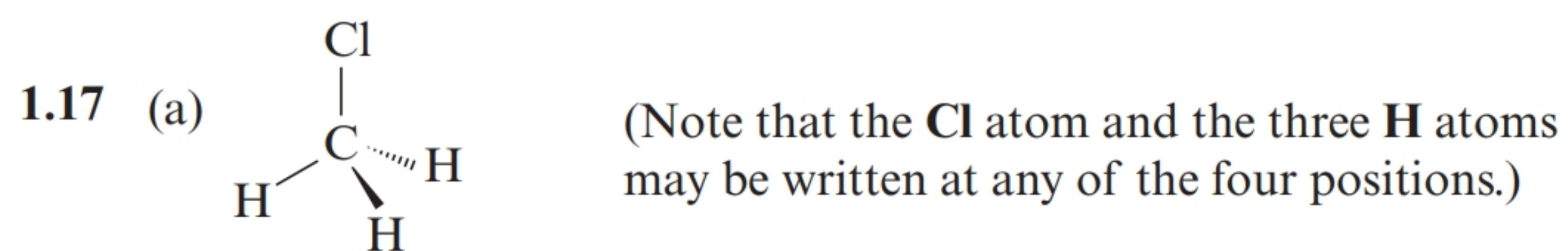


4 THE BASICS: BONDING AND MOLECULAR STRUCTURE

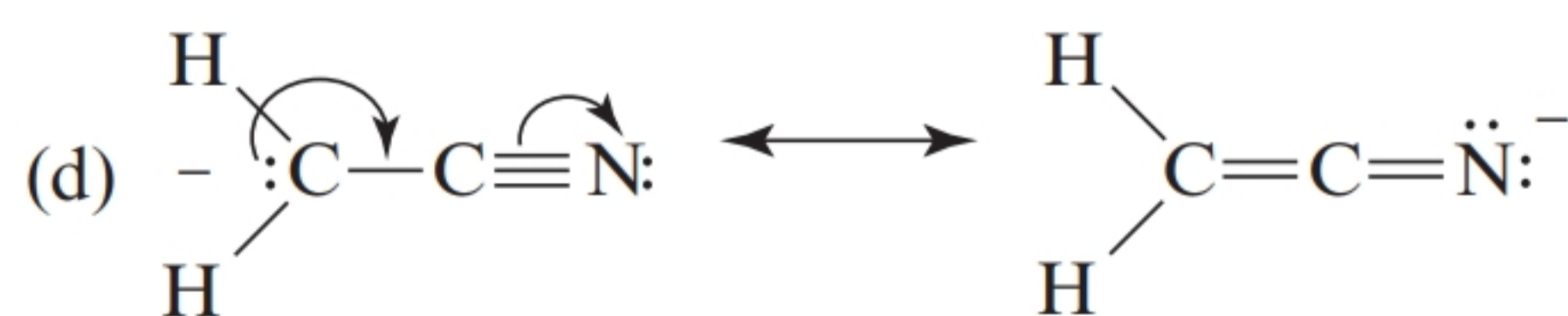
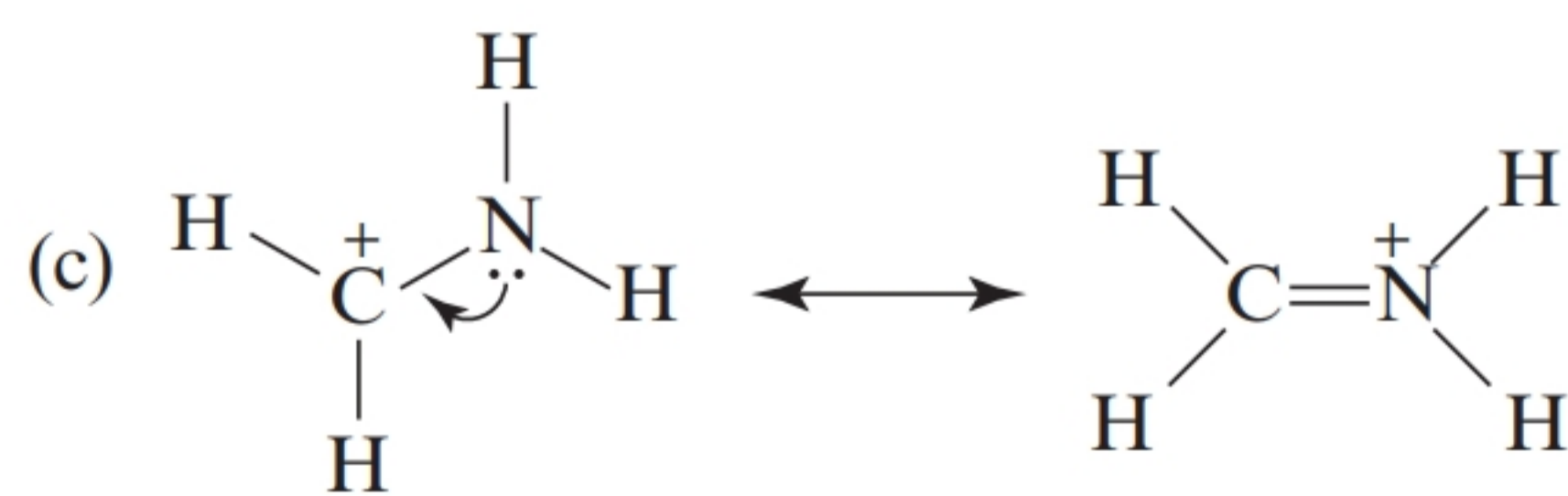
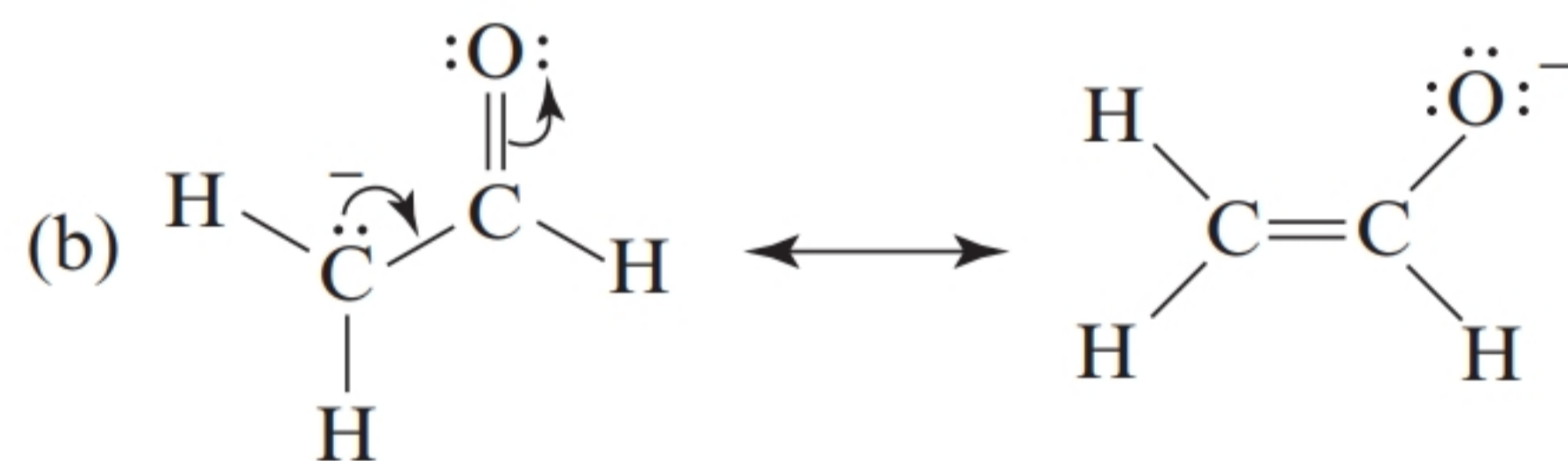
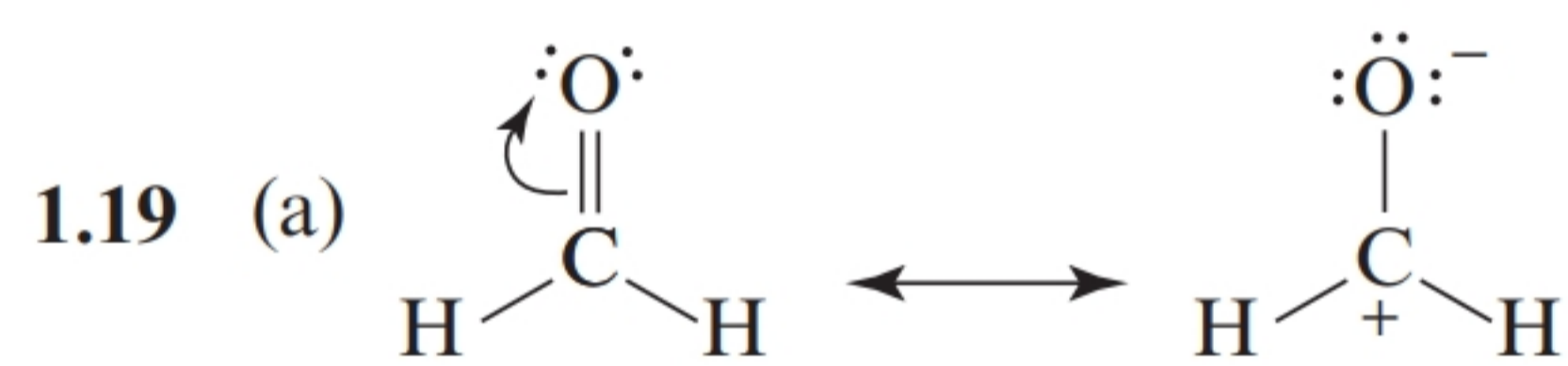


- 1.15** (a) and (d) are constitutional isomers with the molecular formula C_5H_{12} .
 (b) and (e) are constitutional isomers with the molecular formula $C_5H_{12}O$.
 (c) and (f) are constitutional isomers with the molecular formula C_6H_{12} .

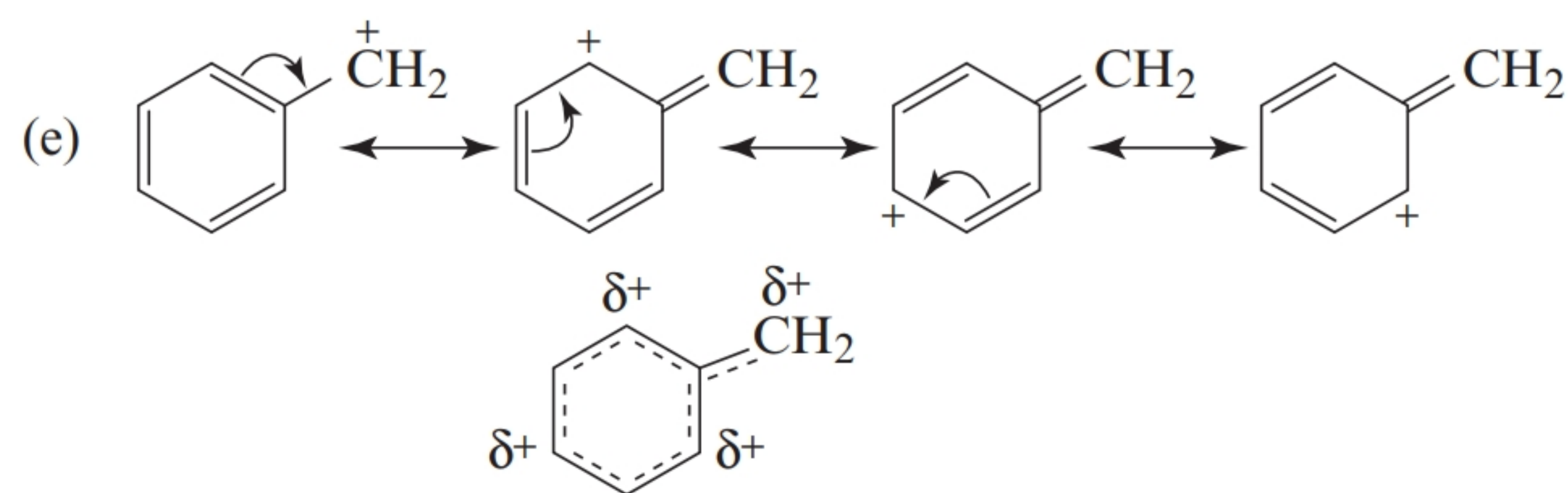
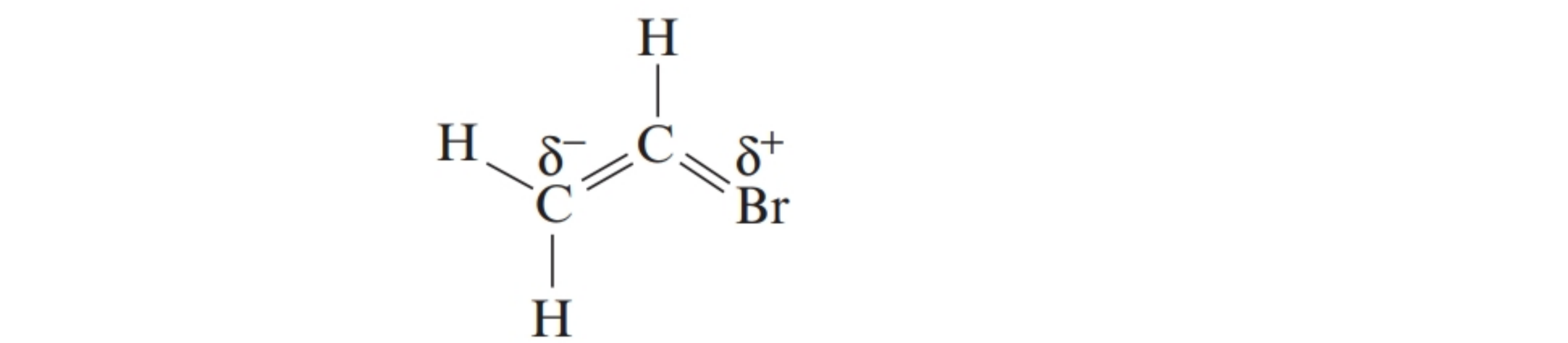
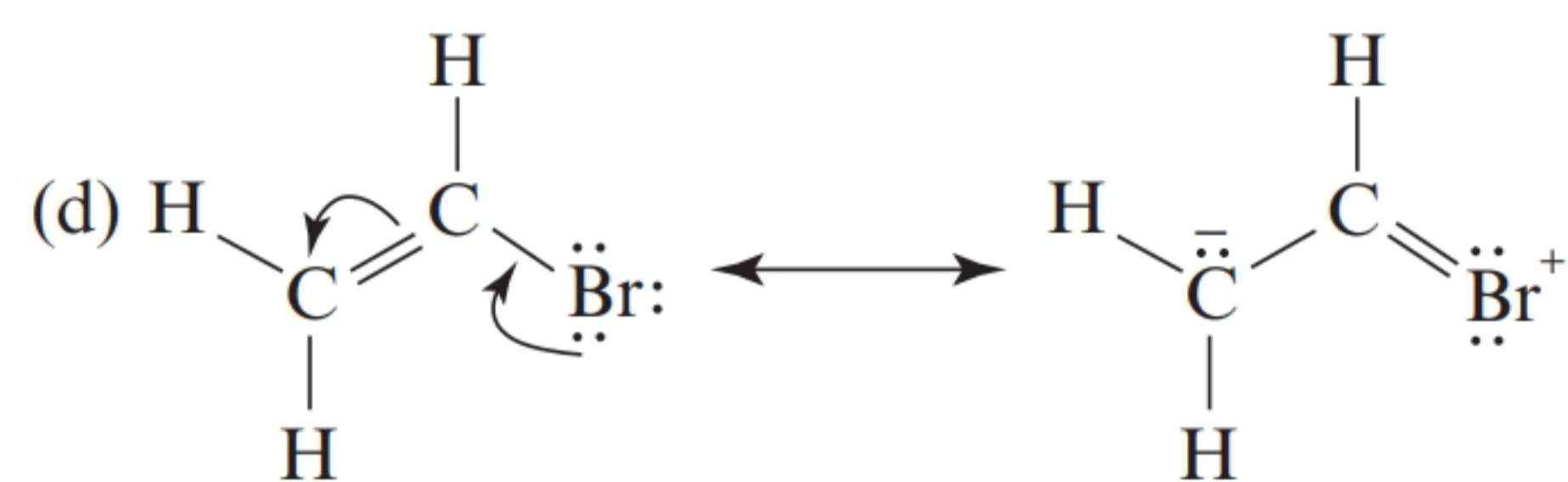
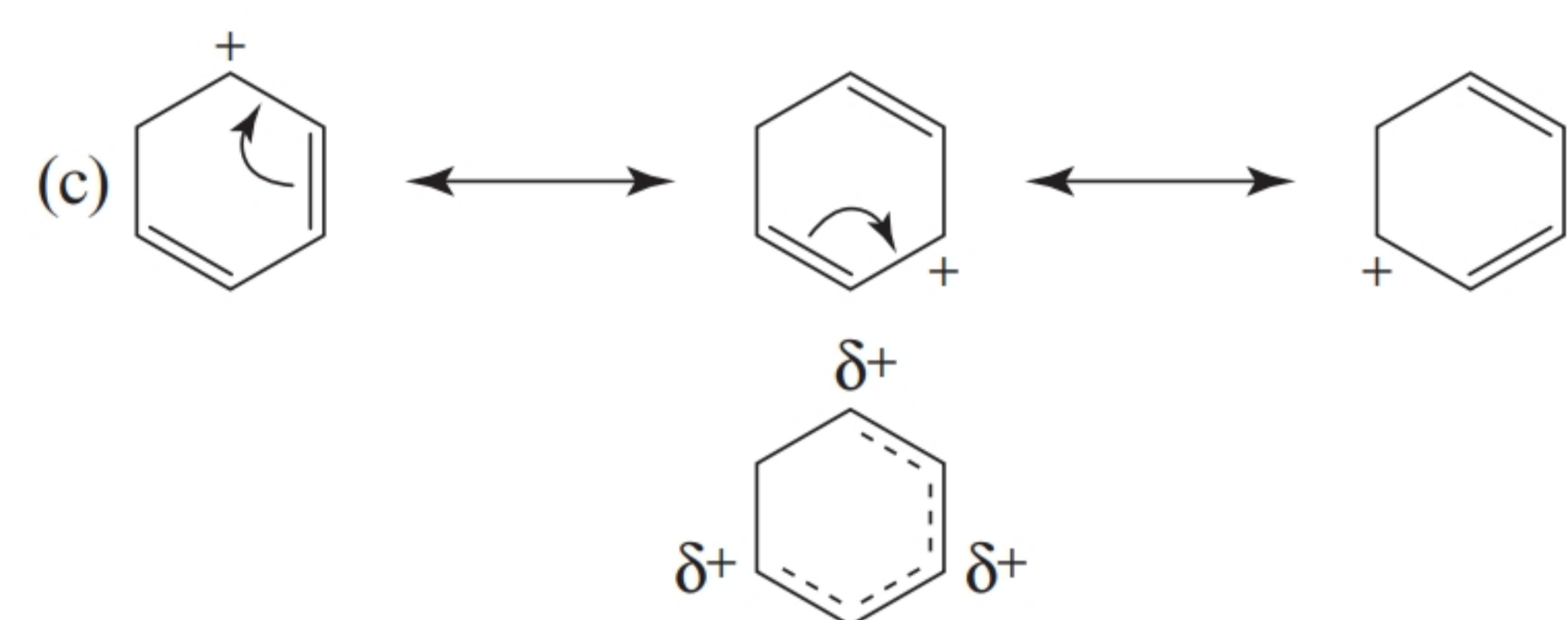
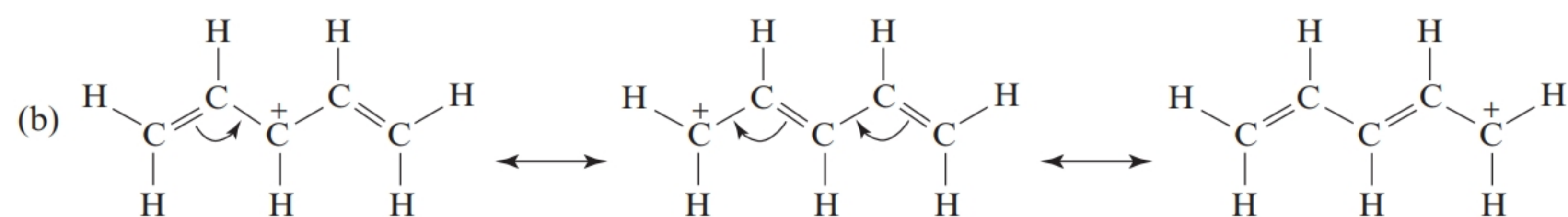
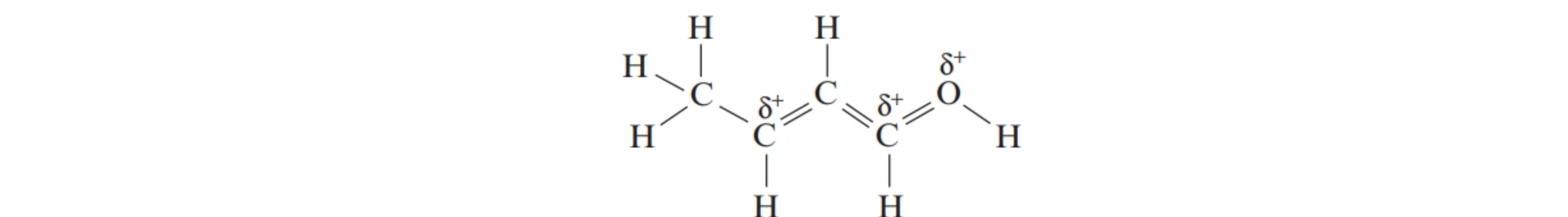
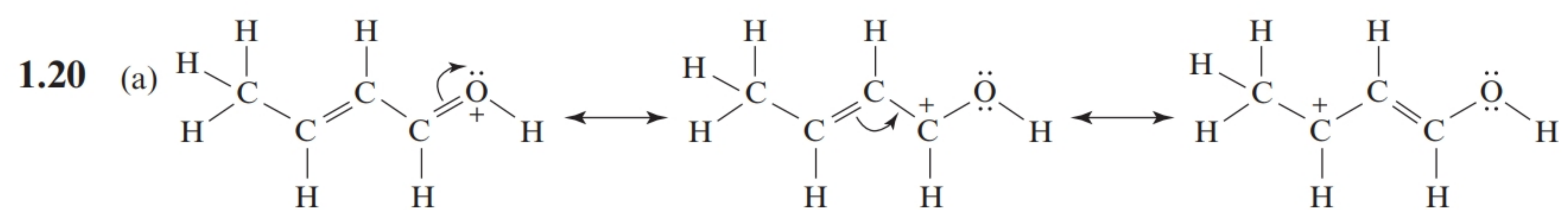


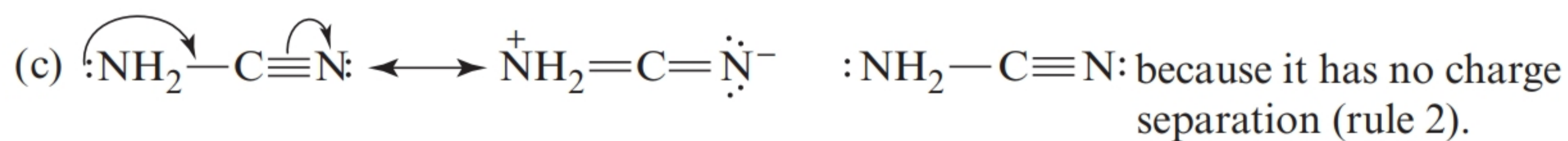
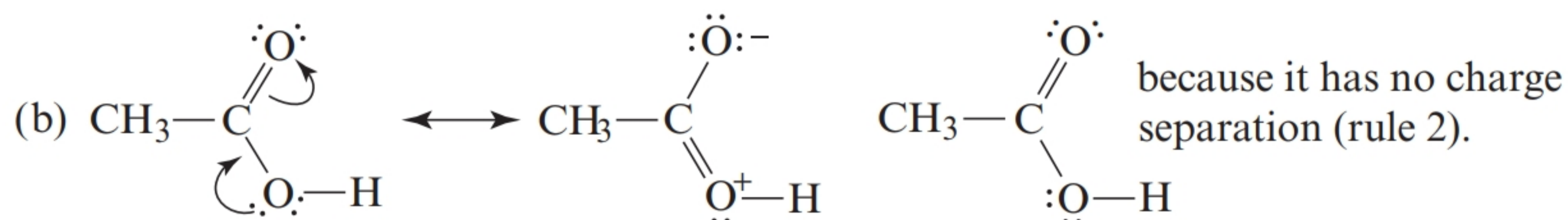
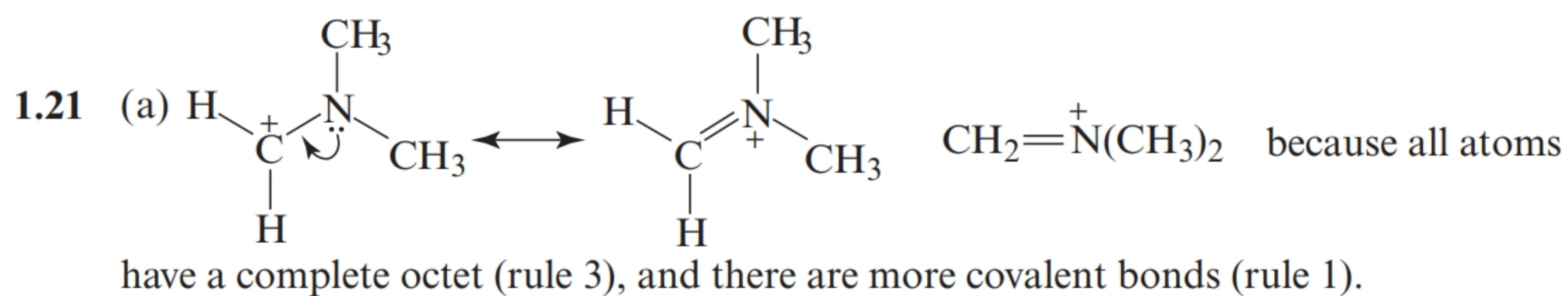
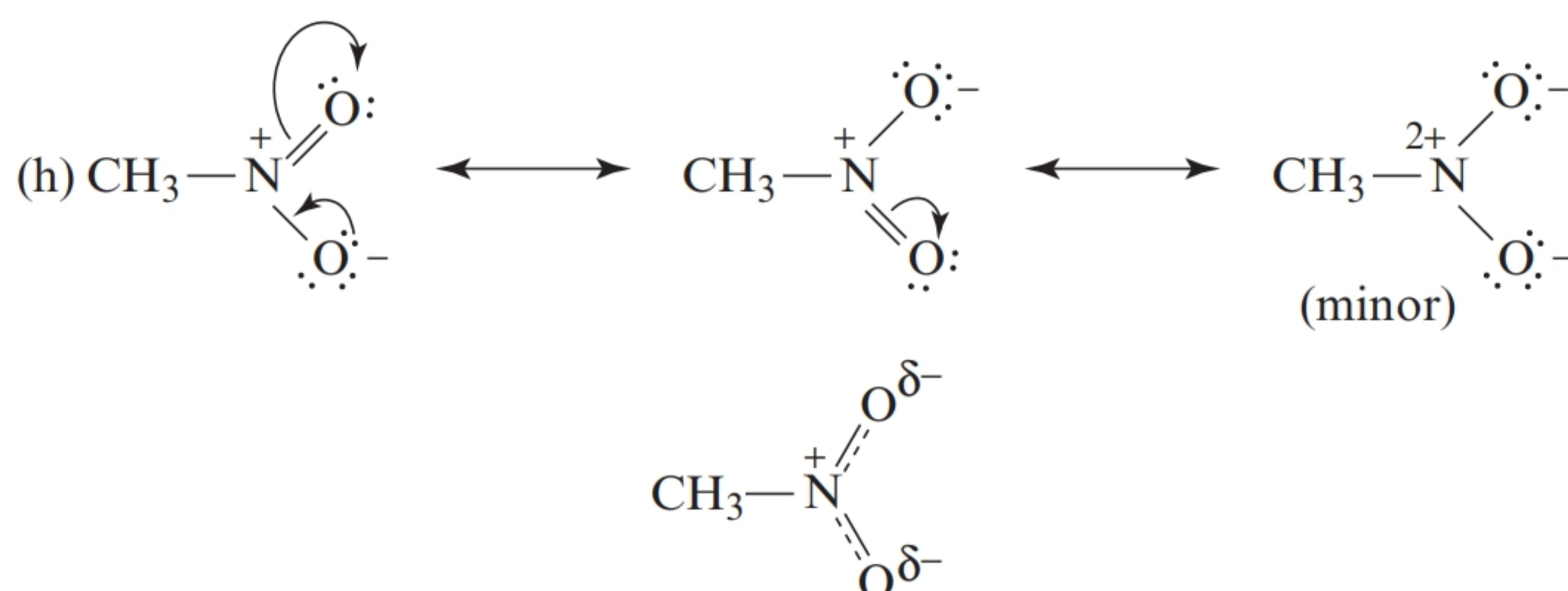
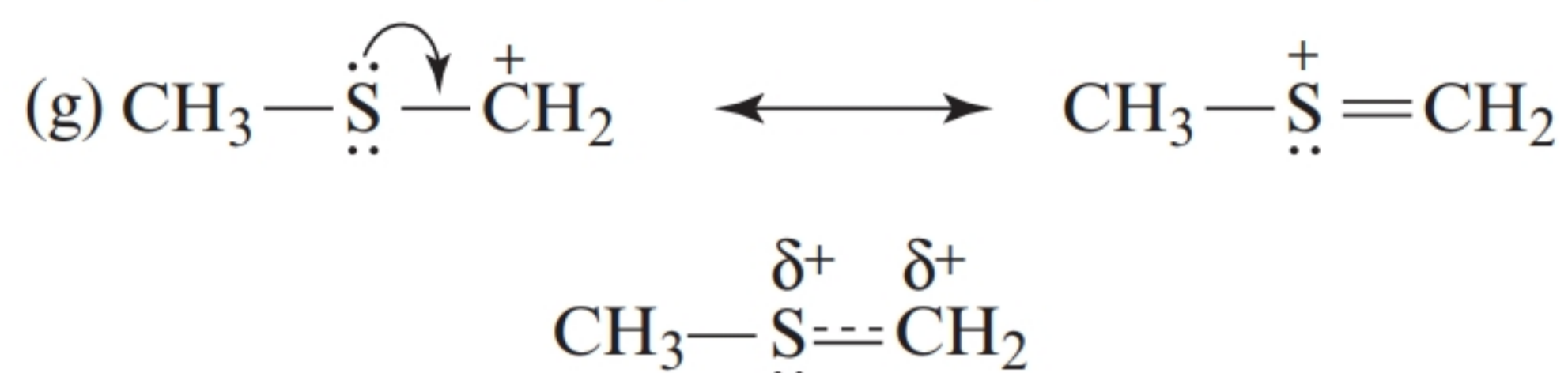
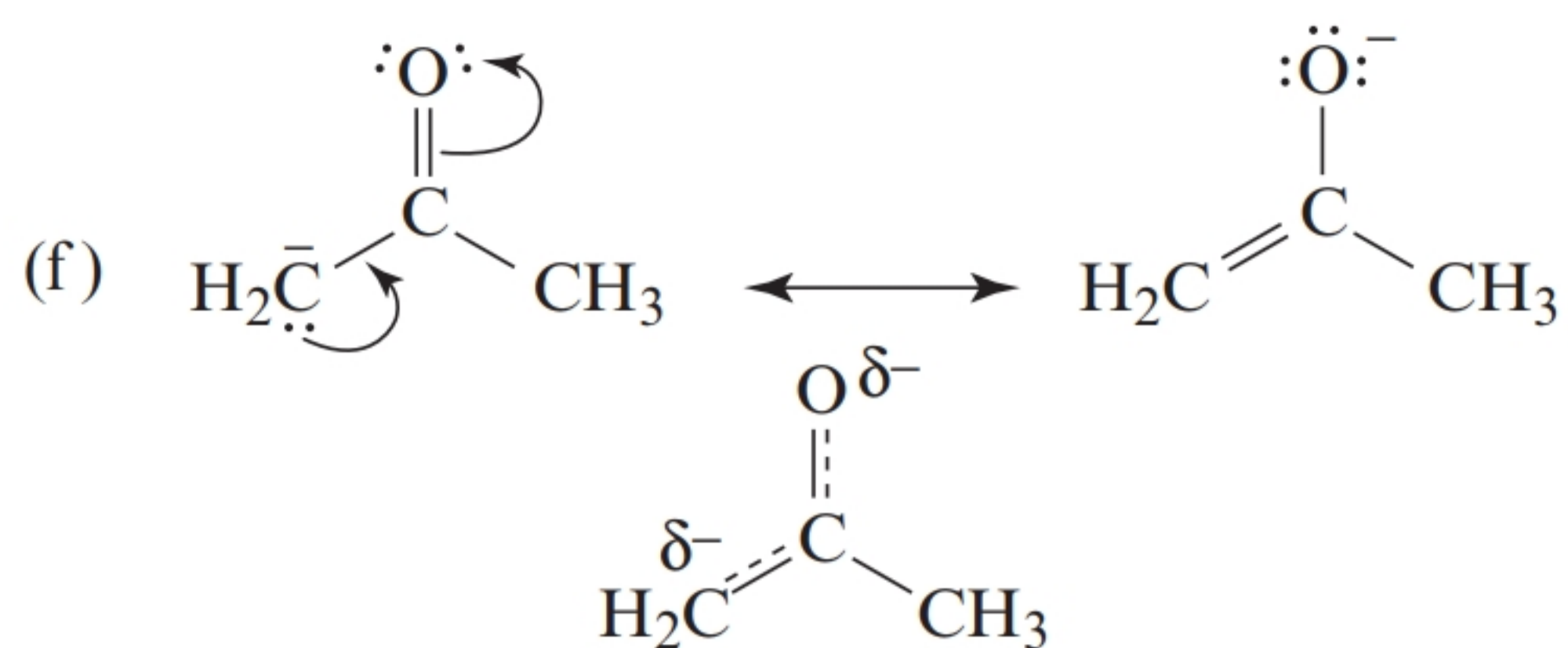


(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C—O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.

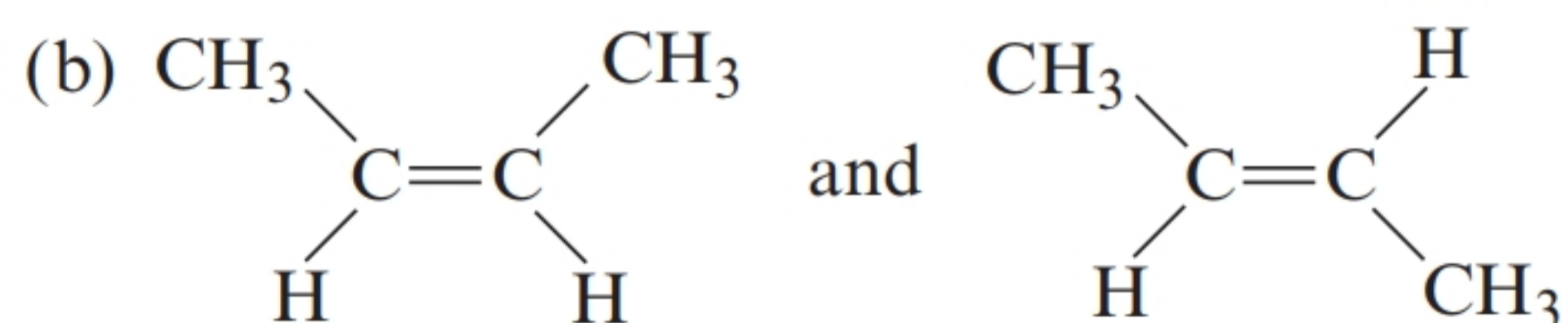


6 THE BASICS: BONDING AND MOLECULAR STRUCTURE

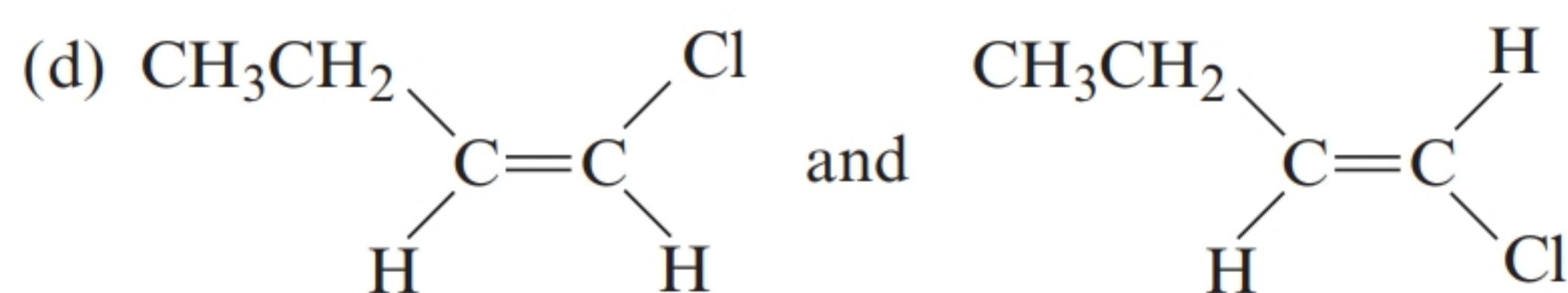




1.22 (a) Cis-trans isomers are not possible.



(c) Cis-trans isomers are not possible.



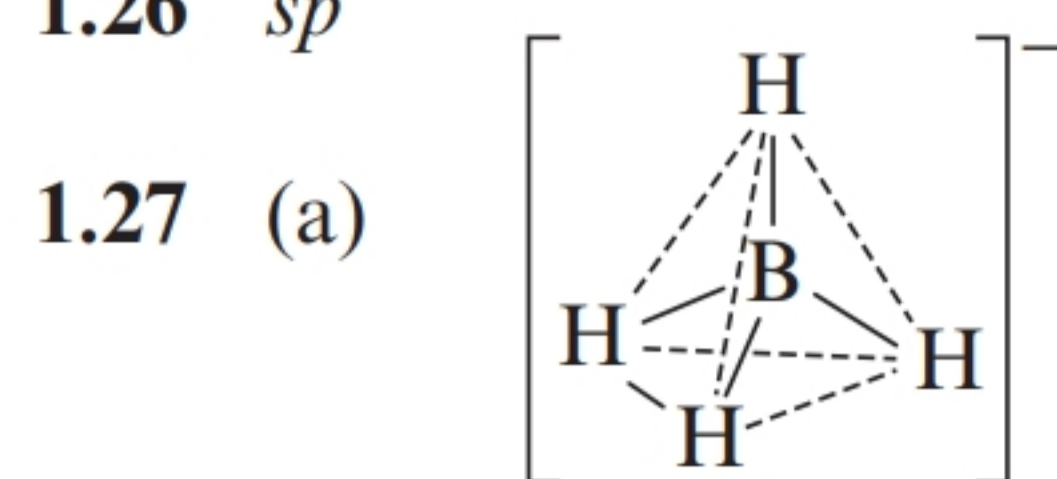
1.23 sp^3

1.24 sp^3

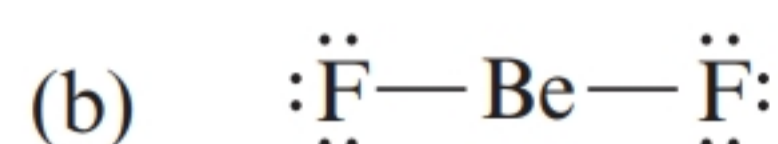
8 THE BASICS: BONDING AND MOLECULAR STRUCTURE

1.25 sp^2

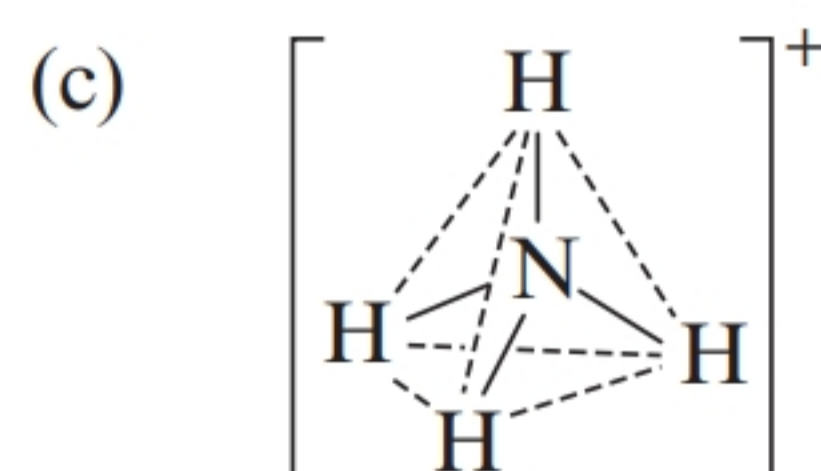
1.26 sp



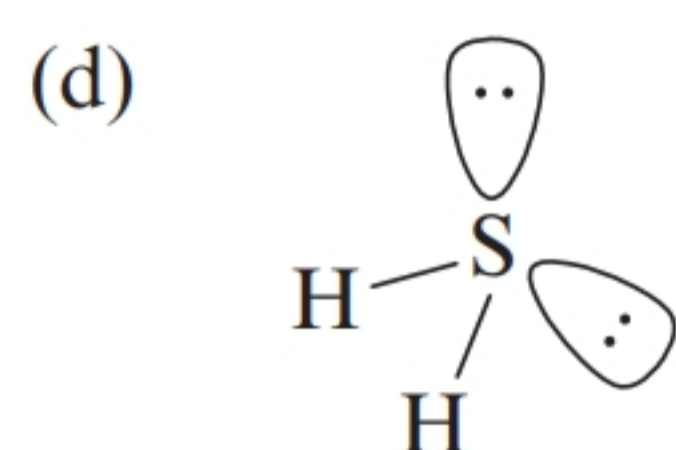
There are four bonding pairs.
The geometry is tetrahedral.



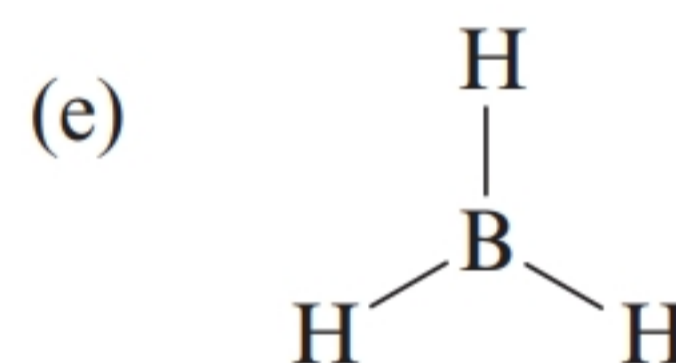
There are two bonding pairs about
the central atom. The geometry is linear.



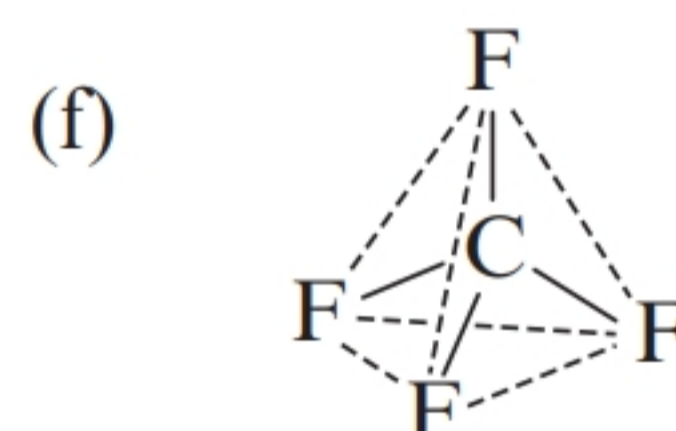
There are four bonding pairs.
The geometry is tetrahedral.



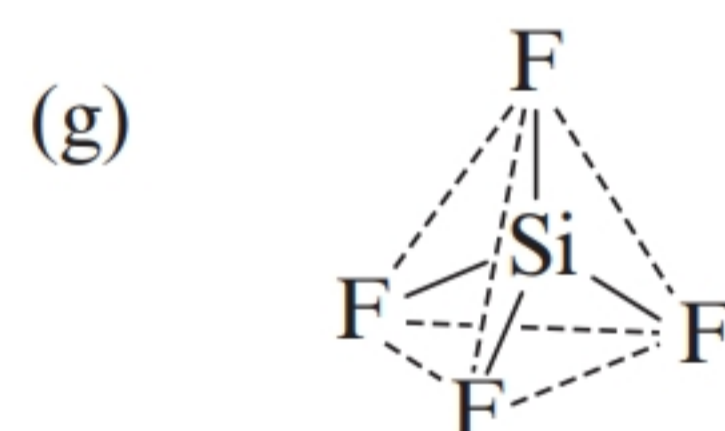
There are two bonding pairs and two nonbonding pairs.
The geometry is tetrahedral and the shape is angular.



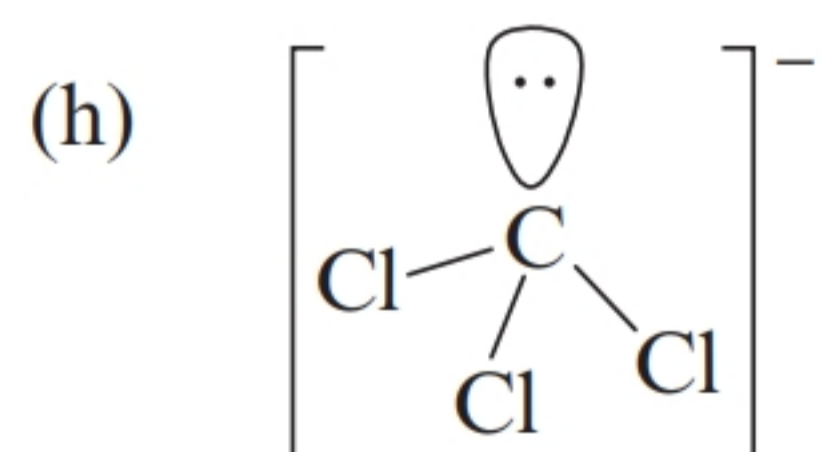
There are three bonding pairs. The geometry
is trigonal planar.



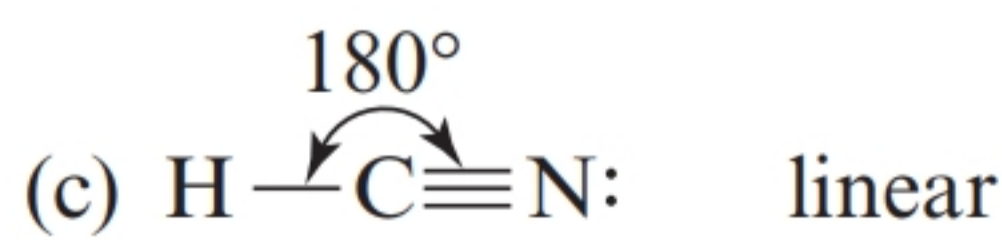
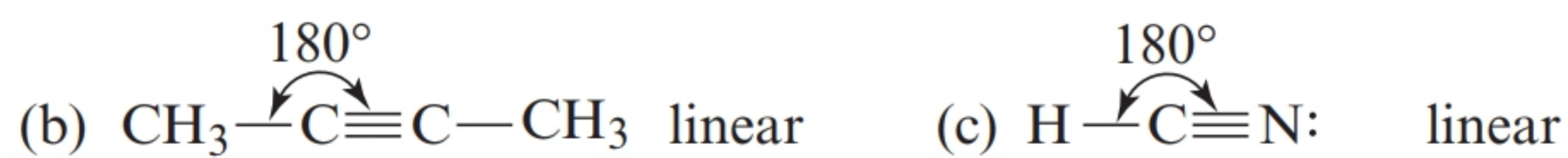
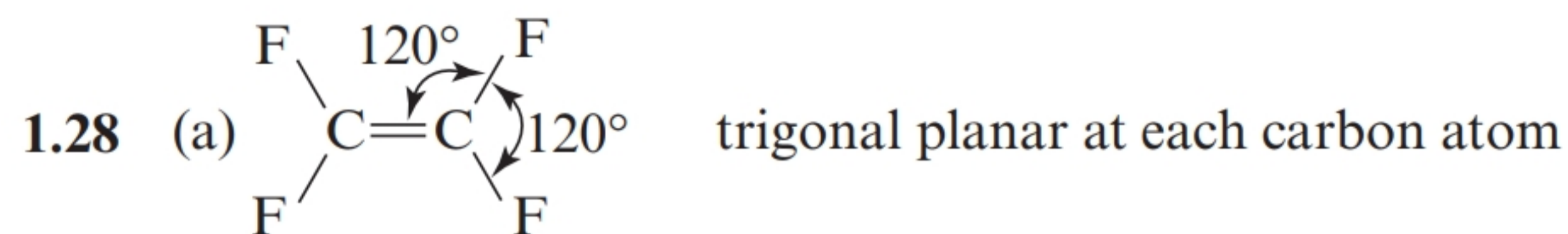
There are four bonding pairs around the central
atom. The geometry is tetrahedral.



There are four bonding pairs around the central atom.
The geometry is tetrahedral.

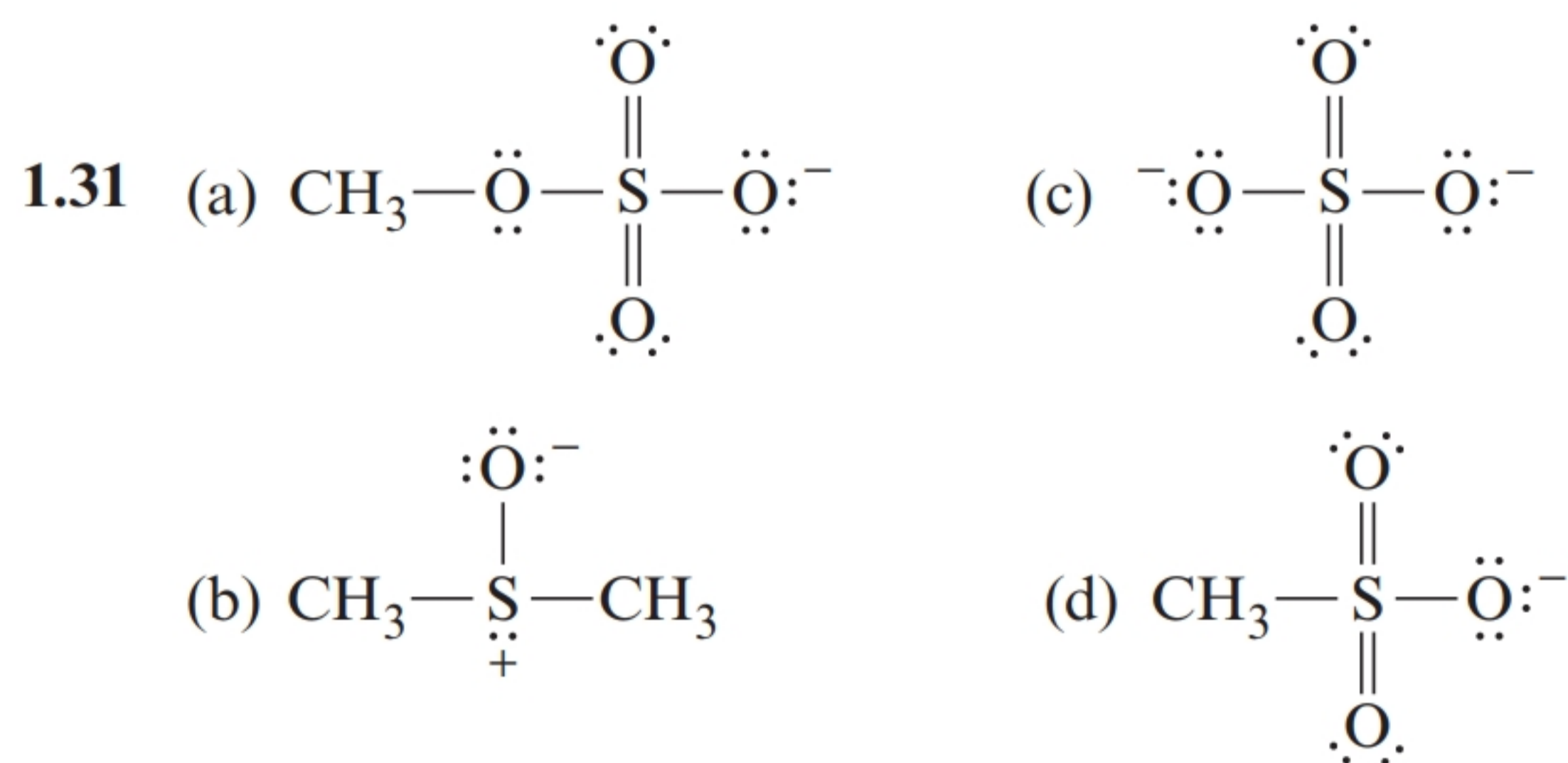
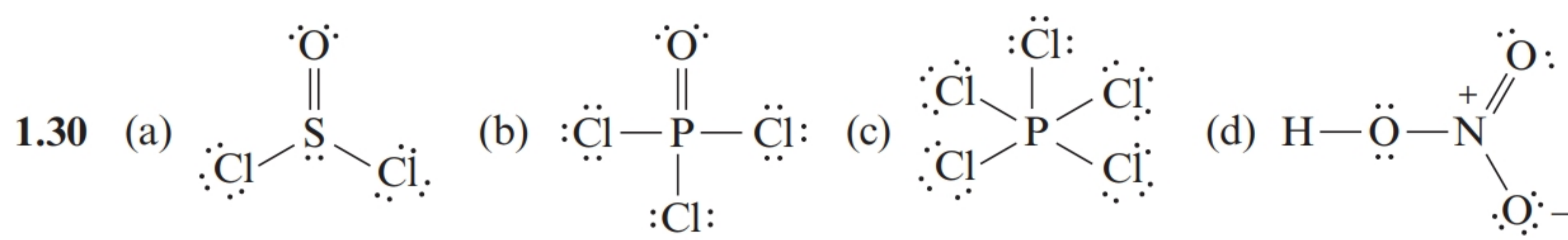


There are three bonding pairs and one nonbonding pair
around the central atom. The geometry is tetrahedral and
the shape is trigonal pyramidal.

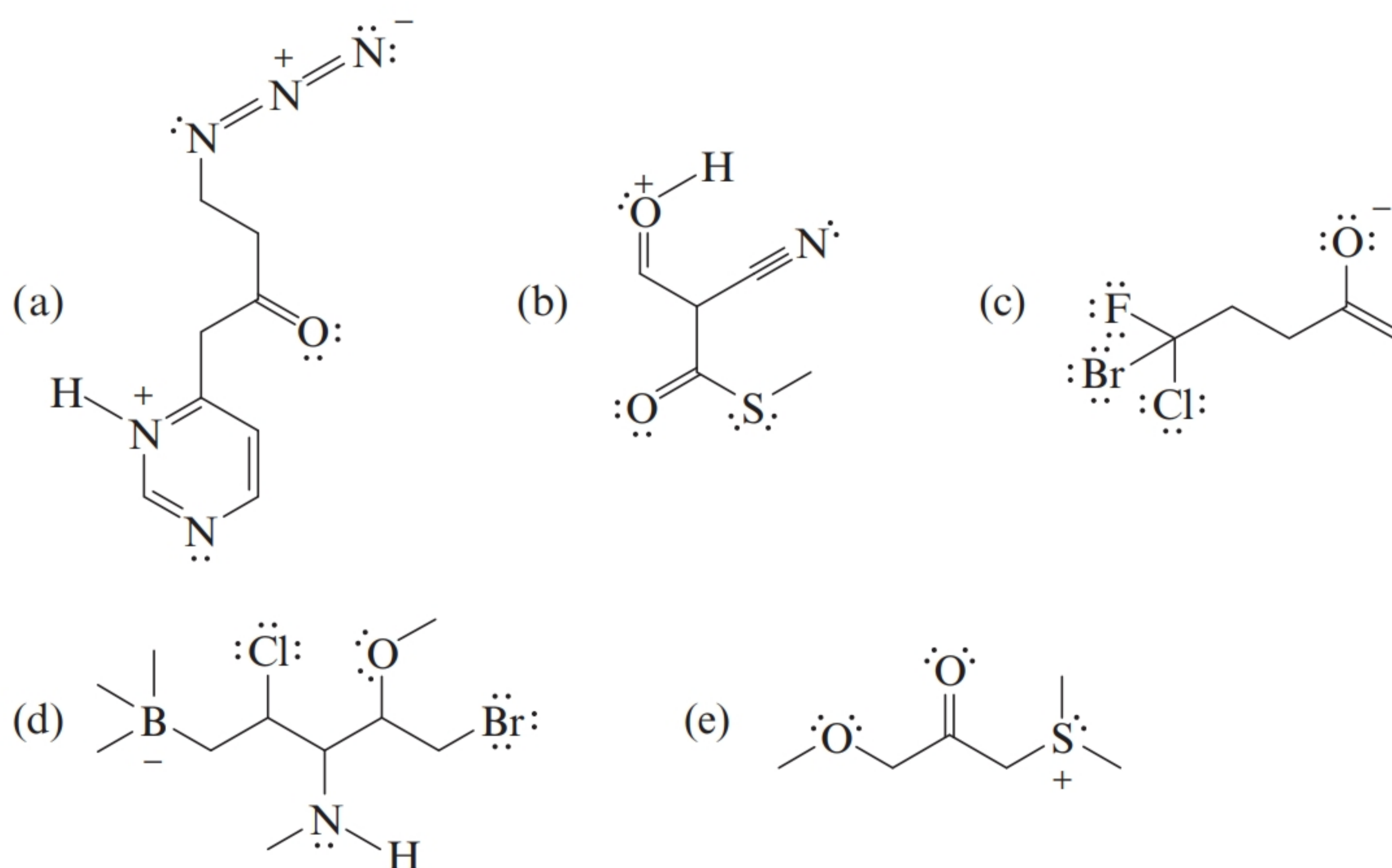


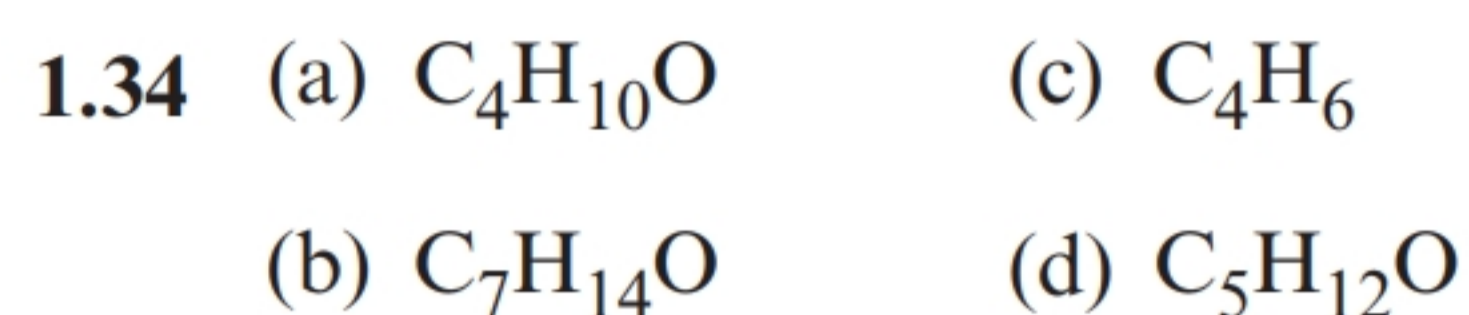
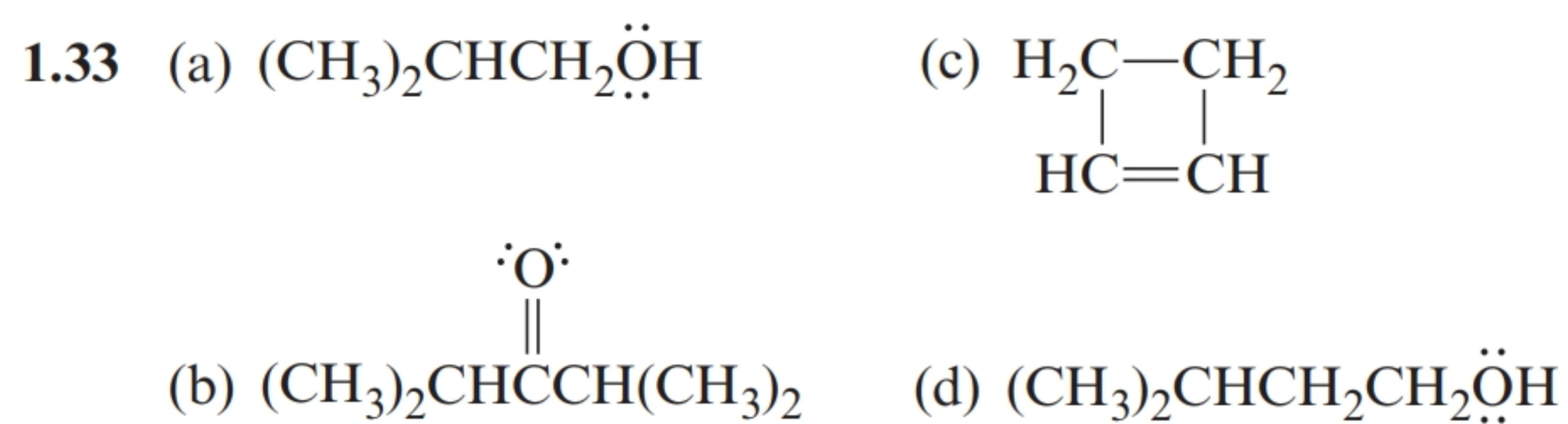
ProblemsElectron Configuration

- 1.29 (a) Na^+ has the electronic configuration, $1s^2 2s^2 2p^6$, of Ne.
 (b) Cl^- has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.
 (c) F^+ and (h) Br^+ do not have the electronic configuration of a noble gas.
 (d) H^- has the electronic configuration, $1s^2$, of He.
 (e) Ca^{2+} has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.
 (f) S^{2-} has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.
 (g) O^{2-} has the electronic configuration, $1s^2 2s^2 2p^6$, of Ne.

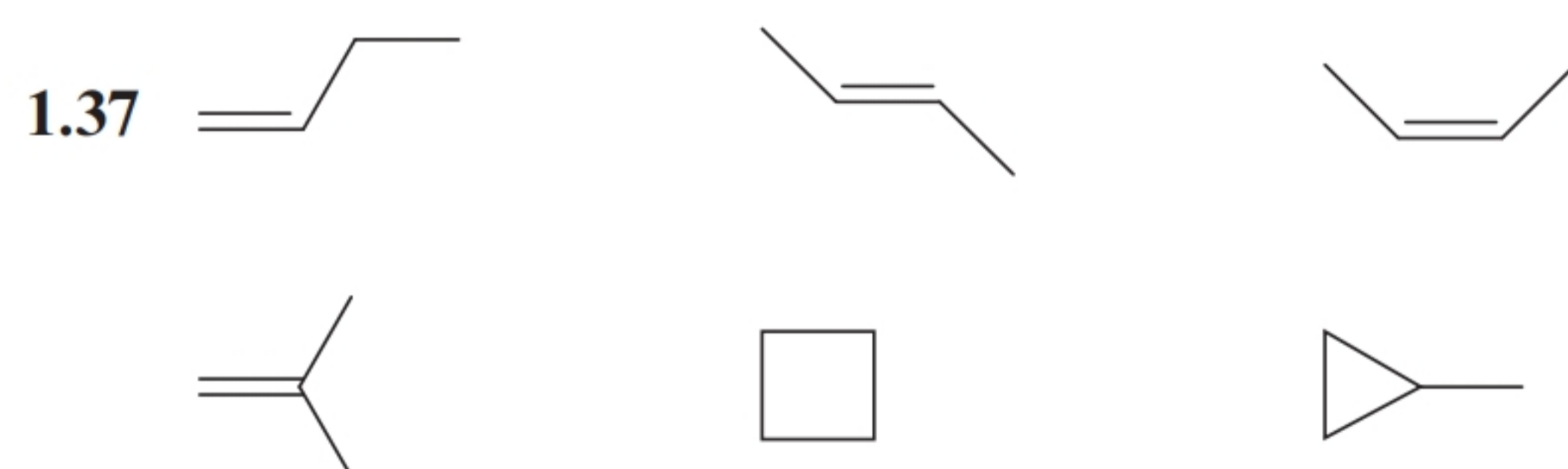
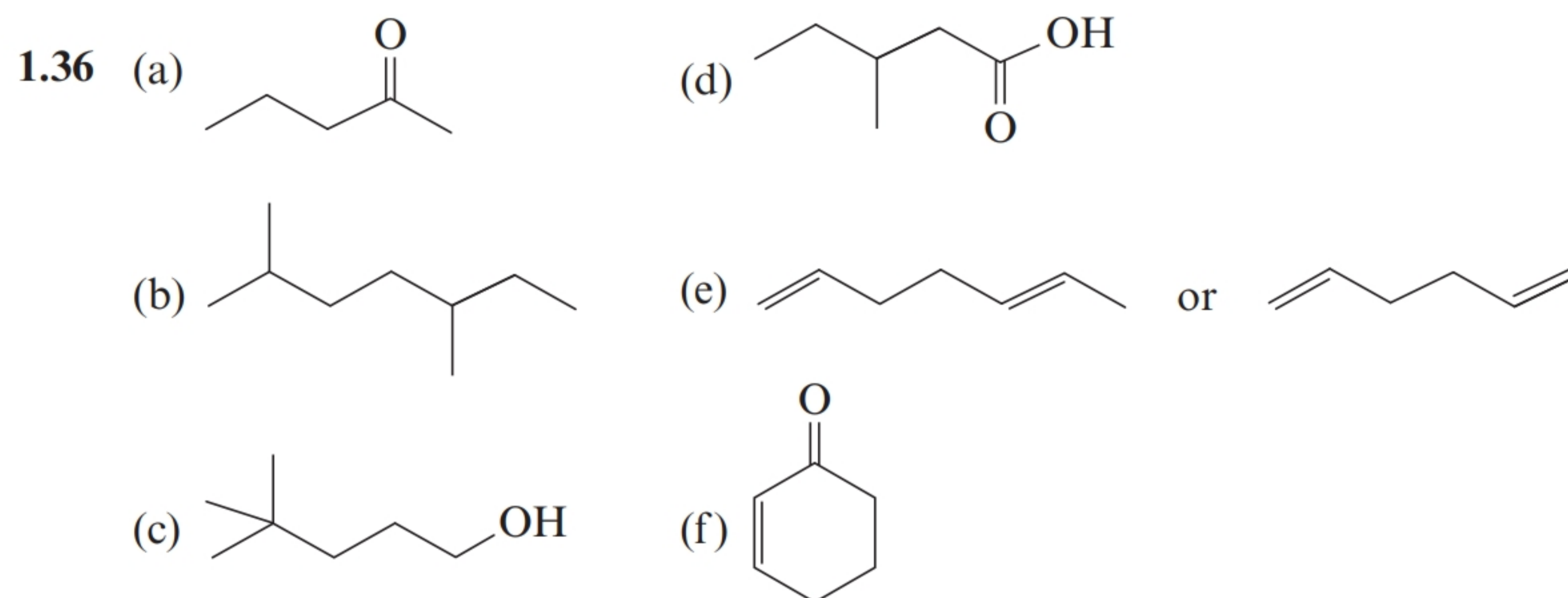
Lewis Structures

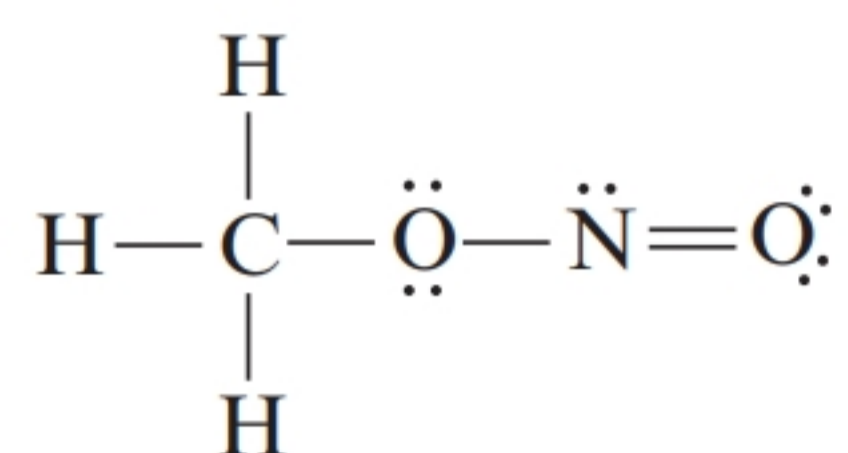
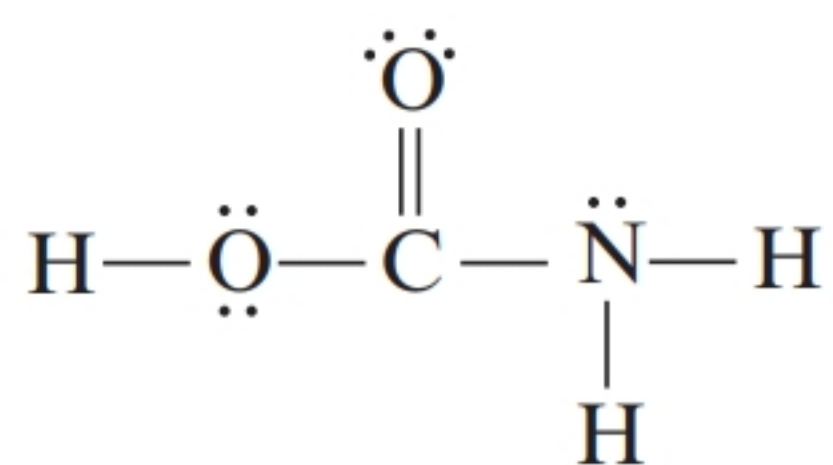
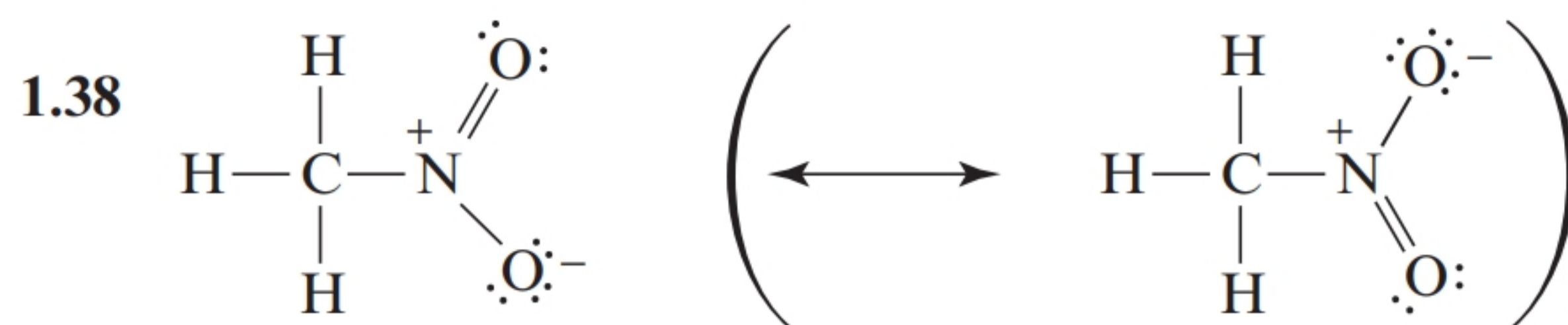
1.32



Structural Formulas and Isomerism

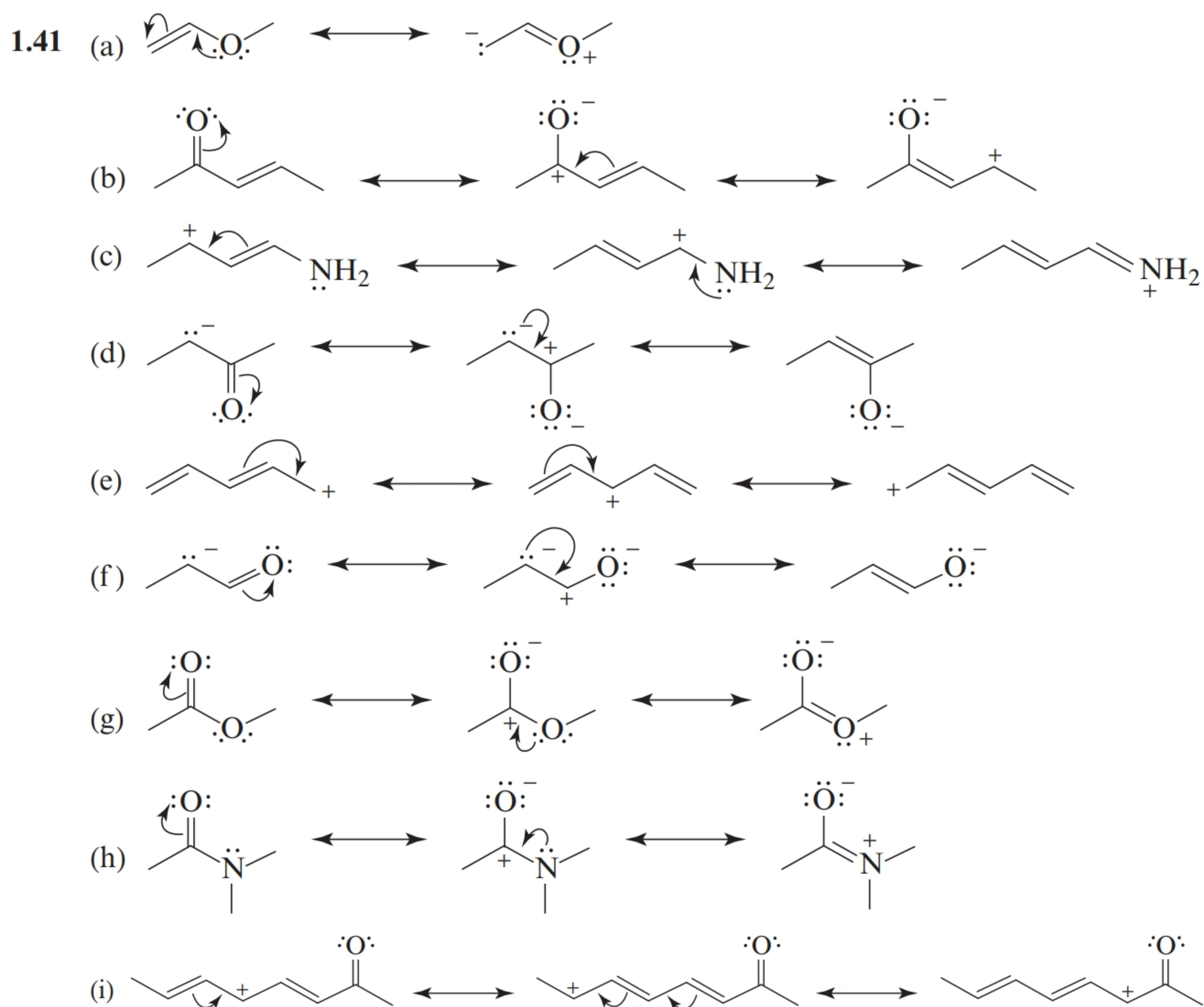
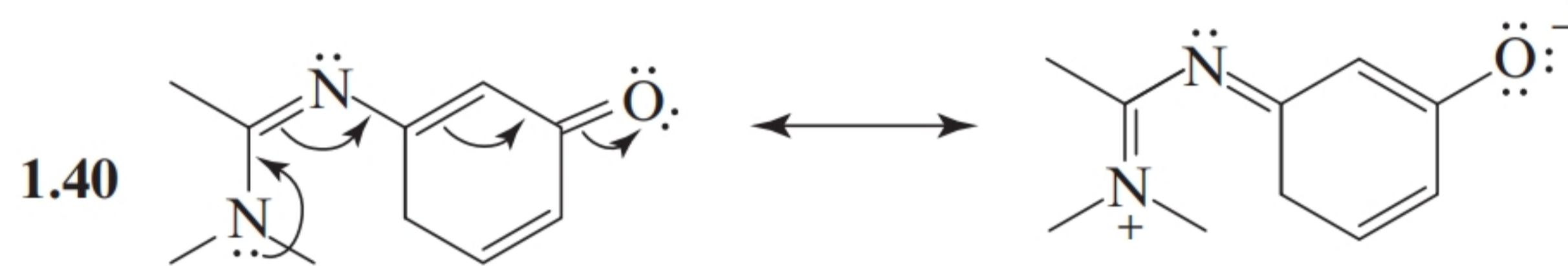
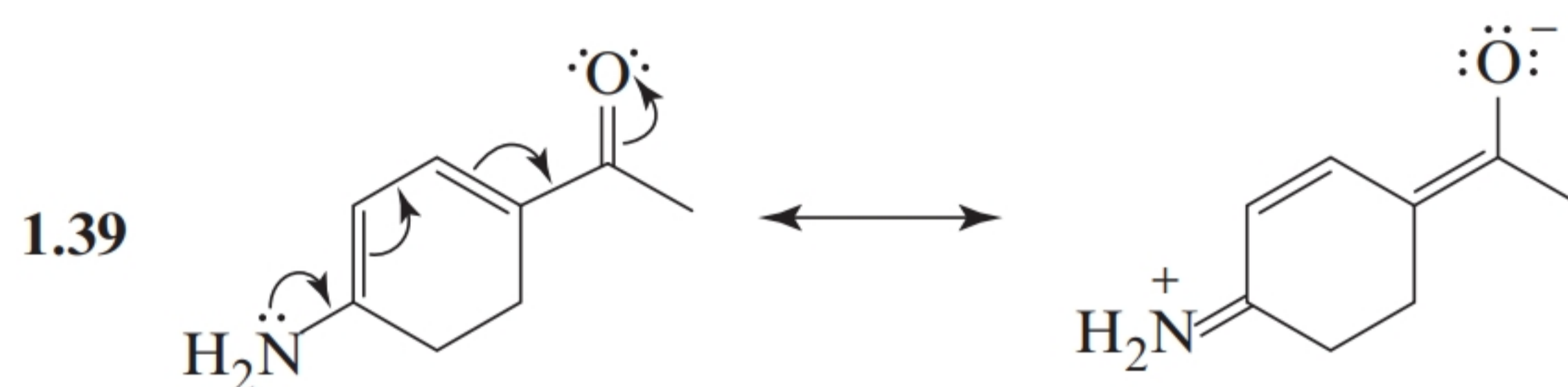
- 1.35 (a) Different compounds, not isomeric (i) Different compounds, not isomeric
 (b) Same compound (j) Same compound
 (c) Same compound (k) Constitutional isomers
 (d) Same compound (l) Different compounds, not isomeric
 (e) Same compound (m) Same compound
 (f) Constitutional isomers (n) Same compound
 (g) Different compounds, not isomeric (o) Same compound
 (h) Same compound (p) Constitutional isomers





(Other structures are possible.)

Resonance Structures



12 THE BASICS: BONDING AND MOLECULAR STRUCTURE

1.42 (a) While the structures differ in the position of their electrons, they also differ in the positions of their nuclei and thus *they are not resonance structures*. (In cyanic acid the hydrogen nucleus is bonded to oxygen; in isocyanic acid it is bonded to nitrogen.)

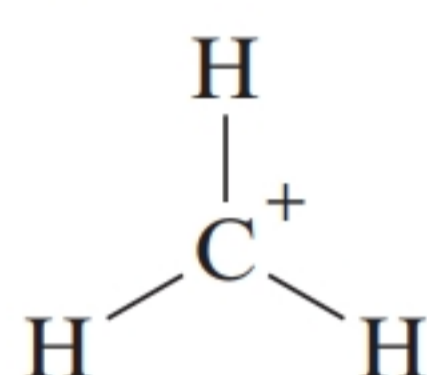
(b) The anion obtained from either acid is a resonance hybrid of the following structures: $^{-}\ddot{\text{O}}-\text{C}\equiv\text{N}:\longleftrightarrow\ddot{\text{O}}=\text{C}=\ddot{\text{N}}:^{-}$



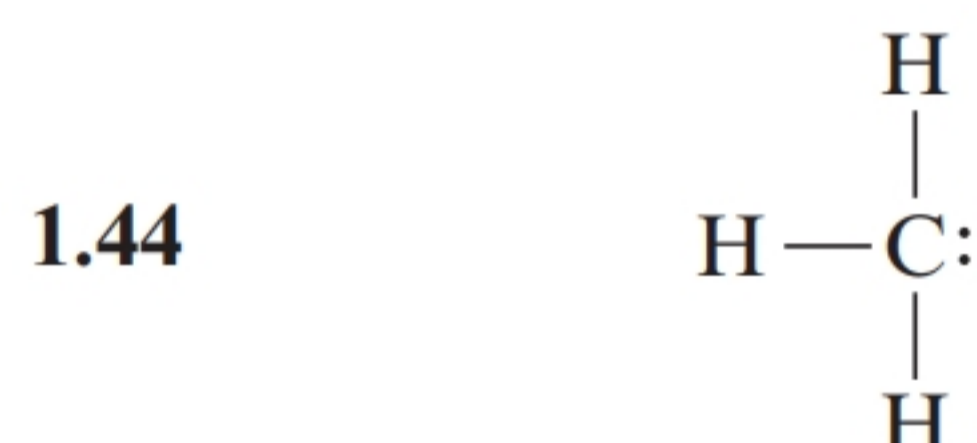
(a) A +1 charge. ($F = 4 - 6/2 - 2 = +1$)

(b) A +1 charge. (It is called a methyl cation.)

(c) Trigonal planar, that is,



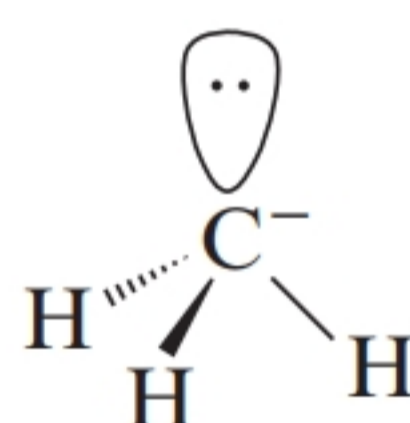
(d) sp^2



(a) A -1 charge. ($F = 4 - 6/2 - 2 = -1$)

(b) A -1 charge. (It is called a methyl anion.)

(c) Trigonal pyramidal, that is



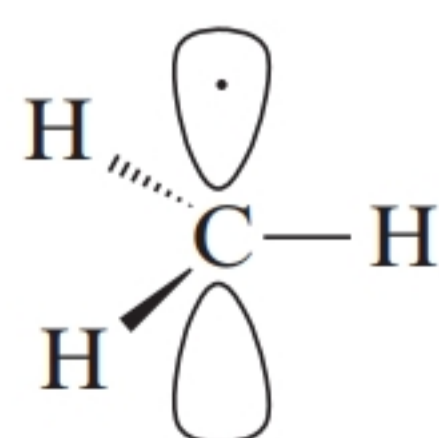
(d) sp^3

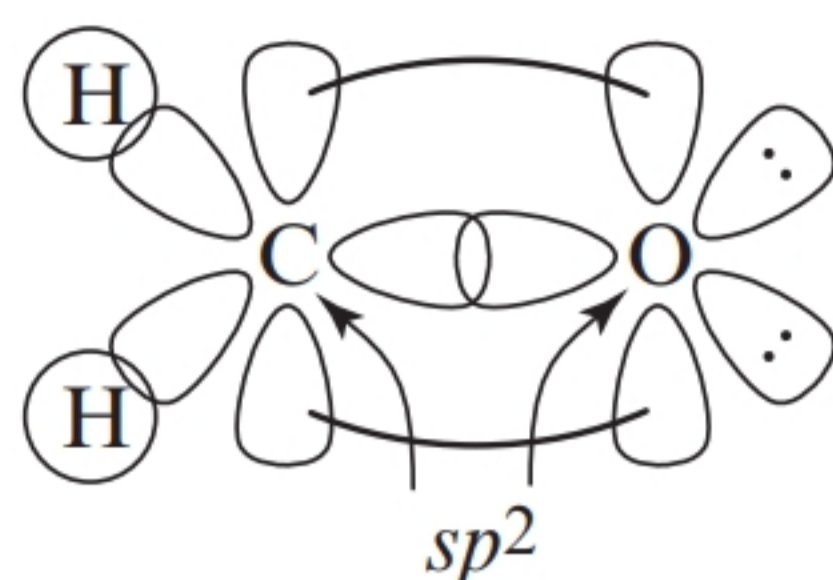
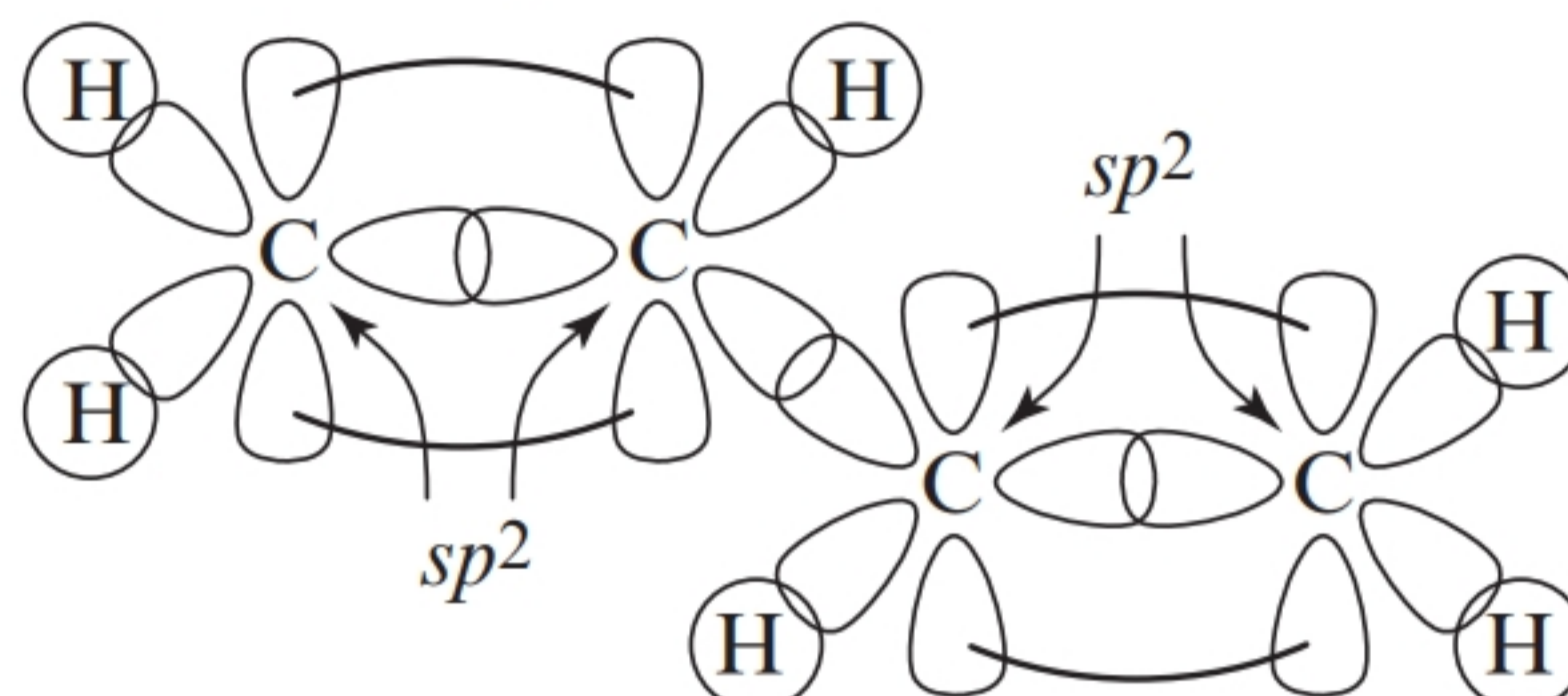
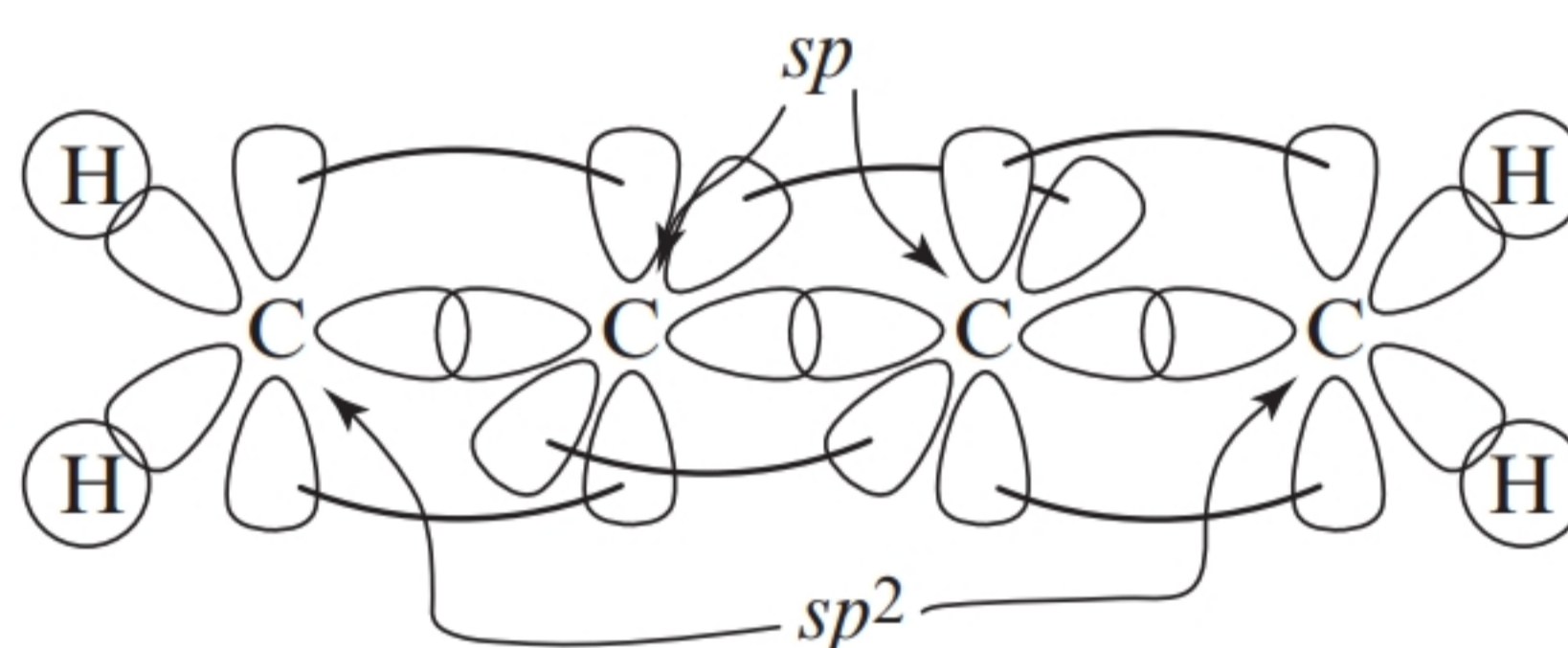


(a) No formal charge. ($F = 4 - 6/2 - 1 = 0$)

(b) No charge.

(c) sp^2 , that is,



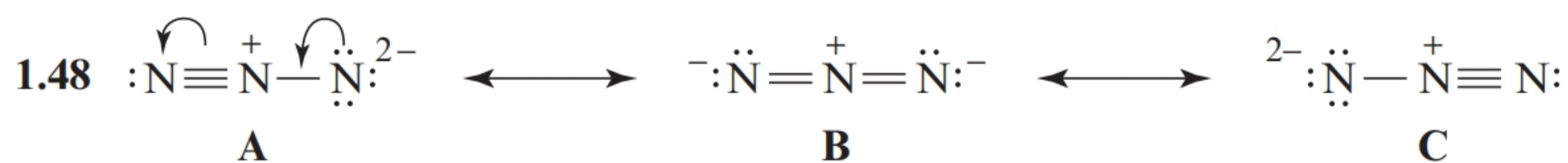
1.46 (a) H_2CO or CH_2O

 (b) $\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$

 (c) $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$


1.47 (a) and (b)

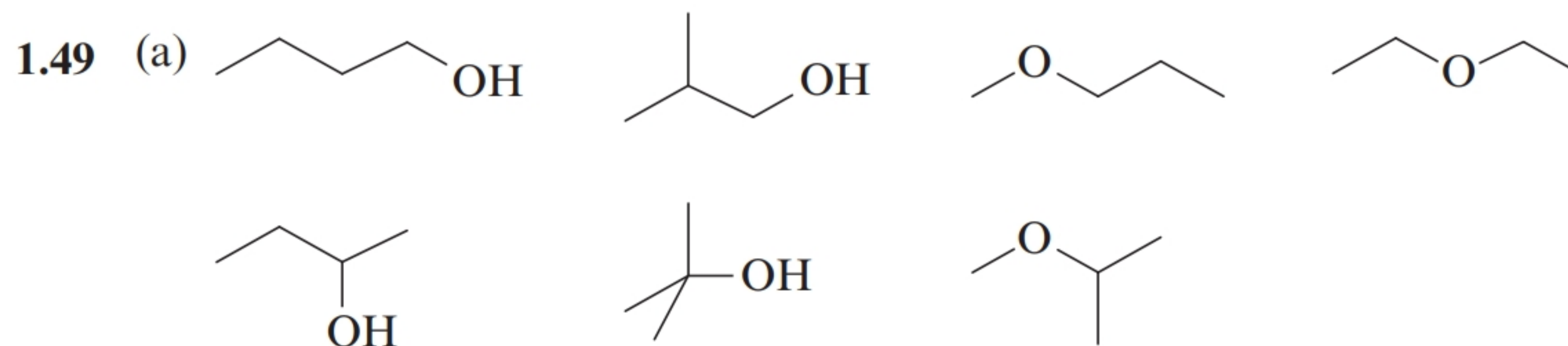


(c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.

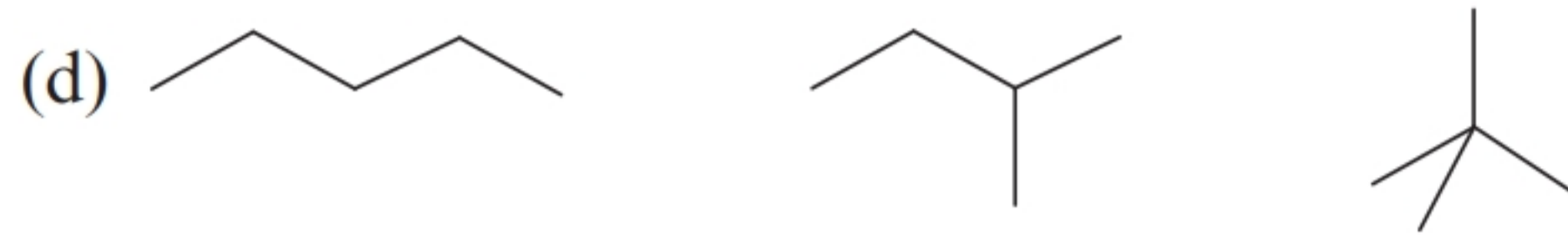
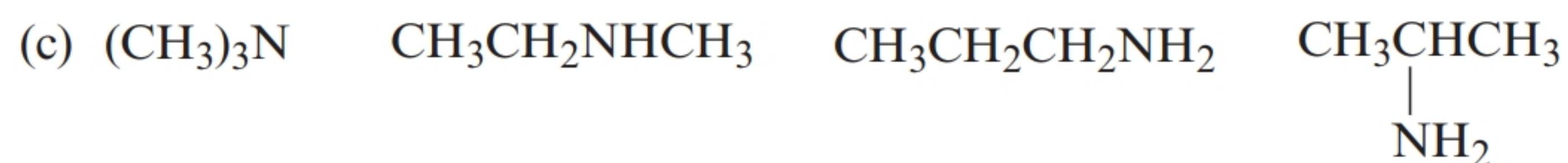
(d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.



Structures A and C are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.



14 THE BASICS: BONDING AND MOLECULAR STRUCTURE



1.50 (a) constitutional isomers

(b) the same

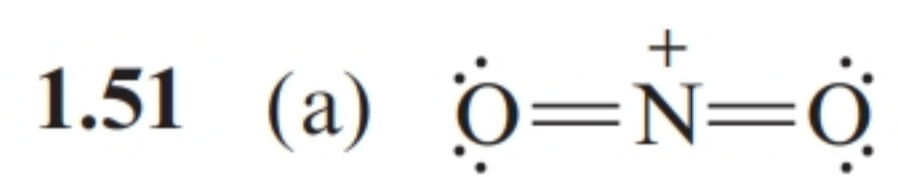
(c) resonance forms

(d) constitutional isomers

(e) resonance forms

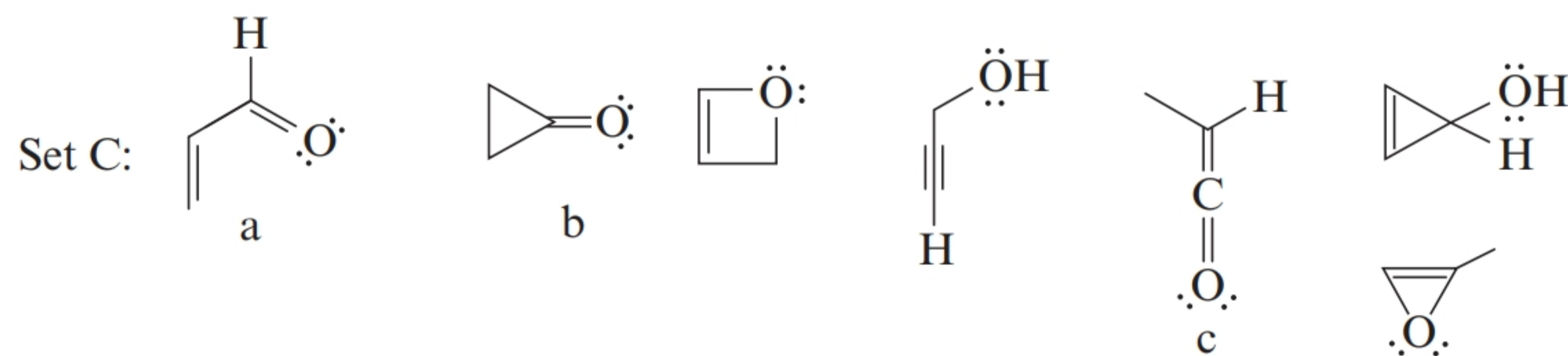
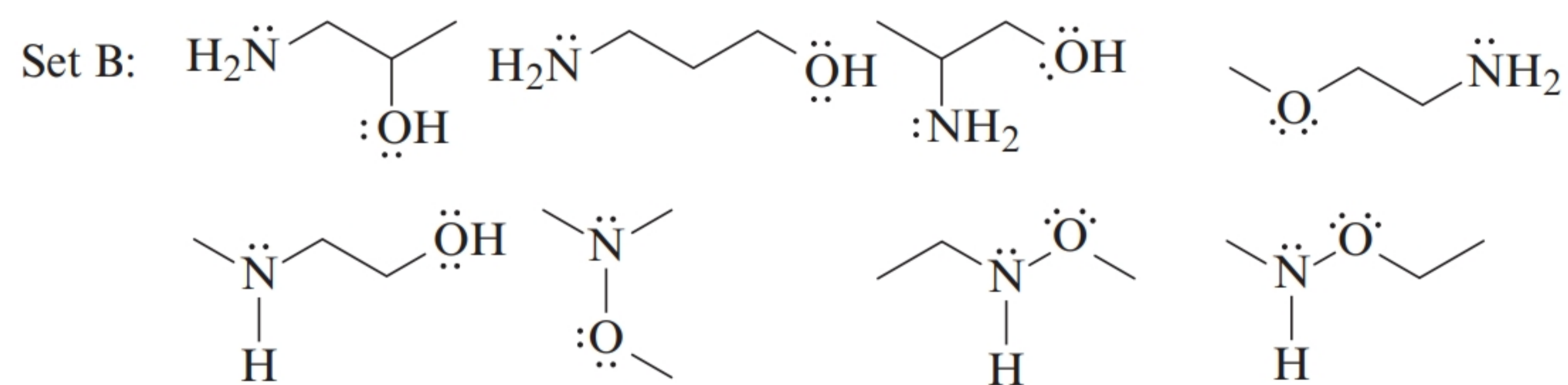
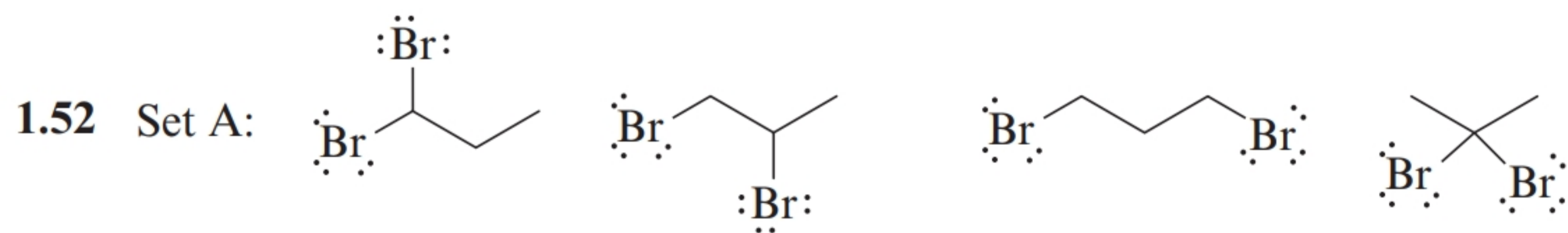
(f) the same

Challenge Problems

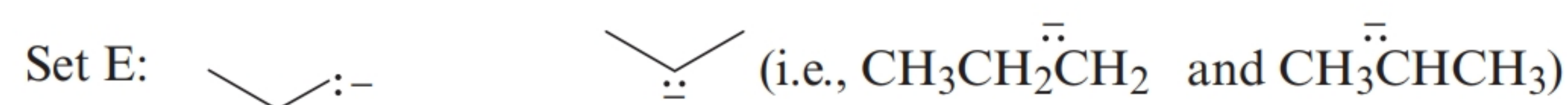
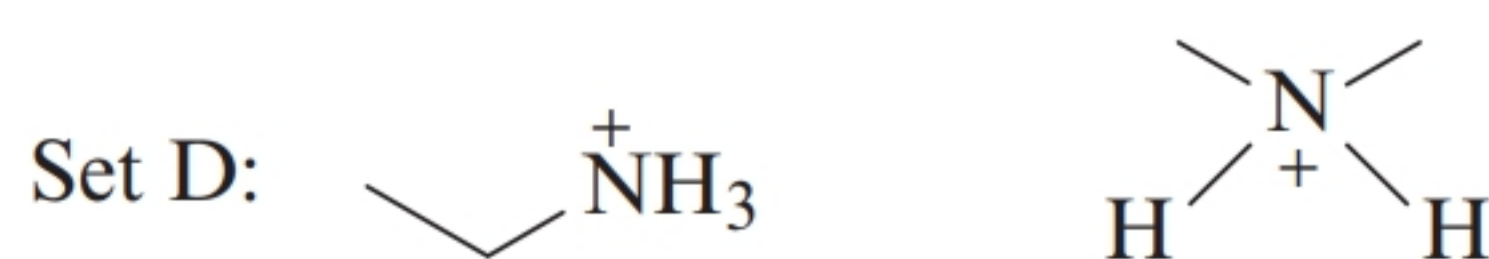


(b) Linear

(c) Carbon dioxide



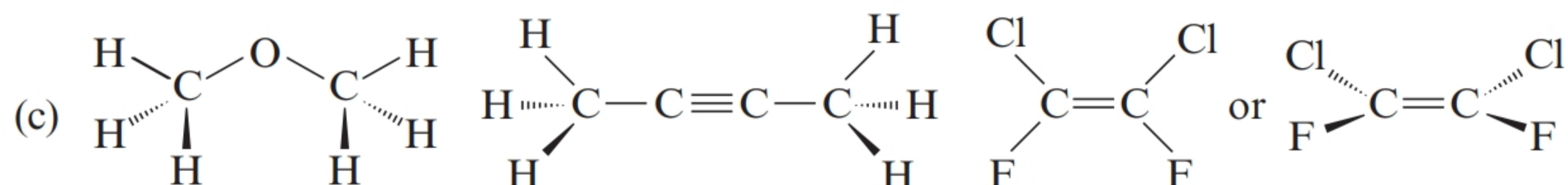
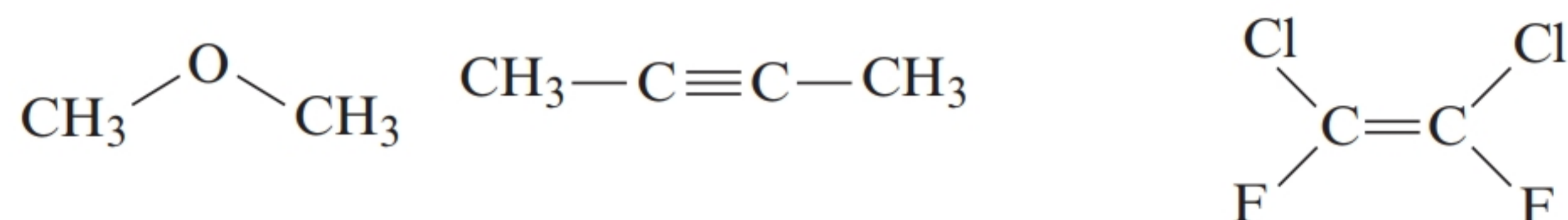
[and unstable enol forms of a, b, and c]



1.53 (a) No, a carbon atom in its ground state would have 2 electrons in the $1s$ orbital, 2 electrons in the $2s$ orbital, and only 2 unpaired electrons in the degenerate $2p_x, 2p_y,$ and $2p_z$ orbitals. So the two unpaired electrons can pair with only 2 hydrogen atoms with their one unpaired electron, respectively to form the compound CH_2 , which would be divalent and have 180 degree bond angles.

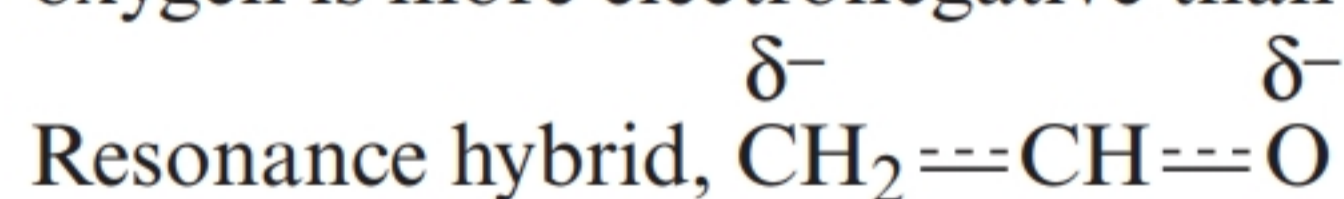
(b) In this case 4 unpaired electrons can combine with 4 hydrogen atoms to give CH_4 , the correct bonding for methane, a tetravalent compound. However, the tetrahedral geometry known to exist for methane would not result from bonding at the $2s$ and three $2p$ orbitals in the excited state. Hybridized sp^3 orbitals are required for tetrahedral geometry.

1.54 (a) Dimethyl ether Dimethylacetylene *cis*-1,2-Dichloro-1,2-difluoroethene



1.55 The large lobes centered above and below the boron atom represent the $2p$ orbital that was not involved in hybridization to form the three $2sp^2$ hybrid orbitals needed for the three boron-fluorine covalent bonds. This orbital is not a pure $2p$ atomic orbital, since it is not an isolated atomic p orbital but rather part of a molecular orbital. Some of the other lobes in this molecular orbital can be seen near each fluorine atom.

1.56 The two resonance forms for this anion are $^-\text{:CH}_2-\text{CH}=\ddot{\text{O}}:$ and $\text{CH}_2=\text{CH}-\ddot{\text{O}}:^-$. The MEP indicates that the resonance contributor where the negative charge on the anion is on the oxygen is more important, which is what we would predict based on the fact that oxygen is more electronegative than carbon.



QUIZ

1.1 Which of the following is a valid Lewis dot formula for the nitrite ion (NO_2^-)?

- (a) $^-\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}:$ (b) $:\ddot{\text{O}}=\ddot{\text{N}}-\ddot{\text{O}}:^-$ (c) $:\ddot{\text{O}}-\ddot{\text{N}}\equiv\ddot{\text{O}}:$ (d) Two of these
(e) None of the above

1.2 What is the hybridization state of the boron atom in BF_3 ?

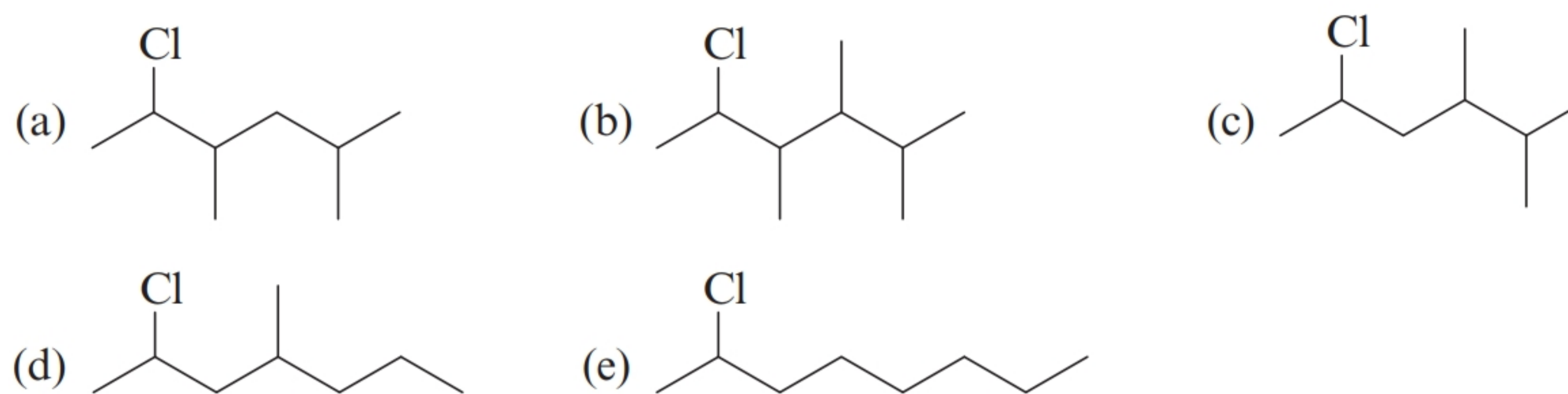
- (a) s (b) p (c) sp (d) sp^2 (e) sp^3

16 THE BASICS: BONDING AND MOLECULAR STRUCTURE

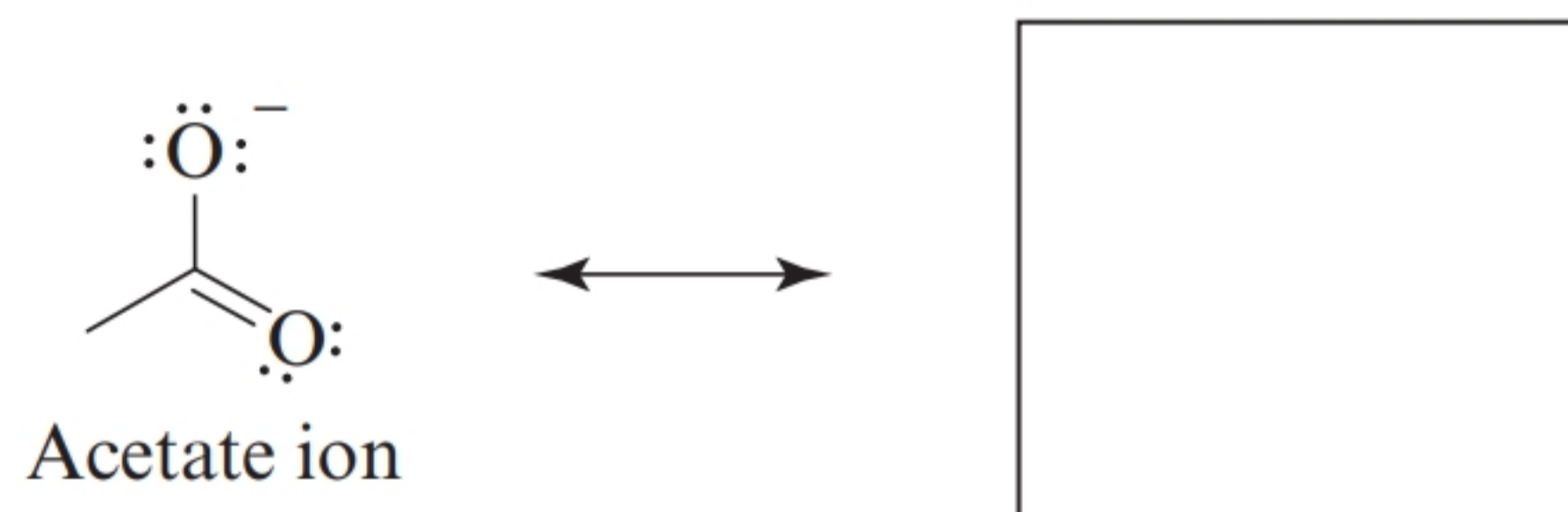
- 1.3 BF_3 reacts with NH_3 to produce a compound, $\text{F}-\text{B}-\text{N}-\text{H}$. The hybridization state of B is
- $$\begin{array}{c} \text{F} \quad \text{H} \\ | \quad | \\ \text{F}-\text{B}-\text{N}-\text{H} \\ | \quad | \\ \text{F} \quad \text{H} \end{array}$$
- (a) s (b) p (c) sp (d) sp^2 (e) sp^3

- 1.4 The formal charge on N in the compound given in Problem 1.3 is
- (a) -2 (b) -1 (c) 0 (d) $+1$ (e) $+2$

- 1.5 The correct bond-line formula of the compound whose condensed formula is $\text{CH}_3\text{CHClCH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ is



- 1.6 Write another resonance structure for the acetate ion.



- 1.7 In the boxes below write condensed structural formulas for constitutional isomers of $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$.

- 1.8 Write a three-dimensional formula for a constitutional isomer of compound A given below. Complete the partial structure shown.

