1

BONDING AND ELECTRON DISTRIBUTION

1.1 THE DECISION-BASED APPROACH TO ORGANIC CHEMISTRY
Decision-based AI Approach of this Text; Problem Spaces as Maps of Possible Alternatives; Types of Tree Searches; Generate and Select Search Strategy; Control Knowledge for Decisions; Overview of the Early Chapters; the Principle of Electron Flow from Electron Rich to Electron Poor; Nucleophiles (Lewis Bases) Seek Positive Charges and Electrophiles (Lewis Acids) Seek Negative Charges

1.2 IONIC AND COVALENT BONDING
Valence Electrons; Electronegativity; Ionic, Covalent, and Polar Covalent Bonds

1.3 LEWIS STRUCTURES AND RESONANCE FORMS
Drawing Lewis Structures to Keep Track of Electrons. Number of Valence Electrons; General Bonding Trends; Formal Charges; In Resonance Forms Only Electrons Move, Not Atoms; Deciding on Major and Minor Resonance Forms

1.4 CURVED-ARROW NOTATION
Full-Headed Curved Arrow Moves Two Electrons; Half-Headed Curved Arrow Moves One Electron; Electron Source; Electron Sink; Charge Is Conserved; Direction of Electron Flow; Good Arrow Pushing Habits; Common Errors

1.5 NOMENCLATURE AND ABBREVIATIONS
Line Structure; First 10 Alkanes; Common Functional Groups; Abbreviations

1.6 THE SHAPES OF MOLECULES
Valence Shell Electron Pair Repulsion (VSEPR) Theory; Groups of Electron Pairs Adopt Positions Around a Central Atom of Least Electron Charge Repulsion

1.7 AN ORBITAL VIEW OF BONDING
Review of *s* and *p* Orbitals Used in Bonding; Using *p* Orbitals to Make the Sigma and Pi Bonds of Nitrogen; Hybridization of the Atomic Orbitals of Carbon, sp, sp^2, sp^3; CC Single Bonds and Free Rotation, Conformational Isomers; CC Double Bonds; High Barrier to Rotation: *Cis* and *Trans*; CC Triple Bonds; Cumulenes

1.8 MOLECULAR REPULSIONS, ATTRACTIONS, AND HYDROGEN BONDING
Steric Hindrance, Nonbonded Repulsion; van der Waals Radii; Common Groups Ordered by Size; Dipole Attractions; Hydrogen Bonding; Cation–Pi Interactions; Donor-Acceptor Complexes

1.9 CONJUGATION, VINYLOGY, AROMATICITY
Overlapping *p* Orbitals Behave as One System, Have Greater Stability; Vinylogy Is the Extension of the Properties of a System by the Insertion of a Double Bond; Unbroken Loop of *p* Orbitals with $4n + 2$ Pi Electrons Has Aromatic Stabilization

1.10 SUMMARY
Structure Determines Reactivity; Lewis Structures and Electron Flow Arrows Allow Us to Keep Track of Electrons and Explain Reactions

COPYRIGHTED MATERIAL

Electron Flow in Organic Chemistry: A Decision-Based Guide to Organic Mechanisms, Third Edition. Paul H. Scudder.
© 2024 John Wiley & Sons, Inc. Published 2024 by John Wiley & Sons, Inc.

1.1 THE DECISION-BASED APPROACH TO ORGANIC CHEMISTRY

The Preface mentioned that this decision-based approach to organic chemistry is modeled after the scientific method. A good hypothesis is just a reasonable guess. You will learn how to recognize alternatives and how to judge which alternative is most reasonable. This is the essence of critical thinking, a crucial skill for scientists, physicians, and life in general. You will develop a good intuition, for intuition can be considered just an internalized decision process. We will use the artificial intelligence concepts of problem spaces and tree searches to help you develop this intuition for organic chemistry.

1.1.1 Introduction to Problem Spaces

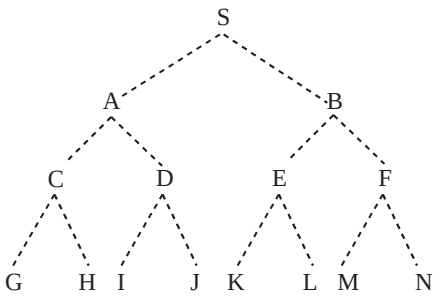
If you were planning a road trip across the US, you would need a map of the highways. It would allow you to see all routes from your starting city to your goal city. You would then choose the best route for what you wanted to see and the time you had for the trip. This is exactly the process you want to go through for understanding organic chemistry. We need a map and the ability to choose the best route. Our maps of problems are called problem spaces and are often shown as trees, with a decision to be made at each branch point.

Figure 1.1A illustrates a generic problem space and some of the approaches to working from the start at the top of the tree at point S down to the expected answer. If that route is from S to A to D to I, some students may attempt to memorize "S goes to I" without understanding the process involved. In order to provide a greater understanding, instructors spend book and class time explaining the expected route to the answer. However, students may see the "lightning strike" to product as shown in Figure 1.1B but not understand the choices that were made along the way. Instructors may feel that, if shown enough times, students will be able to do it themselves. But we can't expect you to make good choices if you have not been taught how to make those decisions. When you work problems and depart from a reasonable route, you need to see your answer discussed to understand how better choices could have been made.

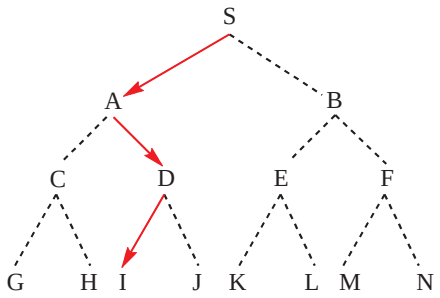
1.1.2 Introduction to Tree Searches

There are several ways to search a problem space tree. Computers often do a "breadth-first" search by considering every possible route and selecting the most efficient one. We might do this, if we planned our road trip with a map of all major roads. However, while working most science problems we are not provided with a complete problem space map, but rather must generate one on our own. We need to employ a different search strategy. New students often approach science problems "depth-first" by going with the first thing that occurs to them and hoping to get lucky (Figure 1.1C). If they don't reach the expected answer, they back up to the last branch and try another route. However, the more complex the problem space is, the less successful this depth-first search process is. Organic chemistry can have complex highly branched problem spaces, so we again need a different tree search strategy. The tree search strategy that excels in complex problem spaces is a "best-first" search, and that is the focus of this text.

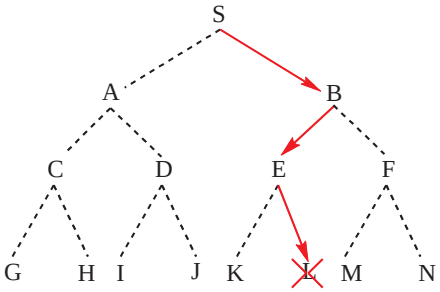
A "best-first" search process is shown in Figure 1.1D, where alternatives are generated and the best alternative is picked at each branch point. Mastering and internalizing this "generate and select" process is crucial to becoming a good scientist or physician. After all, diagnosis is just a physician's search of a complex problem space. An internalized best-first search becomes the essence of a good intuition. If you can master this "generate and select" process and apply it to other fields, it may be the most valuable thing you can take away from a course in organic chemistry.



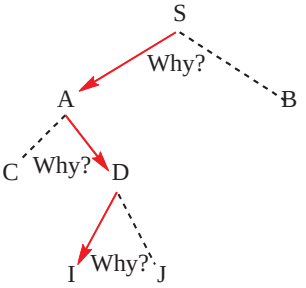
A. Problem space showing all possibilities



B. Instructor lightning strike to expected answer



C. Depth-first impulse to wrong answer



D. Best-first search decision process

Figure 1.1 A generic problem space and some strategies for tree searches in the problem space.

1.1.3 Introduction to Control Knowledge

First, we need to recognize when we are at a branch point and that a decision needs to be made. Then, to be able to make good decisions in a best-first search, we need to master and utilize "control knowledge." These are checks of reasonableness to help you select the best route. For our road trip, this may be the quality of the highway, the season of year, and how much time we have. For organic problems, control knowledge includes the stability of intermediates, reactivity trends of reactants, whether the medium is acidic or basic, evaluation of energetics, and similarity to known processes. We need to understand the principles of stability that will determine which route is of lower energy. This text will use flowcharts and energy surfaces as problem space maps to illustrate what decisions need to be made. The good news is that the control knowledge that applies to thousands of organic reactions is limited and relatively easy to understand.

An important part of control knowledge is to recognize the boundaries of the problem. When we say an answer is in "the ballpark," we are just testing for reasonable bounds. If a friend bragged he or she could run a mile in a minute, you would have good reason not to believe, considering the fastest runners barely break a four-minute mile. You have tested incoming data with control knowledge before deciding, and that is the essence of critical thinking. Table 1.1 illustrates a few common values and upper bounds that are useful in organic chemistry.

Table 1.1 Common Values and Upper Bounds for Common Chemical Reactions

Measurement	Common for organic	Other examples	Upper bound
Density	Often <1 g/cm^3	1.0 g/cm^3 (water)	22.61 g/cm^3 (osmium)
Concentration	11.2 mol/L (benzene)	55.5 mol/L (water)	118.9 mol/L (osmium)
Temperature	–78 to +220°C	25°C (room temp.)	1400°C (glass melts)

Each of the dozen electron flow path alternatives that we build our explanations of more complex organic reactions has boundaries that need to be considered. These path limitations are included as each electron flow path is introduced in Chapter 4 and are summarized in Chapter 7. Another important aspect of control knowledge is using the reactivity trends of reactants to select the hottest site for reaction in a molecule. This allows us to focus on only the most important part of the molecule and not be distracted by differences in parts of the molecule that do not matter, like the unreactive hydrocarbon skeleton. In this way you won't "slip on the grease" when the hydrocarbon section changes, but the hot spot remains the same. Also, the stability trends of intermediates can be used to predict the lowest-energy route when two or more intermediates are possible. Since energy is often limited, the lowest-energy route is the fastest and often the predominant route. Stability trends of products determine the route in reversible systems, as the most stable product is the one formed. More complex decisions involve multiple factors, which contribute to a "decision boundary" between possible choices, as discussed in Chapter 9.

1.1.4 Preview of the Goals of Beginning Chapters

Chapter 1 – Bonding and Electron Distribution

Since favorable organic reactions usually break weak bonds and make stronger ones, you need to understand the different types of bonding. You must be able to represent the structure of molecules with Lewis structures and resonance forms, to be able to find the electron-rich and electron-poor "hot spots" of the molecule. Once the hot spots are identified, you need to be able to draw the process of bond breakage and bond formation with electron flow "curly arrows." The first chapter gives us the means to discuss the "why" of organic reactions using the common language of Lewis dot structures and electron flow arrows. So first we need to understand that "language" of the explanations, to be able to draw a Lewis structure correctly and understand how curly arrows move electrons.

Chapter 2 – The Process of Bond Formation

To be able to judge the most favorable route, we must understand qualitatively both thermodynamics and kinetics. Therefore we need to understand the process of bond making and breaking, what makes bonds strong or weak, and how the energetics of a process makes some routes more favorable than others.

Chapter 3 – Proton Transfer and the Principles of Stability

To ease into the discussion of organic reactions, it is best to start with a familiar reaction like the acid–base reaction of proton transfer and thoroughly understand how structure determines reactivity. If we can understand proton transfer and the energetics associated with various possibilities, we have come a long way toward understanding organic reactions. Organic reactions use the same principles and often have proton transfer as a first step.

Chapter 4 – Important Reaction Archetypes

Other than proton transfer, only about four mechanistic reaction types form the core of an organic course. It is important to recognize and understand these four important reaction archetypes. What does the problem space for each archetype look like, and how do the reactant structures and reaction conditions influence the most favored route?

Later Chapters

The later chapters develop a general approach to all organic reactions by showing how to focus on the most reactive centers and choose the best route. This book provides tools for handling large amounts of information. It will emphasize the grammar of organic chemistry that will help you make sense of all the material. Without this essential logic to guide you, organic chemistry can become a flood of disconnected reactions to be memorized that will challenge even those good at memorization.

This book groups reactions together that have similar processes. Reactants are put into generic groups that behave similarly. General Chemistry did this by grouping all the bases together and all the acids in a separate group. Looking at the chemical structure, we can predict the chemical behavior of HCl would be similar to HBr and the other acids.

A reaction mechanism is our best guess at the steps for how the reaction occurs. Even the most complex reactions can be broken down into a sequence of basic electron flow steps, called electron flow pathways, which become the building blocks of all the common mechanistic processes. The purpose of this text is to teach the understanding and proper combination of these building blocks. Just a dozen electron flow paths can explain almost all of the common reactions found in an undergraduate organic chemistry course. The mechanistic problem space illustrates the correct use of these pathways. The best advantage that a decision-based approach has over memorization is that it engages the mind. We can ask questions like, "Why did it do this and not that?" New reactions become puzzles to solve, not another thing to be memorized.

Our approach is to understand why and when a reaction will occur and to establish a command of organic chemistry based more upon understanding the basics than upon memorization. The most impressive result of organizing the material by mechanistic process is that you will develop a sound chemical intuition and will be capable of making good educated guesses. In addition, the how and why of organic chemistry is far more interesting than the memorization of its components. We will make use of trends and general rules as tools to aid us in understanding what has happened in an organic reaction. These tools have their exceptions and limitations, but they allow us to develop an overall "feel" for organic reactions. We can worry about the exceptions, if necessary, after the bulk of the material is mastered.

1.1.5 The Principle of Electron Flow

A reaction will occur when there is an energetically accessible path by which electrons can flow from an electron source to an electron sink. A reaction is a flow of electron density from an electron-rich region to an electron-deficient region (the obvious exceptions to this are free-radical reactions, treated separately in Chapter 12). To know which regions are electron rich or electron deficient, we must be able to predict the distribution of electron density over a molecule.

A *nucleophile* ("nucleus-loving," $Nu:^-$) is a *Lewis base* (electron pair donor) that has an available electron pair for bonding. Nucleophiles act as electron sources and can be negatively charged like hydroxide anion or neutral like water. An *electrophile* ("electron-loving," E^+) is a *Lewis acid* (electron pair acceptor) that can accept two electrons to form a bond. Electrophiles act as electron sinks and can be positively charged like hydronium cation or neutral like bromine.

Any bond formed is the combination of a nucleophile and an electrophile. The most probable product of a reaction results from the best electron source bonding with the best electron acceptor. The curved-arrow notation (Section 1.4) allows us to describe the flow of electrons from source to sink.

The concept of flow is very important. Just as water flows under the influence of gravity, electrons flow under the influence of charge: from electron-rich atoms to electron-deficient atoms. A poor electron source will not react with a poor electron sink within a useful length of time. One might consider this a case of no push and no pull, so no appreciable electron movement occurs. A poor electron sink requires combination with a good electron source for a reaction to occur.

We need to answer the questions: What properties distinguish a good electron source, a good electron acceptor, and a good pathway for electron flow? There are relatively few

pathways through which the common electron sources and sinks react. The use of generic electron sources and sinks and generic electron flow pathways makes the similarities and interrelationships of the major reactions in organic chemistry become obvious. The electron flow pathways become the building blocks of even complex organic reaction mechanisms, so all the mechanisms seem to "flow" from first principles.

Before we explore the problem space for a simple proton transfer reaction, we need to understand the basics of bonding and define a consistent nomenclature. In order to use the electron flow paths, you first need to be able to keep track of atoms and electrons—write Lewis structures correctly and easily.

1.2 IONIC AND COVALENT BONDING

Before trying to understand stable molecules, let's try to understand stable atomic electron configurations. The outer electrons (valence electrons) are involved in bonding. Figure 1.2 shows the valence electrons of the atoms of elements common in organic chemistry. An atom might achieve the stable filled shell electron configuration of a noble gas (group VIIIA) in any of three ways: lose electrons, gain electrons, or share electrons.

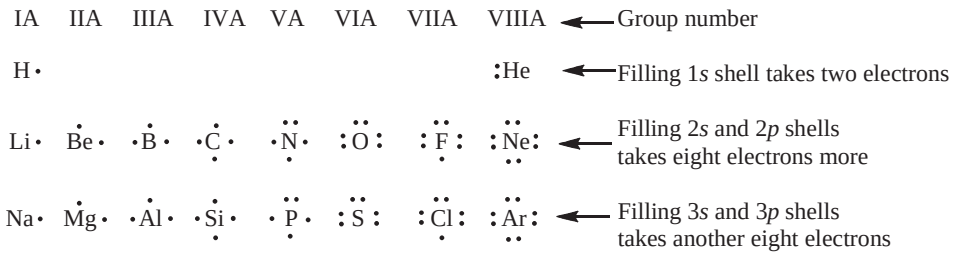
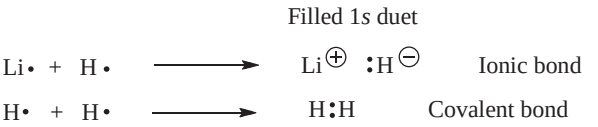


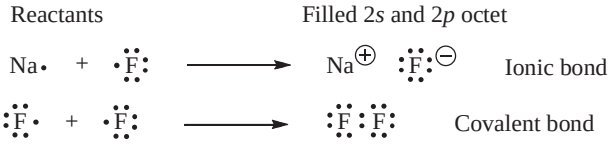
Figure 1.2 The valence electrons of elements in the first three rows of the periodic table.

In the first row of the periodic table, the two valence electrons of helium fill the 1*s* shell, making it very stable. If lithium loses one of its three total electrons, it now has the helium duet and is stable as the Li^+ cation. The hydrogen atom needs two electrons to form the helium duet, and it can achieve that either by gaining an electron outright to form hydride anion or by sharing an electron with another atom. The first row is special in needing only an electron duet for stability; higher rows require an octet of valence electrons for stability. Because hydrogen can add one electron to form hydride, it is sometimes drawn in two places on the periodic table, in Groups IA and in VIIA.



In the second row, neon has a complete valence shell with both the 2*s* and 2*p* orbitals filled (in addition to the filled 1*s* helium core). Sodium has one more electron than neon; losing that electron gives Na^+, which has neon's stable filled shell. If a fluorine atom gains one electron to become fluoride, it has the complete octet of neon and a filled shell.

To generalize, elements of Groups IA and IIA commonly lose their valence electrons to step back to the last noble gas electron configuration. For this reason, it is normal to write all compounds of elements in Groups IA and IIA as ionic. Halogens of Group VIIA can gain an electron to step forward to the next noble gas electron configuration of the halide ion. Groups IIIA through VIIA can gain stable valence octets by sharing electrons in covalent bonds.



Ionic and covalent bonds are the two extremes of bonding. In a covalent bond, a pair of electrons is shared between two atoms. The shared pair of electrons is in a bonding orbital made from the overlap of an atomic orbital from each atom. For a strong covalent bond, these shared atomic orbitals must overlap well and must be similar in energy. In an ionic bond, that pair of electrons resides primarily on one of the two atoms, producing two oppositely charged ions that are attracted to each other. This attraction is expressed mathematically by Coulomb's law, which says the attractive force is directly proportional to the charge of each ion and inversely proportional to the square of the distance between them. A strong ionic bond has opposite charges very close to each other. Reactions tend to break weak bonds and make strong ones, so a reaction can be favored by the formation of strong ionic bonds or strong covalent bonds or both (the HSAB principle, Section 2.4).

Most bonds fall between these two extremes. Pauling defined *electronegativity* as the power of an atom in a molecule to attract electrons to itself. The electronegativity difference of two bonded atoms is an indication of how polarized, how ionic, the bond is. In homonuclear diatomic molecules like H_2 there is pure covalency, no polarization, for the electronegativity difference is zero. Common table salt, Na^+Cl^-, contains a good example of an ionic bond in which the electronegativity difference is large. Table 1.2 is a partial periodic table of the average electronegativities of commonly encountered elements. Elements more electronegative than carbon make up the upper right corner in the periodic table and are in boldface. Electronegativity is the result of increasing nuclear charge on the valence electrons. For example, the electrons in the 2*p* orbital get pulled closer to the nucleus in going from boron to fluorine as the nuclear charge increases. Likewise, Na^+ and F^- both have 10 electrons, but Na^+ is much smaller and its electrons are held tighter than fluoride due to sodium's greater nuclear charge, 11 protons in sodium vs. 9 protons in fluorine.

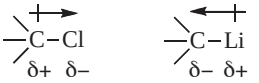
Table 1.2 Average Electronegativities of Selected Elements

H 2.20									
Li 0.98					B 2.04	C 2.55	**N** **3.04**	**O** **3.44**	**F** **3.98**
Na 0.93	Mg 1.31				Al 1.61	Si 1.90	P 2.19	**S** **2.58**	**Cl** **3.16**
K 0.82			Cu (I) 1.90	Zn 1.65				Se 2.55	**Br** **2.96**
				Cd 1.69					**I** **2.66**

The electronegativity of an atom will vary depending on what else is bonded to it. For example, the carbon atom of a CF_3 group is more electronegative than the carbon atom of a CH_3 group. In the CF_3 group, the three highly electronegative fluorines withdraw electron density from the CF_3 carbon atom, which in turn will withdraw more electron density from whatever it's bonded to.

Both the degree and the direction of the polarization of a bond can be predicted by the electronegativity difference. The bonding electron pair is more likely to be found around the more electronegative atom. Carbon can be either partially plus, $\delta+$, or partially minus, $\delta-$, depending on the electronegativity of the group bonded to it. The polarization of the bonding

electrons will become very important in understanding how two species interact, since like charges repel and unlike charges attract. A partially plus carbon will attract a negative ion; a partly negative carbon will attract a positive one.



1.3 LEWIS STRUCTURES AND RESONANCE FORMS

Electron flow paths are written in the language of Lewis dot structures and curved arrows. Lewis dot structures are used to keep track of all valence electrons, and curved arrows are used to symbolize electron movement. You must be able to draw a proper Lewis structure complete with formal charges accurately and quickly. Your command of curved arrows must also be automatic. These two points cannot be overemphasized, since all explanations of reactions will be expressed in the language of Lewis structures and curved arrows. A Lewis structure contains the proper number of valence electrons, the correct distribution of those electrons over the atoms, and the correct formal charge. We will show all valence electrons; lone pairs are shown as darkened dots and bonds by lines.

An atom in a molecule is most stable if it can achieve the electronic configuration of the nearest noble gas, thus having a completely filled valence shell. Hydrogen with two electrons around it, a duet, achieves the configuration of helium. Second-row elements achieve the configuration of neon with an octet of valence electrons. Third-row elements like sulfur achieve an octet but may also expand their valence shell; for example SF_6 is a stable molecule with six single bonds to sulfur (12 bonding electrons total).

1.3.1 Procedure for Drawing Lewis Structures

Use the periodic table to find the valence electrons contributed from each atom. Add an additional electron for a negative charge, or subtract one to account for a positive charge to get the **total number of valence electrons**. Then **draw single bonds between all connected atoms to establish a skeleton**, or preliminary structure. You need to know the pattern in which the atoms are connected. If you have to guess at the connectivity, the most symmetrical structure is often correct. Sulfuric acid, for example, has the one sulfur in the center surrounded by the four oxygens, two of which have attached hydrogens. Since hydrogen forms one covalent bond, it is always on the outside of the structure. **Place any additional bonds between adjacent atoms that both have incomplete octets to satisfy the following general bonding trends**. There may be more than one way to do this (see the next section). Do not exceed the octet for second-row elements. Higher-row elements like phosphorus or sulfur can exceed an octet.

General bonding trend	Example
One bond: H, F, Cl, Br, I	
Two bonds: O, S	
Three bonds: N, P	
Four bonds: C, Si	

Use these trends to connect the atoms. Multiply the number of bonds by two to get the number of electrons shared in bonds. **Subtract the number of shared electrons from the number of valence electrons to get the number of unshared electrons** (if any). Place the unshared electrons as lone pairs on atoms that need them to make octets.

Assign formal charges. Formal charge is a comparison of the number of electrons an atom "owns" in the Lewis structure with the number it would have if it were free. The atom owns half of the electrons that it shares in a bond, but all of its unshared electrons.

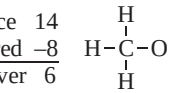
Formal charge = free atom valence − (# of bonds + unshared # of electrons)

The sum of the formal charges must be equal to the total charge of the species. As a cross-check, usually if an atom has more than the number of bonds listed in the general bonding trends, it will have a positive formal charge; if it has less, it will bear a negative formal charge. Formal charge can help identify electron-rich and electron-deficient areas. However, a molecule may have more than one Lewis structure to consider (Section 1.3.2).

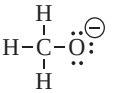
Example: Methoxide anion, CH_3O^-

The total number of valence electrons is 14; we get 6 from O, 4 from C, 1 from each of 3 H's, and 1 for the minus charge. It took four bonds to connect the atoms, so the number of shared electrons is 8. We have used eight electrons, and there are six electrons remaining to be added as lone pairs to complete oxygen's octet.

Valence	14
– Shared	–8
Left over	6



All that is left to do is assign formal charge. Oxygen started with six valence electrons, and in this structure has one bond to it and six unshared electrons, so –1 must be its formal charge. A check shows that the shells are correct for all the atoms, all the valence electrons have been used, and that the sum of the formal charges equals the total charge. The final structure is:

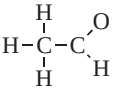


We can't have a bottle of just anions. All compounds are charge balanced, so the methoxide anion above would have a cation to balance the negative charge. This is often a group 1A cation like Li^+, Na^+, or K^+. These cations have the stable configuration of a noble gas, and therefore are just spectator ions. To simplify things, organic chemists often don't bother writing the spectator ions because they don't participate in the reaction.

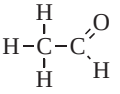
Example: Acetaldehyde, CH_3CHO

The total number of valence electrons is 18; we get 6 from the O, 4 from each of 2 C's, 1 from each of 4 H's. The six-bond skeleton shares 12 electrons.

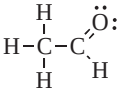
Valence	18
– Shared	–12
Left over	6



Another bond must be made because two adjacent atoms, C and O, have less than expected from the general bonding trends. This bond should go between those two atoms giving the structure:



Seven bonds used 14 electrons; the 4 unshared valence electrons are added as lone pairs to complete the octet of oxygen. Formal charges are all zero; the final structure is:



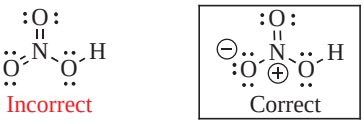
Cross-check: Valid Lewis structures:

- **have correct number of valence electrons,**
- **have correct formal charge (sums to total charge), and**
- **do not exceed octets for second-row elements.**

Common Errors

Throughout the text the incorrect example will appear on the left with the corrected version to the right of it, followed by an explanation on why the left example is incorrect.

Lewis Structure Errors



It is impossible to flow electrons correctly if you cannot keep track of them accurately. The structure on the left has exceeded the octet for nitrogen. Five bonds to N means 10 electrons around it. Since nitrogen is a second-row element, it cannot expand its valence shell.

1.3.2 Resonance Hybrids

Often, one Lewis structure is not sufficient to describe the electron distribution in a molecule. In many cases, the use of a *resonance hybrid* is necessary. All resonance forms are valid Lewis structures. In resonance forms, **only the electrons move and not the atomic nuclei**. Each resonance form does not have a separate existence but is a part of a hybrid whole. The use of a double-headed arrow, ↔, between the forms reinforces the notion of a hybrid representation of a single structure. The forms are not in equilibrium with each other (equilibrium is shown by two opposing arrows).

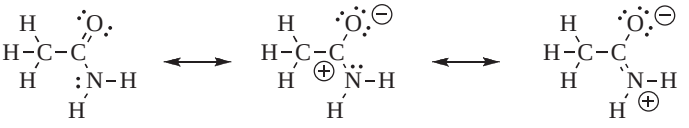
Only one hybrid exists, not individual equilibrating resonance forms. We are trying to describe a molecule's rather diffuse electron cloud with lines and dots; it is not surprising that often one Lewis structure is insufficient. The acetate anion, CH_3COO^-, requires two resonance forms to describe it. Both structures are of equal importance; the carbon–oxygen bond lengths are equal. Generally, an ion is more stable if it has more resonance forms of similar energy (implied by similar structure).



Frequently, the hybrid cannot be represented by equally weighted resonance forms. The hybrid may be more like one form than the other, and thus the resonance forms are denoted as major and minor. For formaldehyde, $H_2C{=}O$, the resonance forms represent the uneven electron distribution of a polarized multiple bond; the charge-separated minor resonance form places a negative charge on the more electronegative atom. Oxygen is winning the electronegativity tug-of-war for the bonding electrons, and mixing in this minor resonance form acknowledges that. The form on the far right does not contribute because it is contrary to the polarization of the bond. A good general rule is to avoid having an incomplete octet on a highly electronegative atom, like nitrogen or oxygen.



Resonance forms for acetamide, CH_3CONH_2, reveal the polarization of the amide group. The partially negative oxygen, not the partially positive nitrogen, will be the reactive site when an amide is used as an electron source.



Major Minor Minor

The major resonance form will have the most covalent bonds and complete shells and the least amount of charge separation. It will seem to be the most stable of the possible resonance forms. Place any negative charges on electronegative atoms. Resonance structures with an incomplete shell are usually minor. Resonance forms having an electronegative atom with an incomplete octet are insignificant.

Occasionally "no-bond" resonance forms are needed to describe the electron distribution in a molecule and are usually associated with very acidic hydrogens. The polarized bond in hydrochloric acid can be represented by using resonance structures to show the partial ionic nature of the bond. The atoms do not move, only the electrons.



Major Minor

Cross-check: The major resonance contributor will have:

- **the most covalent bonds,**
- **the least amount of charge separation,**
- **the most complete octets and duets possible, and**
- **any negative charges on the most electronegative atoms.**

1.4 CURVED-ARROW NOTATION

A full-headed curved arrow indicates the movement of two electrons from the tail of the arrow to the head. A half-headed arrow (fishhook) indicates the shift of one electron likewise. The two ways that a bond can break are *heterolytic* (two electrons) or *homolytic* (one electron). Homolytic processes are unusual and will be treated separately in Chapter 12. For ease of identification, all electron flow arrows in this book will be red.



Heterolytic cleavage (full headed arrow) Homolytic cleavage (fishhook arrows)

Arrows indicate a movement or flow of electrons that **must come from a site of electron density**, either a lone pair or a bond, and move to a site that can accept additional electron density.



If an arrow comes from a bond, that bond is broken. If an arrow comes from a lone pair, the lone pair is removed and a new bond is formed at the head of the arrow. If the head of the arrow points between two atoms, it forms a new bond between them. If it points to an atom, it forms a new lone pair on that atom.



A source of confusion for beginning students is that for intermolecular bond-forming reactions, some authors will point the arrow between the two atoms, whereas others will point

it directly at the second atom. We will try a compromise—when an arrow goes between two molecules, the head of the arrow is drawn close to the appropriate atom on the second molecule. The following are slightly different ways to show the formation of a bond between $Nu:^-$ and E^+ to give the Nu–E bond; we will use the arrow notation on the right. A useful generalization is that an arrow that comes from a lone pair will always form a bond, not another lone pair.



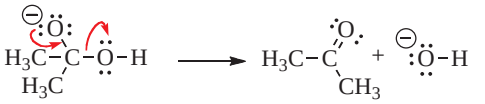
The bond or lone pair from which the first arrow in an electron flow originates is called the *electron source*. The head of the last arrow in an electron flow points to the *electron sink*. **Arrows will always point away from negative charges and toward positive charges.** Sometimes it is useful to use arrows to interconvert resonance structures, but those arrows do not really indicate electron flow.



Some specific examples will help illustrate the correct use of arrows in reactions:

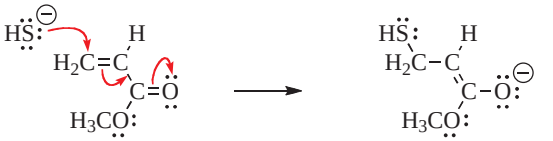


The first arrow on the left comes from the lone pair on the electron-rich hydroxide anion and makes a bond between the hydroxide oxygen and the hydrogen. The second arrow breaks the O–H bond and makes a new lone pair on oxygen. Note that with correct electron bookkeeping **the charge on one side of the transformation arrow will be the same as on the other side** (in this case one minus charge). Charge is conserved. If the electron movement signified by the curved arrows is correct, the products will also be valid Lewis structures.



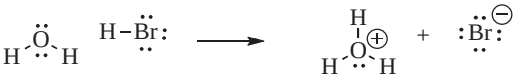
In this second example, the flow comes from the lone pair on the negative oxygen and forms a double bond. The flow continues by breaking the carbon–oxygen bond to form a new lone pair on the oxygen of the hydroxide ion. The electron source in this example changes from negative to neutral because the flow removes electrons from it; the sink becomes negative in accepting the electron flow.

In this last example, the flow starts with the electron-rich sulfur anion and forms a carbon–sulfur bond with the CH_2 group. The pi bond breaks and forms a new pi bond. The flow finishes by breaking the carbon–oxygen pi bond and forming a new lone pair on the electronegative oxygen. Every time an arrow forms a bond to an atom that already has a complete octet, another bond to that atom must break, so the octet is not exceeded.

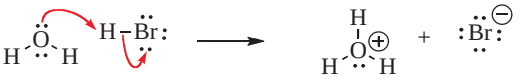


Exercise: Cover the right side of the previous reactions and draw the product.

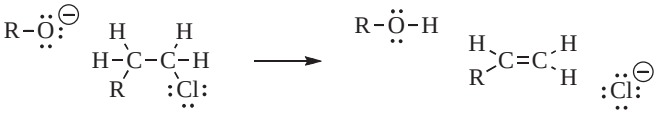
A good way to see whether you have mastered arrows and the concept of electron flow is to provide the arrows given the reactants and products. In these one-step mechanism problems, you must decide which bonds were made and broken and in which direction the electron flow went. Here is an example:



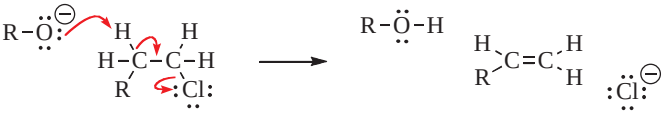
Note the bonding changes: Oxygen has one less lone pair and has formed a new bond to the hydrogen from HBr; the H–Br bond is broken, and bromine now has another lone pair. Now look at the charges: Oxygen is now positive, and bromine is now negative. Electron flow must have come from oxygen (the source) and ended up on bromine (the sink) to account for the change in charge. Only one set of arrows could be correct: The first arrow must come from the oxygen lone pair and form a new O–H bond; the second arrow must break the H–Br bond and form a new lone pair on bromine.



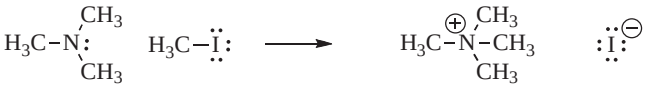
A more complex example might be useful.



Oxygen again has lost a lone pair and formed a bond to hydrogen. A carbon−carbon double bond has formed, the carbon−chlorine bond is broken, and a new lone pair is on chlorine. The minus charge on oxygen in the reactants is now on chlorine in the products; the flow must have come from oxygen (the source) to chlorine (the sink). Again only one set of arrows could be correct: The first arrow must come from the lone pair on the negative oxygen and form an O–H bond; the second arrow must break the C–H bond and form a double bond; the third arrow must break the C–Cl bond and form a lone pair on chlorine.



The flow of negative charge tells you the direction of electron flow in this last example.



The lone pair on nitrogen is gone and a new carbon−nitrogen bond has formed; the carbon−iodine bond is broken and iodine now has an extra lone pair. The charges indicate that electron density has been drained away from nitrogen (which has become positive in the product) and deposited on iodine to give the negative iodide anion. Only one set of arrows could be correct: The first arrow starts from the nitrogen lone pair and forms the N–C bond; the second arrow breaks the C–I bond and forms a new lone pair on iodine.



Exercise: Cover the answers in these previous examples and draw the arrows.

Precautions: It is very important that you pay strict attention to the Lewis structures and arrow positions. **Arrows always point in the same direction as the electron flow, never against it.** Arrows help us keep track of how the charges move. Because arrows move electrons from tail to head, the formal charge on the atom at the tail of the arrow increases by one (becomes more positive) and the formal charge on the atom at the head of the arrow decreases by one (becomes more negative). Never use a curved arrow to indicate the motion of atoms; curved arrows are reserved for electron flow only. Be forewarned that some texts may combine several steps on one structure to avoid redrawing a structure; others may show a partial set of arrows and expect you to fill in the rest mentally. In your study and practice always draw out each electron flow step completely, for errors that would otherwise be easy to find may become difficult to locate if several steps are jumbled together.

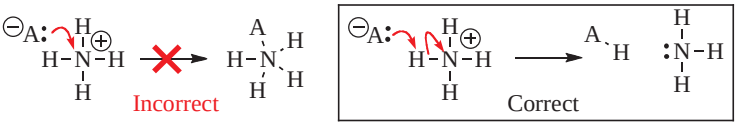
1.4.1 Good Arrow Pushing Habits

- Draw Lewis structures near any arrows (to keep track of atoms and electrons).
- Start every arrow from a **drawn** pair of electrons (not from a minus formal charge).
- Check Lewis structure octets and duets (the most important cross-check).
- Check formal charge and charge balance (or your next step goes astray).
- Use the **known** electron flow paths (introduced over the next few chapters).

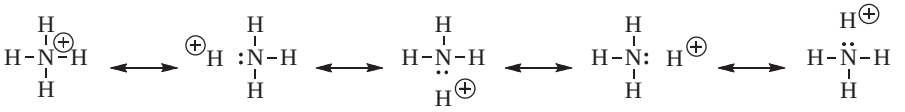
1.4.2 Common Errors

Ligand-Rich vs. Electron-Deficient Errors

Groups like NH_4^+ and H_3O^+ are cationic but not electron deficient because both nitrogen and oxygen have complete octets. For example, the nitrogen in NH_4^+ has four groups bound to it, completing its octet and giving it a formal charge of +1.



Any attack by an anion on the nitrogen would form a fifth bond and exceed its octet. Second-row elements, like C, N, and O, cannot exceed their octet. The resonance forms of the ammonium ion indicate that nitrogen is **winning** the electronegativity tug-of-war. The hydrogen atoms in the ammonium ion are partially positive and therefore acidic.



Similar errors are also seen with the even more acidic hydronium ion, H_3O^+, where again oxygen cannot exceed its octet and is much more electronegative than hydrogen.

Off-the-Path Errors

Until you have the principles of mechanistic organic chemistry thoroughly mastered, it is best to restrict your mechanistic proposals to simple combinations of the electron flow pathways, shown in Chapter 7. You may see a shortcut that with several arrows would allow you to transform the lines and dots of the Lewis structure of the reactant into the lines and dots of the product, but that is not the point of it. What you are trying to do with arrows is guess what is really going on in the reaction, and for that you should use processes that are actually known to exist. The pathways are a very powerful mechanistic vocabulary, and there are very few mechanistic processes that cannot be expressed as a simple combination of them.

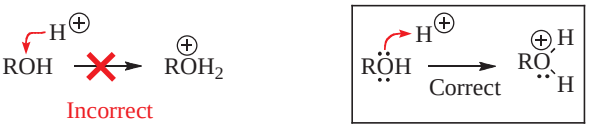
Charge Errors

Typical organic solvents have difficulty stabilizing adjacent like charges. Therefore, avoid forming adjacent like charges unless the reaction solvent is water. **Very few organic intermediates have multiple charges.** Charge must be conserved; the total charge on both sides of the reaction arrow must be the same. Charge is part of your electron count and must balance through each step. Since arrows move electrons, the charges on your final structure must be consistent with the electron movement indicated by your arrows.

Becomes more positive or less negative. Formal charge increases by 1

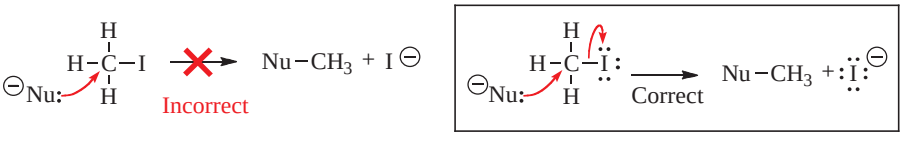
Becomes more negative or less positive. Formal charge decreases by 1

Electron Flow Backwards Error



A proton has no electrons at all, so an arrow cannot start from it. This arrow error is seen in some biochemistry texts to mean, "put the proton there." Always use arrows only for electron movement, nothing else. **Arrows will always head toward positive centers and away from negative ones.**

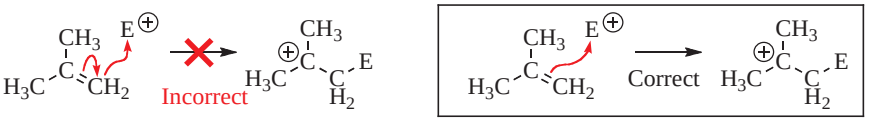
Electron Flow Continuity Errors



To be fair, some authors just draw the first arrow of an electron flow and expect the reader to supply the rest; it is best to see the entire flow drawn out.

Curved Arrows That Bounce or Miss Their Target

Beginners are often not careful in their drawing of arrows and may start an arrow from the wrong bond or put the head in between or on the wrong atoms. Since it is easy to spot, we won't give an example here. Always draw out all the electron pairs on any group that you are going to draw arrows near. Since an electron flow arrow moves electrons, start all arrows from a bond or electron pair, not from the formal charge. A formal charge does not represent or stand in for a drawn electron pair. For example, the anion BH_4^- has two electrons in each of the four boron–hydrogen single bonds. The formal charge just indicates that boron has one more electron than it started with.



This "electron bounce" uses two arrows when only one is required. The second arrow is not starting from a drawn electron pair. **All** arrows must start from a **drawn** electron pair. It is much harder to detect errors when arrows are not used carefully.

1.5 NOMENCLATURE AND ABBREVIATIONS

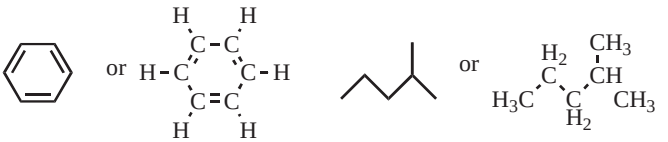
1.5.1 Common Abbreviations

A complete table of abbreviations used in this text is in the Appendix, but a few are so common they need to be learned early.

b	Brønsted–Lowry base, accepts a proton from a Brønsted–Lowry acid
δ+	A partial positive charge
δ–	A partial negative charge
E	Electrophile or Lewis acid, an electron pair acceptor
ERG	Electron-releasing group
EWG	Electron-withdrawing group
Et	Ethyl, CH_3CH_2
HA	Brønsted–Lowry acid, donates a proton to a Brønsted–Lowry base
L	Leaving group, departs with its bonding electron pair
M	Metal
MO	Molecular orbital
Nu	Nucleophile or Lewis base, an electron pair donor
Ph	Phenyl group, C_6H_5, a monosubstituted benzene
R	Any alkyl chain
X	Chlorine, bromine, or iodine
Y, Z	Heteroatoms, commonly oxygen, nitrogen, or sulfur
·····	Partially broken bond (or weak complexation)

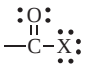
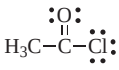
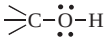
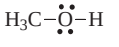
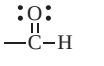
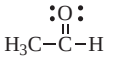
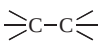
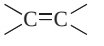
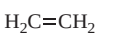
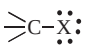
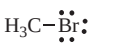
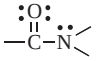
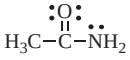
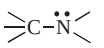
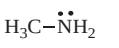
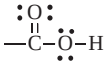
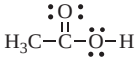
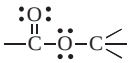
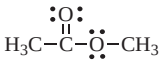
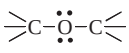
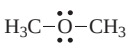
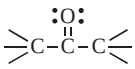
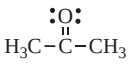
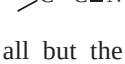
1.5.2 Line Structure

A line structure or skeletal formula is a very easy way to represent organic structures. Each corner in the line corresponds to a carbon atom, and the hydrogen atoms are not drawn. Line structure is fast and convenient to use but can lead to difficult to locate errors. **Any portion of a molecule that is participating in the reaction must be drawn out, showing all the carbons and hydrogens.** It is much too easy to forget about the hydrogen atoms omitted in line structure. The parts of the molecule not participating in the reaction may be shown in line structure or abbreviated. Draw out functional groups (see Table 1.3) and show all H's on heteroatoms.



Organic chemistry is like a foreign language: It is cumulative and requires that vocabulary be learned in addition to grammar. Vocabulary is best learned as you need it, but there is so much to learn that a head start is helpful. You must be able to count in organic, know the common functional groups, and name simple compounds. Compounds are usually numbered from the end with the most oxidized functional group down the longest chain, giving other groups off the chain the lowest numbers if there is a choice. For detail, see Notes on Nomenclature in the Appendix. **Use Table 1.3 to learn the Lewis structures of the common functional groups, so you won't have to draw them from scratch every time they are needed.** A much larger functional group glossary is in the Appendix. In tables, lines off of a carbon are used to denote a bond to R or H.

Table 1.3 Lewis Structures of Common Functional Groups

Name	Functional group	Example	Typed version
Acyl halide			CH_3COCl
Alcohol			CH_3OH
Aldehyde			CH_3CHO
Alkane			CH_3CH_3
Alkene			CH_2CH_2
Alkyl halide			CH_3Br
Alkyne			HCCH
Amide			CH_3CONH_2
Amine			CH_3NH_2
Carboxylic acid			CH_3COOH
Ester			$CH_3CO_2CH_3$
Ether			CH_3OCH_3
Ketone			CH_3COCH_3
Nitrile			CH_3CN

Exercise: Cover all but the far left side of the page and draw Lewis structures for all functional groups. Cover the left side and name all functional groups from the Lewis structures. Flash cards are useful in learning vocabulary like this.

1.5.3 List of the First 10 Alkanes

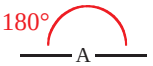
1	Methane	CH_4
2	Ethane	CH_3CH_3
3	Propane	$CH_3CH_2CH_3$
4	Butane	$CH_3CH_2CH_2CH_3$
5	Pentane	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

1.6 THE SHAPES OF MOLECULES

Valence Shell Electron Pair Repulsion (VSEPR) Theory

Once you can draw a good Lewis structure of a molecule, you can use valence shell electron pair repulsion theory (VSEPR) to get its shape. VSEPR theory arises from the fact that repulsion between pairs of bonding and lone pair electrons determine the shape of the molecule. For the purpose of VSEPR, a double or triple bond is considered as a group, and a lone pair acts as if it is larger than a bonding pair. Figure 1.3 shows the shapes of molecules as a function of how many groups crowd around the center atom. The solid wedge in Figure 1.3 symbolizes that the bond is coming out of the paper, and the dashed wedge symbolizes that the bond is going back into the paper. You can demonstrate this VSEPR effect by tying together balloons of the same size, each corresponding to a group of electrons. Only third-row and higher atoms (not carbon) can bond five or six groups.

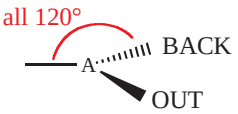
2 groups of electrons around the central atom



Structure : linear

(a multiple bond counts as a single group of electrons)

3 groups of electrons around the central atom



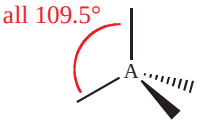
Structure : trigonal planar

One nonbonding pair



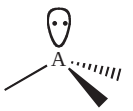
Bent

4 groups of electrons around the central atom



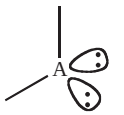
Structure: tetrahedral

One nonbonding pair



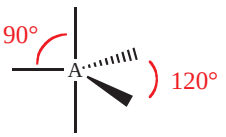
Trigonal pyramidal

Two nonbonding pairs



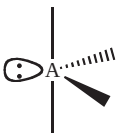
Bent

5 groups of electrons around the central atom



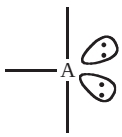
Structure: trigonal bipyramidal

One nonbonding pair



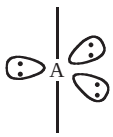
See-saw

Two nonbonding pairs



T-shaped

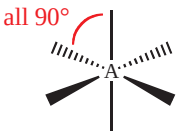
Three nonbonding pairs



Linear

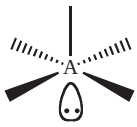
For lone pairs, minimize the number of crowded 90° interactions, especially with other lone pairs

6 groups of electrons around the central atom



Structure: octahedral

One nonbonding pair



Square pyramidal

Two nonbonding pairs



Square planar

Figure 1.3 VSEPR-predicted shapes of molecules.

1.7 AN ORBITAL VIEW OF BONDING

1.7.1 Review of Orbitals Used in Bonding

You may remember from General Chemistry that electrons do not have orbits around an atom but have a cloud-like probability distribution around an atom called an orbital. Each atomic orbital holds two electrons and is described by a mathematical expression called a wave function. We can get the energy of the orbital and the electron's probability distribution from its wave function. The discussion of wave functions is above the level of this text, but if you are interested, a qualitative review and discussion of orbital theory and waves is in the beginning of Chapter 13. For now, we just need to understand qualitatively what the math of quantum mechanics tells us about wave functions.

Figure 1.4 shows several ways of representing a 2*p* orbital. Since a three-dimensional probability distribution cloud of varying electron density is difficult to draw like Figure 1.4a, we often draw orbital surfaces that enclose almost all of the electron cloud as in Figure 1.4b. We arbitrarily shade one lobe of the 2*p* orbital to show that its math sign is different from the other lobe. This math sign is a way of acknowledging the wave nature of the orbital, as in the peak and trough of a wave. There is a planar node in the center, because the math expression of the orbital goes through zero there. The most correct representation is shown in Figure 1.4b, but the commonly used simplified version, Figure 1.4c, is drawn much slimmer so it does not obscure other things in the drawing. When we draw two skinny *p* orbitals next to each other, it may look like they don't overlap, but they actually do.

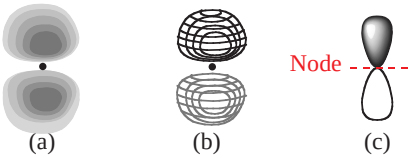


Figure 1.4 Representations of a 2*p* orbital. The nucleus is indicated by a heavy dot in the center. (*a*) Dot density cross-section. (*b*) Three-dimensional surface. (*c*) Simplified version.

The atomic orbitals used for bonding in organic compounds are the 1*s* (for hydrogen), the 2*s*, 2p_x, 2p_y, 2p_z (for carbon), and occasionally the 3*d* (for third row elements). The *s* orbitals are ball shaped, whereas the *p* orbitals are dumbbell shaped and aligned along each of the three coordinate axes, *x*, *y*, and *z*. The four bonding orbitals for carbon are drawn below in Figure 1.5.

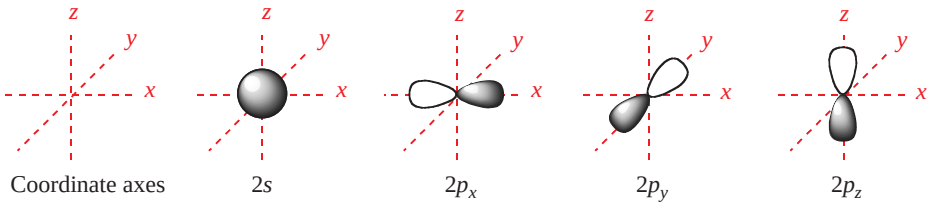


Figure 1.5 Representations of the bonding orbitals of carbon.

1.7.2 Using *p* Orbitals to Make the Sigma and Pi Bonds of Nitrogen

We can make all the bonding orbitals of molecular nitrogen using just the 2p_x, 2p_y, and 2p_z atomic orbitals of Figure 1.5. As we bring two nitrogen atoms together, each with their own set of *p* orbitals, the *p* orbitals will interact. If two orbitals are directly pointed at each other and overlap in phase, a sigma bond is formed. If the orbital overlap is side by side and

in phase, a pi bond is formed. For every in-phase bonding combination of atomic orbitals, there is a higher energy out-of-phase antibonding combination. Figure 1.6 shows the bonding and antibonding molecular orbitals of nitrogen. From six atomic orbitals we built six molecular orbitals; no orbitals were gained or lost. In nitrogen only the three bonding molecular orbitals (not the antibonding) are filled with electrons, giving nitrogen a triple bond. The triple bond of nitrogen is made up of one sigma bond from the overlap of two $2p_x$ atomic orbitals, and there are also two perpendicular pi bonds, one from the overlap of two $2p_y$, and another from the overlap of two $2p_z$ atomic orbitals.

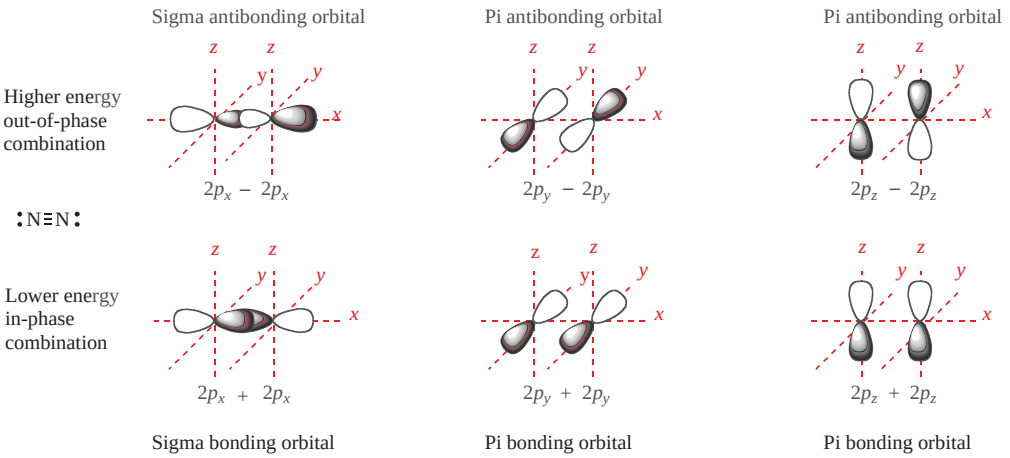


Figure 1.6 The in-phase and out-of-phase mixing of the $2p_x$, $2p_y$, and $2p_z$ atomic orbitals on two nitrogen atoms to give the bonding and antibonding molecular orbitals of molecular nitrogen.

1.7.3 Hybridization

It is convenient to have orbitals for bonding that point along the directions found from VSEPR. Toward this end, we can mathematically mix atomic orbitals on the same atom to get hybrid orbitals that point in the right directions and are useful for the description of bonding with other atoms. Figure 1.7 shows how a 2*s* orbital can be added to and subtracted from a 2*p* orbital to give the two *sp* hybrid orbitals. To subtract, we change the mathematical sign (shading) of the 2*s* orbital and then add it to the 2*p* orbital. The two orbital wave functions reinforce where the mathematical signs are the same (the lobe gets larger) and cancel out where the sign is different (the lobe gets smaller). The number of orbitals is conserved: When we combine two atomic orbitals, we get two hybrid orbitals. We now have two hybrid orbitals pointing 180° from each other able to be used for bonding to two other atoms in a linear arrangement.



Figure 1.7 The mixing of a 2*p* and a 2*s* orbital on an atom giving two *sp* hybrids.

Combining the 2*s* and one of the 2*p* orbitals to get two *sp* hybrids leaves two 2*p* orbitals remaining. This is shown in the orbital energy diagram in Figure 1.8 for *sp* hybridization. Because the 2*s* orbital is lower in energy and closer to the nucleus than a 2*p* orbital, **hybrid orbitals that contain a higher %*s* character will form bonds that will be shorter, stronger, and lower in energy.**

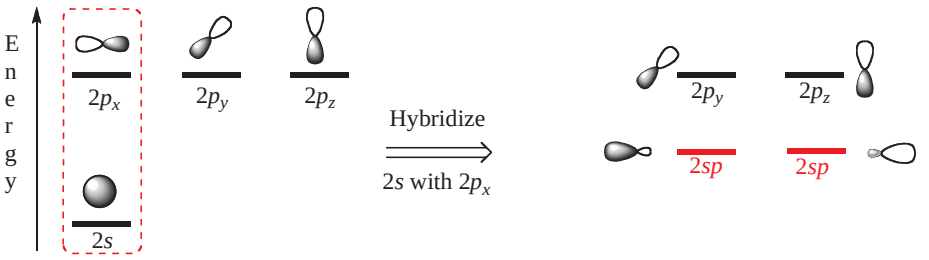


Figure 1.8 Orbital energy levels for mixing a 2*s* and a 2*p* orbital to form two *sp* hybrids.

As shown in Figure 1.5, carbon has one 2*s* and three 2*p* orbitals that can be used for hybridization. Hybridizing the 2*s* with the p_x and the p_y gives three sp^2 hybrid orbitals in the xy plane with a 120° angle between them, Figure 1.9. There is the one p_z orbital left.

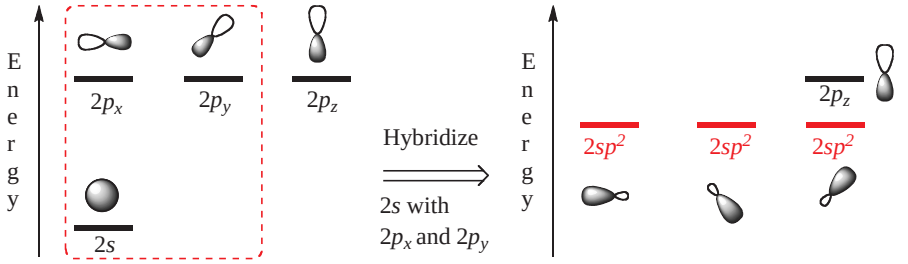


Figure 1.9 Orbital energy levels for mixing a 2*s* with two 2*p* orbitals to form three sp^2 hybrids.

Finally, if we hybridize 2*s* and all three 2*p* orbitals we get four sp^3 hybrid orbitals pointing to the corners of a tetrahedron, Figure 1.10.

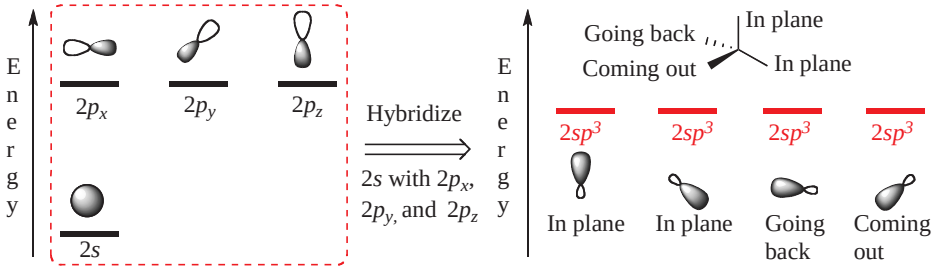


Figure 1.10 Orbital energy levels for mixing a 2*s* with three 2*p* orbitals to form four sp^3 hybrids.

The properties of all possible hybridizations of carbon are summarized in Table 1.4. To determine the hybridization of a carbon atom, just use VSEPR on the Lewis structure. A linear arrangement needs an *sp* carbon; a trigonal planar arrangement needs an sp^2 carbon. A tetrahedral arrangement usually needs sp^3 hybridization, but if a lone pair on the atom is involved in resonance, the lone pair is then in a *p* orbital, and the atom is trigonal planar, sp^2.

Table 1.4 Summary of the Properties of Hybrid Orbitals

Hybridization of carbon	*sp*	sp^2	sp^3
Number of hybrid orbitals	2	3	4
Interorbital angle	180°	120°	109.5°
%*s* character	50	33	25
%*p* character	50	67	75
Orientation	Linear	Trigonal	Tetrahedral
Electronegativity of C	3.29	2.75	2.48
Remaining *p* orbitals	2	1	0

1.7.4 Single Bonds

We can overlap two sp^3 orbitals to produce a sigma bond. The in-phase combination overlaps lobes of the same mathematical sign and is the lower-energy *bonding* orbital. The higher-energy out-of-phase combination is called the *antibonding* orbital and is usually empty. Sigma (σ) bond orbitals are cylindrical along the axis of the bond. Therefore, the ends can rotate about the axis of the bond without losing any overlap. **Strong bonds are due to good overlap of the bonding orbitals**.

To show that an sp^3 carbon is tetrahedral, organic molecules are usually drawn in three dimensions. The solid wedge in Figure 1.11 symbolizes the bond is coming out of the paper, and the dashed wedge symbolizes the bond is going back into the paper. The tetrahedral shape of sp^3 carbon has profound biochemical implications. *Stereochemistry* is the description of how identically connected atoms of a molecule are arranged in space (discussed in Section 2.3). The stereochemistry of a pharmaceutical can make all the difference between potent useful biological activity and undesired effects.



Figure 1.11 The bonding and antibonding orbitals of a carbon–carbon single bond are made from the combination of two sp^3 hybrid orbitals.

Conformational isomers differ only in rotations about single bonds. The eclipsed and staggered conformational isomers of ethane, CH_3CH_3, are shown in Figure 1.12. Although single bonds are drawn as if they were "frozen in space," rotation usually has no significant barrier at room temperature (free rotation at room temperature). Ethane's rotational barrier is tiny, only 3 kcal/mol (13 kJ/mol). One kilocalorie/mol is equal to 4.184 kilojoules/mol.

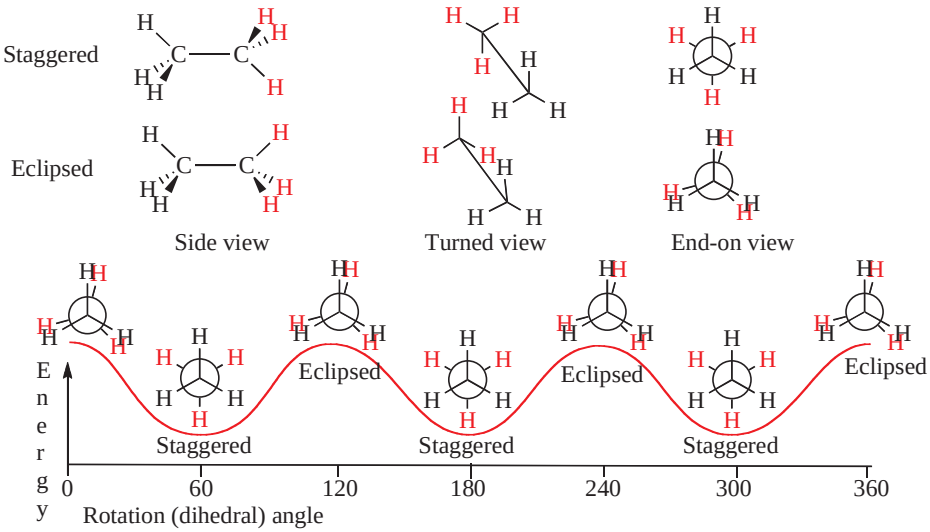


Figure 1.12 Views of two conformational isomers of ethane, staggered and eclipsed. The end-on view is called a Newman projection. Below them is a plot of the energy as the C–C bond rotates.

The staggered conformation is the lowest energy; the eclipsed conformation is highest since the C–H bonds are in the process of passing each other and their electron clouds repel. Rotation about the center C–C bond in butane, $CH_3CH_2CH_2CH_3$, requires passing two methyl

groups with a slightly larger barrier of 4.5 kcal/mol (19 kJ/mol). The staggered form when the methyl groups are opposite (*anti*) is about 0.8 kcal/mol (3.4 kJ/mol) lower in energy than the staggered form, where the methyl groups are 60° to each other (*gauche*). A significant rotation barrier may arise if two very large groups would bump into one another when rotation about the single bond occurs. The best way to learn what organic compounds actually look like is by working with molecular models.

1.7.5 Double Bonds

Pi bonds are made by two *p* orbitals interacting side by side in the same plane and are relatively reactive due to less effective orbital overlap. The in-phase and out-of-phase combination of two 2*p* orbitals yield the pi molecular orbitals for ethene, $CH_2{=}CH_2$, shown in Figure 1.13. Double bonds result from a sigma bond and a pi bond between the two bonding atoms. Since that sigma bond lies in the nodal plane of the pi bond, the sigma and pi bonds of a double bond are considered independent.

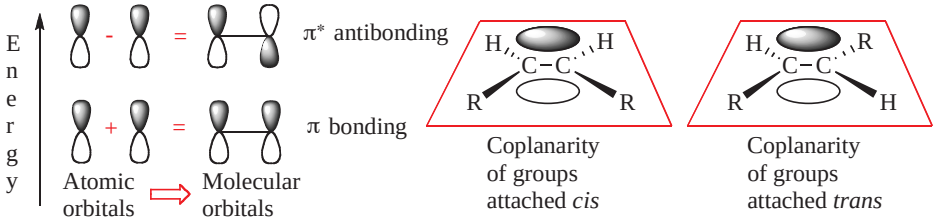


Figure 1.13 The bonding and antibonding orbitals of a carbon–carbon pi bond are made from the side-by-side combination of two 2*p* orbitals by subtraction and addition. Mixing two atomic orbitals gives two molecular orbitals. As shown, all atoms adjacent to the pi bond lie in a plane.

The requirement that the *p* orbitals overlap causes a very large barrier to rotation about the double bond, about 63 kcal/mol (264 kJ/mol). *Cis* (two groups on the same side) and *trans* (two groups on opposite sides) double-bond isomers do not interconvert at any reasonable temperatures. The *trans* isomer tends to be slightly more stable than the *cis* isomer because the groups may bump into one another when they are *cis*. More alkyl substitution on the double bond (replacing an H on the double bond by an R) makes the alkene slightly more stable. For example, an equilibrium mixture of butenes is found to contain 3% 1-butene, 23% *cis*-2-butene (R equals CH_3 above), and 74% *trans*-2-butene.

1.7.6 Triple Bonds

A triple bond is composed of one sigma bond and two pi bonds. Since the two pi bonds are perpendicular to each other, they are treated as two separate, noninteracting pi bonds. **Perpendicular orbitals do not interact.** The triple bond is linear, and atoms bonded to it lie in a straight line (Figure 1.14). Organic chemists tend to draw skinny *p* orbitals (see Figure 1.4); the triple bond is overall cylindrically symmetrical.

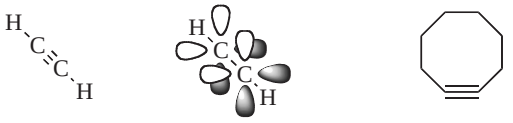


Figure 1.14 The pi orbitals of a triple bond. Cyclooctyne is shown on right.

The average bond strength of a triple bond is 200 kcal/mol (837 kJ/mol); therefore each pi bond is worth about 59 kcal/mol (247 kJ/mol). If placed in a ring, the triple bond can be

bent from collinearity and become weaker and much more reactive. Cyclooctyne is the smallest ring that contains a triple bond and is still stable enough to be isolated.

1.7.7 Cumulenes

Cumulenes are compounds with two adjacent perpendicular double bonds (Figure 1.15). Each double bond can be considered separately. The central carbon is *sp* hybridized, and the two CH_2s lie in perpendicular planes. In heterocumulenes, heteroatoms have replaced one or more of the carbons, as in carbon dioxide, O=C=O.

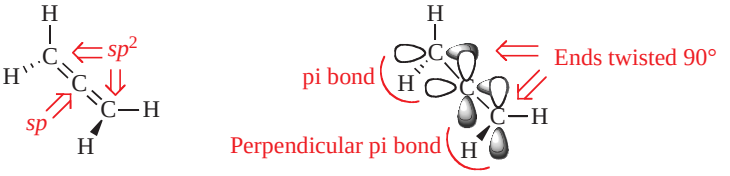


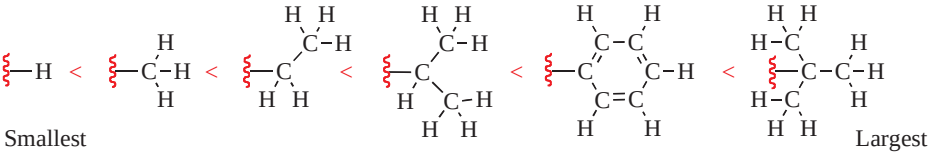
Figure 1.15 The pi orbitals of a cumulene.

1.8 MOLECULAR REPULSIONS, ATTRACTIONS, AND HYDROGEN BONDING

1.8.1 Nonbonded Repulsions

All groups on a molecule take up space, and this occupied space is called *steric bulk*. Interactions that attempt to force two groups to occupy the same space are very unfavorable. The like-charged electron clouds on the two groups repel each other, and as they are forced together the extra energy required is called *steric hindrance*, or nonbonded repulsion. If the path that the nucleophile must follow to satisfy orbital overlap requirements has too much steric hindrance, the reaction will not occur. The nucleophile will just bounce off the group that is in the way. Bulky nucleophiles need very open sites for attack, and hindered sites can be attacked only by small nucleophiles. The steric interactions between site and nucleophile are important in the competition between an anion acting as a nucleophile or acting as a base.

How close is too close? If the distance between two groups is less than the sum of their van der Waals radii, then strong repulsion begins. For most groups, this distance is between 3 and 4 Å, which is about twice the normal C–C single bond length of 1.54 Å. Models are very useful for comparing the relative sizes of groups. Shown below are some common groups ordered by increasing size: hydrogen, methyl, ethyl, isopropyl, phenyl, and *tert*-butyl.



1.8.2 Dipole Attractions and Repulsions

Unlike charges attract, and like charges repel each other. The uneven distribution of electrons in a molecule can result in a pair of partial charges, represented by δ+ and δ− or by ⟶, a dipole moment arrow with the plus end indicated. Polar covalent bonds create bond dipoles. Another dipole arises from a lone pair of electrons in a hybrid orbital. If the center of positive charge (from the nuclei positions) is different from the center of negative charge (from the electron cloud) then the molecule will have a net dipole. Individual dipoles will vector sum to the net dipole. Water has both bond dipoles and lone pair dipoles, Figure 1.16.

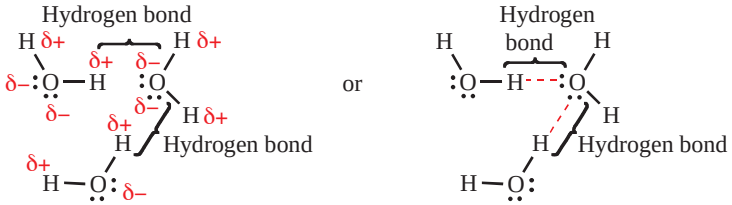


Bond and lone pair dipoles Net dipole

Figure 1.16 The net dipole consists of summing components of bond dipoles and lone pair dipoles. With symmetrical compounds like O=C=O the dipoles will cancel resulting in no net dipole moment.

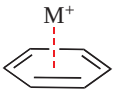
1.8.3 Hydrogen Bonding

Hydrogen bonding is the overlap of a lone pair orbital of a heteroatom with an H atom bonded to another heteroatom, commonly O, N, F, and sometimes S and Cl. With rare exceptions, the C–H bond is not significantly polarized and does not hydrogen bond. The attraction of the permanent δ+ of a polarized hydrogen−heteroatom bond with the δ− of a heteroatom lone pair provides an ionic component. Although the strength of a typical hydrogen bond to oxygen averages about 5 kcal/mol (21 kJ/mol), its importance should not be underestimated. Hydrogen bonding causes water to be a liquid rather than a gas at room temperature. It is calculated that the oxygen in water at room temperature is estimated to be bonding to 3.7 hydrogen atoms. Hydrogen bonding is dynamic and short lived. When water freezes it forms a hexagonal lattice with each oxygen bonded or hydrogen bonded to four hydrogen atoms. This open hexagonal lattice of ice is less dense than liquid water, and that is the reason that ice floats. Hydrogen bonds with a linear arrangement of all three atoms are most common. Often a very weak bond like a hydrogen bond or a complexation is indicated by a dotted line, ·····, which is also used to symbolize a partially broken or made bond. Don't start electron flow arrows from such a line; always use Lewis structures near any arrows to keep track of electrons.



1.8.4 Cation–Pi Interactions

Pi-adducts (formerly called pi-complexes), also often called electron donor−acceptor interactions, are often a weak association of an electron-rich molecule with an electron-poor species. The donor is commonly the electron cloud of a pi bond or a group of pi bonds; the acceptor can be a metal cation, a halogen like Br_2, or an electron-poor organic compound. In the absence of solvent, as can occur in an enzyme cavity, the cation–pi interaction can be stronger than hydrogen bonding. An example is shown below, where a cation snuggles into the face of the aromatic pi cloud of benzene (see aromaticity, Sections 1.9.3 and 13.4).



The gas-phase attraction between benzene and various cations decreases with increasing cation size (Li^+ at 38 kcal/mol, Na^+ at 27 kcal/mol, and K^+ at 18 kcal/mol). Figure 1.17 shows the cation–pi interaction between an alkene and silver ion.

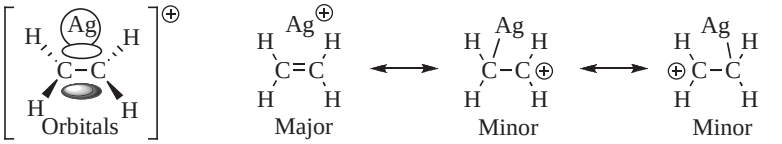


Figure 1.17 A silver ion pi-adduct. Resonance forms describe the orbital overlap shown at left.

1.9 CONJUGATION, VINYLOGY, AND AROMATICITY

1.9.1 Conjugation

Two pi systems connected by a single bond behave as one *conjugated* system because the *p* orbitals of the two pi systems are close enough to have good overlap and additional pi bonding. Figure 1.18 shows how a double bond and a carbonyl group can be placed in a molecule to form both a conjugated system and an unconjugated system. In the conjugated system, the partial plus of the carbonyl is delocalized into the second pi bond. The additional pi bonding makes a conjugated system more stable than the corresponding unconjugated system by about 3.5 kcal/mol (14.6 kJ/mol); any equilibrium between the two favors the conjugated system.

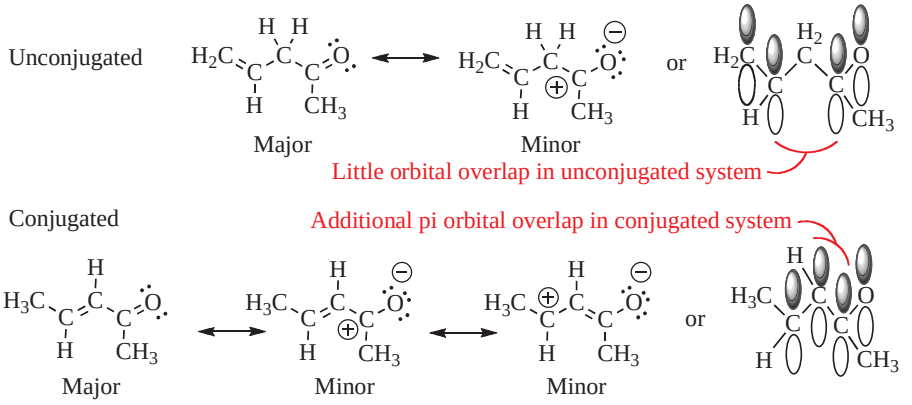


Figure 1.18 The resonance forms and pi overlap of an unconjugated system (top) and a conjugated system (bottom) of a carbon−carbon pi bond and a carbon−oxygen pi bond.

Another example of conjugation is the nitrogen lone pair joined by resonance with a carbonyl group shown in Figure 1.19 for amides. The nitrogen lone pair is not in an sp^3 orbital but in a *p* orbital that overlaps the *p* orbitals of the pi bond to make a three-*p* orbital pi system. Any three-*p* orbital pi system is called an *allylic system*. The conjugated system will have properties different from its individual parts because it now acts as a hybrid and not as two independent functional groups. The third resonance form requires the *p* orbital of the nitrogen lone pair to line up with the *p* orbital on carbon to get the proper overlap for the double bond. This required alignment gives amides a significant C–N rotational barrier of 15 to 20 kcal/mol (63 to 84 kJ/mol). The amide links in proteins do not rotate at room temperature and thus greatly contribute to the three-dimensional stability of proteins.

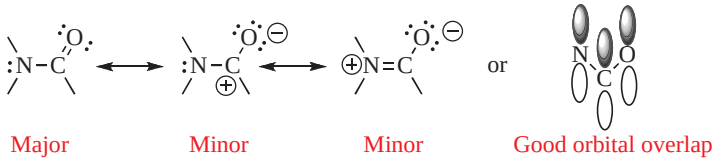
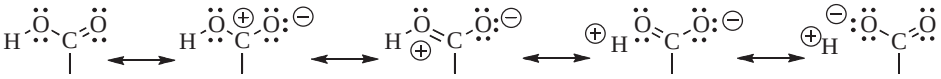


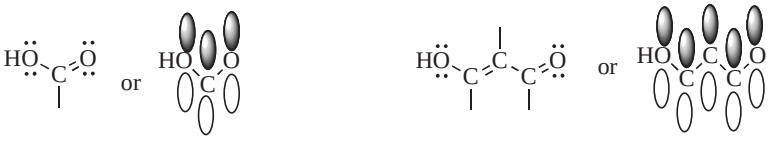
Figure 1.19 Conjugation of a nitrogen lone pair with a carbonyl to give an amide group.

Still another example of conjugation is the carboxylic acid group in which a hydroxyl is conjugated with a carbonyl group. The resonance forms of the carboxylic acid explain the increased acidity of the hydrogen (major form is on the left, with more minor forms to the right):



1.9.2 Vinylogy

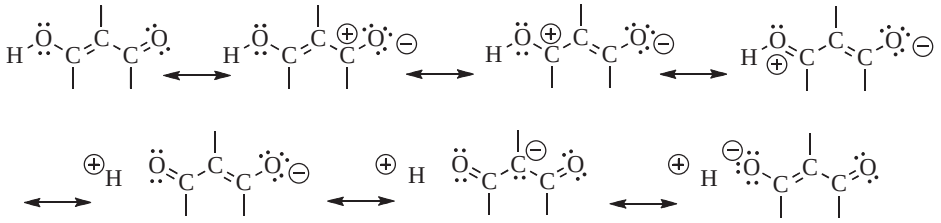
Vinylogy is the extension of the properties of a system by the insertion of a carbon–carbon double bond. The conjugated system increases in length, but the physical properties and chemical reactivity remain approximately the same. A good example of this is the comparison of a carboxylic acid and a vinylogous carboxylic acid (Figure 1.20). The hydroxyl group is still conjugated with the carbonyl through the intervening pi bond.



Carboxylic acid Vinylogous carboxylic acid

Figure 1.20 The insertion of a carbon–carbon double bond between the OH and the C=O of the carboxylic acid creates the vinylogous carboxylic acid on the right.

The resonance forms for a vinylogous carboxylic acid shown below are very similar to the carboxylic acid ones shown above, and likewise can account for an acidic hydrogen.



Ascorbic acid, vitamin C, is an important vinylogous carboxylic acid. The following structures compare several other vinylogous systems with their respective parent systems.



Ester Vinylogous ester



Amide Vinylogous amide



Acyl chloride Vinylogous acyl chloride

1.9.3 Aromaticity

Benzene, C_6H_6, is much more stable and less reactive to electrophiles than simple alkenes, is described by two neutral resonance structures of equal importance, and is the prime example of an aromatic compound:



Any cyclic conjugated compound will be especially stable when the ring contains **$4n + 2$ pi electrons**, where n is any integer (*Hückel's rule*). This extra stability, "resonance stabilization," of the 2, 6, 10, 14, 18, ... pi electron cyclic conjugated systems is termed *aromaticity* and results from the pattern of molecular orbital energies of cyclic conjugated systems (Figure 1.21). Although the derivation of the pattern of these molecular orbitals is beyond the scope of this text, a qualitative explanation of them is given in Section 13.4. As with atomic orbital energy levels that are filled in each noble gas, filled molecular energy levels are more stable than partially filled levels. It takes two electrons to fill the bottom level, then four more to fill the next level, and four more for the next, giving the 2, 6, 10 pattern of stability.

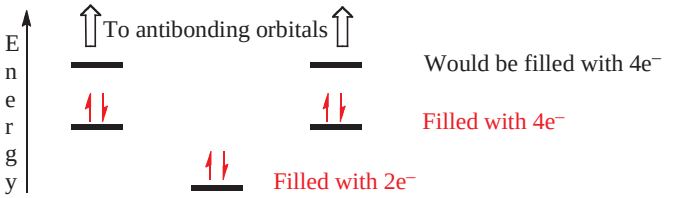


Figure 1.21 The general pattern of molecular orbital energy levels for cyclic conjugated systems. Six electrons are shown, filling the second MO level (stable). A total of four electrons would leave that MO half-filled (unstable).

The resonance stabilization of benzene is estimated to be about 36 kcal/mol (151 kJ/mol), but this is not an experimentally verifiable number. The $4n$ pi electron systems (4, 8, 12, 16, ...), with half-filled energy levels, not only are less stable than the $4n + 2$ systems but are destabilized relative to their open-chain analogs and are called *antiaromatic*.

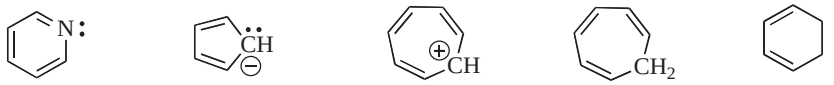
To summarize, **aromatic stabilization occurs in rings that have an unbroken conjugated loop of *p* orbitals (a *p* orbital on each atom in the loop with no big twists between) and $4n + 2$ pi electrons in the loop.**

If the molecule has an unbroken loop of *p* orbitals, you will be able to draw at least two resonance structures that shift the double bonds around the loop, as we did for benzene. If any atom in the ring has four groups bound to it, then there can be no *p* orbital on that atom; the pi loop is broken, and the ring cannot be aromatic.

To determine possible aromaticity, first determine if the loop is intact, then determine how many electrons occupy the loop. Count each double bond as contributing two electrons. A lone pair on an atom in the loop is counted as contributing two electrons if there is no double bond to that atom. (If an atom is doubly bonded and contains a lone pair, the lone pair cannot be counted since it must be in an orbital that is perpendicular to the loop.) If an atom has two lone pairs, just one is counted (only one can align with the loop). A triple bond can contribute only two electrons (one of the two pi bonds must be perpendicular to the loop). A carbocation contributes an empty *p* orbital to the loop (but contributes no electrons).

Example problem

Which of the following compounds are stabilized by aromaticity?



Answer: The first three on the left are aromatic. The far left compound has six electrons in the loop because the nitrogen lone pair is in an sp^2 orbital that is perpendicular to the loop of *p* orbitals, and so is not counted. The anion and the cation both have six electrons in the loop and a *p* orbital on every atom. Neither of the two compounds on the right has a complete loop of *p* orbitals because the CH_2 group(s) breaks the loop of pi conjugation.

1.10 SUMMARY

In this chapter, we learned that **structure determines reactivity**. We have seen that weak bonds are a source of reactivity. Strong bonds are made by good overlap of similar-sized orbitals (same row on periodic table). Bends or twists that decrease orbital overlap weaken bonds. Lewis structures and resonance forms along with electron flow arrows allow us to keep track of electrons and explain the changes that occur in reactions. VSEPR will help us predict the shape of molecules. Next we must review how bonds are made and broken, and what makes reactions favorable. Critical concepts and skills from this chapter are:

Best-First Search

- Generate all reasonable alternatives and select the best one.

Valid Lewis Structures:

- have correct number of valence electrons,
- have correct formal charges that sum to the total charge, and
- do not exceed octets for second-row elements.

The Major Resonance Contributor will have:

- the most covalent bonds,
- the least amount of charge separation,
- the most complete octets and duets as possible, and
- any negative charges on the most electronegative atoms.

Good Arrow Pushing Habits

- Draw full Lewis structures near all arrows (to keep track of electrons and atoms).
- Start every arrow from a **drawn** pair of electrons (not from a minus formal charge).
- Check Lewis structure octets and duets (the most important cross-check).
- Check formal charge and charge balance (or your next step goes astray).
- Use the **known** electron flow paths (introduced over the next few chapters).

VSEPR

- Groups of electrons, bonds and nonbonding pairs, repel each other and arrange themselves in space to minimize this repulsion. Lone pairs are given more space if possible (minimize 90° lone pair interactions).

Conjugation, Vinylogy, and Aromaticity

- Conjugation is the favorable overlap of adjacent p orbitals or pi systems to form a single larger pi system.
- Vinylogy is the extension of the properties of a pi system by the insertion of a pi bond in conjugation.
- Aromatic stabilization is found for cyclic conjugated rings with $4n + 2$ pi electrons.

Essential Skills

- Lewis structures—be able to rapidly draw any compound's major resonance form with the correct formal charges.
- Arrows—understand and be able to supply the arrows for converting between resonance forms, and for one-step reactions given the reactants and products.

CHAPTER 1 EXERCISES

1.1 Draw Lewis structures with resonance for the following neutral compounds. Decide the major resonance form, if any.

O–O–O H_2C–N–N O–C–O H–O–N–O H–O–NO_2

1.2 Draw Lewis structures with resonance for the following charged species. Decide the major resonance form, if any.

$H_2CNH_2^+$ OCN^- $HOCO_2^-$ H_2COH^+ $H_2CCHCH_2^+$

1.3. What is the polarization of the indicated bond?

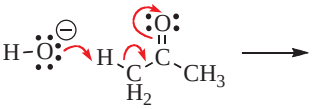
Br–Br HO–Cl H_2B–H H_2C=O I–Cl

1.4 Circle the electrophiles and underline the nucleophiles in the following group.

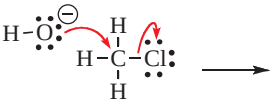
BF_3 H^+ Ne NH_3 ^-CN

1.5 Draw the Lewis structure(s) that would be the product of the arrows.

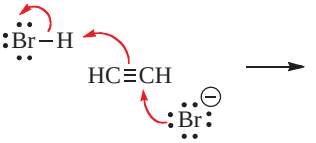
(a)



(b)

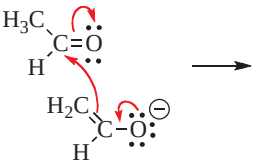


(c)

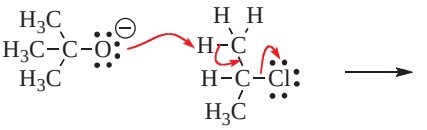


1.6 Draw the Lewis structure(s) that would be the product of the arrows.

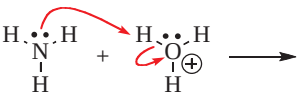
(a)



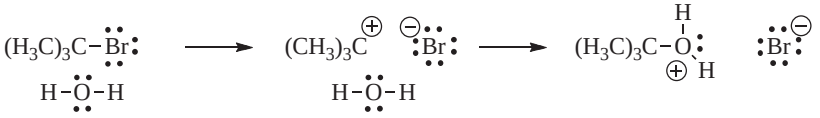
(b)

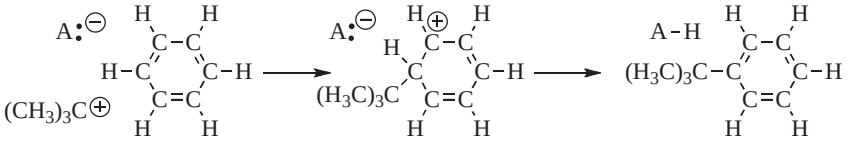


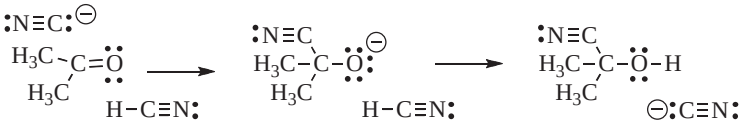
(c)



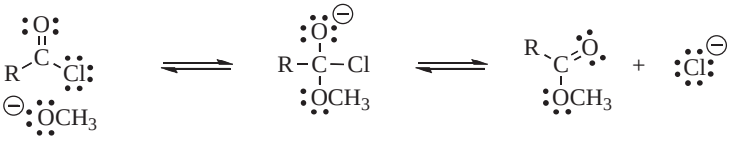
1.7 Give the curved arrows necessary for the following reactions.

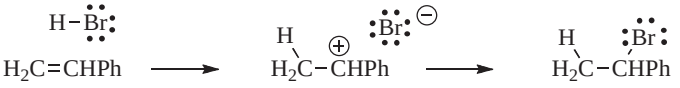
(a) 

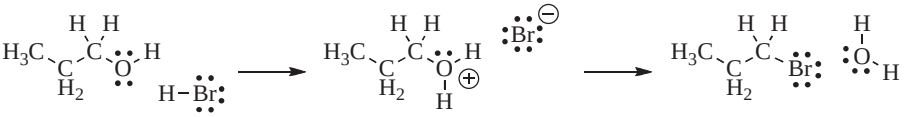
(b) 

(c) 

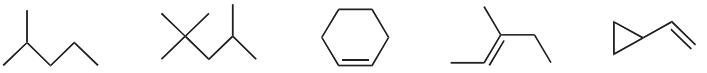
1.8 Give the curved arrows necessary for the following reactions.

(a) 

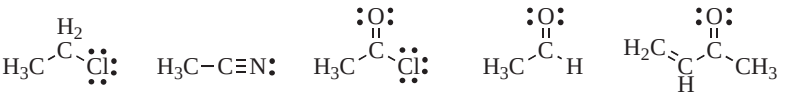
(b) 

(c) 

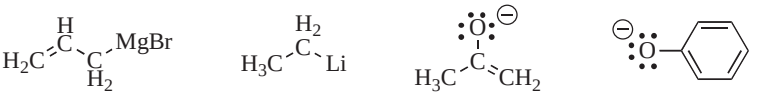
1.9 Draw full Lewis structures for the following line structures.



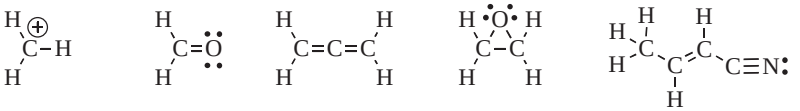
1.10 In the following structures circle any carbon atom that bears a significant partial positive charge. (Hint: look for electronegative atoms.)



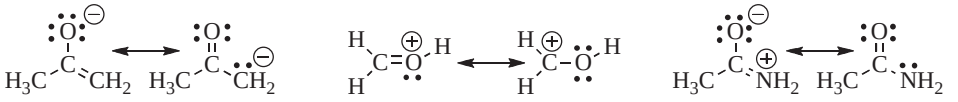
1.11 In the following structures circle any carbon atom that bears a negative or significant partial negative charge. (Hint: draw some resonance forms.)



1.12 Give the hybridization of the carbons in these structures.



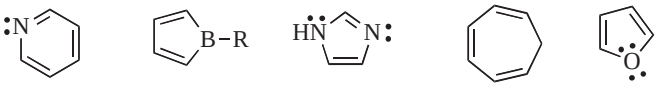
1.13 For each of the resonance pairs below, determine which is the major contributor.



1.14 Draw the pi system for:

(a) an amide (b) carbon dioxide (c) an ester (d) vinylogous amide (e) nitrile

1.15 Circle the aromatic compounds in the following list.



1.16 Circle the conjugated systems in the following list.



1.17 First draw a good Lewis structure, then decide the structure of the following compounds, using VSEPR. For connectivity on these, put the unique atom in the center.

SF_4 CO_2 BF_3 H_2O NH_3

1.18 First draw a good Lewis structure, then decide the structure of the following ions, using VSEPR. For connectivity on these, put the unique atom in the center.

NO_2^- NO_2^+ NO_3^- SO_4^{-2} PO_4^{-3}

1.19 Rank the following on the size of the atom or ion (use #1 for largest).

Ne Na^+ F^- Mg^{2+} Al^{3+}

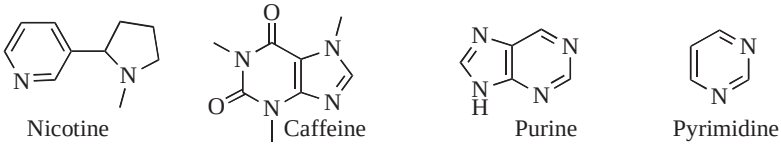
1.20 Circle the molecules that have a dipole moment.

NO_2^- NO_2^+ NO_3^- NH_4^+ $AlCl_4^-$

1.21 Circle the polar covalent and underline the mostly ionic compounds below.

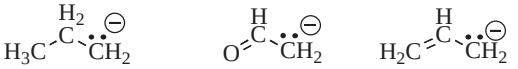
Br_2 LiBr HCl KBr H_2O

1.22 Draw full Lewis structures for the following line structures of biomolecules.



Nicotine Caffeine Purine Pyrimidine

1.23 Decide which of the following anions is the most stable, the least stable.



1.24 Decide which of the following cations is the most stable, the least stable.

