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PREFACE

It is our hope that in writing this *Study Guide and Solutions Manual* we will make the study of organic chemistry more meaningful and worthwhile. To be effective, a study guide should be more than just an answer book. What we present here was designed with that larger goal in mind.

The *Study Guide and Solutions Manual* contains detailed solutions to all the problems in the text. Learning how to solve a problem is, in our view, more important than merely knowing the correct answer. To that end we have included solutions sufficiently detailed to provide the student with the steps leading to the solution of each problem.

In addition, the Self-Test at the conclusion of each chapter is designed to test the student's mastery of the material. Both fill-in and multiple-choice questions have been included to truly test the student's understanding. Answers to the self-test questions may be found in Appendix A at the back of the book.

The completion of this guide was made possible through the time and talents of numerous people. Our thanks and appreciation also go to the many users of the third edition who provided us with helpful suggestions, comments, and corrections. We also wish to acknowledge the assistance and understanding of Kent Peterson, Terry Stanton, and Peggy Selle of McGraw-Hill. Many thanks also go to Linda Davoli for her skillful copyediting. Last, we thank our wives and families for their understanding of the long hours invested in this work.

Francis A. Carey
Robert C. Atkins

TO THE STUDENT

Before beginning the study of organic chemistry, a few words about "how to do it" are in order. You've probably heard that organic chemistry is difficult; there's no denying that. It need not be overwhelming, though, when approached with the right frame of mind and with sustained effort.

First of all you should realize that organic chemistry tends to "build" on itself. That is, once you have learned a reaction or concept, you will find it being used again and again later on. In this way it is quite different from general chemistry, which tends to be much more compartmentalized. In organic chemistry you will continually find previously learned material cropping up and being used to explain and to help you understand new topics. Often, for example, you will see the preparation of one class of compounds using reactions of other classes of compounds studied earlier in the year.

How to keep track of everything? It might be possible to memorize every bit of information presented to you, but you would still lack a fundamental understanding of the subject. It is far better to *generalize* as much as possible.

You will find that the early chapters of the text will emphasize concepts of *reaction theory*. These will be used, as the various classes of organic molecules are presented, to describe *mechanisms* of organic reactions. A relatively few fundamental mechanisms suffice to describe almost every reaction you will encounter. Once learned and understood, these mechanisms provide a valuable means of categorizing the reactions of organic molecules.

There will be numerous facts to learn in the course of the year, however. For example, chemical reagents necessary to carry out specific reactions must be learned. You might find a study aid known as *flash cards* helpful. These take many forms, but one idea is to use 3 × 5 index cards. As an example of how the cards might be used, consider the reduction of alkenes (compounds with carbon–carbon double bonds) to alkanes (compounds containing only carbon–carbon single bonds). The front of the card might look like this:

$$\boxed{\text{Alkenes} \xrightarrow{?} \text{alkanes}}$$

The reverse of the card would show the reagents necessary for this reaction:

$$\boxed{\text{H}_2\text{, Pt or Pd catalyst}}$$

The card can actually be studied in two ways. You may ask yourself: What reagents will convert alkenes into alkanes? Or, using the back of the card: What chemical reaction is carried out with hydrogen and a platinum or palladium catalyst? This is by no means the only way to use the cards—be creative! Just making up the cards will help you to study.

Although study aids such as flash cards will prove helpful, there is only one way to truly master the subject matter in organic chemistry—*do the problems!* The more you work, the more you will learn. Almost certainly the grade you receive will be a reflection of your ability to solve problems.

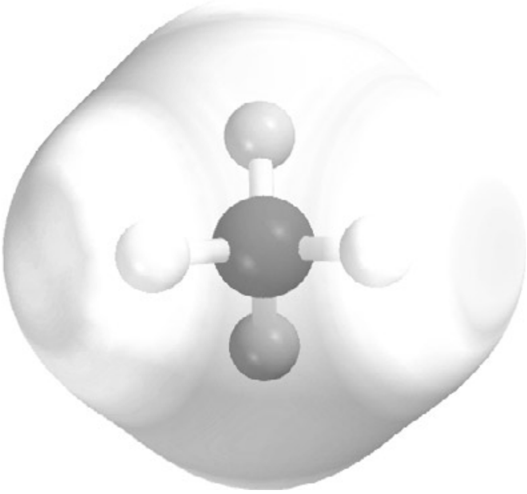
Don't just think over the problems, either; write them out as if you were handing them in to be graded. Also, be careful of how you use the *Study Guide*. The solutions contained in this book have been intended to provide explanations to help you understand the problem. Be sure to write out *your* solution to the problem first and only then look it up to see if you have done it correctly.

Students frequently feel that they understand the material but don't do as well as expected on tests. One way to overcome this is to "test" yourself. Each chapter in the *Study Guide* has a self-test at the end. Work the problems in these tests *without* looking up how to solve them in the text. You'll find it is much harder this way, but it is also a closer approximation to what will be expected of you when taking a test in class.

Success in organic chemistry depends on skills in analytical reasoning. Many of the problems you will be asked to solve require you to proceed through a series of logical steps to the correct answer. Most of the individual concepts of organic chemistry are fairly simple; stringing them together in a coherent fashion is where the challenge lies. By doing exercises conscientiously you should see a significant increase in your overall reasoning ability. Enhancement of their analytical powers is just one fringe benefit enjoyed by those students who attack the course rather than simply attend it.

Gaining a mastery of organic chemistry is hard work. We hope that the hints and suggestions outlined here will be helpful to you and that you will find your efforts rewarded with a knowledge and understanding of an important area of science.

Francis A. Carey
Robert C. Atkins



CHAPTER 1

CHEMICAL BONDING

SOLUTIONS TO TEXT PROBLEMS

1.1 The element carbon has atomic number 6, and so it has a total of six electrons. Two of these electrons are in the 1*s* level. The four electrons in the 2*s* and 2*p* levels (the valence shell) are the valence electrons. Carbon has four valence electrons.

1.2 Electron configurations of elements are derived by applying the following principles:

(*a*) The number of electrons in a neutral atom is equal to its atomic number Z.
(*b*) The maximum number of electrons in any orbital is 2.
(*c*) Electrons are added to orbitals in order of increasing energy, filling the 1*s* orbital before any electrons occupy the 2*s* level. The 2*s* orbital is filled before any of the 2*p* orbitals, and the 3*s* orbital is filled before any of the 3*p* orbitals.
(*d*) All the 2*p* orbitals ($2p_x$, $2p_y$, $2p_z$) are of equal energy, and each is singly occupied before any is doubly occupied. The same holds for the 3*p* orbitals.

With this as background, the electron configuration of the third-row elements is derived as follows [$2p^6 = 2p_x^2 2p_y^2 2p_z^2$]:

Na	(Z = 11)	$1s^22s^22p^63s^1$
Mg	(Z = 12)	$1s^22s^22p^63s^2$
Al	(Z = 13)	$1s^22s^22p^63s^23p_x^1$
Si	(Z = 14)	$1s^22s^22p^63s^23p_x^13p_y^1$
P	(Z = 15)	$1s^22s^22p^63s^23p_x^13p_y^13p_z^1$
S	(Z = 16)	$1s^22s^22p^63s^23p_x^23p_y^13p_z^1$
Cl	(Z = 17)	$1s^22s^22p^63s^23p_x^23p_y^23p_z^1$
Ar	(Z = 18)	$1s^22s^22p^63s^23p_x^23p_y^23p_z^2$

1.3 The electron configurations of the designated ions are:

	Ion	*Z*	Number of Electrons in Ion	Electron Configuration of Ion
(*b*)	He^+	2	1	$1s^1$
(*c*)	H^-	1	2	$1s^2$
(*d*)	O^-	8	9	$1s^22s^22p_x^{\,2}2p_y^{\,2}2p_z^{\,1}$
(*e*)	F^-	9	10	$1s^22s^22p^6$
(*f*)	Ca^{2+}	20	18	$1s^22s^22p^63s^23p^6$

Those with a noble gas configuration are H^-, F^-, and Ca^{2+}.

1.4 A positively charged ion is formed when an electron is removed from a neutral atom. The equation representing the ionization of carbon and the electron configurations of the neutral atom and the ion is:

$$\underset{1s^22s^22p_x^{\,1}2p_y^{\,1}}{\mathrm{C}} \longrightarrow \underset{1s^22s^22p_x^{\,1}}{\mathrm{C}^+} + e^-$$

A negatively charged carbon is formed when an electron is added to a carbon atom. The additional electron enters the $2p_z$ orbital.

$$\underset{1s^22s^22p_x^{\,1}2p_y^{\,1}}{\mathrm{C}} + e^- \longrightarrow \underset{1s^22s^22p_x^{\,1}p_y^{\,1}2p_z^{\,1}}{\mathrm{C}^-}$$

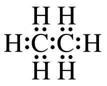
Neither C^+ nor C^- has a noble gas electron configuration.

1.5 Hydrogen has one valence electron, and fluorine has seven. The covalent bond in hydrogen fluoride arises by sharing the single electron of hydrogen with the unpaired electron of fluorine.

Combine $\mathrm{H}\cdot$ and $\cdot\ddot{\underset{\cdot\cdot}{\mathrm{F}}}\colon$ to give the Lewis structure for hydrogen fluoride $\mathrm{H}\colon\ddot{\underset{\cdot\cdot}{\mathrm{F}}}\colon$

1.6 We are told that C_2H_6 has a carbon–carbon bond.

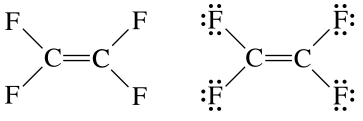
Thus, we combine two $\cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot$ and six $\mathrm{H}\cdot$ to write the Lewis structure of ethane



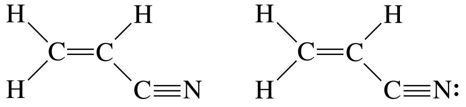
$$\begin{matrix} & \mathrm{H} & \mathrm{H} & \\ \mathrm{H}: & \mathrm{C} & : \mathrm{C} & :\mathrm{H} \\ & \mathrm{H} & \mathrm{H} & \end{matrix}$$

There are a total of 14 valence electrons distributed as shown. Each carbon is surrounded by eight electrons.

1.7 (*b*) Each carbon contributes four valence electrons, and each fluorine contributes seven. Thus, C_2F_4 has 36 valence electrons. The octet rule is satisfied for carbon only if the two carbons are attached by a double bond and there are two fluorines on each carbon. The pattern of connections shown (below left) accounts for 12 electrons. The remaining 24 electrons are divided equally (six each) among the four fluorines. The complete Lewis structure is shown at right below.



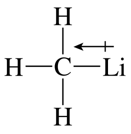
(*c*) Since the problem states that the atoms in C_3H_3N are connected in the order CCCN and all hydrogens are bonded to carbon, the order of attachments can only be as shown (below left) so as to have four bonds to each carbon. Three carbons contribute 12 valence electrons, three hydrogens contribute 3, and nitrogen contributes 5, for a total of 20 valence electrons. The nine bonds indicated in the partial structure account for 18 electrons. Since the octet rule is satisfied for carbon, add the remaining two electrons as an unshared pair on nitrogen (below right).



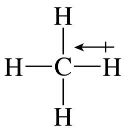
1.8 The degree of positive or negative character at carbon depends on the difference in electronegativity between the carbon and the atoms to which it is attached. From Table 1.2, we find the electronegativity values for the atoms contained in the molecules given in the problem are:

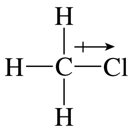
Li	1.0
H	2.1
C	**2.5**
Cl	3.0

Thus, carbon is more electronegative than hydrogen and lithium, but less electronegative than chlorine. When bonded to carbon, hydrogen and lithium bear a partial positive charge, and carbon bears a partial negative charge. Conversely, when chlorine is bonded to carbon, it bears a partial negative charge, and carbon becomes partially positive. In this group of compounds, lithium is the least electronegative element, chlorine the most electronegative.



Methyllithium; most negative character at carbon

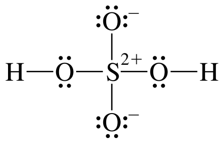




Chloromethane; most positive character at carbon

1.9 (*b*) The formal charges in sulfuric acid are calculated as follows:

	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2) = 1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4) + 4 = 6$	0
Oxygen:	6	$\frac{1}{2}(2) + 6 = 7$	-1
Sulfur:	6	$\frac{1}{2}(8) + 0 = 4$	$+2$

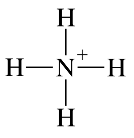


(*c*) The formal charges in nitrous acid are calculated as follows:

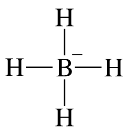
	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2) = 1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4) + 4 = 6$	0
Oxygen:	6	$\frac{1}{2}(4) + 4 = 6$	0
Nitrogen:	5	$\frac{1}{2}(6) + 2 = 5$	0

$$H-\underset{\cdot\cdot}{\ddot{O}}-\ddot{N}=\ddot{O}\colon$$

1.10 The electron counts of nitrogen in ammonium ion and boron in borohydride ion are both 4 (one half of 8 electrons in covalent bonds).



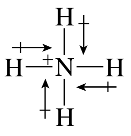
Ammonium ion

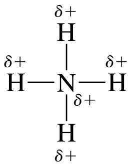


Borohydride ion

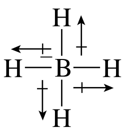
Since a neutral nitrogen has 5 electrons in its valence shell, an electron count of 4 gives it a formal charge of $+1$. A neutral boron has 3 valence electrons, and so an electron count of 4 in borohydride ion corresponds to a formal charge of -1.

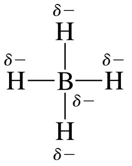
1.11 As shown in the text in Table 1.2, nitrogen is more electronegative than hydrogen and will draw the electrons in N—H bonds toward itself. Nitrogen with a formal charge of $+1$ is even more electronegative than a neutral nitrogen.



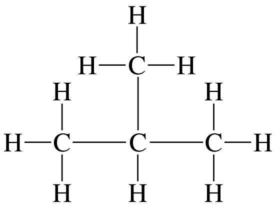


Boron (electronegativity = 2.0) is, on the other hand, slightly less electronegative than hydrogen (electronegativity = 2.1). Boron with a formal charge of -1 is less electronegative than a neutral boron. The electron density in the B—H bonds of BH_4^- is therefore drawn toward hydrogen and away from boron.



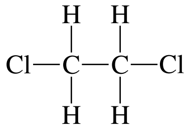


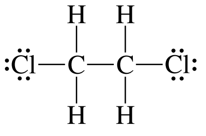
1.12 (*b*) The compound $(CH_3)_3CH$ has a central carbon to which are attached three CH_3 groups and a hydrogen.



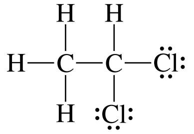
Four carbons and 10 hydrogens contribute 26 valence electrons. The structure shown has 13 covalent bonds, and so all the valence electrons are accounted for. The molecule has no unshared electron pairs.

(*c*) The number of valence electrons in $ClCH_2CH_2Cl$ is 26 (2Cl = 14; 4H = 4; 2C = 8). The constitution at the left below shows seven covalent bonds accounting for 14 electrons. The remaining 12 electrons are divided equally between the two chlorines as unshared electron pairs. The octet rule is satisfied for both carbon and chlorine in the structure at the right below.

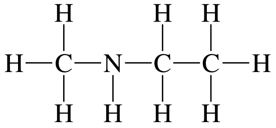


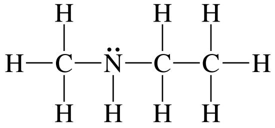


(*d*) This compound has the same molecular formula as the compound in part (*c*), but a different structure. It, too, has 26 valence electrons, and again only chlorine has unshared pairs.

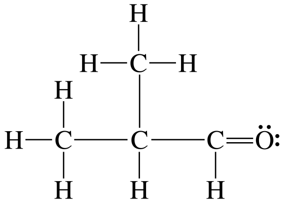


(*e*) The constitution of $CH_3NHCH_2CH_3$ is shown (below left). There are 26 valence electrons, and 24 of them are accounted for by the covalent bonds in the structural formula. The remaining two electrons complete the octet of nitrogen as an unshared pair (below right).

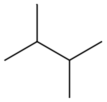




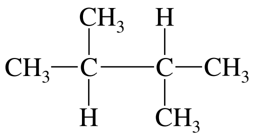
(*f*) Oxygen has two unshared pairs in $(CH_3)_2CHCH{=}O$.



1.13 (*b*) This compound has a four-carbon chain to which are appended two other carbons.

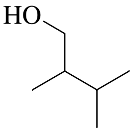


is equivalent to



which may be rewritten as $(CH_3)_2CHCH(CH_3)_2$

(*c*) The carbon skeleton is the same as that of the compound in part (*b*), but one of the terminal carbons bears an OH group in place of one of its hydrogens.



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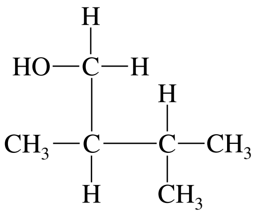
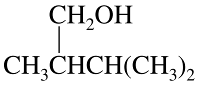
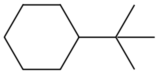


which may be rewritten as

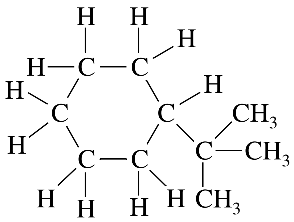


$$CH_3\overset{CH_2OH}{C}HCH(CH_3)_2$$

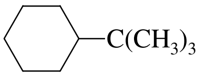
(*d*) The compound is a six-membered ring that bears a —$C(CH_3)_3$ substituent.



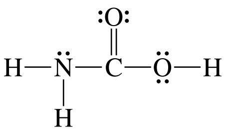
is equivalent to



which may be rewritten as



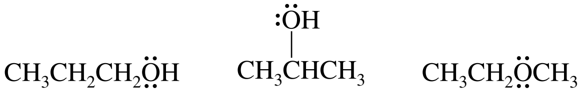
1.14 The problem specifies that nitrogen and both oxygens of carbamic acid are bonded to carbon and one of the carbon–oxygen bonds is a double bond. Since a neutral carbon is associated with four bonds, a neutral nitrogen three (plus one unshared electron pair), and a neutral oxygen two (plus two unshared electron pairs), this gives the Lewis structure shown.



$\mathrm{H{-}\ddot{N}H{-}C({=}\ddot{O}){-}\ddot{O}{-}H}$

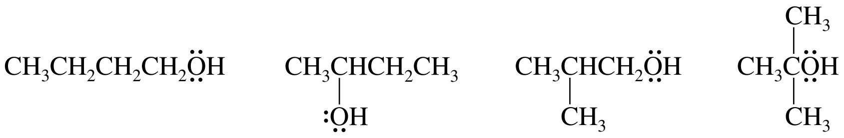
Carbamic acid

1.15 (*b*) There are three constitutional isomers of C_3H_8O:



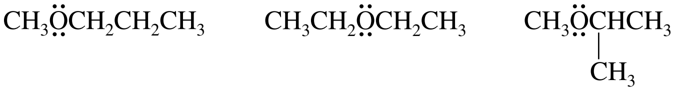
$\mathrm{CH_3CH_2CH_2\ddot{O}H}$ $\mathrm{CH_3CH(\ddot{O}H)CH_3}$ $\mathrm{CH_3CH_2\ddot{O}CH_3}$

(*c*) Four isomers of $C_4H_{10}O$ have —OH groups:



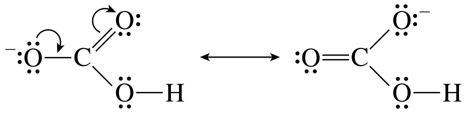
$\mathrm{CH_3CH_2CH_2CH_2\ddot{O}H}$ $\mathrm{CH_3CH(\ddot{O}H)CH_2CH_3}$ $\mathrm{CH_3CH(CH_3)CH_2\ddot{O}H}$ $\mathrm{CH_3C(CH_3)_2\ddot{O}H}$

Three isomers have C—O—C units:



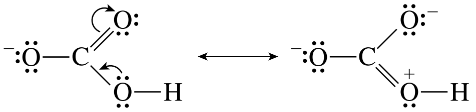
$\mathrm{CH_3\ddot{O}CH_2CH_2CH_3}$ $\mathrm{CH_3CH_2\ddot{O}CH_2CH_3}$ $\mathrm{CH_3\ddot{O}CH(CH_3)CH_3}$

1.16 (*b*) Move electrons from the negatively charged oxygen, as shown by the curved arrows.



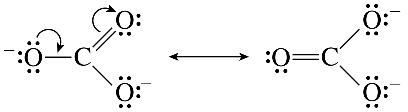
Equivalent to original structure

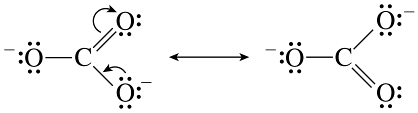
The resonance interaction shown for bicarbonate ion is more important than an alternative one involving delocalization of lone-pair electrons in the OH group.



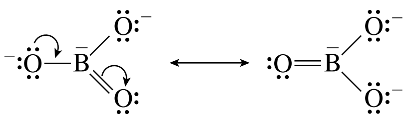
Not equivalent to original structure; not as stable because of charge separation

(*c*) All three oxygens are equivalent in carbonate ion. Either negatively charged oxygen can serve as the donor atom.

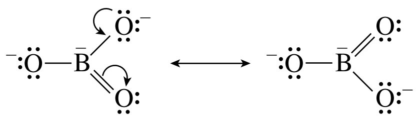




(*d*) Resonance in borate ion is exactly analogous to that in carbonate.

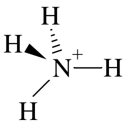


and



1.17 There are four B—H bonds in BH_4^-. The four electron pairs surround boron in a tetrahedral orientation. The H—B—H angles are 109.5°.

1.18 (*b*) Nitrogen in ammonium ion is surrounded by 8 electrons in four covalent bonds. These four bonds are directed toward the corners of a tetrahedron.

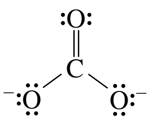


Each HNH angle is 109.5º.

(*c*) Double bonds are treated as a single unit when deducing the shape of a molecule using the VSEPR model. Thus azide ion is linear.

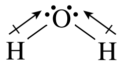
$^{-}{:}\ddot{N}{=}\overset{+}{N}{=}\ddot{N}{:}^{-}$ The NNN angle is 180°.

(*d*) Since the double bond in carbonate ion is treated as if it were a single unit, the three sets of electrons are arranged in a trigonal planar arrangement around carbon.

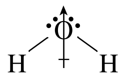


The OCO angle is 120º.

1.19 (*b*) Water is a bent molecule, and so the individual O—H bond dipole moments do not cancel. Water has a dipole moment.



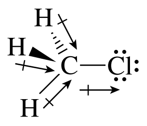
Individual OH bond moments in water



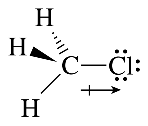
Direction of net dipole moment

(*c*) Methane, CH_4, is perfectly tetrahedral, and so the individual (small) C—H bond dipole moments cancel. Methane has no dipole moment.

(*d*) Methyl chloride has a dipole moment.

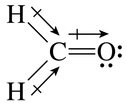


Directions of bond dipole moments in CH_3Cl

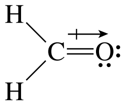


Direction of molecular dipole moment

(*e*) Oxygen is more electronegative than carbon and attracts electrons from it. Formaldehyde has a dipole moment.

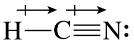


Direction of bond dipole moments in formaldehyde

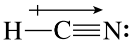


Direction of molecular dipole moment

(*f*) Nitrogen is more electronegative than carbon. Hydrogen cyanide has a dipole moment.

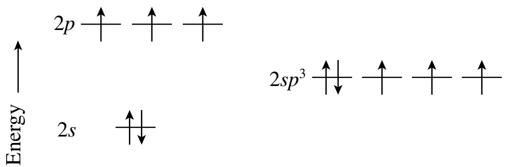


Direction of bond dipole moments in HCN



Direction of molecular dipole moment

1.20 The orbital diagram for sp^3-hybridized nitrogen is the same as for sp^3-hybridized carbon, except nitrogen has one more electron.

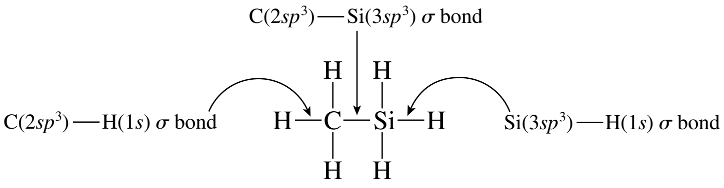


Ground electronic state of nitrogen
(*a*)

sp^3 hybrid state of nitrogen
(*b*)

The unshared electron pair in ammonia ($:NH_3$) occupies an sp^3-hybridized orbital of nitrogen. Each N—H bond corresponds to overlap of a half-filled sp^3 hybrid orbital of nitrogen and a 1*s* orbital of hydrogen.

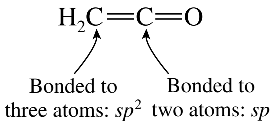
1.21 Silicon lies below carbon in the periodic table, and it is reasonable to assume that both carbon and silicon are sp^3-hybridized in H_3CSiH_3. The C—Si bond and all of the C—H and Si—H bonds are σ bonds.



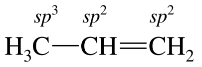
The principal quantum number of the carbon orbitals that are hybridized is 2; the principal quantum number for the silicon orbitals is 3.

1.22 (*b*) Carbon in formaldehyde ($H_2C{=}O$) is directly bonded to three other atoms (two hydrogens and one oxygen). It is sp^2-hybridized.

(*c*) Ketene has two carbons in different hybridization states. One is sp^2-hybridized; the other is *sp*-hybridized.



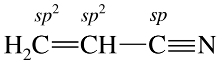
(*d*) One of the carbons in propene is sp^3-hybridized. The carbons of the double bond are sp^2-hybridized.



$$\overset{sp^3}{\mathrm{H_3C}}{-}\overset{sp^2}{\mathrm{CH}}{=}\overset{sp^2}{\mathrm{CH_2}}$$

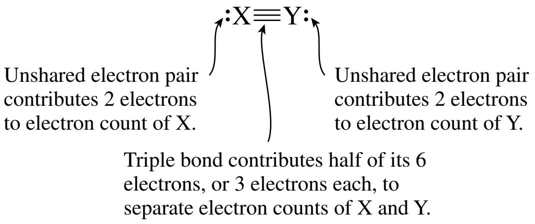
(*e*) The carbons of the CH_3 groups in acetone [$(CH_3)_2C{=}O$] are sp^3-hybridized. The C=O carbon is sp^2-hybridized.

(*f*) The carbons in acrylonitrile are hybridized as shown:



$$\overset{sp^2}{\mathrm{H_2C}}{=}\overset{sp^2}{\mathrm{CH}}{-}\overset{sp}{\mathrm{C}}{\equiv}\mathrm{N}$$

1.23 All these species are characterized by the formula :X≡Y:, and each atom has an electron count of 5.



Unshared electron pair contributes 2 electrons to electron count of X.

Unshared electron pair contributes 2 electrons to electron count of Y.

Triple bond contributes half of its 6 electrons, or 3 electrons each, to separate electron counts of X and Y.

Electron count X = electron count Y = 2 + 3 = 5

(*a*) :N≡N: A neutral nitrogen atom has 5 valence electrons: therefore, each atom is electrically neutral in molecular nitrogen.

(*b*) :C≡N: Nitrogen, as before, is electrically neutral. A neutral carbon has 4 valence electrons, and so carbon in this species, with an electron count of 5, has a unit negative charge. The species is cyanide anion; its net charge is −1.

(*c*) :C≡C: There are two negatively charged carbon atoms in this species. It is a dianion; its net charge is −2.

(*d*) :N≡O: Here again is a species with a neutral nitrogen atom. Oxygen, with an electron count of 5, has 1 less electron in its valence shell than a neutral oxygen atom. Oxygen has a formal charge of +1; the net charge is +1.

(*e*) :C≡O: Carbon has a formal charge of −1; oxygen has a formal charge of +1. Carbon monoxide is a neutral molecule.

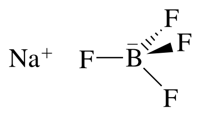
1.24 All these species are of the type $:\ddot{\mathrm{Y}}{=}\mathrm{X}{=}\ddot{\mathrm{Y}}:$. Atom X has an electron count of 4, corresponding to half of the 8 shared electrons in its four covalent bonds. Each atom Y has an electron count of 6; 4 unshared electrons plus half of the 4 electrons in the double bond of each Y to X.

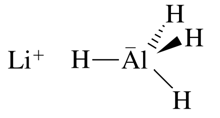
(*a*) $:\ddot{\mathrm{O}}{=}\mathrm{C}{=}\ddot{\mathrm{O}}:$ Oxygen, with an electron count of 6, and carbon, with an electron count of 4, both correspond to the respective neutral atoms in the number of electrons they “own.” Carbon dioxide is a neutral molecule, and neither carbon nor oxygen has a formal charge in this Lewis structure.

(*b*) $:\ddot{\mathrm{N}}{=}\mathrm{N}{=}\ddot{\mathrm{N}}:$ The two terminal nitrogens each have an electron count (6) that is one more than a neutral atom and thus each has a formal charge of −1. The central N has an electron count (4) that is one less than a neutral nitrogen; it has a formal charge of +1. The net charge on the species is (−1 + 1 − 1), or −1.

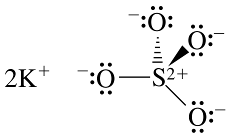
(*c*) $:\ddot{\mathrm{O}}{=}\mathrm{N}{=}\ddot{\mathrm{O}}:$ As in part (*b*), the central nitrogen has a formal charge of +1. As in part (*a*), each oxygen is electrically neutral. The net charge is +1.

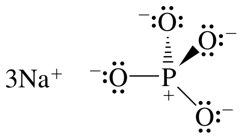
1.25 (*a*, *b*) The problem specifies that ionic bonding is present and that the anion is tetrahedral. The cations are the group I metals Na^+ and Li^+. Both boron and aluminum are group III elements, and thus have a formal charge of −1 in the tetrahedral anions BF_4^- and AlH_4^- respectively.


Sodium tetrafluoroborate


Lithium aluminum hydride

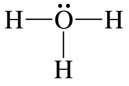
(*c*, *d*) Both of the tetrahedral anions have 32 valence electrons. Sulfur contributes 6 valence electrons and phosphorus 5 to the anions. Each oxygen contributes 6 electrons. The double negative charge in sulfate contributes 2 more, and the triple negative charge in phosphate contributes 3 more.


Potassium sulfate


Sodium phosphate

The formal charge on each oxygen in both ions is −1. The formal charge on sulfur in sulfate is +2; the charge on phosphorus is +1. The net charge of sulfate ion is −2; the net charge of phosphate ion is −3.

1.26 (*a*) Each hydrogen has a formal charge of 0, as is always the case when hydrogen is covalently bonded to one substituent. Oxygen has an electron count of 5.



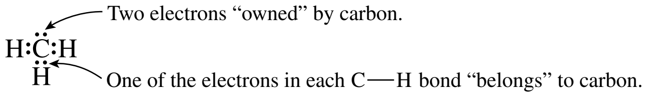
$$\text{Electron count of oxygen} = 2 + \tfrac{1}{2}(6) = 5$$

Unshared pair

Covalently bonded electrons

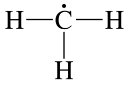
A neutral oxygen atom has 6 valence electrons; therefore, oxygen in this species has a formal charge of +1. The species as a whole has a unit positive charge. It is the hydronium ion, H_3O^+.

(*b*) The electron count of carbon is 5; there are 2 electrons in an unshared pair, and 3 electrons are counted as carbon's share of the three covalent bonds to hydrogen.



An electron count of 5 is one more than that for a neutral carbon atom. The formal charge on carbon is −1, as is the net charge on this species.

(*c*) This species has 1 less electron than that of part (*b*). None of the atoms bears a formal charge. The species is neutral.



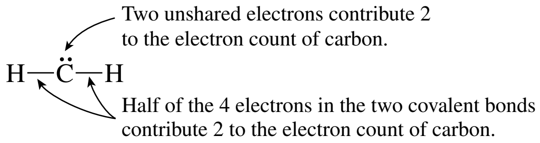
$$\text{Electron count of carbon} = 1 + \tfrac{1}{2}(6) = 4$$

Unshared electron

Electrons shared in covalent bonds

(*d*) The formal charge of carbon in this species is +1. Its only electrons are those in its three covalent bonds to hydrogen, and so its electron count is 3. This corresponds to 1 less electron than in a neutral carbon atom, giving it a unit positive charge.

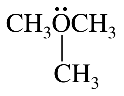
(*e*) In this species the electron count of carbon is 4, or, exactly as in part (*c*), that of a neutral carbon atom. Its formal charge is 0, and the species is neutral.



1.27 Oxygen is surrounded by a complete octet of electrons in each structure but has a different "electron count" in each one because the proportion of shared to unshared pairs is different.

(*a*) $CH_3\overset{..}{\underset{..}{O}}:$

(*b*) $CH_3\overset{..}{\underset{..}{O}}CH_3$

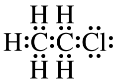
(*c*)

$\underset{\displaystyle CH_3}{CH_3\overset{..}{O}CH_3}$

Electron count $= 6 + \frac{1}{2}(2) = 7$; formal charge $= -1$

Electron count $= 4 + \frac{1}{2}(4) = 6$; formal charge $= 0$

Electron count $= 2 + \frac{1}{2}(6) = 5$; formal charge $= +1$

1.28 (*a*) Each carbon has 4 valence electrons, each hydrogen 1, and chlorine has 7. Hydrogen and chlorine each can form only one bond, and so the only stable structure must have a carbon–carbon bond. Of the 20 valence electrons, 14 are present in the seven covalent bonds and 6 reside in the three unshared electron pairs of chlorine.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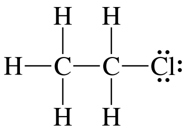
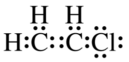


(*b*) As in part (*a*) the single chlorine as well as all of the hydrogens must be connected to carbon. There are 18 valence electrons in C_2H_3Cl, and the framework of five single bonds accounts for only 10 electrons. Six of the remaining 8 are used to complete the octet of chlorine as three unshared pairs, and the last 2 are used to form a carbon–carbon double bond.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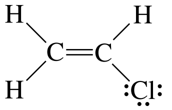
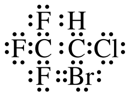


(*c*) All of the atoms except carbon (H, Br, Cl, and F) are monovalent; therefore, they can only be bonded to carbon. The problem states that all three fluorines are bonded to the same carbon, and so one of the carbons is present as a CF_3 group. The other carbon must be present as a CHBrCl group. Connect these groups together to give the structure of halothane.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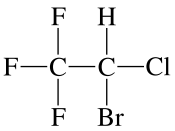
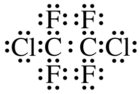

(Unshared electron pairs omitted for clarity)

(*d*) As in part (*c*) all of the atoms except carbon are monovalent. Since each carbon bears one chlorine, two $ClCF_2$ groups must be bonded together.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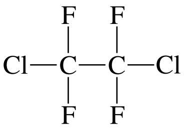
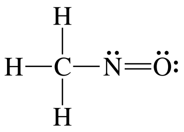
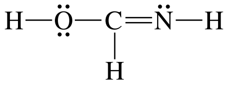

(Unshared electron pairs omitted for clarity)

1.29 Place hydrogens on the given atoms so that carbon has four bonds, nitrogen three, and oxygen two. Place unshared electron pairs on nitrogen and oxygen so that nitrogen has an electron count of 5 and oxygen has an electron count of 6. These electron counts satisfy the octet rule when nitrogen has three bonds and oxygen two.

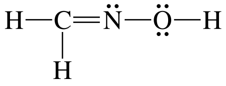
(*a*)



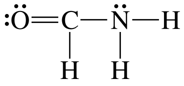
(*c*)



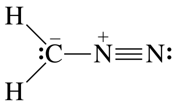
(*b*)



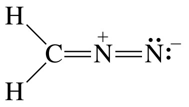
(*d*)



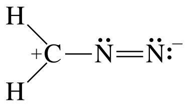
1.30 (*a*) Species A, B, and C have the same molecular formula, the same atomic positions, and the same number of electrons. They differ only in the arrangement of their electrons. They are therefore resonance forms of a single compound.



A



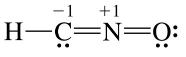
B



C

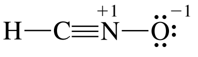
(*b*) Structure A has a formal charge of −1 on carbon.
(*c*) Structure C has a formal charge of +1 on carbon.
(*d*) Structures A and B have formal charges of +1 on the internal nitrogen.
(*e*) Structures B and C have a formal charge of −1 on the terminal nitrogen.
(*f*) All resonance forms of a particular species must have the same net charge. In this case, the net charge on A, B, and C is 0.
(*g*) Both A and B have the same number of covalent bonds, but the negative charge is on a more electronegative atom in B (nitrogen) than it is in A (carbon). Structure B is more stable.
(*h*) Structure B is more stable than structure C. Structure B has one more covalent bond, all of its atoms have octets of electrons, and it has a lesser degree of charge separation than C. The carbon in structure C does not have an octet of electrons.
(*i*) The CNN unit is linear in A and B, but bent in C according to VSEPR. This is an example of how VSEPR can fail when comparing resonance structures.

1.31 The structures given and their calculated formal charges are:



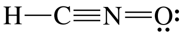
$H-\overset{-1}{C}=\overset{+1}{N}=O$

A



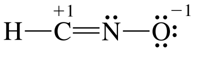
$H-C\equiv\overset{+1}{N}-\overset{-1}{O}$

B



$H-C\equiv N=O$

C

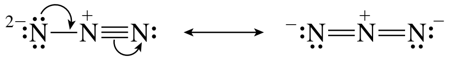


$H-\overset{+1}{C}=N-\overset{-1}{O}$

D

(*a*) Structure D contains a positively charged carbon.
(*b*) Structures A and B contain a positively charged nitrogen.
(*c*) None of the structures contain a positively charged oxygen.
(*d*) Structure A contains a negatively charged carbon.
(*e*) None of the structures contain a negatively charged nitrogen.
(*f*) Structures B and D contain a negatively charged oxygen.
(*g*) All the structures are electrically neutral.
(*h*) Structure B is the most stable. All the atoms except hydrogen have octets of electrons, and the negative charge resides on the most electronegative element (oxygen).
(*i*) Structure C is the least stable. Nitrogen has five bonds (10 electrons), which violates the octet rule.

1.32 (*a*) These two structures are resonance forms since they have the same atomic positions and the same number of electrons.



16 valence electrons (net charge = −1)

16 valence electrons (net charge = −1)

(*b*) The two structures have different numbers of electrons and, therefore, can't be resonance forms of each other.

16 valence electrons (net charge −1)

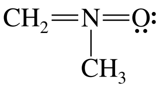
14 valence electrons (net charge +1)

(*c*) These two structures have different numbers of electrons; they are not resonance forms.

16 valence electrons (net charge = −1)

20 valence electrons (net charge = −5)

1.33 Structure C has 10 electrons surrounding nitrogen, but the octet rule limits nitrogen to 8 electrons. Structure C is incorrect.

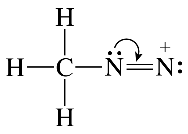


$CH_2{=}N(CH_3){=}O$

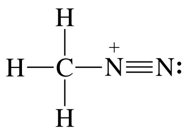
Not a valid Lewis structure!

1.34 (*a*) The terminal nitrogen has only 6 electrons; therefore, use the unshared pair of the adjacent nitrogen to form another covalent bond.

By moving electrons of the nitrogen lone pair as shown by the arrow

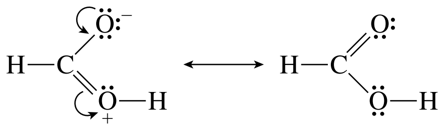


a structure that has octets about both nitrogen atoms is obtained.

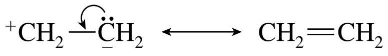


In general, move electrons from sites of high electron density toward sites of low electron density. Notice that the location of formal charge has changed, but the net charge on the species remains the same.

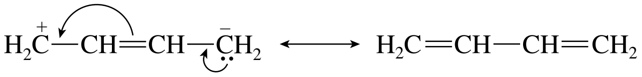
(*b*) The dipolar Lewis structure given can be transformed to one that has no charge separation by moving electron pairs as shown:



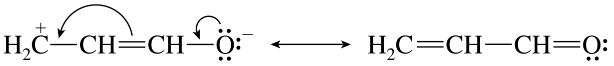
(*c*) Move electrons toward the positive charge. Sharing the lone pair gives an additional covalent bond and avoids the separation of opposite charges.



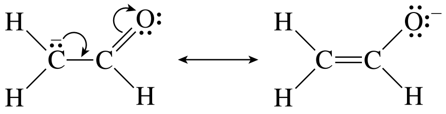
(*d*) Octets of electrons at all the carbon atoms can be produced by moving the electrons toward the site of positive charge.



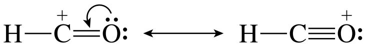
(*e*) As in part (*d*), move the electron pairs toward the carbon atom that has only 6 electrons.



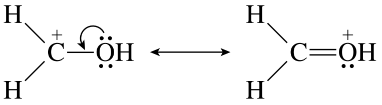
(*f*) The negative charge can be placed on the most electronegative atom (oxygen) in this molecule by moving electrons as indicated.



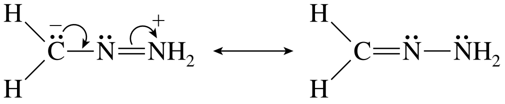
(*g*) Octets of electrons are present around both carbon and oxygen if an oxygen unshared electron pair is moved toward the positively charged carbon to give an additional covalent bond.



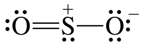
(*h*) This exercise is similar to part (*g*); move electrons from oxygen to carbon so as to produce an additional bond and satisfy the octet rule for both carbon and oxygen.



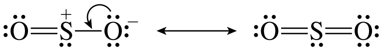
(*i*) By moving electrons from the site of negative charge toward the positive charge, a structure that has no charge separation is generated.



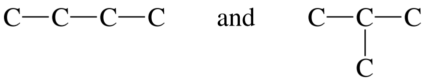
1.35 (*a*) Sulfur is in the same group of the periodic table as oxygen (group VI A) and, like oxygen, has 6 valence electrons. Sulfur dioxide, therefore, has 18 valence electrons. A Lewis structure in which sulfur and both oxygens have complete octets of electrons is:



(*b*) Move an electron pair from the singly bonded oxygen in part (*a*) to generate a second double bond. The resulting Lewis structure has 10 valence electrons around sulfur. It is a valid Lewis structure because sulfur can expand its valence shell beyond 8 electrons by using its 3*d* orbitals.

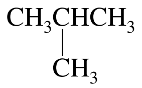


1.36 (*a*) To generate constitutionally isomeric structures having the molecular formula C_4H_{10}, you need to consider the various ways in which four carbon atoms can be bonded together. These are



Filling in the appropriate hydrogens gives the correct structures:

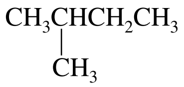
$CH_3CH_2CH_2CH_3$ and

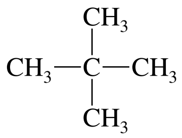

$CH_3\underset{CH_3}{CH}CH_3$

Continue with the remaining parts of the problem using the general approach outlined for part (*a*).

(*b*) C_5H_{12}

$CH_3CH_2CH_2CH_2CH_3$


$CH_3\underset{CH_3}{CH}CH_2CH_3$

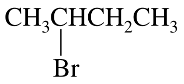

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

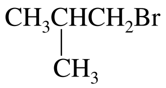
(*c*) $C_2H_4Cl_2$

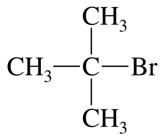
CH_3CHCl_2 and $ClCH_2CH_2Cl$

(*d*) C_4H_9Br

$CH_3CH_2CH_2CH_2Br$

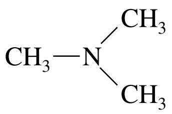

$CH_3\underset{Br}{CH}CH_2CH_3$

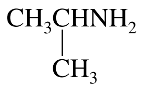

$CH_3\underset{CH_3}{CH}CH_2Br$


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$

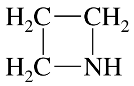
(*e*) C_3H_9N

$CH_3CH_2CH_2NH_2$ $CH_3CH_2NHCH_3$



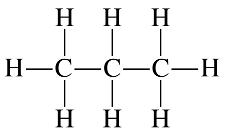

$CH_3\underset{CH_3}{CH}NH_2$

Note that when the three carbons and the nitrogen are arranged in a ring, the molecular formula based on such a structure is C_3H_7N, not C_3H_9N as required.



(not an isomer)

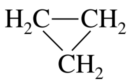
1.37 (*a*) All three carbons must be bonded together, and each one has four bonds; therefore, the molecular formula C_3H_8 uniquely corresponds to:


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

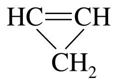
$(CH_3CH_2CH_3)$

(*b*) With two fewer hydrogen atoms than the preceding compound, either C_3H_6 must contain a carbon–carbon double bond or its carbons must be arranged in a ring; thus the following structures are constitutional isomers:

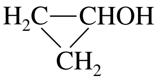
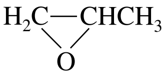
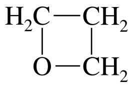
$H_2C{=}CHCH_3$ and



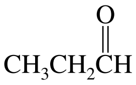
(*c*) The molecular formula C_3H_4 is satisfied by the structures

$H_2C{=}C{=}CH_2$ $HC{\equiv}CCH_3$ 

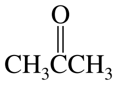
1.38 (*a*) The only atomic arrangements of C_3H_6O that contain only single bonds must have a ring as part of their structure.

(*b*) Structures corresponding to C_3H_6O are possible in noncyclic compounds if they contain a carbon–carbon or carbon–oxygen double bond.

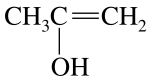


$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$



$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

$CH_3CH{=}CHOH$ $CH_3OCH{=}CH_2$

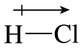


$CH_3\underset{\underset{\displaystyle OH}{|}}{C}{=}CH_2$

$H_2C{=}CHCH_2OH$

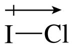
1.39 The direction of a bond dipole is governed by the electronegativity of the atoms it connects. In each of the parts to this problem, the more electronegative atom is partially negative and the less electronegative atom is partially positive. Electronegativities of the elements are given in Table 1.2 of the text.

(*a*) Chlorine is more electronegative than hydrogen.



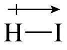
$\overset{+\!\!\longrightarrow}{H{-}Cl}$

(*b*) Chlorine is more electronegative than iodine.



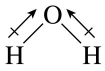
$\overset{+\!\!\longrightarrow}{I{-}Cl}$

(*c*) Iodine is more electronegative than hydrogen.

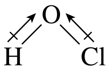


$\overset{+\!\!\longrightarrow}{H{-}I}$

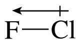
(*d*) Oxygen is more electronegative than hydrogen.



(*e*) Oxygen is more electronegative than either hydrogen or chlorine.

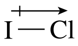


1.40 The direction of a bond dipole is governed by the electronegativity of the atoms involved. Among the halogens the order of electronegativity is F > Cl > Br > I. Fluorine therefore attracts electrons away from chlorine in FCl, and chlorine attracts electrons away from iodine in ICl.



$\overset{\longleftarrow\!\!+}{F{-}Cl}$

$\mu = 0.9$ D



$\overset{+\!\!\longrightarrow}{I{-}Cl}$

$\mu = 0.7$ D

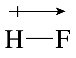
Chlorine is the positive end of the dipole in FCl and the negative end in ICl.

1.41 (*a*) Sodium chloride is ionic; it has a unit positive charge and a unit negative charge separated from each other. Hydrogen chloride has a polarized bond but is a covalent compound. Sodium chloride has a larger dipole moment. The measured values are as shown.

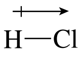
$Na^+ Cl^-$ is more polar than $H{-}Cl$

μ 9.4 D μ 1.1 D

(*b*) Fluorine is more electronegative than chlorine, and so its bond to hydrogen is more polar, as the measured dipole moments indicate.

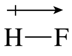


is more polar than

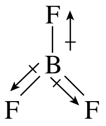


μ 1.7 D μ 1.1 D

(*c*) Boron trifluoride is planar. Its individual B—F bond dipoles cancel. It has no dipole moment.

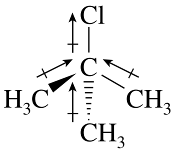


is more polar than

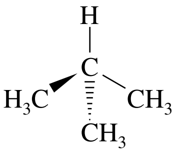


μ 1.7 D μ 0 D

(*d*) A carbon–chlorine bond is strongly polar; carbon–hydrogen and carbon–carbon bonds are only weakly polar.

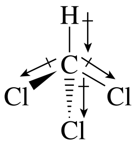


is more polar than

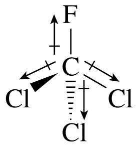


μ 2.1 D μ 0.1 D

(*e*) A carbon–fluorine bond in CCl_3F opposes the polarizing effect of the chlorines. The carbon–hydrogen bond in $CHCl_3$ reinforces it. $CHCl_3$ therefore has a larger dipole moment.

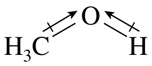


is more polar than

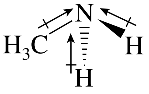


μ 1.0 D μ 0.5 D

(*f*) Oxygen is more electronegative than nitrogen; its bonds to carbon and hydrogen are more polar than the corresponding bonds formed by nitrogen.

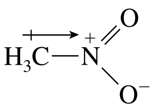


is more polar than

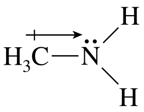


μ 1.7 D μ 1.3 D

(*g*) The Lewis structure for CH_3NO_2 has a formal charge of +1 on nitrogen, making it more electron-attracting than the uncharged nitrogen of CH_3NH_2.

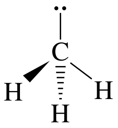


is more polar than

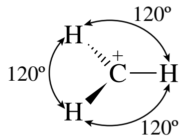


μ 3.1 D μ 1.3 D

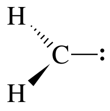
1.42 (*a*) There are four electron pairs around carbon in $:\bar{C}H_3$; they are arranged in a tetrahedral fashion. The atoms of this species are in a trigonal pyramidal arrangement.



(*b*) Only three electron pairs are present in $\overset{+}{C}H_3$, and so it is trigonal planar.

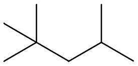


(*c*) As in part (*b*), there are three electron pairs. When these electron pairs are arranged in a plane, the atoms in $:CH_2$ are not collinear. The atoms of this species are arranged in a bent structure according to VSEPR considerations.



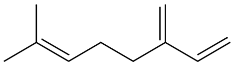
1.43 The structures, written in a form that indicates hydrogens and unshared electrons, are as shown. Remember: A neutral carbon has four bonds, a neutral nitrogen has three bonds plus one unshared electron pair, and a neutral oxygen has two bonds plus two unshared electron pairs. Halogen substituents have one bond and three unshared electron pairs.

(*a*)



is equivalent to $(CH_3)_3CCH_2CH(CH_3)_2$

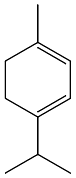
(*b*)



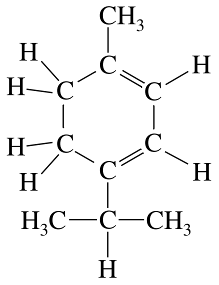
is equivalent to

$$(CH_3)_2C{=}CHCH_2CH_2\overset{\overset{\displaystyle CH_2}{\|}}{C}CH{=}CH_2$$

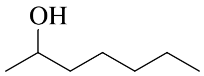
(*c*)



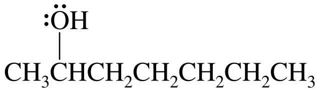
is equivalent to



(*d*)

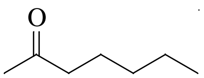


is equivalent to

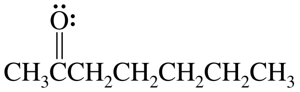


$$CH_3\overset{\overset{:\ddot{O}H}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$$

(*e*)

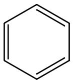


is equivalent to



$$CH_3\overset{\overset{\ddot{O}:}{\|}}{C}CH_2CH_2CH_2CH_2CH_3$$

(*f*)



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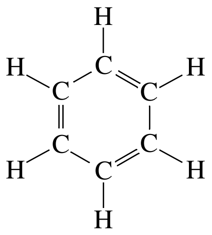
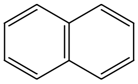


(*g*)



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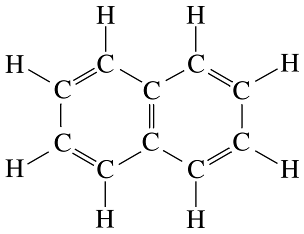
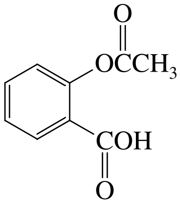


(*h*)



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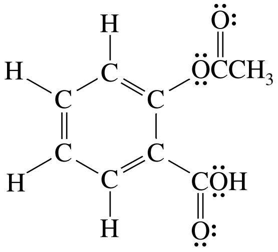
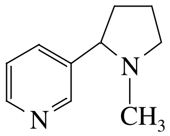


(*i*)



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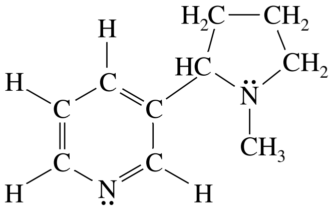
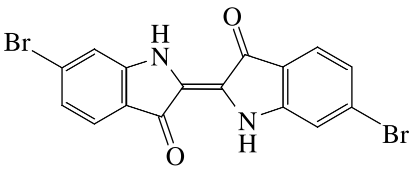


(*j*)



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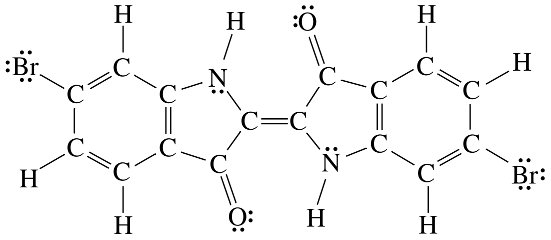
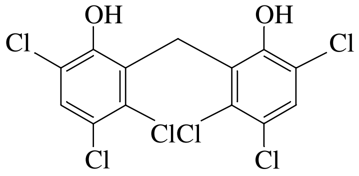


(*k*)



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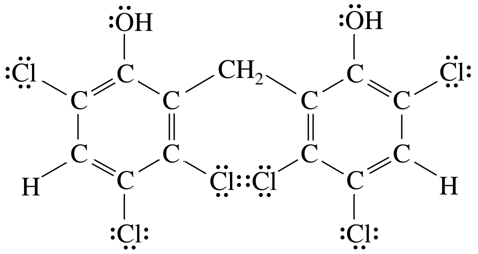
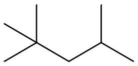
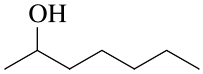


1.44 (*a*) C_8H_{18}
(*b*) $C_{10}H_{16}$
(*c*) $C_{10}H_{16}$
(*d*) $C_7H_{16}O$
(*e*) $C_7H_{14}O$
(*f*) C_6H_6
(*g*) $C_{10}H_8$
(*h*) $C_9H_8O_4$
(*i*) $C_{10}H_{14}N_2$
(*j*) $C_{16}H_8Br_2N_2O_2$
(*k*) $C_{13}H_6Cl_6O_2$

Isomers are different compounds that have the same molecular formula. Two of these compounds, (*b*) and (*c*), have the same molecular formula and are isomers of each other.

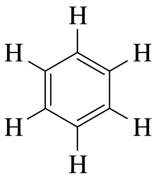
1.45 (*a*) Carbon is sp^3-hybridized when it is directly bonded to four other atoms. Compounds (*a*) and (*d*) in Problem 1.43 are the only ones in which *all* of the carbons are sp^3-hybridized.


(*a*)

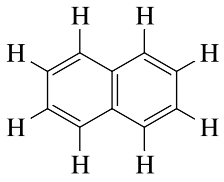


(*d*)

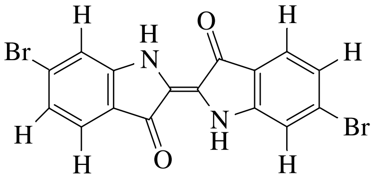
(*b*) Carbon is sp^2-hybridized when it is directly bonded to three other atoms. Compounds (*f*), (*g*), and (*j*) in Problem 1.43 have only sp^2-hybridized carbons.



(*f*)



(*g*)

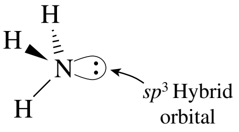


(*j*)

None of the compounds in Problem 1.43 contain an *sp*-hybridized carbon.

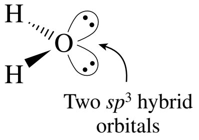
1.46 The problem specifies that the second-row element is sp^3-hybridized in each of the compounds. Any unshared electron pairs therefore occupy sp^3-hybridized orbitals, and bonded pairs are located in σ orbitals.

(*a*) Ammonia



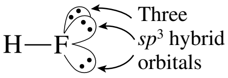
Three σ bonds formed by sp^3–s overlap

(*b*) Water



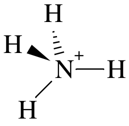
Two σ bonds formed by sp^3–s overlap

(*c*) Hydrogen fluoride



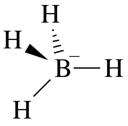
One σ bond formed by sp^3–s overlap

(*d*) Ammonium ion



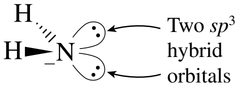
Four σ bonds formed by sp^3–s overlap

(*e*) Borohydride anion



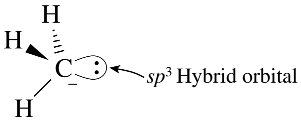
Four σ bonds formed by sp^3–s overlap

(*f*) Amide anion



Two σ bonds formed by sp^3–s overlap

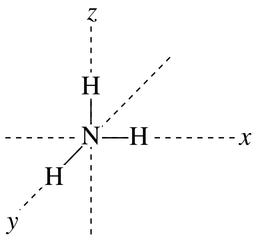
(*g*) Methyl anion



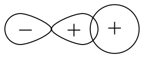
Three σ bonds formed by sp^3–s overlap

1.47 (*a*) The electron configuration of N is $1s^2 2s^2 2p_x^{\,1} 2p_y^{\,1} 2p_z^{\,1}$. If the half-filled $2p_x$, $2p_y$, and $2p_z$ orbitals are involved in bonding to H, then the unshared pair would correspond to the two electrons in the $2s$ orbital.

(*b*) The three *p* orbitals $2p_x$, $2p_y$, and $2p_z$ have their axes at right angles to one another. The H—N—H angles would therefore be 90°.

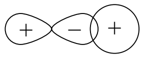


1.48 A bonding interaction exists when two orbitals overlap "in phase" with each other, that is, when the algebraic signs of their wave functions are the same in the region of overlap. The following orbital is a bonding orbital. It involves overlap of an *s* orbital with the lobe of a *p* orbital of the same sign.



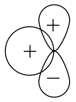
(*c*) (bonding)

On the other hand, the overlap of an *s* orbital with the lobe of a *p* orbital of opposite sign is antibonding.



(*b*) (antibonding)

Overlap in the manner shown next is nonbonding. Both the positive lobe and the negative lobe of the *p* orbital overlap with the spherically symmetrical *s* orbital. The bonding overlap between the *s* orbital and one lobe of the *p* orbital is exactly canceled by an antibonding interaction between the *s* orbital and the lobe of opposite sign.



(*a*) (nonbonding)

1.49–1.55 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual.* You should use *Learning By Modeling* for these exercises.

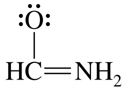
SELF-TEST

PART A

A-1. Write the electronic configuration for each of the following:
(*a*) Phosphorus (*b*) Sulfide ion in Na_2S

A-2. Determine the formal charge of each atom and the net charge for each of the following species:

(*a*) $:\ddot{N}{=}C{=}\ddot{S}:$ (*b*) $:O{\equiv}N{-}\ddot{\underset{\cdot\cdot}{O}}:$ (*c*)



$$\begin{array}{c}:\ddot{O}:\\ |\\ HC{=}NH_2\end{array}$$

A-3. Write a second Lewis structure that satisfies the octet rule for each of the species in Problem A-2, and determine the formal charge of each atom. Which of the Lewis structures for each species in this and Problem A-2 is more stable?

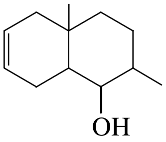
A-4. Write a correct Lewis structure for each of the following. Be sure to show explicitly any unshared pairs of electrons.

(*a*) Methylamine, CH_3NH_2

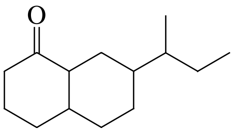
(*b*) Acetaldehyde, C_2H_4O (the atomic order is CCO; all the hydrogens are connected to carbon.)

A-5. What is the molecular formula of each of the structures shown? Clearly draw any unshared electron pairs that are present.

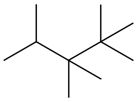
(*a*)



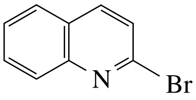
(*c*)



(*b*)



(*d*)



A-6. Which compound in Problem A-5 has

(*a*) Only sp^3-hybridized carbons

(*b*) Only sp^2-hybridized carbons

(*c*) A single sp^2-hybridized carbon atom

A-7. Account for the fact that all three sulfur–oxygen bonds in SO_3 are the same by drawing the appropriate Lewis structure(s).

A-8. The cyanate ion contains 16 valence electrons, and its three atoms are arranged in the order OCN. Write the most stable Lewis structure for this species, and assign a formal charge to each atom. What is the net charge of the ion?

A-9. Using the VSEPR method,

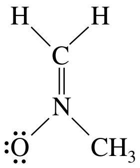
(*a*) Describe the geometry at each carbon atom and the oxygen atom in the following molecule: $CH_3OCH{=}CHCH_3$.

(*b*) Deduce the shape of NCl_3, and draw a three-dimensional representation of the molecule. Is NCl_3 polar?

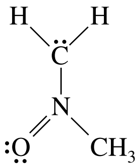
A-10. Assign the shape of each of the following as either linear or bent.

(*a*) CO_2 (*b*) NO_2^+ (*c*) NO_2^-

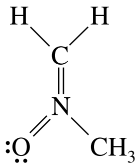
A-11. Consider structures A, B, C, and D:



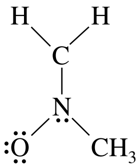
A



B



C



D

(*a*) Which structure (or structures) contains a positively charged carbon?

(*b*) Which structure (or structures) contains a positively charged nitrogen?

(*c*) Which structure (or structures) contains a positively charged oxygen?

(*d*) Which structure (or structures) contains a negatively charged carbon?

(*e*) Which structure (or structures) contains a negatively charged nitrogen?

(*f*) Which structure (or structures) contains a negatively charged oxygen?

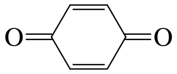
(*g*) Which structure is the most stable?

(*h*) Which structure is the least stable?

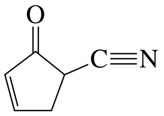
A-12. Given the following information, write a Lewis structure for urea, CH_4N_2O. The oxygen atom and both nitrogen atoms are bonded to carbon, there is a carbon–oxygen double bond, and none of the atoms bears a formal charge. Be sure to include all unshared electron pairs.

A-13. How many σ and π bonds are present in each of the following?

(*a*) $CH_3CH{=}CHCH_3$

(*c*)


(*b*) $HC{\equiv}CCH_2CH_3$

(*d*)


A-14. Give the hybridization of each carbon atom in the preceding problem.

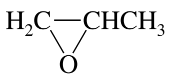
PART B

B-1. Which one of the following is most likely to have ionic bonds?
(*a*) HCl (*b*) Na_2O (*c*) N_2O (*d*) NCl_3

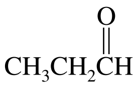
B-2. Which of the following is *not* an electronic configuration for an atom in its ground state?
(*a*) $1s^22s^22p_x^22p_y^12p_z^1$ (*c*) $1s^22s^22p_x^22p_y^22p_z^1$
(*b*) $1s^22s^22p_x^22p_y^22p_z^0$ (*d*) $1s^22s^22p_x^22p_y^22p_z^2$

B-3. The formal charge on phosphorus in $(CH_3)_4P$ is
(*a*) 0 (*b*) −1 (*c*) +1 (*d*) +2

B-4. Which of the following is an isomer of compound 1?

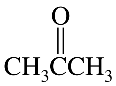


1



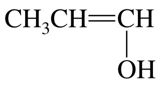
$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

2



$CH_3\overset{\overset{O}{\|}}{C}CH_3$

3



$CH_3CH{=}\underset{\underset{OH}{|}}{CH}$

4

(*a*) 2 (*c*) 2 and 3
(*b*) 4 (*d*) All are isomers.

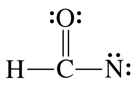
B-5. In which of the following is oxygen the positive end of the bond dipole?
(*a*) O—F (*b*) O—N (*c*) O—S (*d*) O—H

B-6. What two structural formulas are resonance forms of one another?

(*a*) $H-C\equiv\overset{+}{N}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$ and $H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-C\equiv N:$

(*b*) $H-\underset{\cdot\cdot}{\overset{+}{O}}=C=\overset{\cdot\cdot}{N}:^{-}$ and $H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-C\equiv N:$

(*c*) $H-C\equiv\overset{+}{N}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$ and



$H-\overset{\overset{:O:}{\|}}{C}-\overset{\cdot\cdot}{N}:$

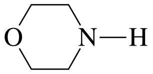
(*d*) $H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-C\equiv N:$ and $H-\overset{\cdot\cdot}{N}=C=\overset{\cdot\cdot}{O}:$

B-7. The bond identified (with the arrow) in the following structure is best described as:

$$HC{\equiv}C\underset{\uparrow}{-}CH{=}CH_2$$

(*a*) $2sp$–$2sp^2$ σ (*c*) $2sp^2$–$2sp^3$ σ (*e*) $2p$–$2p$ σ
(*b*) $2p$–$2p$ π (*d*) $2sp^2$–$2sp^2$ σ

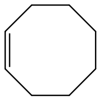
B-8. The total number of *unshared pairs* of electrons in the molecule

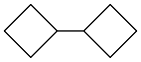


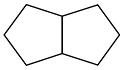
is
(*a*) 0 (*b*) 1 (*c*) 2 (*d*) 3

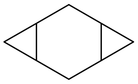
B-9. Which of the following contains a triple bond?
(*a*) SO_2 (*b*) HCN (*c*) C_2H_4 (*d*) NH_3

B-10. Which one of the compounds shown is *not* an isomer of the other three?


(*a*)


(*b*)


(*c*)


(*d*)

B-11. Which one of the following is the most stable Lewis structure? The answer must be correct in terms of bonds, unshared pairs of electrons, and formal charges.

(*a*) $:\ddot{O}{=}N{=}CH_2$ (*c*) $:\ddot{O}{=}\ddot{N}{-}\underset{-}{\ddot{C}}H_2$ (*e*) $:\underset{\cdot\cdot}{\ddot{O}}{-}\underset{\cdot\cdot}{\ddot{N}}{-}\ddot{C}H_2$

(*b*) $^{-}:\underset{\cdot\cdot}{\ddot{O}}{-}\ddot{N}{=}CH_2$ (*d*) $:\ddot{O}{=}\underset{-}{\ddot{N}}{=}CH_2$

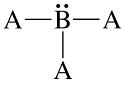
B-12. Repeat the previous question for the following Lewis structures.

(*a*) $^{-}:\underset{\cdot\cdot}{\ddot{N}}{-}\underset{\cdot\cdot}{\ddot{N}}{-}\overset{+}{C}H_2$ (*c*) $:\ddot{N}{=}\ddot{N}{-}\overset{-}{\ddot{C}}H_2$ (*e*) $^{-}:\ddot{N}{=}\overset{+}{N}{=}CH_2$

(*b*) $^{-}:\underset{\cdot\cdot}{\ddot{N}}{-}\ddot{N}{=}CH_2$ (*d*) $:N{\equiv}\overset{+}{N}{-}CH_2$

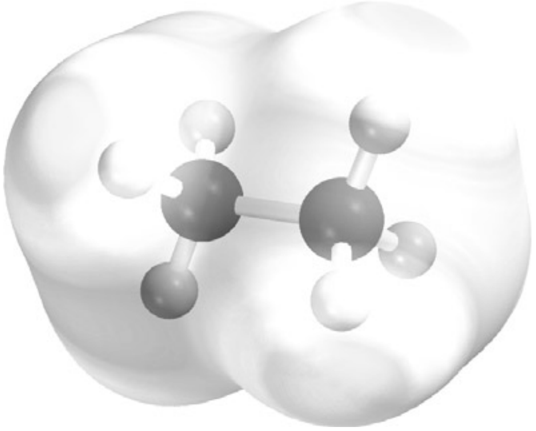
B-13. Which of the following molecules would you expect to be *nonpolar*?
1. CH_2F_2 2. CO_2 3. CF_4 4. CH_3OCH_3
(*a*) 1 and 2 (*b*) 1 and 3 (*c*) 1 and 4 (*d*) 2 and 3 (*e*) 2, 3, and 4

The remaining two questions refer to the hypothetical compounds:

$A{-}B{-}A$	$A{=}\ddot{B}{-}A$	$A{=}B{=}A$	 $A{-}\underset{\underset{A}{\vert}}{\ddot{B}}{-}A$
1	2	3	4

B-14. Which substance(s) is (are) linear?
(*a*) 1 only (*b*) 1 and 3 (*c*) 1 and 2 (*d*) 3 only

B-15. Assuming A is more electronegative than B, which substance(s) is (are) polar?
(*a*) 1 and 3 (*b*) 2 only (*c*) 4 only (*d*) 2 and 4

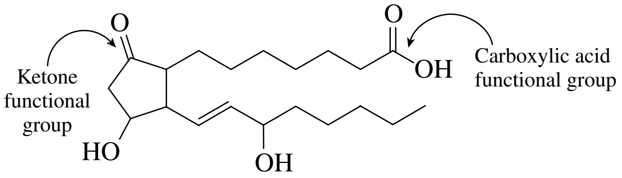


CHAPTER 2

ALKANES

SOLUTIONS TO TEXT PROBLEMS

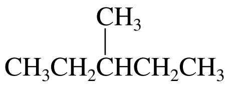
2.1 A carbonyl group is C═O. Of the two carbonyl functions in prostaglandin E_1 one belongs to the ketone family, the other to the carboxylic acids.



2.2 An unbranched alkane (*n*-alkane) of 28 carbons has 26 methylene (CH_2) groups flanked by a methyl (CH_3) group at each end. The condensed formula is $CH_3(CH_2)_{26}CH_3$.

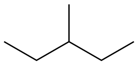
2.3 The alkane represented by the carbon skeleton formula has 11 carbons. The general formula for an alkane is C_nH_{2n+2}, and thus there are 24 hydrogens. The molecular formula is $C_{11}H_{24}$; the condensed structural formula is $CH_3(CH_2)_9CH_3$.

2.4 In addition to $CH_3(CH_2)_4CH_3$ and $(CH_3)_2CHCH_2CH_2CH_3$, there are three more isomers. One has a five-carbon chain with a one-carbon (methyl) branch:

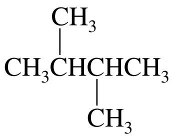


$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$$

or

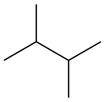


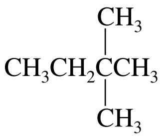
The remaining two isomers have two methyl branches on a four-carbon chain.



$$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_3$$

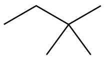
or





$$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$$

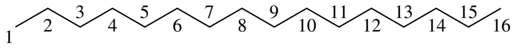
or



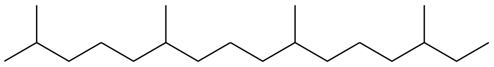
2.5 (*b*) Octacosane is not listed in Table 2.4, but its structure can be deduced from its systematic name. The suffix -cosane pertains to alkanes that contain 20–29 carbons in their longest continuous chain. The prefix octa- means "eight." Octacosane is therefore the unbranched alkane having 28 carbon atoms. It is $CH_3(CH_2)_{26}CH_3$.

(*c*) The alkane has an unbranched chain of 11 carbon atoms and is named **undecane.**

2.6 The ending -hexadecane reveals that the longest continuous carbon chain has 16 carbon atoms.



There are four methyl groups (represented by tetramethyl-), and they are located at carbons 2, 6, 10, and 14.



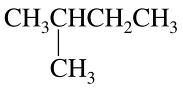
2,6,10,14-Tetramethylhexadecane
(phytane)

2.7 (*b*) The systematic name of the unbranched C_5H_{12} isomer is **pentane** (Table 2.4).

$CH_3CH_2CH_2CH_2CH_3$

IUPAC name: **pentane**
Common name: *n*-pentane

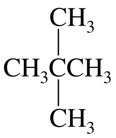
A second isomer, $(CH_3)_2CHCH_2CH_3$, has four carbons in the longest continuous chain and so is named as a derivative of butane. Since it has a methyl group at C-2, it is **2-methylbutane.**



$$\begin{array}{l} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3 \end{array}$$

IUPAC name: **2-methylbutane**
Common name: isopentane
methyl group at C-2

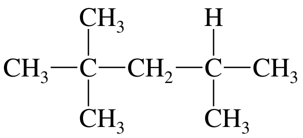
The remaining isomer, $(CH_3)_4C$, has three carbons in its longest continuous chain and so is named as a derivative of propane. There are two methyl groups at C-2, and so it is a 2,2-dimethyl derivative of propane.



$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_3$$

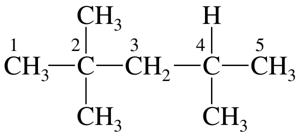
IUPAC name: **2,2-dimethylpropane**
Common name: neopentane

(*c*) First write out the structure in more detail, and identify the longest continuous carbon chain.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

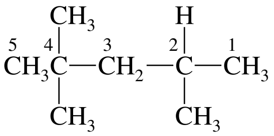
There are five carbon atoms in the longest chain, and so the compound is named as a derivative of pentane. This five-carbon chain has three methyl substituents attached to it, making it a trimethyl derivative of pentane. Number the chain in the direction that gives the lowest numbers to the substituents at the first point of difference.



$$\overset{1}{\mathrm{CH_3}}{-}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\overset{2}{\mathrm{C}}}}{-}\overset{3}{\mathrm{CH_2}}{-}\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\overset{4}{\mathrm{C}}}}{-}\overset{5}{\mathrm{CH_3}}$$

2,2,4-Trimethylpentane (correct)

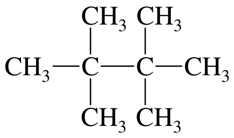
not



$$\overset{5}{\mathrm{CH_3}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\overset{4}{\mathrm{C}}}}{-}\overset{3}{\mathrm{CH_2}}{-}\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\overset{2}{\mathrm{C}}}}{-}\overset{1}{\mathrm{CH_3}}$$

2,4,4-Trimethylpentane (incorrect)

(*d*) The longest continuous chain in $(CH_3)_3CC(CH_3)_3$ contains four carbon atoms.



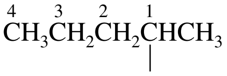
$$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3}$$

The compound is named as a tetramethyl derivative of butane; it is **2,2,3,3-tetramethylbutane.**

2.8 There are three C_5H_{11} alkyl groups with unbranched carbon chains. One is primary, and two are secondary. The IUPAC name of each group is given beneath the structure. Remember to number the alkyl groups from the point of attachment.

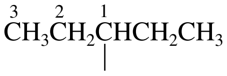
$CH_3CH_2CH_2CH_2CH_2—$

Pentyl group (primary)



$$\overset{4}{\mathrm{CH_3}}\overset{3}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\underset{|}{\overset{1}{\mathrm{C}}}\mathrm{HCH_3}$$

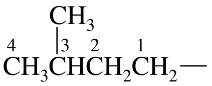
1-Methylbutyl group (secondary)



$$\overset{3}{\mathrm{CH_3}}\overset{2}{\mathrm{CH_2}}\underset{|}{\overset{1}{\mathrm{C}}}\mathrm{HCH_2CH_3}$$

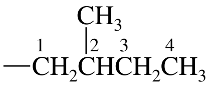
1-Ethylpropyl group (secondary)

Four alkyl groups are derived from $(CH_3)_2CHCH_2CH_3$. Two are primary, one is secondary, and one is tertiary.



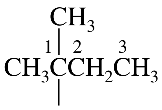
$$\overset{4}{\mathrm{CH_3}}\overset{\mathrm{CH_3}}{\overset{3}{\mathrm{C}}}\mathrm{H}\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_2}}{—}$$

3-Methylbutyl group (primary)



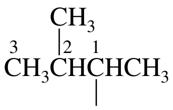
$${—}\overset{1}{\mathrm{CH_2}}\overset{\mathrm{CH_3}}{\overset{2}{\mathrm{C}}}\mathrm{H}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$$

2-Methylbutyl group (primary)



$$\mathrm{CH_3}\underset{|}{\overset{\mathrm{CH_3}}{\overset{1}{\mathrm{C}}}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_3}}$$

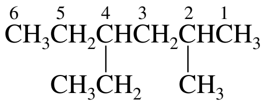
1,1-Dimethylpropyl group (tertiary)



$$\overset{3}{\mathrm{CH_3}}\overset{\mathrm{CH_3}}{\overset{2}{\mathrm{C}}}\mathrm{H}\underset{|}{\overset{1}{\mathrm{C}}}\mathrm{HCH_3}$$

1,2-Dimethylpropyl group (secondary)

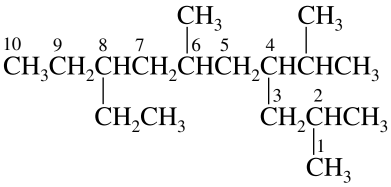
2.9 (*b*) Begin by writing the structure in more detail, showing each of the groups written in parentheses. The compound is named as a derivative of hexane, because it has six carbons in its longest continuous chain.



$$\overset{6}{\mathrm{CH_3}}\overset{5}{\mathrm{CH_2}}\underset{\mathrm{CH_3CH_2}}{\overset{4}{\mathrm{C}}}\mathrm{H}\overset{3}{\mathrm{CH_2}}\underset{\mathrm{CH_3}}{\overset{2}{\mathrm{C}}}\mathrm{H}\overset{1}{\mathrm{CH_3}}$$

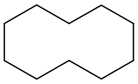
The chain is numbered so as to give the lowest number to the substituent that appears closest to the end of the chain. In this case it is numbered so that the substituents are located at C-2 and C-4 rather than at C-3 and C-5. In alphabetical order the groups are ethyl and methyl; they are listed in alphabetical order in the name. The compound is 4-ethyl-2-methylhexane.

(*c*) The longest continuous chain is shown in the structure; it contains ten carbon atoms. The structure also shows the numbering scheme that gives the lowest number to the substituent at the first point of difference.

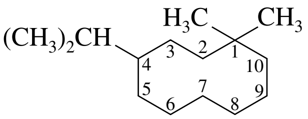


In alphabetical order, the substituents are ethyl (at C-8), isopropyl at (C-4), and two methyl groups (at C-2 and C-6). The alkane is 8-ethyl-4-isopropyl-2,6-dimethyldecane. The systematic name for the isopropyl group (1-methylethyl) may also be used, and the name becomes 8-ethyl-2,6-dimethyl-4-(1-methylethyl)decane.

2.10 (*b*) There are ten carbon atoms in the ring in this cycloalkane, thus it is named as a derivative of cyclodecane.

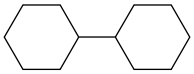


Cyclodecane



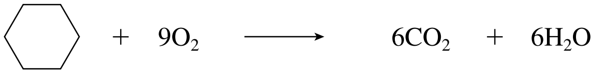
The numbering pattern of the ring is chosen so as to give the lowest number to the substituent at the first point of difference between them. Thus, the carbon bearing two methyl groups is C-1, and the ring is numbered counterclockwise, placing the isopropyl group on C-4 (numbering clockwise would place the isopropyl on C-8). Listing the substituent groups in alphabetical order, the correct name is 4-isopropyl-1,1-dimethylcyclodecane. Alternatively, the systematic name for isopropyl (1-methylethyl) could be used, and the name would become 1,1-dimethyl-4-(1-methylethyl)cyclodecane.

(*c*) When two cycloalkyl groups are attached by a single bond, the compound is named as a cycloalkyl-substituted cycloalkane. This compound is cyclohexylcyclohexane.



2.11 The alkane that has the most carbons (nonane) has the highest boiling point (151°C). Among the others, all of which have eight carbons, the unbranched isomer (octane) has the highest boiling point (126°C) and the most branched one (2,2,3,3-tetramethylbutane) the lowest (106°C). The remaining alkane, 2-methylheptane, boils at 116°C.

2.12 All hydrocarbons burn in air to give carbon dioxide and water. To balance the equation for the combustion of cyclohexane (C_6H_{12}), first balance the carbons and the hydrogens on the right side. Then balance the oxygens on the left side.



Cyclohexane Oxygen Carbon dioxide Water

2.13 (*b*) Icosane (Table 2.4) is $C_{20}H_{42}$. It has four more methylene (CH_2) groups than hexadecane, the last unbranched alkane in Table 2.5. Its calculated heat of combustion is therefore (4 × 653 kJ/mol) higher.

$$\begin{aligned}\text{Heat of combustion of icosane} &= \text{heat of combustion of hexadecane} + 4 \times 653\ \text{kJ/mol}\\ &= 10{,}701\ \text{kJ/mol} + 2612\ \text{kJ/mol}\\ &= 13{,}313\ \text{kJ/mol}\end{aligned}$$

2.14 Two factors that influence the heats of combustion of alkanes are, in order of decreasing importance, (1) the number of carbon atoms and (2) the extent of chain branching. Pentane, isopentane, and neopentane are all C_5H_{12}; hexane is C_6H_{14}. Hexane has the largest heat of combustion. Branching leads to a lower heat of combustion; neopentane is the most branched and has the lowest heat of combustion.

Hexane	$CH_3(CH_2)_4CH_3$	Heat of combustion 4163 kJ/mol (995.0 kcal/mol)
Pentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 3527 kJ/mol (845.3 kcal/mol)
Isopentane	$(CH_3)_2CHCH_2CH_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
Neopentane	$(CH_3)_4C$	Heat of combustion 3514 kJ/mol (839.9 kcal/mol)

2.15 (*b*) In the reaction

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

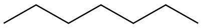
carbon becomes bonded to an atom (Br) that is more electronegative than itself. Carbon is *oxidized.*

(*c*) In the reaction

$$6CH_2{=}CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2)_3B$$

one carbon becomes bonded to hydrogen and is, therefore, *reduced.* The other carbon is also reduced, because it becomes bonded to boron, which is less electronegative than carbon.

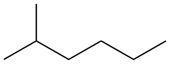
2.16 It is best to approach problems of this type systematically. Since the problem requires all the isomers of C_7H_{16} to be written, begin with the unbranched isomer heptane.



$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

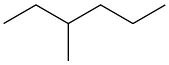
Heptane

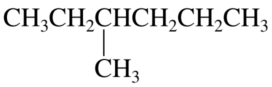
Two isomers have six carbons in their longest continuous chain. One bears a methyl substituent at C-2, the other a methyl substituent at C-3.



$(CH_3)_2CHCH_2CH_2CH_2CH_3$

2-Methylhexane

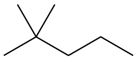




$$CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_3$$

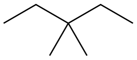
3-Methylhexane

Now consider all the isomers that have two methyl groups as substituents on a five-carbon continuous chain.



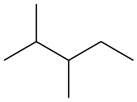
$(CH_3)_3CCH_2CH_2CH_3$

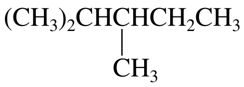
2,2-Dimethylpentane



$(CH_3CH_2)_2C(CH_3)_2$

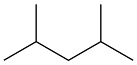
3,3-Dimethylpentane





$$(CH_3)_2CH\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3$$

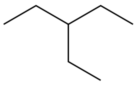
2,3-Dimethylpentane



$(CH_3)_2CHCH_2CH(CH_3)_2$

2,4-Dimethylpentane

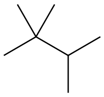
There is one isomer characterized by an ethyl substituent on a five-carbon chain:



$(CH_3CH_2)_3CH$

3-Ethylpentane

The remaining isomer has three methyl substituents attached to a four-carbon chain.

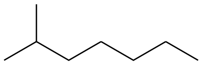


$(CH_3)_3CCH(CH_3)_2$

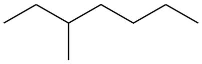
2,2,3-Trimethylbutane

2.17 In the course of doing this problem, you will write and name the 17 alkanes that, in addition to octane, $CH_3(CH_2)_6CH_3$, comprise the 18 constitutional isomers of C_8H_{18}.

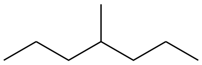
(*a*) The easiest way to attack this part of the exercise is to draw a bond-line depiction of heptane and add a methyl branch to the various positions.



2-Methylheptane



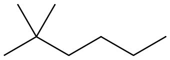
3-Methylheptane



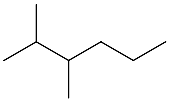
4-Methylheptane

Other structures bearing a continuous chain of seven carbons would be duplicates of these isomers rather than unique isomers. "5-Methylheptane," for example, is an incorrect name for 3-methylheptane, and "6-methylheptane" is an incorrect name for 2-methylheptane.

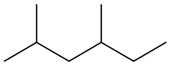
(*b*) Six of the isomers named as derivatives of hexane contain two methyl branches on a continuous chain of six carbons.



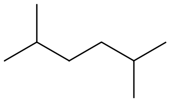
2,2-Dimethylhexane



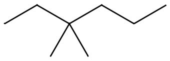
2,3-Dimethylhexane



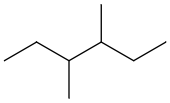
2,4-Dimethylhexane



2,5-Dimethylhexane

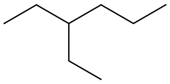


3,3-Dimethylhexane



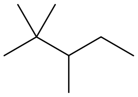
3,4-Dimethylhexane

One isomer bears an ethyl substituent:

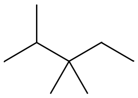


3-Ethylhexane

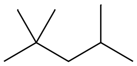
(*c*) Four isomers are trimethyl-substituted derivatives of pentane:



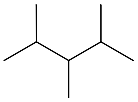
2,2,3-Trimethylpentane



2,3,3-Trimethylpentane

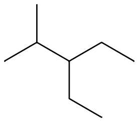


2,2,4-Trimethylpentane

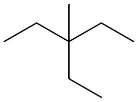


2,3,4-Trimethylpentane

Two bear an ethyl group and a methyl group on a continuous chain of five carbons:

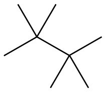


3-Ethyl-2-methylpentane



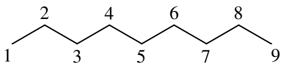
3-Ethyl-3-methylpentane

(*d*) Only one isomer is named as a derivative of butane:

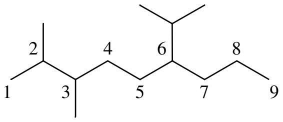


2,2,3,3-Tetramethylbutane

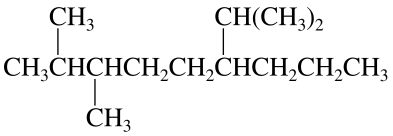
2.18 (*a*) The longest continuous chain contains nine carbon atoms. Begin the problem by writing and numbering the carbon skeleton of nonane.



Now add two methyl groups (one to C-2 and the other to C-3) and an isopropyl group (to C-6) to give a structural formula for 6-isopropyl-2,3-dimethylnonane.

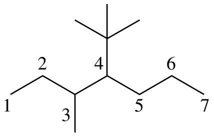


or

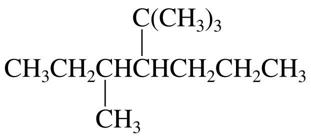


$$CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH(CH_3)_2}{|}}{C}HCH_2CH_2CH_3$$

(*b*) To the carbon skeleton of heptane (seven carbons) add a *tert*-butyl group to C-4 and a methyl group to C-3 to give 4-*tert*-butyl-3-methylheptane.

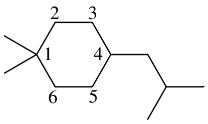


or



$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}H\overset{\overset{C(CH_3)_3}{|}}{C}HCH_2CH_2CH_3$$

(*c*) An isobutyl group is —$CH_2CH(CH_3)_2$. The structure of 4-isobutyl-1,1-dimethylcyclohexane is as shown.



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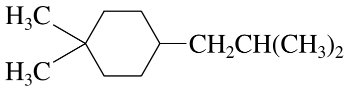
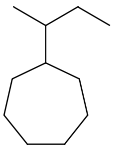


(*d*) A *sec*-butyl group is $CH_3\underset{|}{C}HCH_2CH_3$. *sec*-Butylcycloheptane has a *sec*-butyl group on a seven-membered ring.



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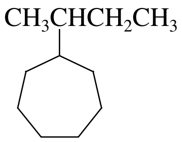
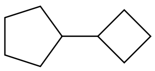
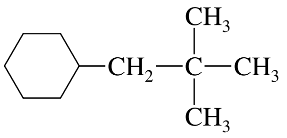


(*e*) A cyclobutyl group is a substituent on a five-membered ring in cyclobutylcyclopentane.

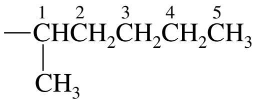


(*f*) Recall that an alkyl group is numbered from the point of attachment. The structure of (2,2-dimethylpropyl)cyclohexane is



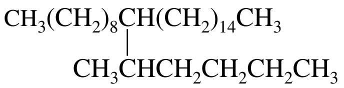
(*g*) The name "pentacosane" contains no numerical locants or suffixes indicating the presence of alkyl groups. It must therefore be an unbranched alkane. Table 2.4 in the text indicates that the suffix -cosane refers to alkanes with 20–29 carbons. The prefix penta- stands for "five," and so pentacosane must be the unbranched alkane with 25 carbons. Its condensed structural formula is $CH_3(CH_2)_{23}CH_3$.

(*h*) We need to add a 1-methylpentyl group to C-10 of pentacosane. A 1-methylpentyl group is:



$$-\underset{\displaystyle CH_3}{\overset{1}{C}H}\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$$

It has five carbons in the longest continuous chain counting from the point of attachment and bears a methyl group at C-1. 10-(1-Methylpentyl)pentacosane is therefore:



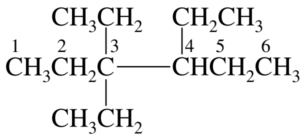
$$CH_3(CH_2)_8\underset{\displaystyle CH_3CHCH_2CH_2CH_2CH_3}{CH}(CH_2)_{14}CH_3$$

2.19 (*a*) This compound is an unbranched alkane with 27 carbons. As noted in part (*g*) of the preceding problem, alkanes with 20–29 carbons have names ending in -cosane. Thus, we add the prefix hepta- ("seven") to -cosane to name the alkane $CH_3(CH_2)_{25}CH_3$ as **heptacosane.**

(*b*) The alkane $(CH_3)_2CHCH_2(CH_2)_{14}CH_3$ has 18 carbons in its longest continuous chain. It is named as a derivative of **octadecane.** There is a single substituent, a methyl group at C-2. The compound is **2-methyloctadecane.**

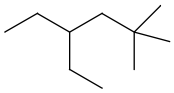
(*c*) Write the structure out in more detail to reveal that it is **3,3,4-triethylhexane.**

$(CH_3CH_2)_3CCH(CH_2CH_3)_2$ is rewritten as

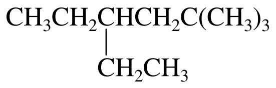


$$\overset{1}{C}H_3\overset{2}{C}H_2\underset{\displaystyle CH_3CH_2}{\overset{\displaystyle CH_3CH_2}{\overset{3}{C}}}—\overset{\displaystyle CH_2CH_3}{\overset{4}{C}H}\overset{5}{C}H_2\overset{6}{C}H_3$$

(*d*) Each line of a bond-line formula represents a bond between two carbon atoms. Hydrogens are added so that the number of bonds to each carbon atom totals four.



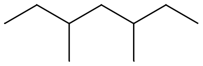
is the same as



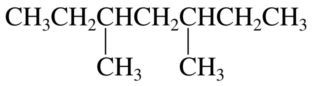
$$CH_3CH_2\underset{\displaystyle CH_2CH_3}{C}HCH_2C(CH_3)_3$$

The IUPAC name is **4-ethyl-2,2-dimethylhexane.**

(*e*)



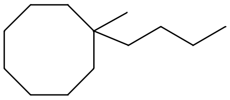
is the same as



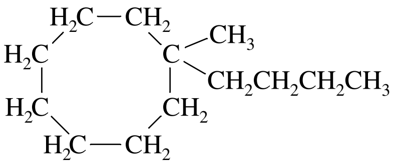
$$CH_3CH_2\underset{\displaystyle CH_3}{C}HCH_2\underset{\displaystyle CH_3}{C}HCH_2CH_3$$

The IUPAC name is **3,5-dimethylheptane.**

(*f*)

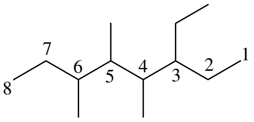


is the same as



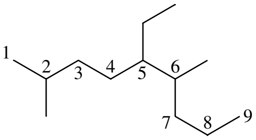
The IUPAC name is **1-butyl-1-methylcyclooctane.**

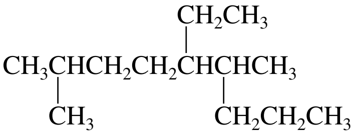
(*g*) Number the chain in the direction shown to give **3-ethyl-4,5,6-trimethyloctane.** When numbered in the opposite direction, the locants are also 3, 4, 5, and 6. In the case of ties, however, choose the direction that gives the lower number to the substituent that appears first in the name. "Ethyl" precedes "methyl" alphabetically.



2.20 (*a*) The alkane contains 13 carbons. Since all alkanes have the molecular formula C_nH_{2n+2}, the molecular formula must be $C_{13}H_{28}$.

(*b*) The longest continuous chain is indicated and numbered as shown.





$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}H\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}}HCH_3$$

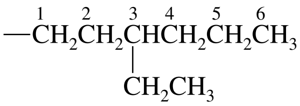
In alphabetical order, the substituents are ethyl (at C-5), methyl (at C-2), methyl (at C-6). The IUPAC name is **5-ethyl-2,6-dimethylnonane.**

(*c*) Fill in the hydrogens in the alkane to identify the various kinds of groups present. There are five **methyl** (CH_3) groups, five **methylene** (CH_2) groups, and three **methine** (CH) groups in the molecule.

(*d*) A primary carbon is attached to one other carbon. There are five primary carbons (the carbons of the five CH_3 groups). A secondary carbon is attached to two other carbons, and there are five of these (the carbons of the five CH_2 groups). A tertiary carbon is attached to three other carbons, and there are three of these (the carbons of the three methine groups). A quaternary carbon is attached to four other carbons. None of the carbons is a quaternary carbon.

2.21 (*a*) The group $CH_3(CH_2)_{10}CH_2—$ is an unbranched alkyl group with 12 carbons. It is a **dodecyl group.** The carbon at the point of attachment is directly attached to only one other carbon. It is a primary alkyl group.

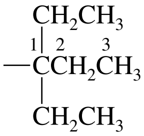
(*b*) The longest continuous chain from the point of attachment is six carbons; it is a hexyl group bearing an ethyl substituent at C-3. The group is a **3-ethylhexyl group.** It is a primary alkyl group.



$$-\overset{1}{C}H_2\overset{2}{C}H_2\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{3}{C}}}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

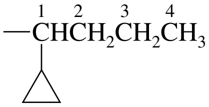
(*c*) By writing the structural formula of this alkyl group in more detail, we see that the longest continuous chain from the point of attachment contains three carbons. It is a **1,1-diethylpropyl** group. Because the carbon at the point of attachment is directly bonded to three other carbons, it is a tertiary alkyl group.

$—C(CH_2CH_3)_3$ is rewritten as

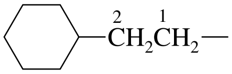


$$-\overset{\displaystyle CH_2CH_3}{\overset{|\,1}{\underset{|}{\underset{\displaystyle CH_2CH_3}{C}}}}\overset{2}{C}H_2\overset{3}{C}H_3$$

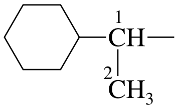
(*d*) This group contains four carbons in its longest continuous chain. It is named as a butyl group with a cyclopropyl substituent at C-1. It is a **1-cyclopropylbutyl** group and is a secondary alkyl group.



(*e*, *f*) A two-carbon group that bears a cyclohexyl substituent is a **cyclohexylethyl** group. Number from the point of attachment when assigning a locant to the cyclohexyl group.

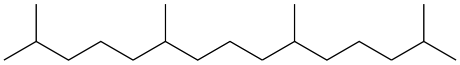


2-Cyclohexylethyl
(primary)



1-Cyclohexylethyl
(secondary)

2.22 The IUPAC name for pristane reveals that the longest chain contains 15 carbon atoms (as indicated by -pentadecane). The chain is substituted with four methyl groups at the positions indicated in the name.



Pristane (2,6,10,14-tetramethylpentadecane)

2.23 (*a*) An alkane having 100 carbon atoms has 2(100) + 2 = 202 hydrogens. The molecular formula of hectane is $C_{100}H_{202}$ and the condensed structural formula is $CH_3(CH_2)_{98}CH_3$. The 100 carbon atoms are connected by 99 σ bonds. The total number of σ bonds is 301 (99 C—C bonds + 202 C—H bonds).

(*b*) Unique compounds are formed by methyl substitution at carbons 2 through 50 on the 100-carbon chain (C-51 is identical to C-50, and so on). There are 49 *x*-methylhectanes.

(*c*) Compounds of the type 2,*x*-dimethylhectane can be formed by substitution at carbons 2 through 99. There are 98 of these compounds.

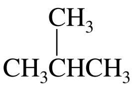
2.24 Isomers are different compounds that have the same molecular formula. In all these problems the safest approach is to write a structural formula and then count the number of carbons and hydrogens.

(*a*) Among this group of compounds, only butane and isobutane have the same molecular formula; only these two are isomers.

$CH_3CH_2CH_2CH_3$

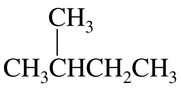
Butane
C_4H_{10}

Cyclobutane
C_4H_8



$CH_3\overset{CH_3}{C}HCH_3$

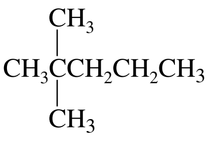
Isobutane
C_4H_{10}



$CH_3\overset{CH_3}{C}HCH_2CH_3$

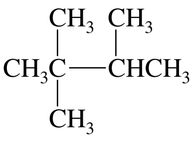
2-Methylbutane
C_5H_{12}

(*b*) The two compounds that are isomers, that is, those that have the same molecular formula, are 2,2-dimethylpentane and 2,2,3-trimethylbutane.



$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2CH_2CH_3$

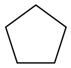
2,2-Dimethylpentane
C_7H_{16}



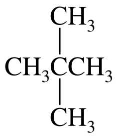
$CH_3\underset{CH_3}{\overset{CH_3}{C}}—\overset{CH_3}{C}HCH_3$

2,2,3-Trimethylbutane
C_7H_{16}

Cyclopentane and neopentane are not isomers of these two compounds, nor are they isomers of each other.



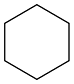
Cyclopentane
C_5H_{10}



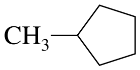
$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3$$

Neopentane
C_5H_{12}

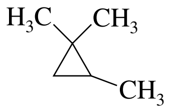
(*c*) The compounds that are isomers are cyclohexane, methylcyclopentane, and 1,1,2-trimethylcyclopropane.



Cyclohexane
C_6H_{12}



Methylcyclopentane
C_6H_{12}

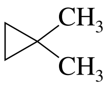


1,1,2-Trimethylcyclopropane
C_6H_{12}

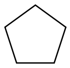
Hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$, has the molecular formula C_6H_{14}; it is not an isomer of the others.

(*d*) The three that are isomers all have the molecular formula C_5H_{10}.

Ethylcyclopropane
C_5H_{10}

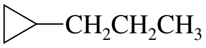


1,1-Dimethylcyclopropane
C_5H_{10}

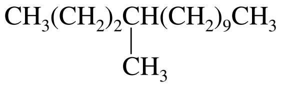


Cyclopentane
C_5H_{10}

Propylcyclopropane is not an isomer of the others. Its molecular formula is C_6H_{12}.



(*e*) Only 4-methyltetradecane and pentadecane are isomers. Both have the molecular formula $C_{15}H_{32}$.

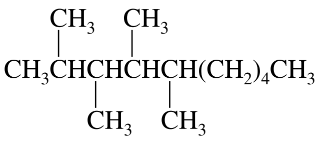


$$CH_3(CH_2)_2\underset{CH_3}{CH}(CH_2)_9CH_3$$

4-Methyltetradecane
$C_{15}H_{32}$

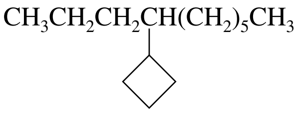
$CH_3(CH_2)_{13}CH_3$

Pentadecane
$C_{15}H_{32}$



$$CH_3\overset{CH_3}{CH}\underset{CH_3}{CH}\overset{CH_3}{CH}\underset{CH_3}{CH}(CH_2)_4CH_3$$

2,3,4,5-Tetramethyldecane
$C_{14}H_{30}$



4-Cyclobutyldecane
$C_{14}H_{28}$

2.25 The oxygen and two of the carbons of C_3H_5ClO are part of the structural unit that characterizes epoxides. The problem specifies that a methyl group (CH_3) is *not* present; therefore, add the