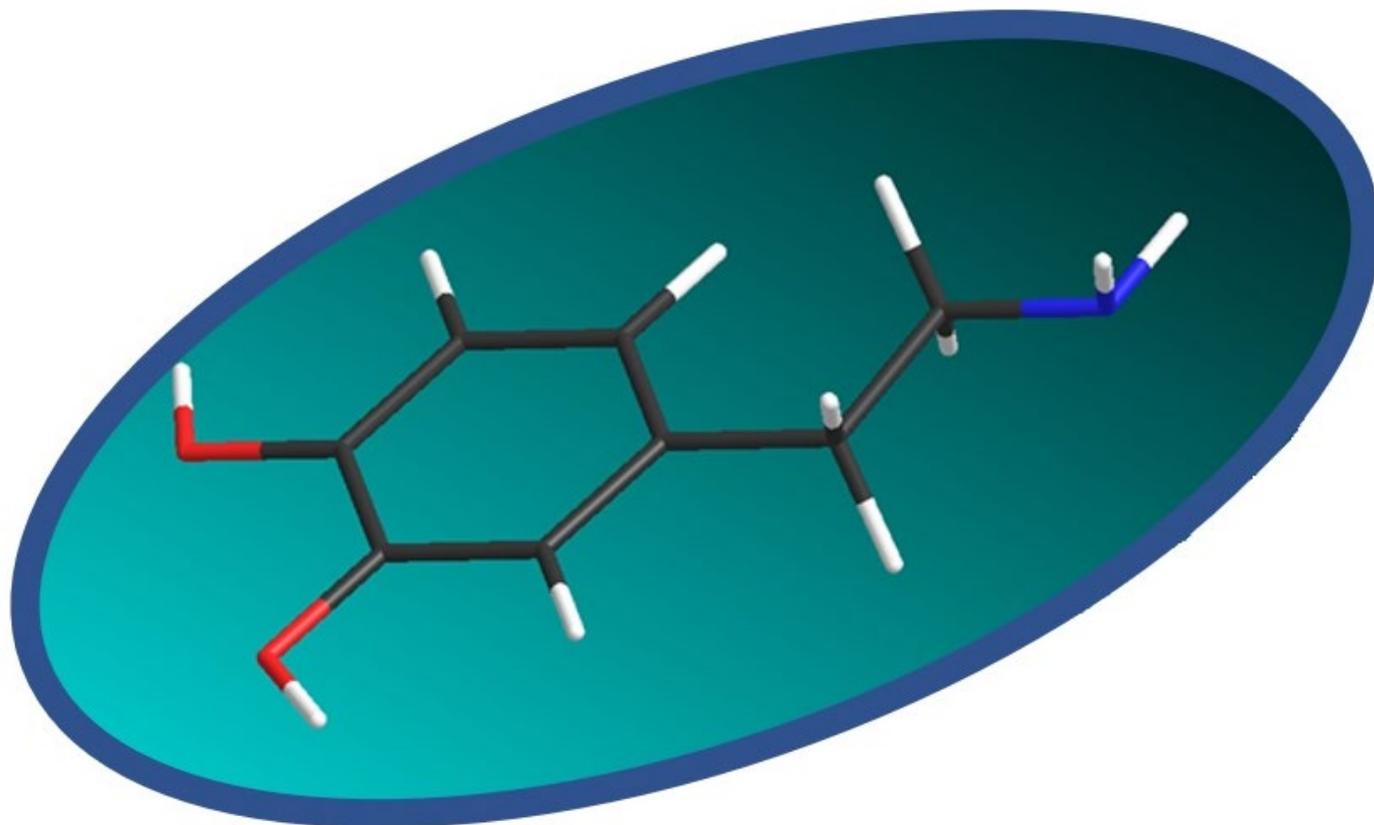


# Thinking Organically

Version 1.0



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*With gratitude to Prof. Guillermo Gerona-Navarro for his work in developing the course curriculum and advice on this text.*



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## Organic Chemistry: What are the Facts and Why the Reputation?

The challenge of organic chemistry has been mythologized out of all proportion to its content. At its heart, organic chemistry takes simple ideas of atomic and molecular structure and uses them to understand the reactions of carbon. The versatile nature of carbon means that infinite variations are possible, but all arise from the same simple themes. Why, then, do bleary-eyed pre-medical students declare that the course is devouring their souls and sending them spiraling into madness? Why do students planning their schedules look at courses on organic chemistry with the same dread that the sailing ship captains of old eyed poorly-mapped reefs and hurricanes?

The problem is not that organic chemistry is harder than first-year chemistry, the problem is that it is different. What is more, students who developed bad habits that worked passably in general chemistry will find them to be useless when studying organic chemistry.

First-year chemistry is based heavily in mathematics. Conceptual material is important to the course, but it is often possible to learn how to do mathematical problems without really understanding of the concepts underlying them. This is a sub-optimal approach in first-year chemistry, but it is outright self-destructive in organic chemistry. Organic chemistry is in large part a course on conceptual logic and spatial reasoning. Trying to memorize how to do organic chemistry problems without understanding the basic concepts is like trying to learn how to win a chess game by memorizing every possible combination of moves. There are simply too many possible configurations, and even seemingly superficial differences between scenarios can have important consequences. The only possible approach is to understand the basic principles underlying the game and apply them anew to each unique problem.

The transition to this different style of learning is challenging for many students. Logic and spatial reasoning are skills that can take time to develop, but a full course in organic chemistry moves rapidly through advanced subject matter. This textbook, and the course it supports, are intended to provide an opportunity to build those skills at a slower pace. Topics such as structure and nomenclature – mainstays of organic chemistry – are applied to limited sets of molecules rather than covering the full breadth of chemistry. Once students have some familiarity with these topics, they can assimilate the broader subject matter of organic chemistry far more easily.

This book departs from the style of most current textbooks by having relatively few blocks labeled as “Examples”. There are many examples presented, but they are integrated with the text. This is to emphasize the tight connection between concept and problem. Breaking out separate problems encourages skipping or skimming other material, a practice this book avoids encouraging. If you feel a book should not be telling you how to learn, consider that every textbook you have ever read has done exactly that. If you miss having blocks labeled as “Example,” ask yourself whether you might be undervaluing other components of the text.

If none of the rest of this page strikes you as useful, let me offer you one piece of unassailably good advice: **Get a model kit.** No one succeeds without one. Organic chemistry is inherently three-dimensional and visualization is an essential skill. In many cases, the best-rendered two-dimensional images in the world are less helpful than a simple, hand-held model. Find any model kit you think is convenient, or use marshmallows and toothpicks or similar household items. But once this book enters Chapters 4-6, models will be essential for your success.

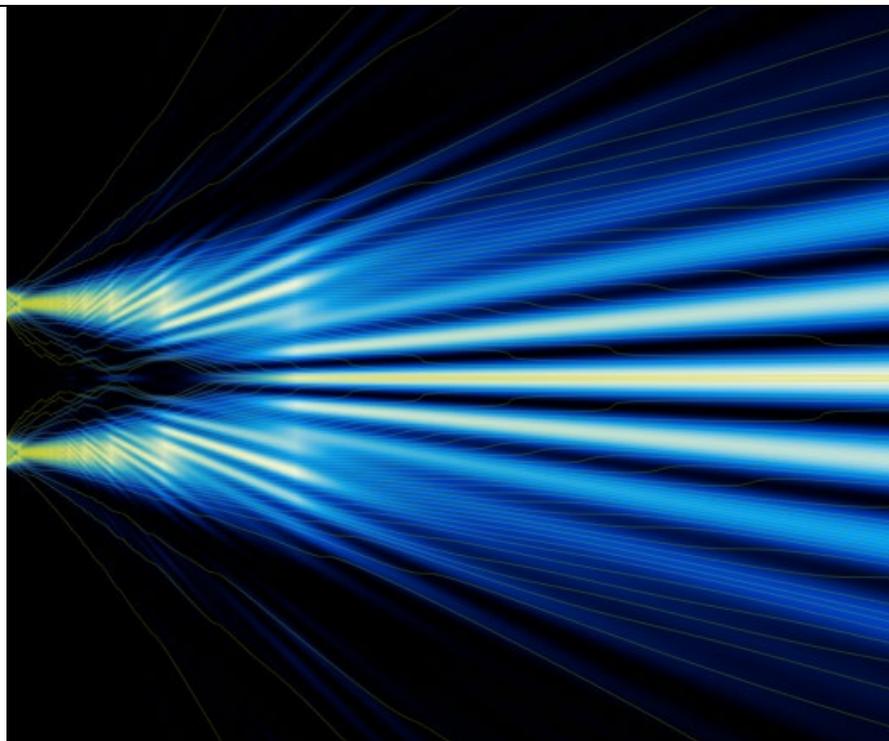
I wish you success in your studies, and I hope this book is of use.

-Mark Kobrak, August 6, 2021

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# CHAPTER 1: The Wave Nature of Electrons



*A simulation of the diffraction of atoms passed through a pair of slits. This is an example of particles behaving as if they were waves.*

*From: Gondran, M. and Gondran, A., Numerical Simulation of the Double Slit Interference with Ultracold Atoms, Am. J. Phys., **2007**, 73, 605908. Courtesy of Wikimedia Commons, [https://commons.wikimedia.org/wiki/File:100\\_trajectories\\_guided\\_by\\_the\\_wave\\_function.png](https://commons.wikimedia.org/wiki/File:100_trajectories_guided_by_the_wave_function.png), accessed July 7, 2021.*

GOD DOES NOT  
PLAY DICE WITH  
THE UNIVERSE

-ALBERT EINSTEIN

THE UNIVERSE IS  
UNDER NO  
OBLIGATION TO  
MAKE SENSE TO  
YOU.

-NEIL DEGRASSE  
TYSON

*The early investigators of quantum mechanics were shocked to discover that the beautiful simplicity of Newton's Laws was replaced by far more subtle and complex rules when studying the motion of electrons and protons. Scientists have had to come to terms with the idea that many natural phenomena will be counterintuitive.*

## BEFORE YOU BEGIN, MAKE SURE YOU KNOW

- The structure of the atom (Flowers, secs 2.3 and 6.3)
- The nature of quantum numbers for atomic orbitals (Flowers, sec 6.4)
- The rules for Aufbau in atomic orbitals, including the Pauli Exclusion Principle and Hund's Rule (Flowers, sec 6.4)

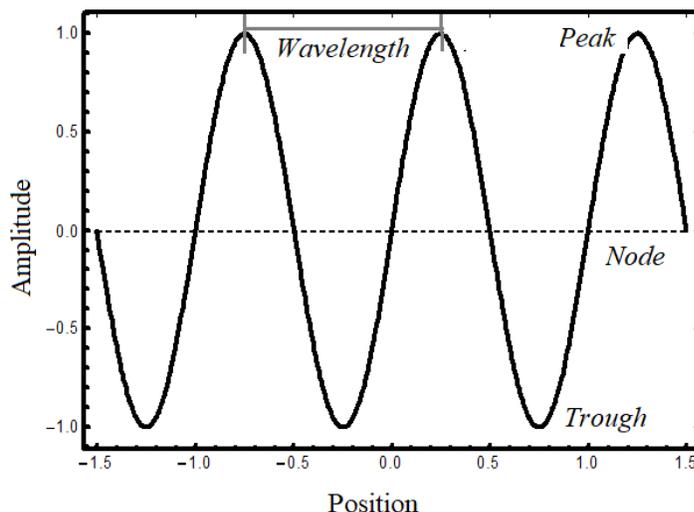
## Section 1.1: The Nature of Waves

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand basic ideas behind the nature of waves, including amplitude, wavelength, and the existence of nodes.
- Understand the nature of interference between waves, including both constructive and destructive interference.
- Understand the idea of a standing wave.

A central concept in modern atomic theory is that electrons behave as waves. This is only helpful if you know what a wave does. That will be the focus of this section.

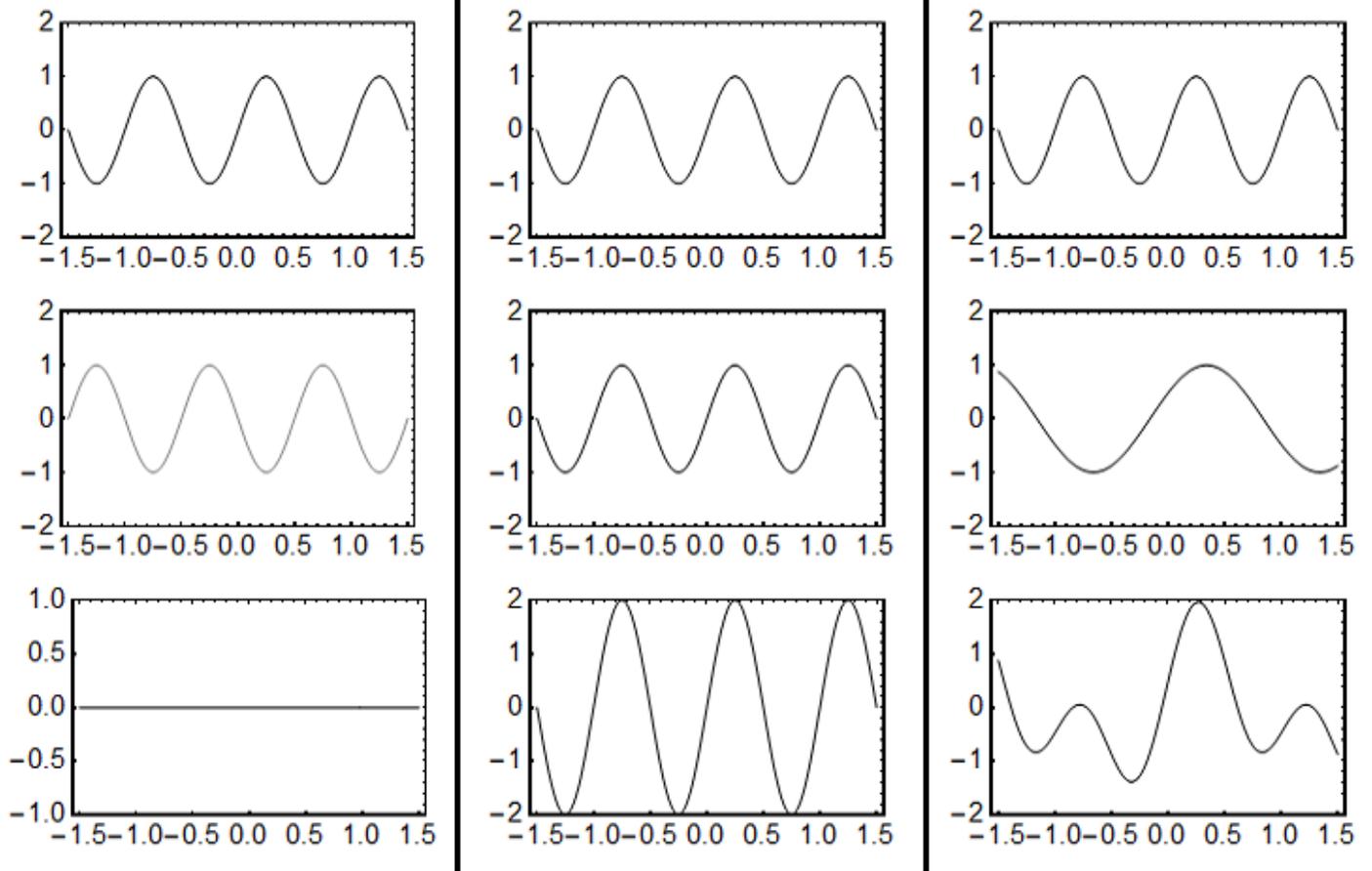
If you've ever tossed a pebble in a pond or pushed a rubber duck in a bathtub, you have made waves. Waves in water are easy to understand – they have an amplitude that corresponds to their height above (peak) or below (trough) the level of the surrounding water. Water waves also have a wavelength that corresponds to the distance between peaks in the waves. Figure 1.1.1 gives an example of this.



**Figure 1.1.1:** Left: Ripple tank used to study water waves. Right: Illustration of a simple, one-dimensional wave.

Left image from University of New Hampshire Center for Coastal and Ocean Mapping, <http://ccom.unh.edu/facilities/test-tanks/wave-tank>, accessed July 2, 2021.

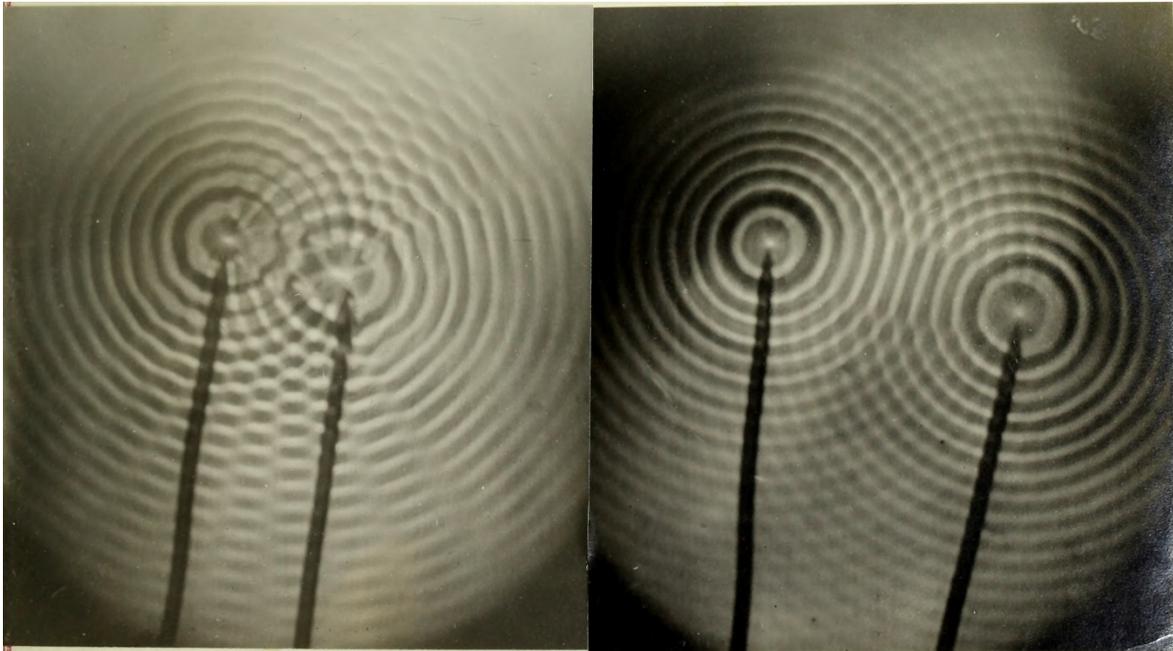
An important feature of waves is interference. If you toss two pebbles in a pond so that the waves are traveling in opposite directions, they will reinforce each other where peaks overlap with each other or troughs overlap with each other. This is an example of constructive interference. Waves can also cancel each other out where a peak and a trough meet each other. This is an example of destructive interference. See Figure 1.1.2 for an illustration of these effects.



**Figure 1.1.2:** Illustration of the interference patterns of waves. Summing the top two waves in each column gives the pattern shown in the third row. Left: Destructive interference (adding two waves that are out of phase but otherwise identical leads to cancellation). Center: Constructive interference (adding two identical waves reinforces the pattern). Right: A combination of constructive and destructive interference (summing waves with different wavelengths leads to more complex waveforms).

One of the most interesting properties of waves is something we take for granted: They can have nodes. Nodes are points in space where the amplitude of the wave changes sign. For water, that means a point between a region where the wave height is above the level of the surrounding water, and a region where the level of the water is below it.

Nodes are easy to understand in a straight line (1-dimensional), but the patterns can become more varied in a surface (2-dimensional). Nodes can be straight lines, or they can curve into circles. Figure 1.1.3 illustrates some patterns of nodes.



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**Figure 1.1.3:** Water waves generated in a ripple tank. Each dipping rod moves up and down to generate circular waves that diffuse outward from it. The patterns interfere with each other in ways that depend on factors including the distance between the dipping rods. Note that the pattern of waves and nodes in the right-hand image consists of nearly-straight lines between the two sources, strikingly different from the circular patterns the produced in isolation.

Image from Shewhart, W.A., *A Study of the Propagation, Refraction, Reflection, Interference and Diffraction of Ripple Waves*, University of Illinois, 1913; accessed via Wikimedia Commons, <http://commons.wikimedia.org>, July 2, 2021.

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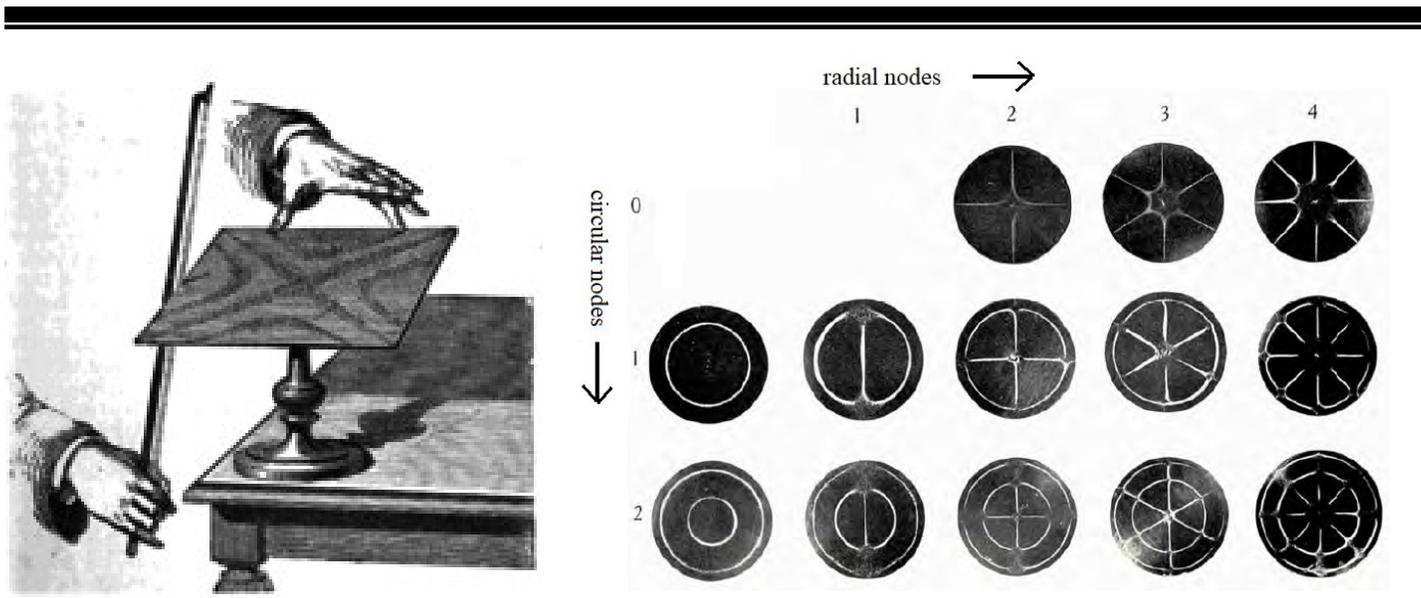
Waves in water are most often seen to move through space, and are referred to as traveling waves. Sound waves and light waves generally work the same way in everyday experience. But there is another category of waves called standing waves. Standing waves do not move from one place to another. Instead, they remain within some region of space and cycle through a repeating pattern.

A common example of this is the waves generated on a drumhead or a metal plate when struck. These objects generate sound when struck because they vibrate in a repeating pattern. While it is too fast for the human eye to see, it can be visualized by placing sand on top of the plate. The sand will be kicked away from the parts of the plate that are in motion, and will come to rest at nodes where the plate is stationary.

This phenomenon is illustrated in Figure 1.1.4. It is striking that such complex patterns can emerge in an object as simple as a circular metal plate. The standing wave can be understood as a flow of energy through the plate, in the form of vibrations. Energy can flow in an infinite number of patterns, but only a certain number of these patterns will repeat themselves. The details of which patterns lead to repetition are determined by the geometry of the plate and its mechanical characteristics, such as rigidity. But the bottom line is that these limitations mean that only certain energies of vibration will produce standing waves, and only certain patterns can emerge.

Nodes come about because as energy flows back and forth in the wave, it creates positive and negative amplitudes in different parts of the plate that are out of phase with each other (i.e. one is up when the other is down, and vice versa). The opposing forces cancel out in the line between them, making those regions into immobile nodes, where the amplitude is always zero.

Nodal patterns also help us understand the nature of the mode in question. In the example in Figure 1.1.4, we see that various allowed standing waves have either circular nodes (rings) or radial nodes (lines from center to edge). While the relationships are complicated, in general, the more energy a standing wave has the more nodes it has. Another way to say this is that as the spacing between nodes decreases, the wavelength of the wave decreases, and higher energy is generally associated with shorter wavelength (wavelength can actually be difficult to define in a circular species, but there is a broad analogy with the one-dimensional waves discussed above).



**Figure 1.1.4:** Left: Forcing the square plate to vibrate by drawing a violin bow across it. Right: Patterns in sand created in vibrating circular plates, illustrating where the nodes are. These images were generated using a somewhat more sophisticated technique than drawing the bow across them, but the end result is the same.

Left image from Stone, W. H., *Elementary Lessons on Sound*, Macmillan and Co., 1879. Accessed via Wikimedia Commons, [https://commons.wikimedia.org/wiki/File:Bowling\\_chladni\\_plate.png](https://commons.wikimedia.org/wiki/File:Bowling_chladni_plate.png), July 2, 2021.

Right image from Waller, M.D., *Vibrations of Free Circular Plates, Part I: Normal Modes*, Proc. Physical Society **1937**, 50, 70-76.

It is worth stopping to consider how perfect the relationships have to be to create a standing wave. Imagine trying to create a standing wave in a bathtub by pushing down on a floating object such as a rubber duck. Pushing down once creates ripples that will hit the wall of the tub and bounce back, dissipating as they go, and the pattern will not repeat and will eventually fade away. But if you were to push the rubber duck up and down with your hand repeatedly, you would create a pattern of ripples. And if you could time it just right, the pattern would repeat and make a standing wave. You might even be able to find other speeds at which you could bob the rubber duck and create standing waves, albeit with different patterns of nodes.

Standing waves in the plate are similar. The plate has to move up and down at just the right frequency to cause the repeating pattern. Each of those frequencies has a particular energy, and there are no standing waves at energies between them. In other words, the energies are discrete.

This should ring a bell related to electrons. Electrons moving around an atom reside in orbitals, and those orbitals have discrete energies. Each of these orbitals corresponds to a standing wave, so of course each has a discrete energy. Take a moment and consider the points made in Table 1.1.1 about standing waves – they will connect directly to understanding electrons in atomic orbitals.

**Take Note!** Static images do not do justice to the nature of standing waves. Here are some videos that might help:

[Vibrating plates \(Chladni plates\)](#)

<https://www.youtube.com/watch?v=IRFysSAxWxI&t=21s>

[Cymatics: Chladni Plate - Sound, Vibration and Sand](#)

<https://www.youtube.com/watch?v=tFAcYruShow>

[Vibrations of a Drumhead](#)

<https://www.youtube.com/watch?v=v4ELxKKT5Rw>

General Features of Standing Waves	Connection to Vibrations of Plates
Energies are discrete	The structure and composition of an object determine how rapidly energy moves through it. Only certain specific energies will move in a way that leads to a repeating pattern (i.e. a standing wave). The patterns shown in Figure 1.1.4 can only exist if the plate has a very specific energy. Sometimes it is possible that two different standing waves have different structures but the same energy (i.e. they are degenerate in energy), but there is still only one energy at which a given wave may exist.
Each standing wave has a distinct pattern of nodes	As with the plate in Figure 1.1.4, every standing wave solution will have some set of nodes. There may be different types of nodes (for the plate, radial vs. circular), and they will be placed differently for every wave.
In general, the number of nodes increases as the energy increases	Based on this principle, the energies of the modes shown in Figure 1.1.4 will increase for the images going from right to left and from top to bottom.
The nodes can be translated into “quantum numbers” that identify the mode	The number of radial nodes and the number of circular nodes, given on the axes of Figure 1.1.4, could each be viewed as a quantum number. For instance, labeling the number of circular modes $n_c$ and the number of radial modes $n_r$ , one could tell a reader exactly which mode is of interest by specifying “ $n_c=2, n_r=3$ ”.

**Table 1.1.1:** Some key properties of standing waves.

## Section 1.2: The Wave Nature of Electrons

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand the wave nature of matter, including the ideas of probability amplitude and probability density.
- Understand the nature of interference in waves, and how it leads to behavior that is different from the behavior of particles.

The idea that electrons might behave like waves rather than particles was first proposed by Louis DeBroglie in 1924, and was proven experimentally by Clinton Davisson and Lester Germer. The experiment involved firing a beam of electrons at a crystal of nickel, and observing that the electrons scattered in a way that was only possible if the electrons behaved as waves. Other experimental demonstrations have followed since.

Year	Discoverer	Discovery
1924	Louis DeBroglie	Theory that matter could behave like waves in some circumstances, rather than behaving like particles. Was able to determine the wavelength matter would have if this were true.
1925	Clinton Davisson and Lester Germer	Observed that firing a beam of electrons at a crystalline piece of nickel metal created a diffraction pattern that was only possible if the electrons were behaving as waves.
1926	Max Born	Publishes an interpretation of the probability amplitude and the probability density of the wavefunction. This interpretation is described in the main text.
1927	Erwin Schrödinger	Developed an equation that allowed one to predict the behavior of an electron wave through knowledge of its probability amplitude. The equation is in some ways for quantum mechanics what Newton's Laws are for classical mechanics.

**Table 1.2.1:** Some key developments in the development of quantum mechanics.

But DeBroglie's theory did not include a key detail: If the electrons were behaving as waves, what did their amplitude mean? When discussing water waves, one can speak of the height of the water as an amplitude. What was the "amplitude" of an electron?

It was Max Born who proposed the idea that the wave – or, as it was known, the wavefunction – represented something completely outside of prior human experience. He proposed a property called the probability amplitude and a related property called the probability density.

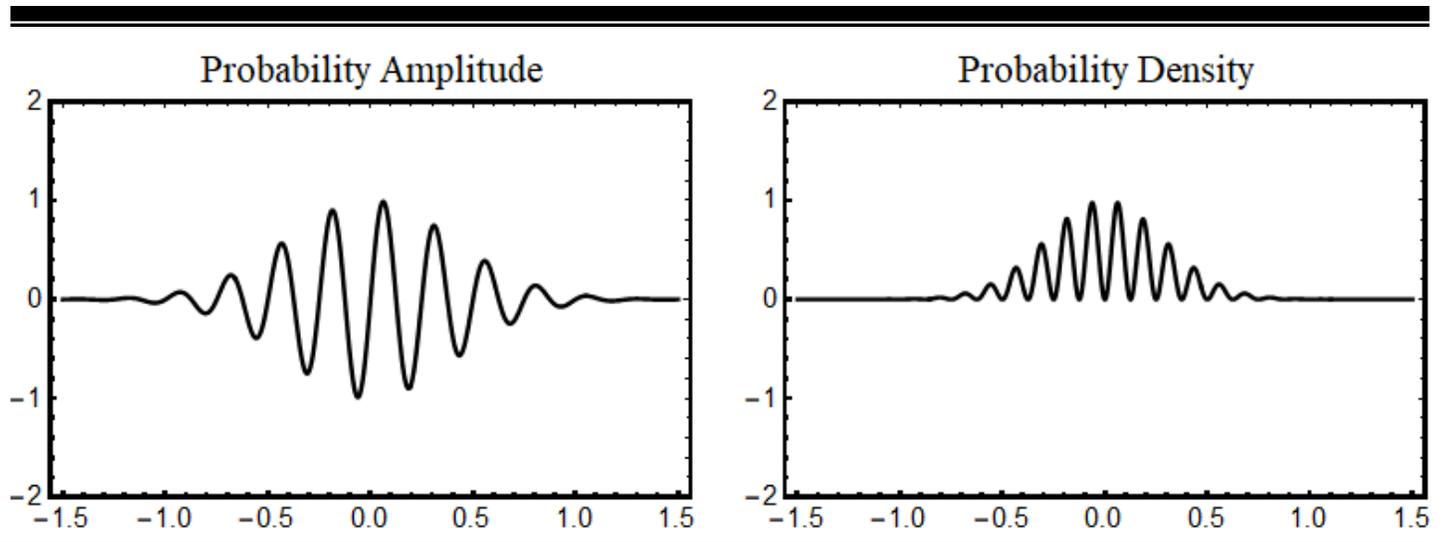
The probability density is the easier quantity to understand. It represents the likelihood of finding the electron at a particular point in space. The higher the probability density, the more likely it is to be found there. If the probability density is zero, the electron cannot be found at that point. Because it is proportional to probability, probability density is always a positive number.

The probability amplitude is the stranger property. It is not "like" anything in human experience. It is a property of the electron and can be positive or negative. At every point  $x$  in space, the electron has a probability amplitude  $\psi(x)$  and a probability density  $\Psi(x)$ . The two are connected by the relationship:

$$\Psi(x) = |\psi(x)|^2 \quad (1.2.1)$$

In other words, the probability density is just the magnitude of the probability amplitude squared. This definition is consistent with the requirement that probability amplitude can be positive or negative but probability density can only be positive.

When we want to describe the behavior of a particle like a baseball, we can talk about it having a position and a velocity which can change in time as it moves. When we want to describe the behavior of an electron, we have to talk about its probability amplitude, and how that changes in response to the presence of other forces. The probability amplitude can be described using a mathematical expression called the Schrödinger Equation, a mathematical equation that looks a lot like the equations used to describe waves. So, even though the probability amplitude is unlike anything in human experience, its behavior maps closely to that of waves we are familiar with (which was the point of looking at waves in Section 1.1.1).



**Figure 1.2.1:** Sample probability amplitude and its probability density for an electron in one-dimension. Note that nodes in the probability amplitude correspond to points where the probability density is zero.

But stopping to consider the nature of the probability density makes clear that this quantum mechanical realm is alien to our experience. First, waves do not end cleanly at some point in space; they tail off gradually to zero. The wavefunction defining an electron has to have a value at *every* point in space, even if it is a very small one. If one asks, “Where is this electron?” the answer is that there is some probability of finding it anywhere. It could be up your nose, or on the Moon. Physically, of course, an electron would never be spread out enough to have a significant probability of finding it in both places. Your nose and the Moon have different potential energies and a great many objects between them which prevent the electron from spanning the space. But the principle – that the electron is spread through space – has important implications.

One of these is the idea of localization. The electron cannot be confined to a single point, but the range over which it can be found can be relatively small if the probability density decreases quickly with distance from some central point. So we can talk about an electron being localized or delocalized depending on its width

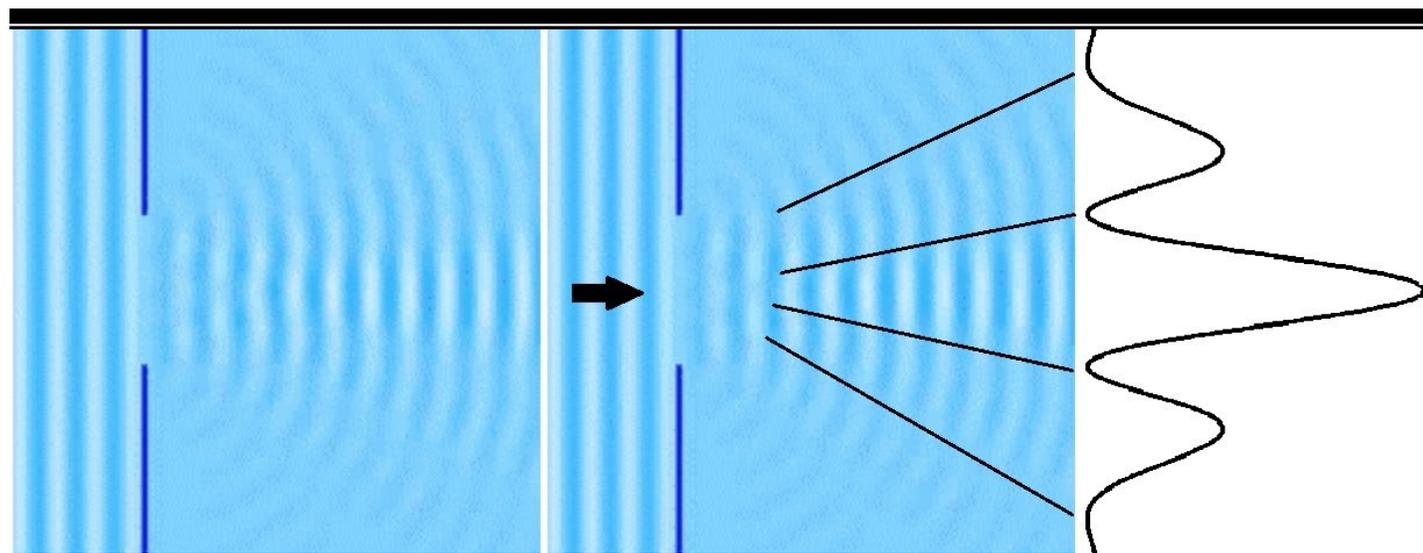
in space (though those terms are arbitrary – a chemist talks about an electron being localized in a bond, and a nuclear physicist talks about a proton being localized in a nucleus, which is 100,000 times smaller).

It is also important to realize that some basic ideas of physics have not gone out the window just because we realize that the electron behaves as a wave. Like charges still repel each other, and opposite charges attract. That means electrons will be repelled by each other, and they will be drawn to the nucleus of an atom or to other positively charged objects. This will be reflected in the distribution of probability density. The probability density will be higher near positively charged objects and lower near negatively charged ones. It may also change in time, shifting toward or away them.

You may be wondering why we need the probability amplitude, since the probability density tells us where the electron is (which is usually what we want to know). The answer is that the probability density itself does not explain all of the properties of an electron in motion. Probability amplitude is necessary to explain many of these, including interference.

Look back at the water waves shown in Figure 1.1.3, and note the complex patterns that arise because of interference between the waves. You likely find it intuitive that the height of the water should be affected by interference in this way. Now imagine that the *existence* of the water – the likelihood of finding it somewhere – could be affected by interference of this type, that waves of water could run into each other and not just change the height of the water but actually make it cease to exist at points where you would find a node. This is what quantum mechanics tells us is happening with electrons.

Let us look at the property of interference in a little more detail by studying the passage of waves through a slit, as shown in Figure 1.2.2. This could represent the heights of water waves or the probability density of electrons passing through a slit. In either case, a key feature in passage is the existence of nodes, marked with lines in the right-hand side of the figure. If one were to draw a line across the wavefront and measure the intensity as shown, one would find points where the intensity of the wave was zero.



**Figure 1.2.2:** Motion of waves passing through a slit. Straight (plane) waves enter the slit from left to right, and are diffracted during passage. Left: Unaltered image. Right: Nodes marked with lines, and intensity indicated by peaks to right.

Left image taken from Wikimedia Commons, <https://commons.wikimedia.org/wiki/File:Wave-diffraction-2.gif>, July 2, 2021.

This illustrates the difference between waves and particles. Imagine throwing a series of baseballs at the slit and looking at where they strike. Like the waves, their impacts would also make a pattern on the wall, but probably one that changed smoothly from a point of highest likelihood on the wall directly behind the slit and then tailed off as the angle between the wall and the slit became larger. There would not be points analogous to nodes, where the baseball could not hit even though it could hit the wall to either side of that point. This was the phenomenon that made it possible for Davisson and Germer to conclude that electrons were behaving as waves rather than particles, and it is a critical property of electrons.

Interference can only arise if the amplitude of a wave could be either positive or negative. This is why we need the concept of probability amplitude to understand the behavior of electrons, even though it is the probability density that we can directly observe through measurement. It also means that when we look at electrons in orbitals we will need to take interference into account to understand their behavior. Electron interference leads to complex, alternating patterns of positive and negative probability amplitude, and this is ultimately what gives rise to the shapes of atomic orbitals.

One final question to consider is the question of why the laws of physics seem to work differently for electrons and baseballs. The answer is that they do not work differently, and that every object in the universe – including you – should be described by a wavefunction.

The reason Major League Baseball pitchers do not need to worry about the baseball undergoing diffraction when they throw it is that it is a very heavy object by the standards of quantum mechanics. It turns out that the more mass an object has, the more localized the wavefunction that describes it. Baseballs, human beings, and other objects we can perceive directly with our senses have wavefunctions that are so localized that we can consider them as occupying a single point in space. In other words, the distribution of probability density is so narrow that their wave nature is unimportant and we can think of them as particles, recovering the ideas of position and velocity that are intuitive to us.

It turns out that the dividing line where the mass becomes large enough that wavefunctions can be ignored falls between the masses of electrons and the masses of nuclei. That is, in most circumstances, chemists can view nuclei as particles and electrons as waves. While there are times this approximation leads to poor results, most of organic chemistry can be understood within this framework.

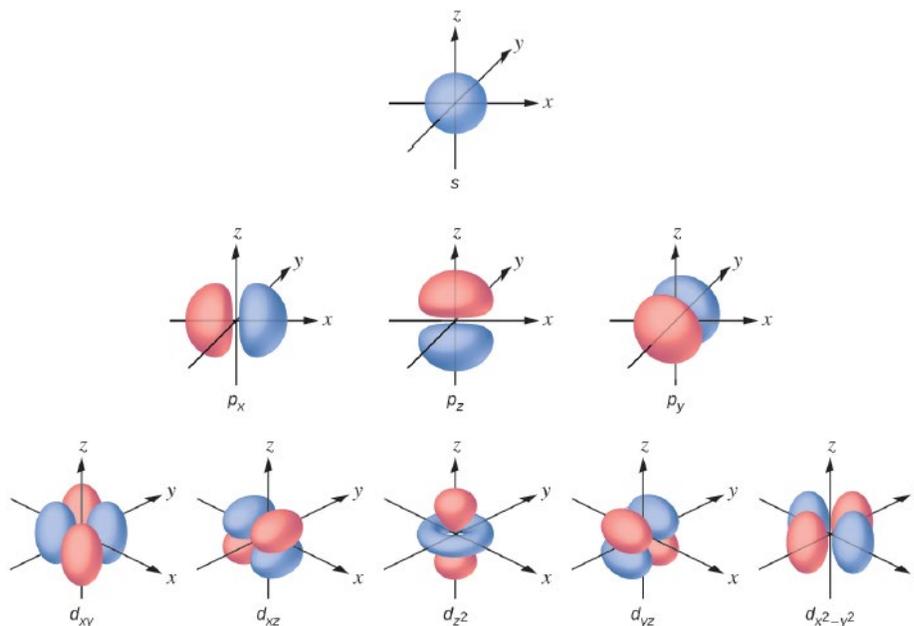
## Section 1.3: Atomic Orbitals as Standing Waves

### LEARNING OBJECTIVES FOR THIS SECTION

- Be able to recognize the features of atomic orbitals that correspond to those of standing waves.
- Recognize that the quantum numbers associated with atomic orbitals relate to the distribution of nodes of the wavefunction, and therefore determine the relative sign of the probability amplitude in different regions of space.
- Understand the significance of spin as an intrinsic property of an electron.
- Be able to use the Aufbau rules to fill atomic orbitals in many-electron atoms, making proper account of the Pauli Exclusion Principle and Hund's Rule.

We began this chapter with a general discussion of waves, including the idea of standing waves that repeat in a cycle without changing their position in space. We then discussed some of the principles underlying the idea that electrons should be viewed as waves, noting that the Schrödinger equation – which describes the behavior of the probability amplitude – looks very much like the equations describing waves that are familiar to us. Perhaps unsurprisingly, the Schrödinger equation indicates that electrons can form standing waves.

One example of such a standing wave are the orbitals of a hydrogen atom. The electron is attracted to the positively-charged nucleus, so tends to stay near it. But its wave nature means that it cannot just exist in a single point sitting on top of the nucleus, so it is spread out through space around it.



**Figure 1.3.1:** Atomic orbitals. Relative phases are indicated by color (i.e. the probability amplitude of lobes marked in red have an opposite sign to lobes marked in blue). Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).

How the electron moves depends on its energy and its interactions with surrounding objects. An electron with high energy can move right past a nucleus and off into space again. But electrons with lower energies will be trapped by the attractive force of the nucleus. The classical analog to this is the behavior of planets around the Sun. An astronomical body with a high energy may swing past the Sun and have its course

changed, but it will move back out into deep space again. Those with lower energies will be trapped in orbits, moving in a repeating pattern around the Sun as the planets do. The key is that, as waves, electrons do not move in orbits like planets. Instead, in order to be in a repeating pattern of motion around the nucleus, they have to be in a standing wave like the plates shown in Figure 1.1.4.

And, like those standing waves in the plates, there are rules that mean that only certain energies are possible for the electrons, and their standing waves have specific patterns of nodes. In other words, the energies of the orbitals are discrete, with only some values allowed and others forbidden.

An important distinction between electrons and planets is that electrons are not found on a single path. The wavefunction describing them is spread out through all of 3D space so that, for every point (x,y,z) in space, there is a probability amplitude  $\psi(x,y,z)$ .

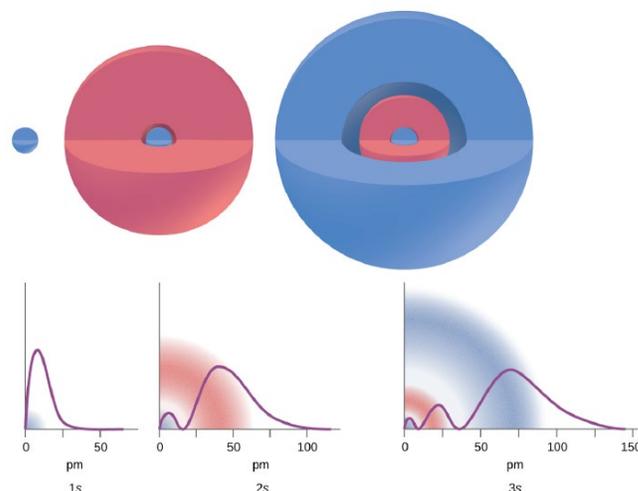
Visualizing a three-dimensional wave like this is a challenge that is usually met by drawing a surface that satisfies two rules. First, the value of the probability density  $\Psi(x,y,z)$  is the same for every point on the surface, and second, the surface is drawn in a way that 90% of the probability density for the electron is contained within the surface (i.e. there is a 90% probability that the electron will be found in the area bounded by the surface). Those two rules lead to the familiar shapes for the orbitals of a H-atom. They are a good guide to the distribution of the electron, but it is important to remember that the reality is a bit more complex.

Like conventional standing waves, the H-atom orbitals include nodes at various positions. Because they are 3D distributions, it is not as simple as having a node being a point or a line. Instead, nodes in wavefunctions show up as “nodal planes” (flat planes cutting through the wavefunction) or some other structure; this is a bit like the radial and circular nodes in the 2D standing waves of the plates shown in Figure 1.1.4. As in conventional waves, the electronic wavefunction has different signs on each side of the node.

Looking at the wavefunctions in Figure 1.3.1, it is clear that the p-orbitals have a nodal plane dissecting them. Their differing orientations in part reflect the fact that they are dissected by a different plane. The  $p_x$  orbital is dissected by the yz-plane, the  $p_z$ -orbital is dissected by the xy-plane, and so on. The d-orbitals have four lobes because, with the exception of the  $d_{z^2}$ -orbital, they are dissected by two planes that are separated from each other by  $90^\circ$ . The  $d_{z^2}$ -orbital can be imagined as having nodes arranged as cones pointing up and down along the z-axis (don't worry if you have trouble visualizing this), which are a bit like the circular nodes in Figure 1.3.1.

---

**Figure 1.3.2:** Atomic s-orbitals, with radial dependence of the wavefunction shown. Probability density as a function of distance from the nucleus is shown in the lower part of the image. Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).



But there is an additional layer of complication. The wavefunctions can also have nodes of spherical symmetry, which are hard to visualize. In essence, the wavefunction changes sign at some distance away from the nucleus, which is shown for s-orbitals in Figure 1.3.2. Atomic 3p- and 4d-orbitals, and higher-numbered orbitals, have similar changes in sign with distance from the nucleus. This seems like it ought to be significant, but in fact in most circumstances the interaction between orbitals on neighboring atoms is governed by the outermost layer of the orbital so changes in sign of this type are moot.

We emphasize again that the presence of nodes in atomic wavefunctions means there are points at which the probability amplitude is zero. This means that the probability density at these points is also zero, so the electron cannot be found there, which seems counterintuitive. But in practice it is more important that we understand that the wavefunction changes sign across those nodes, because it is the relative sign of the wavefunctions that will dominate interference effects that are important in the construction of covalent bonds.

General Features of Standing Waves	Connection to Atomic Orbitals
Energies are discrete	Atomic orbitals have discrete energies, determined by their structure (e.g. 1s-orbitals have a different energy from 2s- or 2p-orbitals).
Each standing wave has a distinct pattern of nodes	Orbital structures range from spheres for s-orbitals to cloverleaves for d-orbitals, as shown in Figure 1.3.1.
In general, the number of nodes increases as the energy increases	2s-orbitals have a higher energy than 1s-orbitals, and (for many-electron atoms) 3d-orbitals have a higher energy than 3p-orbitals.
The nodes can be translated into “quantum numbers” that identify the mode	The quantum numbers $n$ , $l$ , and $m_l$ provide enough information to identify a specific atomic orbital.

**Table 1.3.1:** Some key properties of standing waves.

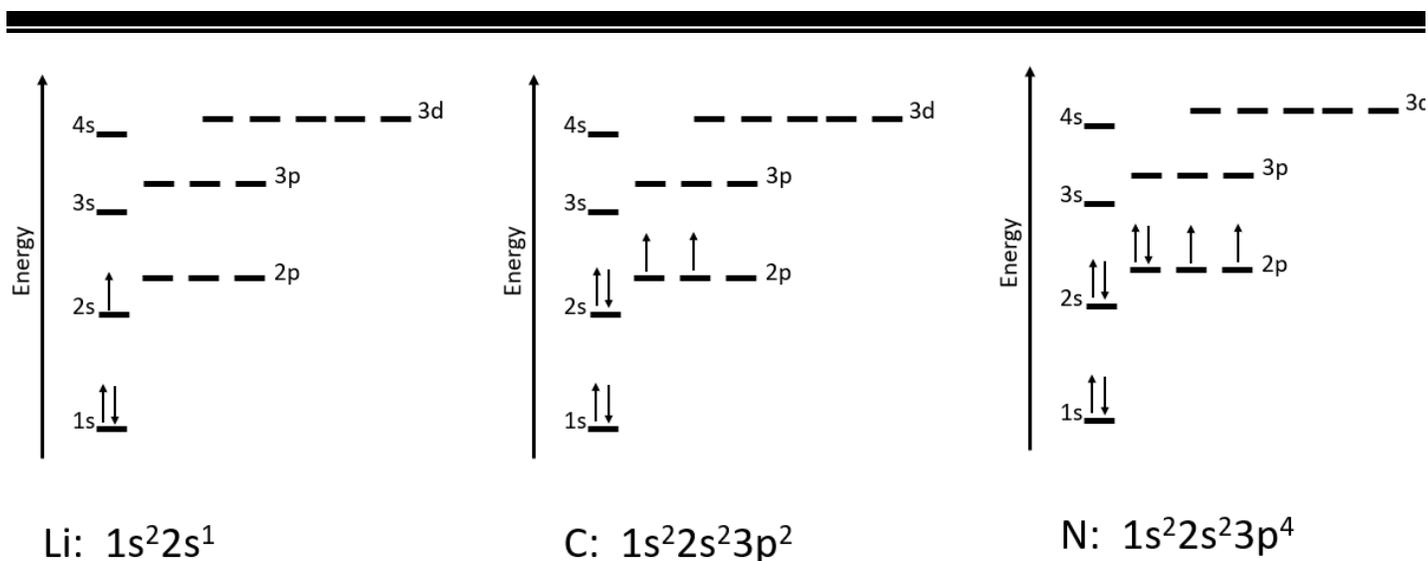
Table 1.3.1 applies the general features of standing waves to atomic orbitals, as Table 1.1.1 tied the features of standing waves to vibrating plates. The point here is to clarify the nature of atomic orbitals as standing waves, in preparation for the discussion of bonding in Chapter 2. The emergence of quantum numbers, for example, is not unique to quantum mechanics but rather is a consequence of the wave nature of matter. The three-dimensional standing waves of the hydrogen atom can be described by three quantum numbers, the familiar  $n$ ,  $l$ , and  $m_l$  (there is in fact a rule that the number of necessary quantum numbers equals the number of dimensions). These are analogous to the two quantum numbers (radial and circular) for the vibrating two-dimensional plates. Other aspects of the analogy are equally strong.

One can tighten the connection further by noting that each quantum number gives information about the nodal pattern of the wavefunction. The principal

**Take Note!** You should have learned previously that there are specific relationships between the allowed quantum numbers  $n$ ,  $l$ , and  $m_l$  (e.g.  $l$  cannot be larger than  $n-1$ ). These relationships emerge from specific features of the Schrödinger equation that are beyond the scope of this discussion. We do not review the relationships between quantum numbers here, but you should review them if you do not remember them.

quantum number  $n$  gives the number of radial nodes (0 for  $n=1$ , 2 for  $n=2$ , etc.) and the azimuthal quantum number  $l$  gives the number of nodal planes (0 for  $l=0$  corresponding to a s-orbital, 1 for  $l=1$  corresponding to a p-orbital, 2 for  $l=2$  corresponding to a d-orbital). The magnetic quantum number does not give a distribution of nodes *per se*, but it does control the orientation of the nodal surfaces in the orbital (cycling through the yz-plane, xz-plane, and xy-plane for the p-orbitals, for instance).

You will note that we have not discussed the spin quantum number  $m_s$ . That is because we have been discussing the standing wave solutions of the H atom, which are distributions in space. The spin quantum number describes a “spin state” for the electron, variously referred to as either “up or down” or “+1/2 or -1/2”. The “spin” is a property of a quantum object that does not have an analog in our daily experience – it is not really like anything we can perceive directly through our senses. The quantum numbers  $n$ ,  $l$ , and  $m_l$  are properties of the motion of the electron in an atomic orbital, and cannot be used to describe the electron when it is in other circumstances (e.g. moving through free space, with no nearby atoms). Spin is an intrinsic property of an electron, and it will always have a spin state, regardless of its circumstances.



**Figure 1.3.3:** Electronic structures for lithium and carbon.

Before concluding our discussion of atomic orbitals, it is probably worthwhile to review the Aufbau rules for many-electron atoms. You should remember that the energies for atomic orbitals follow the pattern laid out in Figure 1.3.3, and that the ground state (lowest energy state) of an atom is constructed by putting atoms into the lowest-energy atomic orbitals first.

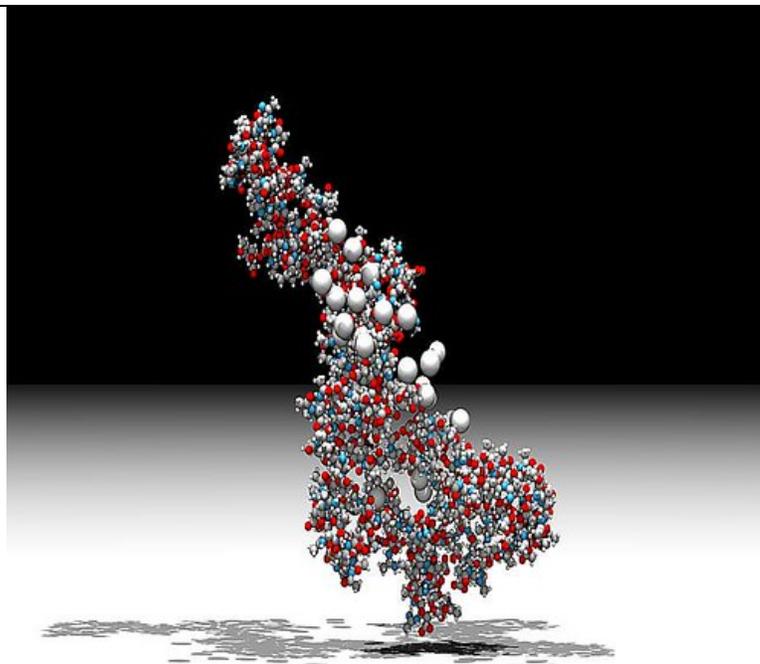
There are two rules to keep in mind for the Aufbau process. The first rule is the Pauli Exclusion Principle, which states that no two electrons can occupy the same state. In the context of atoms, that means that no electrons can have the same set of four quantum numbers ( $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ). Three of those quantum numbers determine the identity of the orbital (e.g.  $1s$  specifies  $n=1$ ,  $l=0$ , and  $m_l=0$ ), and the fourth determines the spin state. That means that there can be two electrons in every orbital, provided that one is spin-up and the other spin-down. This is why for the case of lithium in Figure 1.3.3 the first two electrons go in the lowest-lying orbital, and the third goes in the next orbital up.

The second rule one needs to remember is Hund’s Rule, which states that if there is a series of degenerate orbitals (i.e. orbitals that are equivalent in energy) then electrons should be placed into orbitals so that the number of unpaired electrons is maximized, with the spins of unpaired electrons are aligned. For

carbon, that means that the only two electrons in the 2p orbitals are placed in separate orbitals with their spins aligned (here, spin-up, though it would be equally correct to place them both spin-down). For nitrogen, with four electrons in the 2p-orbitals, one needs one set of paired electrons and two unpaired electrons with spins aligned.

This is a very cursory review, and you may want to review these subjects more fully in your general chemistry text. The review is motivated by the fact that while all atomic orbitals are standing waves for electrons, not all standing waves are atomic orbitals. As we will see in the next chapter, one can have molecular orbitals, in which standing waves of electrons are formed in the presence of two or more atoms. This leads to bonding, resonance, and other important chemical phenomena. And the principles used in atomic orbitals – the Aufbau rules, the Pauli Exclusion Principle, and Hund's rule – are also used for molecular orbitals

## CHAPTER 2: Chemical Bonds



*A portion of the cell membrane of pseudomonas aeruginosa, a bacterium. Representation is a result of simulations run by the U.S. Department of Energy's Environmental Molecular Sciences Laboratory.*

*Courtesy of Wikimedia Commons,  
<https://search.creativecommons.org/photos/532a7a2c-25ed-4af5-80dc-998276e79334>, accessed July 7, 2021.*

CONCLUSION: BIG  
HELIX IN SEVERAL  
CHAINS, PHOSPHATES  
ON OUTSIDE,  
PHOSPHATE-  
PHOSPHATE INTER-  
HELICAL BONDS  
DISRUPTED BY  
WATER. PHOSPHATE  
LINKS AVAILABLE TO  
PROTEINS.

-ROSALIND FRANKLIN

*From the deceptively simple geometry of water to the intricacies of DNA, molecular structure arises from chemical bonds. Understanding the nature of the covalent bond is the first step toward the modern practice of chemistry.*

### BEFORE YOU BEGIN, MAKE SURE YOU KNOW

- The shapes of atomic orbitals (Flowers, sec 6.3)
- The rules for Aufbau in atomic orbitals, including the Pauli Exclusion Principle and Hund's Rule (Flowers, sec 6.4)
- Drawing and interpreting Lewis structures (Flowers, sec 7.3)
- Valence Shell Electron Pair Repulsion (VSEPR) Theory (Flowers, sec 7.6)

## Section 2.1: The Challenge of the Chemical Bond

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand how interactions between electrons and nuclei create chemical bonds.
- Understand that a stable bond requires a standing electronic wavefunction.
- Understand how the standing wavefunction for a bond can be approximated using the constructive interference of two atomic orbitals.

Moving now from atoms to molecules, we consider the simplest molecule:  $\text{H}_2$ . Two nuclei and two electrons that are held together by their electrical charges and nothing else.

That is an important realization. Take a moment and step back from the fact that you know that  $\text{H}_2$  is a “molecule,” whatever that means, and just perceive it as 4 objects: Two heavy nuclei and two electrons buzzing around them. Try to find it in you to be surprised that those 4 objects stick together, but if you try to throw in two more electrons the group will not stay together.  $\text{H}_2^-$  can exist, but  $\text{H}_2^{2-}$  cannot. Why should that be true?

As we discussed in the last chapter, the nuclei are heavy enough that we can safely think of them as particles sitting at specific points, but the electrons must be considered as waves with probability amplitude smeared out through space. How are these objects going to assemble themselves?

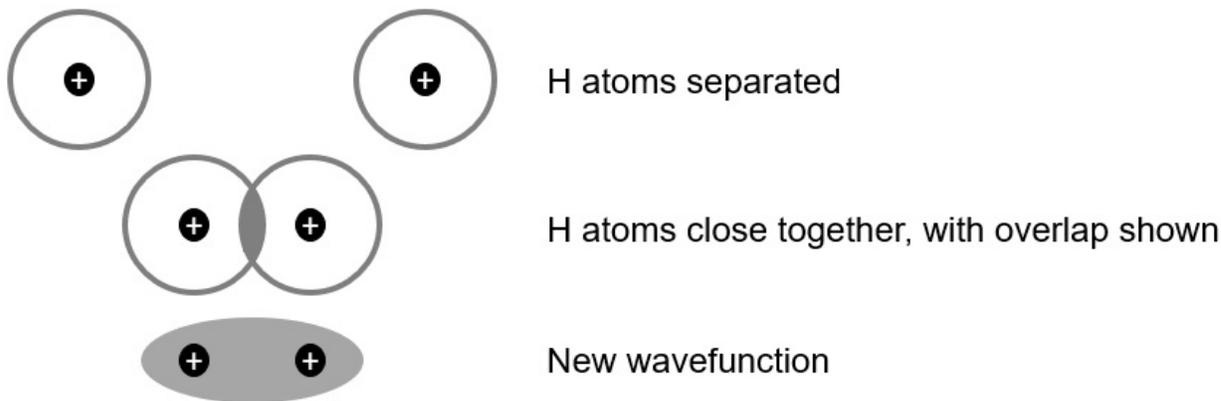
Whether they are electrons around atoms or boulders rolling down hill, objects in nature tend to move in ways that minimize their energy. Since the forces here are all between charged objects, they will maximize the interactions between oppositely charged objects (which are attractive) and minimize the interaction between like-charged objects.

The obvious way to minimize the energy is to put most of the electron density between the two nuclei. Each electron is repelled by one negatively-charged object (the other electron), but is close to both nuclei and is attracted to each. Likewise, the nuclei are closer to the electrons than they are to each other, so there is a net force keeping them together.

This balance of forces is sensitive to the distance between the nuclei. If the nuclei get too close to each other, the repulsive charge between the nuclei will push them apart despite the presence of the electrons. Likewise, if the nuclei move too far away from each other the electrons will no longer be close enough to interact favorably with them. The result is that the nuclei stay at a relatively constant distance from each other, giving the molecule a bond length.

But if these four objects are going to stay in this configuration indefinitely, then the electrons have to occupy a standing wave state. This will be a bit like the atomic orbitals we discussed in the last chapter, except that now this wavefunction is responding to the presence of two nuclei rather than one. Most of the probability density has to sit between the two nuclei for the reasons we described above, but because waves do not just “stop” the wavefunction will also extend into other regions of space. Some probability density will be found around one or the other of the nuclei rather than between them, and the probability density should decay smoothly as the distance from the nuclei increases in any direction.

It is possible to solve the Schrödinger equation for this system, at least approximately, and find the standing wave that best describes the distribution. Even for this simplest of molecules, that is a challenging problem. But it turns out that the essential physics of the problem can be captured by constructing a new orbital using the  $1s$  orbitals of each H atom as a starting point.



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**Figure 2.1.1:** Formation of a H<sub>2</sub> molecule from the overlap of 1s orbitals around H atoms.

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Let us imagine that we move the two H atoms close enough to each other that their 1s orbitals overlap in space, as shown in Figure 2.1.1. Remember that the orbitals are waves, and when two waves come into contact they can interfere with each other. In this case, we combine them in a way that leads to constructive interference, so that the probability amplitude where they overlap is larger than the overlap of a 1s orbital in isolation. This reinforcement of probability amplitude also increases the probability density.

The result, then, is a region of increased probability density between the two nuclei. What is more, the new wavefunction that is created by the overlap has the properties we wanted for the standing wave describing the distribution of electrons: It puts most of the probability density along the axis between the two nuclei, leaves some of it in the regions around each of the nuclei, and tails off into space beyond those regions. So, we can *build* something close to the standing wave we need by combining the atomic orbitals in ways that exploit their interference properties. This is not a perfect representation of the standing wave for the electrons, but much of chemistry can be understood with this approximation.

The standing wave that defines the bond is subject to many of the same rules as the standing waves for atomic orbitals, the most important being that no two electrons can have exactly the same state. So, once again, only two electrons are allowed to move in this standing wave: One spin up, and one spin down. Double and triple bonds are not formed by putting more electrons into the same standing wave, but rather by building additional standing waves with distributions that span the distance between the two nuclei; we'll discuss this point further in Section 2.2.

Hydrogen is the simplest molecule, and the wavefunction describing it can be built using only one wavefunction on each nucleus. Other atoms require dealing with more nuclei and more atomic orbitals, and it is necessary to make some strategic decisions about how to do it.

There are two broad strategies: Valence Bond Theory and Molecular Orbital Theory. Valence Bond Theory works by changing atomic orbitals into what are called "hybrid orbitals," which allow bonds and bond angles to emerge naturally. Molecular Orbital Theory works by combining atomic orbitals in more complex ways than the simple structures we've shown here for H<sub>2</sub>. The virtue of Valence Bond Theory is simplicity, and

the virtue of Molecular Orbital Theory is its ability to account for phenomena such as resonance that are not well-described by Valence Bond Theory. We will discuss each in turn.

## Section 2.2: Valence Bond Theory

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand how hybrid orbitals are constructed, and how they are used in Valence Bond Theory.
- Be able to recognize the hybridization of an atom in a molecule.
- Understand the relationship between Valence Bond Theory and VSEPR geometry.
- Understand the nature of pi- and sigma-bonds, be able to recognize each, and understand the significance of unhybridized p-orbitals on neighboring atoms.

When we looked at the H<sub>2</sub> molecule in the example above we saw that what we needed was a standing wave to describe the bond. It put electron density between the two nuclei, where the energies of interaction were most favorable.

But there is an additional challenge when three or more atoms are present in a molecule. We have to rationalize what we know about electrons and wavefunctions with what we know about molecular geometry. You should be familiar with the fundamental ideas of Valence Shell Electron Pair Repulsion (VSEPR) theory. VSEPR treats electron pairs as if they were localized in bonds or in lone pairs, and arranges atoms in space to minimize their energies of interaction. A lone pair or bond (including a double or triple bond) is viewed as an electron domain, and the molecular geometry is determined by the need to minimize the energies of interaction between the different electron domains in the molecule. If there are two electron domains present, the electron domains sit 180° apart. If there are three, they sit 120° degrees apart, and if there are four they sit 109.5° apart.

You should understand from your prior studies that these angles will be adjusted based on the details of the forces between them (e.g. an electron pair is more repulsive than a bond, so bonds will move away from it). You should also understand that the geometry of the *molecule* will be distinct from the geometry created by the *electron domains*. This means that, for instance, a NH<sub>3</sub> molecule has 3 bonds and one lone pair of electrons, so the electron domain geometry is tetrahedral, but the three bonds mean that the molecular geometry is trigonal pyramidal. If you are not confident in your understanding of these ideas, you should review them in your general chemistry text.

**Table 2.2.1:** Features of Valence Bond Theory.

### Valence Bond Theory

Strategy:

- 1) Convert atomic orbitals into “hybrid orbitals”
- 2) Describe a wavefunction for the chemical bond as the overlap of hybrid orbitals on neighboring atoms
- 3) Assume there are exactly two electrons per bond

Pros:

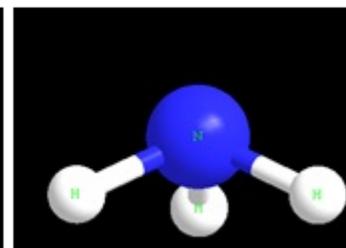
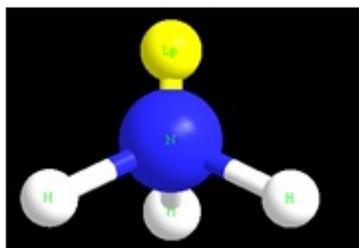
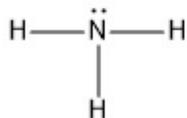
- Simple, quick, and accurate most of the time

Cons:

- Fails for phenomena such as paramagnetism that involve unpaired electrons
- Very clumsy in its treatment of resonance (discussed in Section 2.4)

Formula	Lewis Structure	Electron Domain Geometry	Molecular Geometry
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NH<sub>3</sub>



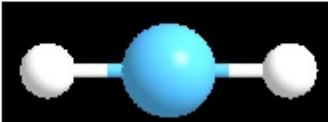
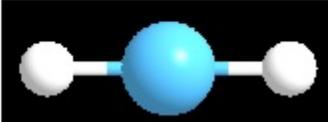
**Figure 2.2.1:** Lewis structure, electron domain geometry, and molecular geometry for ammonia. In the electron domain geometry, the lone pair is shown in yellow, but the labels for molecular geometry include only information on atomic positions. Here, that means that the electron domain geometry is tetrahedral but the molecular geometry is trigonal planar.

In the last section, we saw that combining the 1s orbitals on each H atom in H<sub>2</sub> led to a standing wave like the one we needed. But VSEPR theory says that the standing waves between atoms have to have certain angles between them, usually roughly 109.5°, 120°, or 180° (we are mostly ignoring the cases where the valence shell is expanded and other angles are possible). How do we build standing waves that put regions of electron density at those angles, starting with atomic orbitals?

The answer is that we can take advantage of the interference between atomic orbitals to build a new type of wavefunction called a hybrid orbital. A hybrid orbital is a wavefunction that puts probability amplitude in a lobe somewhere near the atomic nucleus. By combining a s-orbital with 1, 2, or 3 p-orbitals we can create hybrid orbitals that put lobes of electron density at angles corresponding to the angles required by VSEPR theory, leading to bonds positioned at the appropriate angles.

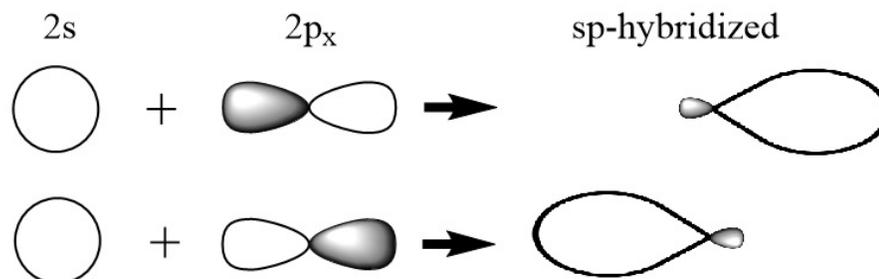
**sp-hybridization:** The simplest example of this is the BeH<sub>2</sub> molecule. At first glance, BeH<sub>2</sub> looks like it should be an ionic compound, because it combines a metal with a non-metal. But in fact it behaves as a molecule, forming covalent Be-H bonds and creating a BeH<sub>2</sub> structure that can float around as a single chemical object in the gas phase (something genuinely ionic compounds like NaCl do not do). It violates the octet rule (Be has too few electrons), but nature can do that occasionally and that makes the BeH<sub>2</sub> molecule a particularly easy starting point for this discussion.

There are only 2 electron domains in BeH<sub>2</sub>, the two bonds, so they have to be 180° apart by the VSEPR rules. When we built the H<sub>2</sub> molecule, we did it by creating interference between the 1s-orbitals on each H-atom. We would like to find similar orbitals for the Be atom that will put electron density between the two atoms. But we cannot just use, say, a 2p<sub>x</sub> orbital for one bond and a 2p<sub>y</sub> orbital for the other, because that would put two regions of electron density at an angle of 90° apart because the p-orbitals are 90° apart. Using the 2s orbital seems like it might help, but that just means the electron density is smeared all over a spherical space rather than localized into a lobe where a bond could form. We want wavefunctions on the Be atom that will put electron probability amplitude in specific spots that are 180° away from each other.

Formula	Lewis Structure	Electron Domain Geometry	Molecular Geometry
$\text{BeH}_2$	$\text{H}—\text{Be}—\text{H}$		

**Figure 2.2.2:** Lewis structure, electron domain geometry, and molecular geometry for  $\text{BeH}_2$ . The Be atom has only 4 electrons, so the octet rule is violated, but in fact this molecule exists. With only two domains, VSEPR rules demand a linear geometry.

We can construct the wavefunctions we need by taking advantage of interference between a 2s and a 2p orbital, as shown in Figure 2.2.3. Remember that the 2p orbital has a nodal plane at the center, and the wavefunction has opposite signs on each side. In contrast, the 2s orbital is spherical, and its probability amplitude is the same on both sides. Recalling that waves can interfere with each other, that means the 2s and 2p orbitals will interfere constructively on one side of the nucleus (where the probability amplitudes have the same sign) and destructively on the other (where the probability amplitudes have opposite signs). The result will be a wavefunction with a large lobe on one side of the atom and a much smaller lobe on the other. This is the result of constructive and destructive interference between the wavefunctions, similar to the way constructive interference between the two 1s orbitals on the H atoms led to increased probability amplitude



**Figure 2.2.3:** The combination of the 2s and  $2p_x$  atomic wavefunctions creates two new orbitals, called sp-hybrid orbitals. The shading of the lobes indicates the sign of the probability amplitude of the wavefunction (here, light for positive, dark for negative, though the choices are arbitrary). Where the signs are the same, the waves reinforce and probability amplitude increases; where they are opposite in sign, they interfere destructively and the probability amplitude decreases. Note that the enhanced lobes of the wavefunction are  $180^\circ$  apart, consistent with the VSEPR rules.

between the two nuclei.

If that were the end of the story, we would have only one hybrid orbital corresponding to a single lobe on one side of the molecule. But there is a rule in quantum mechanics that dictates that if you combine two

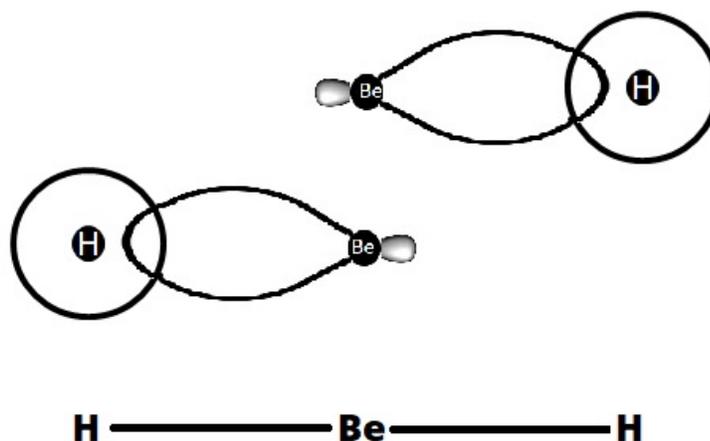
orbitals you must create two new orbitals (i.e. it is inconsistent to create only one orbital out of two). Here, the second orbital is created by reversing the phase of one of the orbitals – as if we have subtracted one from the other rather than adding them. The result is a second lobe on the opposite side of the molecule, 180° from the first.

You may be tempted to ask why these orbitals should exist. Why has the atom suddenly decided that the atomic orbitals are no longer good standing waves? The answer is energy. Placing a second nucleus near the Be changes the forces acting on the electrons, and the unhybridized orbitals no longer minimize the energy of the system. But the hybrid orbitals, which move electron density into the space between the nuclei, do minimize the energy.

**Take Note!** The number of hybrid orbitals out must equal the number of atomic orbitals in. This will be useful in relating the hybridization of the atom to the number of bonds it forms.

Once the hybrid orbitals form and place electron density at the specified sites around the Be nucleus, atomic orbitals centered on the H atom will overlap with it and create a region of constructive interference, exactly the same way that the 1s orbitals overlapped for the H-atom. Again, we are using the overlap of atomic wavefunctions (in this case, hybrid orbitals) to place electron density between the two nuclei to minimize the energy.

**Figure 2.2.4:** Overlap between the sp-hybrid orbitals and the 1s orbitals on the H atoms that create the Be-H bonds.



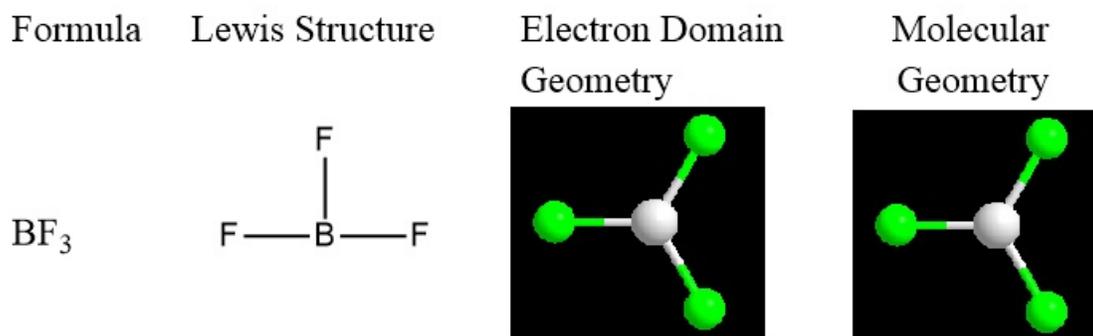
This is exactly what we needed to match the predictions of VSEPR. With only 2 bonds, there are only 2 electron domains, and they are 180° apart, exactly as we need them to be.

Astute readers will notice that there are two p-orbitals left on the Be atom that are not involved in bonding. Here, they are simply empty orbitals because there are only 4 electrons around the Be. But in other molecules they will have a role to play in double and triple bonds.

**sp<sup>2</sup>-hybridization:** As you would expect, different combinations of atomic orbitals give different hybrid orbitals. Given the rule above about the number of hybrid orbitals being the same as the number of atomic

orbitals used to construct them, we can conclude that if we want a 3-lobed structure we need to combine three atomic orbitals. It turns out we need one s-orbital with two p-orbitals, as we will show below.

Looking at  $\text{BF}_3$  – another octet-rule violating species that is useful as an example – we see 3 electron domains (all bonds) around the boron atom. This means the bonds must be  $120^\circ$  apart, creating a trigonal planar structure. It is difficult to see how to combine a pair of p-orbitals (each  $90^\circ$  apart) and a s-orbital (spherical) in such a way that their interference pattern creates three wavefunctions with lobes that are  $120^\circ$  apart.



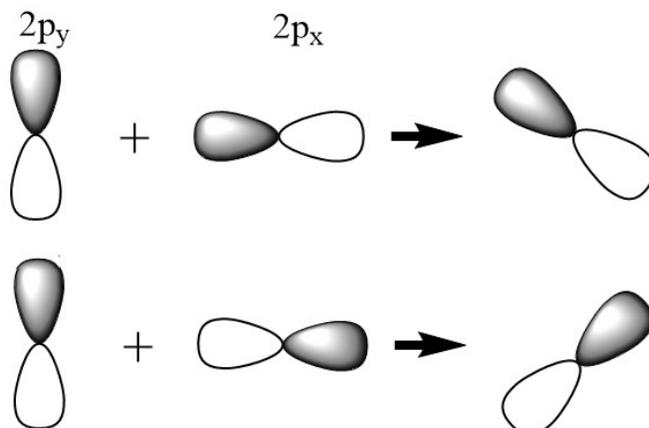
**Figure 2.2.4:** Lewis structure, electron domain geometry, and molecular geometry for  $\text{BF}_3$ . The B atom has only 6 electrons, so the octet rule is violated, but in fact this molecule exists. With only three domains, VSEPR rules demand a trigonal planar geometry.

The answer to this riddle is twofold. First, the interference between two p-orbitals can lead to a lobe that sits between them. And second, new wavefunctions can be built using more amplitude from one wavefunction than another. So, if one were to simply add a  $2p_x$  orbital to a  $2p_y$  orbital, one would get a new wavefunction with an orientation at a  $45^\circ$  between them. But if one were to add more amplitude of the  $2p_x$  than the  $2p_y$  orbital, the new orbital would be at an angle closer to the x-axis than to the y-axis. Throw in the interference with the  $2s$  orbital, which will also contribute, and you can build the necessary 3 lobes.

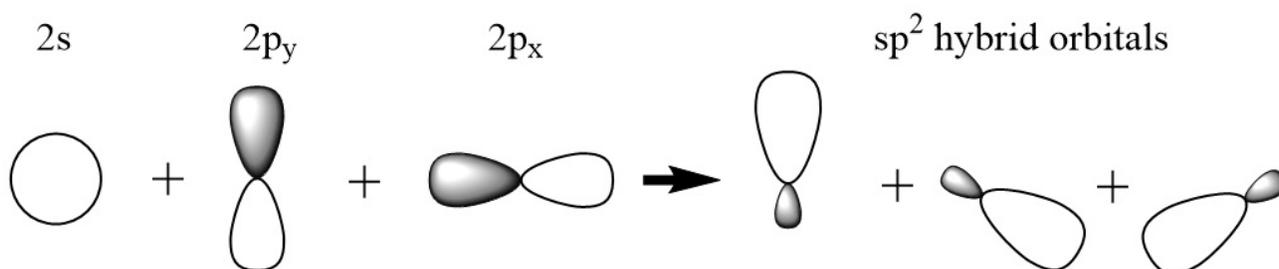
We are not going to get into the mathematics underlying this, which are quite complicated, but it is important to understand how this rotation works because it places limits on where the 3 lobes can sit. Because only two p-orbitals are involved ( $p_x$  and  $p_y$  in the example) the lobes must exist in the plane created by the two axes of the p-orbitals (the xy-plane). That is consistent with the molecular geometry associated with  $\text{BF}_3$  (trigonal planar).

Here again, we are left with one unhybridized p-orbital. This one is perpendicular to the plane made by the 3 lobes of the hybrid orbitals (i.e. the  $p_z$ -orbital, which sticks out of the xy-plane for the example above). This will be important in understanding double bonds.

**Figure 2.2.5:** Top: The combination of p-orbitals can rotate probability amplitude within the plane created by the two orbitals. The addition of the  $2p_x$  and  $2p_y$  added together in equal amounts to create two new orbitals, rotated by  $45^\circ$  relative to the axes but still  $90^\circ$  relative to each other.



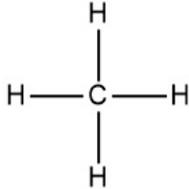
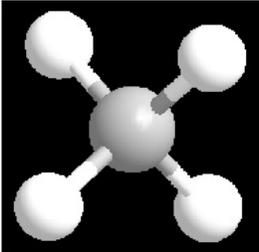
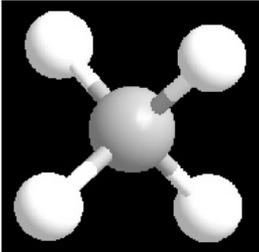
Bottom: The addition of the  $2s$ ,  $2p_y$ , and  $2p_x$  orbitals creates three new atomic orbitals with lobes at  $120^\circ$  relative to each other. This image does not include the details of the interference patterns that produce the orbitals, it is simply a schematic.



**$sp^3$ -hybridization:** Finally, we come to the case where we combine all three p-orbitals with a s-orbital and create 4 new hybrid orbitals. The structure here is fully 3-dimensional, with the four lobes separated by  $109.5^\circ$  creating a tetrahedral structure. Here it is very difficult to show how this construction can work, but it is analogous to that for the  $sp^2$ -hybridization so we ask that you take it on faith.

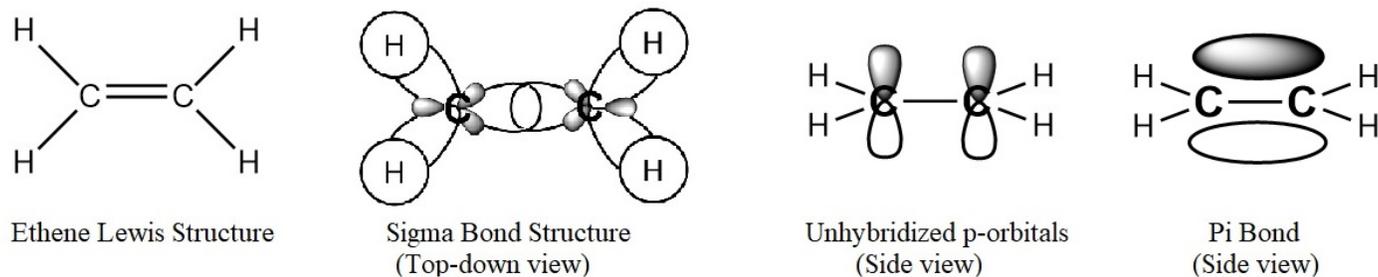
Obviously, there are no unhybridized p-orbitals present in a molecule of this type.

Expanded valence shell species exist such as  $PF_5$  ( $sp^3d$ -hybridized P) and  $SF_6$  ( $sp^3d^2$ -hybridized S), but will not be discussed in this supplement.

Formula	Lewis Structure	Electron Domain Geometry	Molecular Geometry
CH <sub>4</sub>			

**Figure 2.2.6:** Lewis structure, electron domain geometry, and molecular geometry for CH<sub>4</sub>. With four domains, VSEPR rules demand a tetrahedral geometry.

**Unhybridized p-orbitals and the creation of multiple bonds:** We have not yet considered the question of double and triple bonds. We know these exist in Lewis structures, and somehow involve 4 electrons for double bonds or 6 electrons for triple bonds. But we also know from the Pauli Exclusion Principle that we can only have 2 electrons in each wavefunction. That means there must be more than one wavefunction present in double and triple bonds.



**Figure 2.2.7:** Representations of the electronic structure of ethene. All atoms in ethene are in the same plane, with the sigma bonds lying entirely in the plane and the lobes of the pi bond rising above and below it.

This is where the unhybridized p-orbitals come in. Consider the ethene molecule shown in Figure 2.2.7. Each C atom has 3 domains around it, so it must undergo sp<sup>2</sup>-hybridization and leave one unhybridized p-orbital in place. This creates three lobes around each C, which go into the 2 C-H bonds and 1 C-C bond.

These lobes put electron density on a line directly between the two nuclei. This is energetically the most stable place to put it because it maximizes the energy of interaction between the electrons and the nuclei. Bonds of this type are referred to as sigma bonds (sometimes written σ-bonds), because they are blobby and look a bit like a Greek letter “σ”. (Chemists can be very silly sometimes.)

However, only two electrons can sit in the wavefunctions corresponding to sigma bonds. That is fine for the two C-H single bonds, but it leaves the C=C double bond incomplete. We need an additional wavefunction that can accommodate those last two electrons.

This new wavefunction is subject to some of the constraints we have already talked about. It can only contain two electrons, and it should form in a way that minimizes the energy for the system. But the best place to put electron density – on the line between the two nuclei – is already taken by the sigma bond. We cannot build a new wavefunction that puts electron density there, so we need electron density to sit *near* the line between the two nuclei, but not actually on it.

We can construct that using the unhybridized p-orbitals on each C atom. If they are parallel to each other, they can create constructive interference above and below the sigma bond. The result is a second-best place for electron density, and represents the wavefunction occupied by the second pair of electrons in the bond. This is called a pi-bond (or  $\pi$ -bond) because it looks a bit like a Greek letter “ $\pi$ ”. (Again, silly.)

**Figure 2.2.8:** Constructing a pi bond from two p-orbitals. The p-orbitals must be aligned parallel to each other, and must be no more than one bondlength away from each other (i.e. there must be unhybridized p-orbitals on atoms with a sigma bond between them).

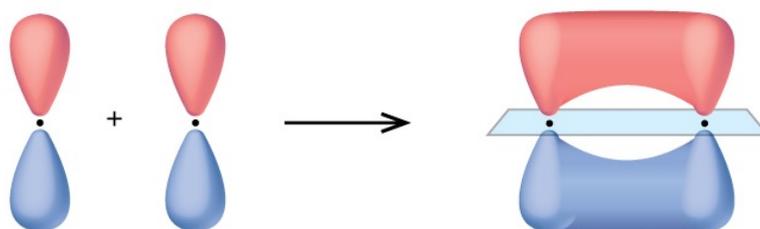
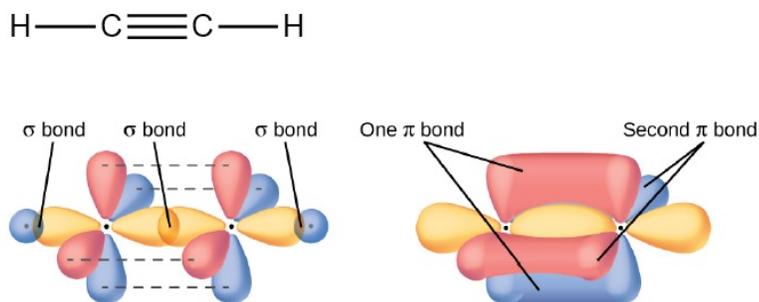


Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).

There are some important issues of geometry illustrated in Figure 2.2.7. First, the pi-bond can only form if the two p-orbitals are parallel to each other. Otherwise, they will not overlap and create constructive interference. Second, the rules for hybridization mean that the p-orbital is perpendicular to the plane defined by the H-C-H bonds. After all, the three sigma bonds are the result of  $sp^2$ -hybridization, and were formed from two p-orbitals (say,  $p_x$  and  $p_y$ ) that were perpendicular to the unhybridized p-orbital ( $p_z$ ). The same thing is true for the C-atoms on each side, meaning that in order for the p-orbitals to be parallel to each other, both C atoms and all four H atoms must be in the same plane.

**Take Note!** Each pi bond contains two lobes, one “above” the sigma bond and one “below” it. Both lobes are part of the same pi-bond.

**Figure 2.2.9:** Top: Lewis structure for acetylene. Bottom: Sigma- and pi-bonding structures for acetylene. Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).



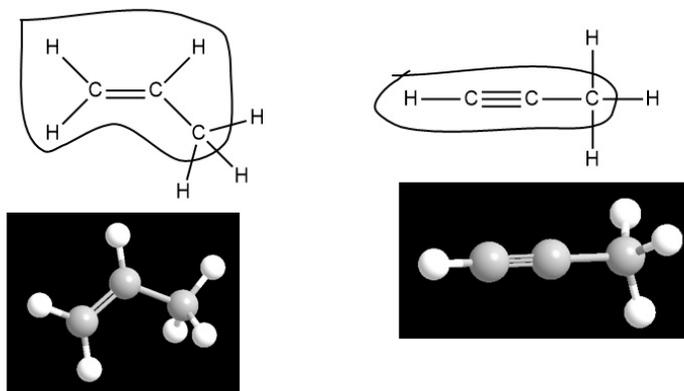
This is a key principle for understanding molecular structure. A double bond between two atoms not only sets the distance between them, it also dictates that the atoms bound to them must be within a plane. See Figure 2.2.10 for a closer look at this phenomenon.

Looking now at acetylene, we see that the carbons are each  $sp$ -hybridized, leaving two unhybridized  $p$ -orbitals on each C atom. The  $sp$ -hybridization means that all four atoms are in a straight line, as both C-C-H angles are  $180^\circ$ . And the presence of two unhybridized  $p$ -orbitals means that the C atoms can each form two  $\pi$  bonds, as shown in Figure 2.2.9.

A triple bond can only exist if the two atoms involved are  $sp$ -hybridized, meaning there must be  $180^\circ$  angles associated with each atom. But extended molecules will not be collinear, only those bound to the  $sp$ -hybridized atoms will be.

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**Figure 2.2.10:** Compounds containing double and triple bonds. Left: Circled atoms must all be within the same plane, and the lobes of the  $\pi$ -bond are perpendicular to that plane. Right: Circled atoms must be collinear, with the lobes of the two  $\pi$ -bonds parallel to that line.

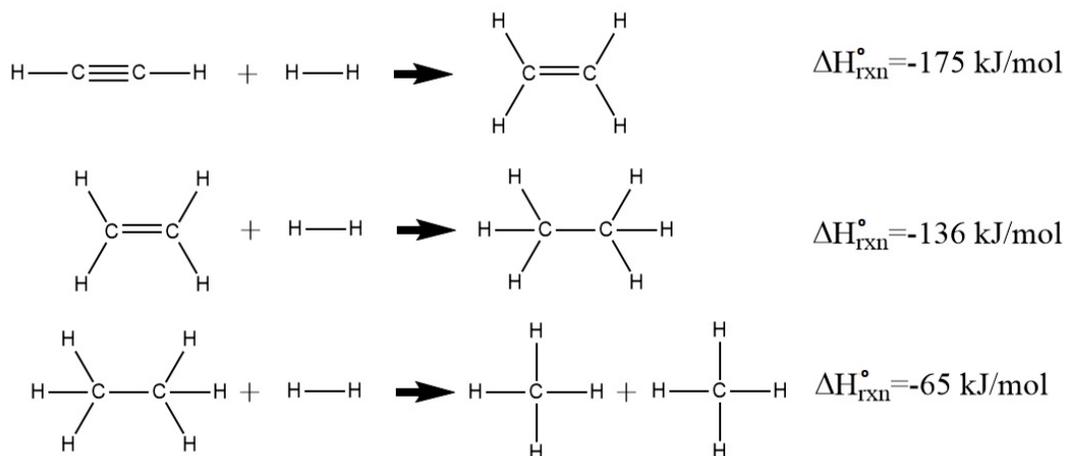


Looking back at the structure of the  $\pi$ -bond, one might expect that the electrons placed above and below the line between the atoms should not interact as strongly with the nuclei as electrons placed between them (i.e. electrons in the  $\sigma$ -bond).  $\pi$ -bonds are in fact weaker than  $\sigma$ -bonds, and this can be seen experimentally. A series of hydrogenation reactions are given in Figure 2.2.11, with each corresponding to the elimination of either a C-C  $\pi$ - or  $\sigma$ -bond (along with the H-H bond) and the creation of two C-H bonds. The heat of reaction for breaking the  $\sigma$ -bond is far smaller than the heat of reaction for breaking either of the  $\pi$ -bonds, reflecting the fact that the  $\sigma$ -bond is much more stable than the  $\pi$ -bonds. Likewise, removing the (second)  $\pi$  bond from acetylene releases more energy than releasing the (first)  $\pi$  bond from ethene. This is because the second  $\pi$  bond is less stable than the first, because forcing 6 electrons into close proximity in a triple bond creates more electron-electron repulsion than forcing 4 electrons into a double bond.

A caveat to the discussion above is that there are other factors that affect the energies in question, and the differences in enthalpy do not arise purely from the bond effects described. But the principle is correct, and will generally be true for the energies of  $\sigma$ - and  $\pi$ -bonds.

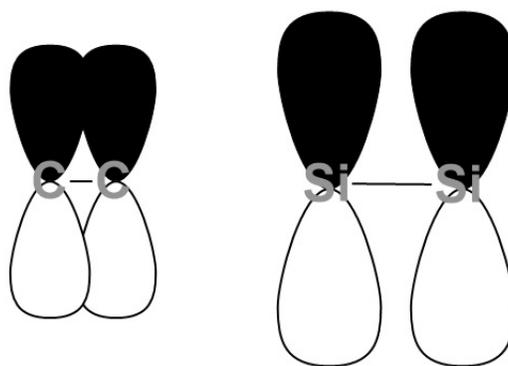
**Figure 2.2.11:**

Reactions of H<sub>2</sub> with acetylene (C<sub>2</sub>H<sub>2</sub>), ethene (C<sub>2</sub>H<sub>4</sub>), and ethane (C<sub>2</sub>H<sub>6</sub>). In each reaction, a C-C pi- or sigma-bond is broken and two C-H bonds are broken. The differences in the heat of reaction illustrate the differing strengths of pi bonds and sigma bonds.



Double and triple bonds between 2<sup>nd</sup> row elements are very common, as in N<sub>2</sub> or CO<sub>2</sub>, but one rarely finds comparable 3<sup>rd</sup> row examples. This is because 3p-orbitals are more diffuse than 2p-orbitals, so their overlap does not lead to localized electron density in a way that interacts strongly with the nuclei. Also, the larger atomic radii in the third row push the atomic centers further apart, reducing overlap between the p-orbitals. In other words, the p-orbitals can overlap, but they do not lead to strong bonds. Consequently, while researchers sometimes study compounds engineered to contain bonds of this type, they are unstable and rarely found outside of controlled experiments. More often, attempting to create a third row element containing a double or triple bond will lead to a network of sigma bonds (e.g. attempting to create P<sub>2</sub> will lead to a solid with each P atom bound to three other P atoms).

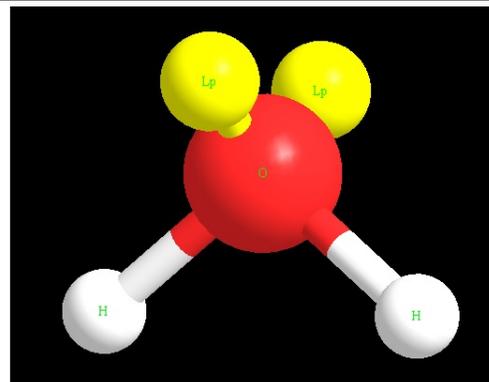
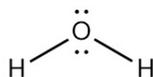
**Figure 2.2.12:** Comparison of the overlap of p-orbitals for C-C and Si-Si bonds. The 3p-orbitals for in the Si valence state are larger and therefore more diffuse than the 2-p orbitals for C, and the Si-Si bondlength is longer than that for C-C. Both of these factors reduce the overlap between neighboring p-orbitals, making pi-bonds unstable for elements of the 3<sup>rd</sup> row or higher.



**Lone pairs in hybridized orbitals:** As should be clear by now, the rules for hybridization also apply to lone pairs of electrons. This is consistent with the knowledge that lone pairs of electrons have to be accounted for in VSEPR theory. Lone pairs act as electron domains that repel bonds (and each other), which means that they have to be localized in space, and the only way to do that is to occupy hybrid orbitals. For example, the oxygen in water is sp<sup>3</sup>-hybridized and two of the orbitals are occupied by lone pairs, as shown in Figure 2.2.13.

The electrons sit in hybrid orbitals, meaning that the oxygen has  $sp^3$ -hybridization, a tetrahedral domain geometry, and a bent molecular geometry. The H-O-H bond angle for water is  $104.5^\circ$ , slightly less than the  $109.5^\circ$  that would correspond to a perfect tetrahedron.

**Figure 2.2.13:** Lewis structure and 3D model of a water molecule. In the model, H atoms are shown in white and the lone pairs in yellow.



You may be wondering why we only considered hybridization through  $sp^3$  here and, more generally, while hybridization never exceeds  $sp^3d^2$ . The reason is simply that hybrid orbitals can only be constructed from orbitals of roughly the same energy, in this case meaning having the same principal quantum number  $n$ . Combining, say, a  $2p_x$  orbital with a  $3d_{xy}$  orbital will not produce a localized lobe that is useful in bonding, and therefore the energy of the system will not be reduced (there are other reasons they don't combine, but this one is sufficient for our purposes). So, for  $n=2$  the highest possible hybridization is  $sp^3$ . This covers the elements C, N, and O, which are the most common in organic chemistry. Hybridizations involving d-orbitals require 3<sup>rd</sup> row elements (commonly P or S) in combination with strongly electronegative elements. These exist, but are less central to organic chemistry and so are not addressed here.

Valence Bond Theory is a powerful tool for understanding chemistry, but it is incomplete. There are phenomena that it does not explain such as paramagnetism, and phenomena that it describes awkwardly, such as resonance. We will discuss both of these below.

**Take Note!** If you do not understand why the H-O-H bond angle is less than  $109.5^\circ$ , you should review the VSEPR rules in your general chemistry text. Focus in particular on how the structure is refined based on the presence of domains like electron pairs that are more repulsive than sigma-bonds.

## Section 2.3: Molecular Orbital Theory

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand basic concepts in Molecular Orbital theory.
- Be able to construct molecular orbitals from atomic orbitals in homonuclear diatomic molecules.
- Be able to apply the Aufbau rules to fill molecular orbitals and obtain the electronic configuration of a diatomic molecule in this way.
- Be able to use sigma and pi notation to write the electronic configuration of a diatomic molecule.
- Be able to calculate the bond order and predict paramagnetism from the electronic configuration of a diatomic molecule.

Stepping back, we should remember that we discussed valence bond theory as an attempt to build appropriate wavefunctions to describe chemical bonds. This amounts to identifying wavefunctions that put electron density between atomic centers to create attractive forces. Valence Bond Theory (VBT) does this by creating hybrid orbitals that lead to appropriate lobed structures, and then putting the atoms next to each other so that the lobes on neighboring atoms interfere with each other and create an appropriate wavefunction.

**Problems with Valence Bond Theory:** But there are assumptions that underlie valence bond theory that are sometimes inconsistent with nature. One is that the electrons are always localized in some combination of sigma- and pi-bonds, and there are only two electrons in each. These assumptions are often very good, but they are worth thinking through more clearly.

If we wanted to rigorously describe a molecule, we would be better off starting with the positions of nuclei and then solving the Schrödinger equation to get the possible standing wavefunctions. There would be a lowest energy state and a series of higher energy states as well, as we see in the atomic orbitals. As in the atomic orbitals, we might encounter some standing wavefunctions with equivalent energies (i.e. that are degenerate). When we have our list of wavefunctions, we would fill them by an Aufbau process in exactly the same way we do with atomic orbitals to obtain electronic configurations.

In fact, modern computations can do exactly this, and can predict molecular geometries and energies with remarkable accuracy. One of the revealing features of such studies is that the wavefunctions are spread out in ways that make it difficult to assign pairs of electrons to particular atoms or bonds. When one finishes adding all of the electrons to appropriate orbitals and sums up the electron densities, one finds that electron density will most often sit between two nuclei, as expected from valence bond arguments. But the details of the motion of individual electrons may be quite different.

An example of the results of this type of calculation is given in Figure 2.3.1, in which the authors of a research paper have performed quantum mechanical calculations on methane. Three wavefunctions are shown in the image. Of these three, the lowest-energy state is the one on the left, with a wavefunction that is

**Table 2.3.1:** Features of Molecular Orbital Theory

### Molecular Orbital Theory

#### Strategy:

- 1) Use atomic orbitals to build both “bonding” and “antibonding” orbitals between atoms (can include more than two atoms)
- 2) Use Aufbau rules to fill molecular orbitals

#### Pros:

- Easily describes phenomena involving unpaired electrons
- Easily describes resonance, and is a necessary concept in explaining the delocalization of electrons

#### Cons:

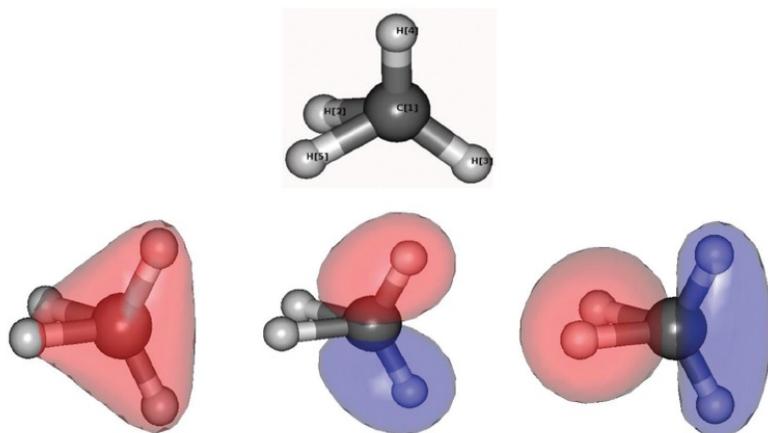
- Very difficult to implement for molecules with more than two atoms

distributed between all five of the atoms in the molecule. The other two are higher energy states, and contain some nodes. This is only a small subset of the available states, there are many others that contribute. The states would fill with pairs of electrons in the lowest-energy orbitals first (in this case, two electrons in the left-most orbital), and other states would fill according to the Aufbau rules.

Individually, these states look quite different from our expectations based on Valence Bond Theory, where we expected to find pairs of electrons sitting between bonds. But if we took all of the occupied molecular orbitals for methane and added their probability densities together, we would get a distribution that put most of the electron density in the spaces between pairs of atoms, summing up to about two electrons in each of those spaces. In other words, we would do a lot of work and recover something that looked very much like what we could get from two minutes of work with VBT. In essence, both constructions are different and reasonably good representations of the same phenomenon, so of course their results have to agree in most cases.

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**Figure 2.3.1:** Molecular orbitals for methane (CH<sub>4</sub>). Modified from Baptista, L. da Silveira, E. F., A Theoretical Study of Three Gas-Phase Reactions Involving the Production or Loss of Methane Cations, *Phys. Chem. Chem. Phys.* **2014**, 16, 21867-21875.



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So why is Molecular Orbital Theory (MOT) useful? Well, occasionally, one encounters a phenomenon where the assumptions underlying VBT break down, such as phenomena involving unpaired electrons. One example is the paramagnetism of oxygen.

Materials that do not react strongly to a magnetic field are said to be diamagnetic, and usually represent compounds where all electrons are present in pairs. Recall that electron spin corresponds to the orientation of a magnetic dipole for the molecule, and electrons with opposite spins ( $+\frac{1}{2}$  or  $-\frac{1}{2}$ ) are oriented in different directions. In other words, the north pole of one is pointed in the same direction as the south pole of another. If you put paired electrons in a magnetic field, their opposite orientations mean that one will be attracted to the dipole while the other will be repelled. Thus, their interactions cancel out, and there is no net interaction with the field.

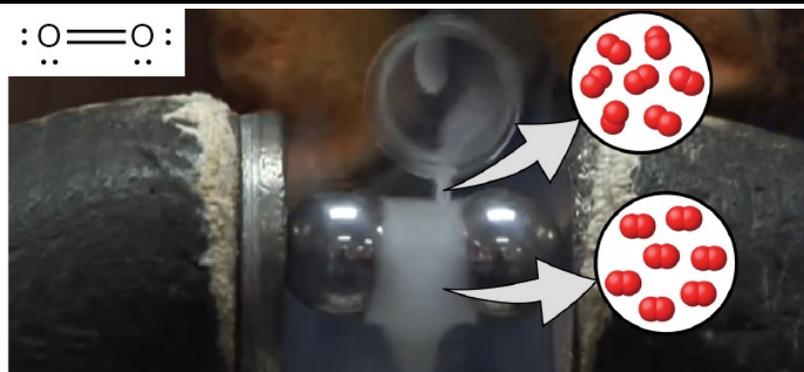
Paramagnetic materials do not have a net magnetic field themselves (i.e. they are not like “permanent magnets” that always have a magnetic field), but if you put them in a magnetic field they will be attracted to it. Most paramagnetic materials contain unpaired electrons, which can orient themselves to interact favorably with the magnetic field (i.e. align the south end of the electron with the north end of the field). Metal complexes are frequently paramagnetic.

It has been observed experimentally that oxygen is attracted to magnetic fields, and is therefore paramagnetic. But how is this possible? Its Lewis structure indicates O<sub>2</sub> has a double bond between two O atoms, each of which has two lone pairs of electrons. Octets on both O atoms are filled, and all electrons are

paired. Valence Bond Theory offers no insight that can explain this discrepancy, because it operates based on the assumption that the electrons are paired. We see below how to address it in Molecular Orbital Theory.

**Figure 2.3.2:** Liquid oxygen attracted to a magnet ( $O_2$  Lewis structure inset)

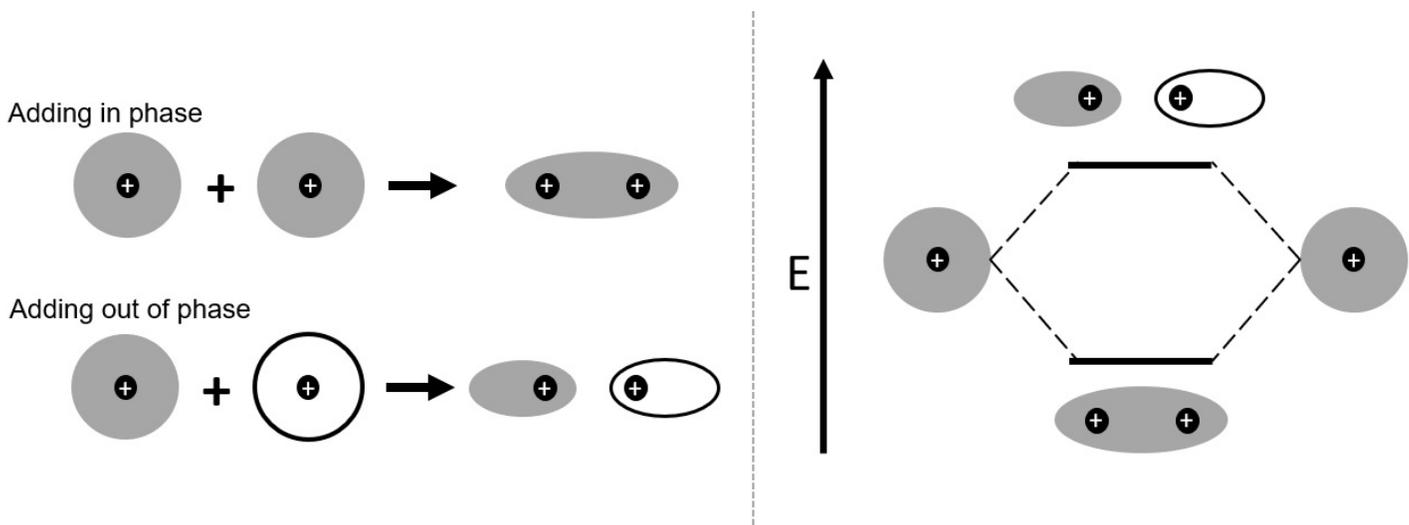
Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).



**Molecular Orbital Theory for Homonuclear Diatomic Molecules:** Solving molecular orbitals for molecules containing three or more atoms is extremely challenging, and a high level of accuracy generally requires the aid of a computer. But one can obtain good descriptions of molecular orbitals for homonuclear diatomic molecules (i.e. molecules containing two identical nuclei) by hand. We do so here to illustrate how MOT can explain some phenomena that are not well-described by VBT.

The simplest homonuclear diatomic molecule is  $H_2$ , and we were halfway to obtaining the molecular orbital description of  $H_2$  in our discussion of overlapping  $1s$  orbitals in Section 2.1. But we only considered the case where the two overlapping orbitals were in-phase with each other and interfered constructively. To properly implement MO theory, we need to consider the possibility that they will be out of phase and interfere destructively as well. This is another manifestation of the rule we mentioned for creating hybrid orbitals: The number of orbitals out must equal the number of orbitals in. In this case, the number of molecular orbitals formed must equal the number of atomic orbitals that contribute to it.

It is easy to see that where constructive interference creates electron density between nuclei, one achieves a stable configuration with favorable energies of interaction between electrons and nuclei. In contrast, destructive interference puts electron density in regions that interact strongly with one nucleus or the other, but not both. This is an unstable configuration. The orbitals that lead to stable formations are said to be bonding orbitals, and they are stable because they have energies lower than those of the isolated atoms. That means that once formed, energy has to be put into the molecule to cause the bond to break. In contrast, the unstable configurations are referred to as antibonding orbitals, and have energies that are higher than those of the isolated atoms. If there are electrons in the antibonding orbital and none in the bonding orbital, the nuclei will move apart because they are more stable as isolated atoms.

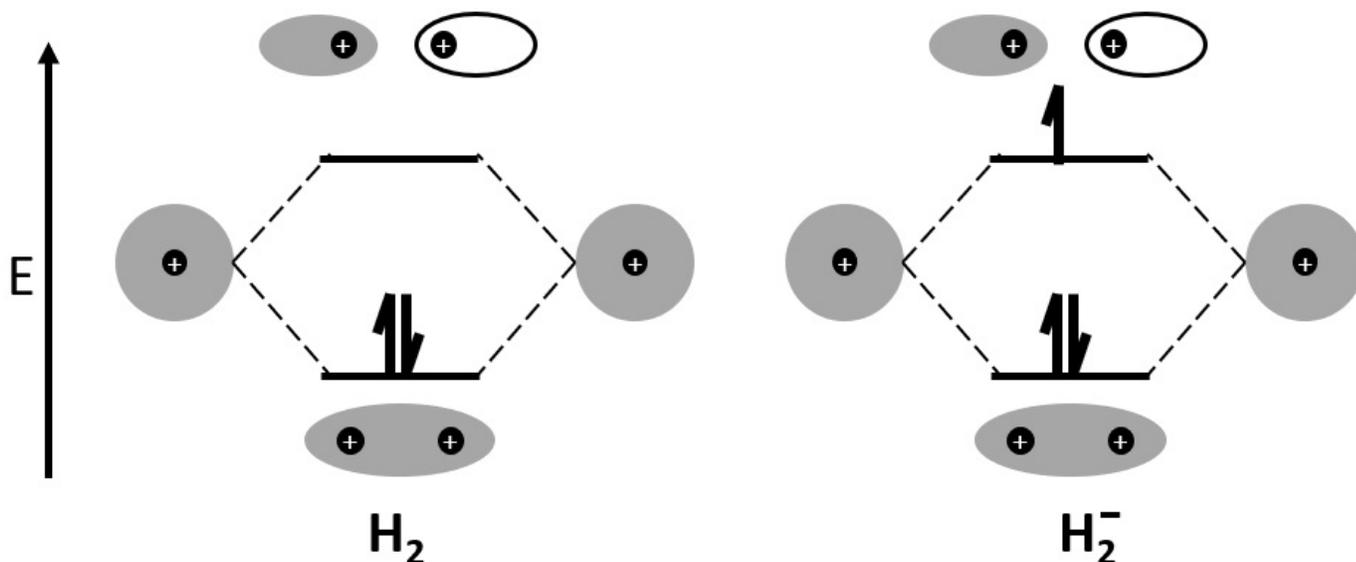


**Figure 2.3.3:** Left: Schematic diagram of the addition of hydrogen 1s orbitals in-phase and out-of-phase. Right: Molecular Orbital diagram for  $H_2$ . Note that energy increases as one moves up the page, per the arrow on the left. The in-phase wavefunction has a lower energy than the isolated H atoms, while the out-of-phase wavefunction has a higher energy.

Once these orbitals are constructed, one uses the same Aufbau rules as are used in atomic orbitals to work out the electron configuration of the molecule, discussed in Section 1.3. There are 2 electrons in  $H_2$ , and they will both go in the bonding orbital, one spin-up and one spin down.

One might ask whether it is worth going to this trouble, as we have not really gained more insight on  $H_2$  than we had before. Except that we can use MO theory to answer a question that VB theory cannot address: Is  $H_2^-$  stable?

We can answer this question using a Molecular Orbital Diagram, as shown in Figure 2.3.4. We have laid out the allowed molecular orbital states, and filled them according to the Aufbau rules for atomic orbitals. The first two electrons go into the lowest-energy state, with opposite spins per the Pauli Exclusion Principle.  $H_2^-$  has three electrons, so the Aufbau rules tell us the next one goes into the next-lowest (which happens to be the antibonding orbital). We can crudely estimate the energy by saying we've got two electrons sitting in a favorable orbital and one in an unfavorable one, so the molecule will be stable.



**Figure 2.3.4:** Molecular Orbital Diagrams for  $H_2$  and  $H_2^-$ . Electrons are added according to the Aufbau rules, so  $H_2$  has 2 electrons in the lowest-energy (bonding) state and  $H_2^-$  has 2 electrons in the lowest-energy state and one in the highest-energy state.

This leads to an idea called bond order. The bond order is defined by the equation

$$\text{Bond order} = (\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals})/2$$

So, the bond order for  $H_2$  would be  $(2-0)/2=1$ , corresponding to a single bond, while the bond order for  $H_2^-=(2-1)/2=1/2$ . The bond is expected to be weaker for  $H_2^-$  than for  $H_2$ .

A note of caution is in order here: This simple model ignores some important factors in the energy of the system, such as the repulsion between electrons. Pairs of electrons in the same region of space, including within the same orbital, repel each other. That means that some of the favorable energy gained by having two electrons in a bonding orbital is lost to unfavorable electron-electron interactions, so putting a second electron in the bonding orbital gains less energy than putting a third electron in the antibonding orbital. For  $H_2^-$ , this means that even though the bond order of  $H_2^-$  is  $1/2$ , the energy required to break the bond in  $H_2^-$  is less than  $1/2$  the energy required to break the bond in  $H_2$ .

The MO approach is also important in understanding other molecules. For instance, we can use the same MO diagram to describe  $He_2$  as the overlap of two 1s orbitals but with 4 electrons present. According to MO theory, a pair of He atoms in close proximity will have two bonding electrons and two antibonding electrons. Since the energy penalty associated with the latter is greater than the favorable energy associated with the former, the molecule is unstable and will break apart to form isolated He atoms. In other words,  $He_2$  does not form.

Another important feature in MO theory is that we can model molecules like  $H_2^-$ , which have an odd number of electrons. VB theory does not have a good way to treat such structures, beyond noting that they violate the octet rule. But with MO theory we could predict the stability of  $H_2^-$ .

We can also use MO Theory in the presence of unpaired electrons. As mentioned above, molecules with unpaired electrons are paramagnetic (attracted to magnetic fields) and molecules where all electrons are paired are diamagnetic (not interacting with magnetic fields). We can see from these MO diagrams that  $\text{H}_2$  is diamagnetic, and  $\text{H}_2^-$  is paramagnetic. This is information we could not obtain using VB theory.

Turning now to second row elements, we start by looking at how atomic orbitals on different atoms can overlap. We have to worry about the overlap of  $2s$  and  $2p_x$ ,  $2p_y$ , and  $2p_z$  on the neighboring atoms. We do not hybridize these orbitals, but instead simply look at the orbitals they form when the nuclei are placed close to each other.

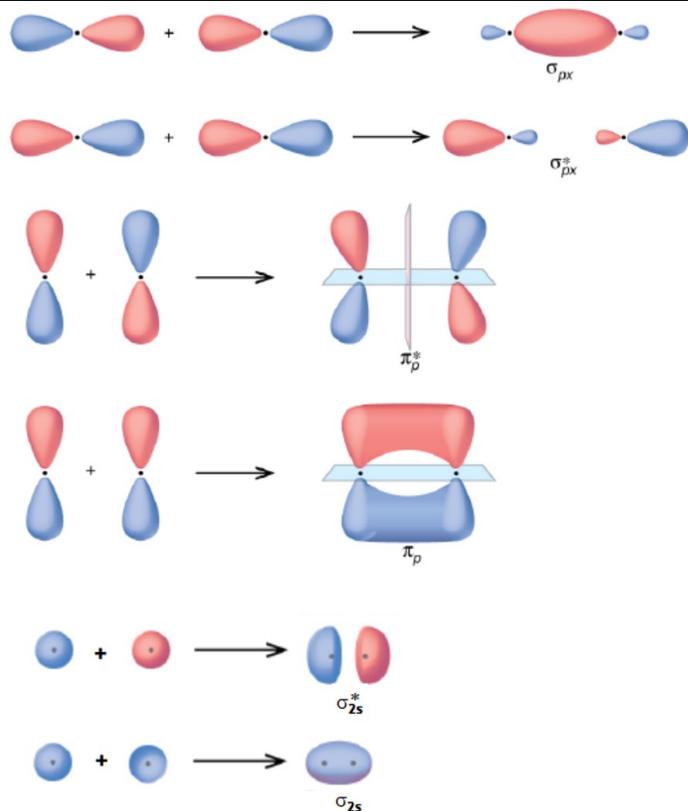
One can understand most of the properties of molecular orbitals for second row elements by assuming that only orbitals with comparable energies will interfere with each other (though this is not quite true, as we will discuss below). You can understand this simply as the wavefunctions having certain frequencies, and if their energies are very different their frequencies will be different and they will not interfere in a consistent way. So, the  $2s$  orbital on one atom will form molecular orbitals by overlapping with the  $2s$  orbital on the other atom, but will not create molecular orbitals by overlapping with orbitals of different energy.

The  $2s$  orbitals will have the same kind of bonding and antibonding molecular orbitals (MOs) as the  $1s$  orbitals of the H atoms did in Figure 2.3.3. Figure 2.3.5 shows how the  $p$ -orbitals will overlap and create molecular orbitals. We take the  $x$ -axis to be the line connecting the two atoms, though this is not a universal convention (the choice is arbitrary, some sources label this line the  $z$ -axis). We obtain four different types of orbitals: Bonding and antibonding orbitals formed by the overlap of  $p_x$  orbitals, which lie parallel to the axis; and bonding and antibonding orbitals of  $p_y$  and  $p_z$ , which are perpendicular to it. The bonding orbitals for  $p_y$  and  $p_z$  look very much like the pi-bonds we constructed in MO theory, as would be expected, as pi-bonds are built from unhybridized MOs perpendicular to the line between the molecules.

**Figure 2.3.5:** Overlap of second row atomic orbitals on neighboring atoms. The  $x$ -axis is taken as the line connecting the two nuclei. The top orbitals are the bonding and antibonding orbitals of the  $p_x$ -orbitals, and the central orbitals are the bonding and antibonding orbitals of the  $p_y$  and  $p_z$ . At the bottom are the bonding and antibonding molecular orbitals made by the overlap of the  $2s$  atomic orbitals.

Note that only one pair of orbitals for the  $p_y$  and  $p_z$  atomic orbitals are shown. There are in fact four (two bonding and two antibonding), but they are identical, simply rotated by  $90^\circ$  relative to each other (i.e. one on the  $y$ -axis, and one on the  $z$ -axis).

Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).



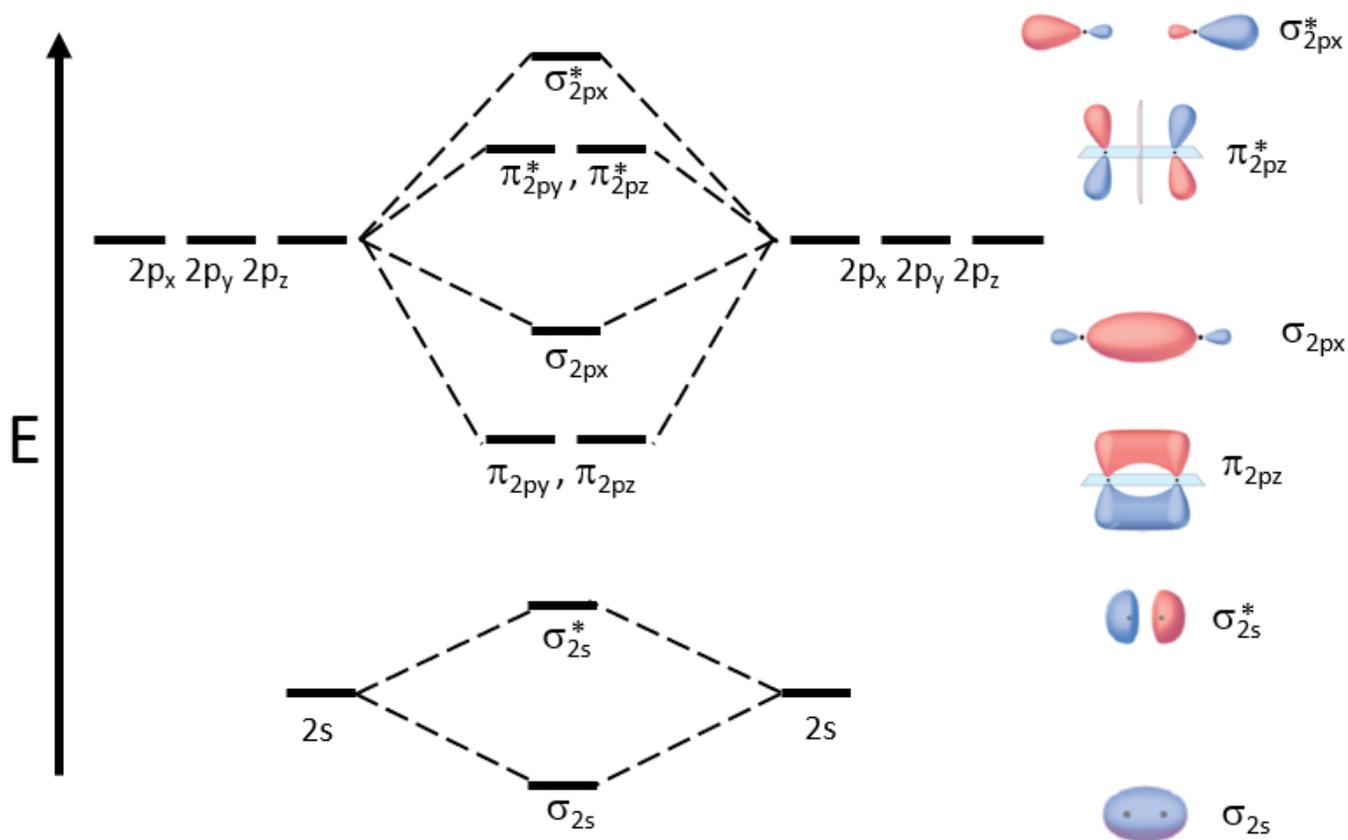
These wavefunctions have different symmetries, and are identified by special notation. The orbitals formed by the overlap of the 2s orbitals or the 2p<sub>x</sub> orbitals are said to be  $\sigma$  orbitals, and are labeled by the atomic orbitals that create them as  $\sigma_{2s}$  or  $\sigma_{2p_x}$ . The orbitals formed by the overlap of the perpendicular p-orbitals are said to be  $\pi$ -orbitals, and are labeled by their atomic orbitals as  $\pi_{2p_y}$  and  $\pi_{2p_z}$ . Obviously this is similar to the notation used for bond types in VBT, and indicates the same symmetries.

The overlap of each pair of atomic orbitals creates two molecular orbitals: One bonding and one antibonding. The bonding and antibonding orbitals have the same symmetry, but the antibonding orbitals are denoted with a \* superscript. So, the overlap of the 2p<sub>y</sub> orbitals creates a bonding orbital labeled  $\pi_{2p}$  and an antibonding orbital labeled  $\pi_{2p}^*$ .

As you might expect, placing electron density between the two nuclei creates a lower-energy wavefunction than placing it along the sides. This is the reason that even though the atomic p-orbitals have the same energies, the  $\sigma_{2p_x}$  molecular orbital has a lower energy than the  $\pi_{2p_y}$  and  $\pi_{2p_z}$  orbitals.

An issue to consider is that as the principal quantum number  $n$  increases, the average distance between the nucleus and the electron increases. So, to create overlap between 2s orbitals, the nuclei have to sit further apart than they do when creating overlap between 1s orbitals. This is why 2<sup>nd</sup> row elements have longer bond lengths than H<sub>2</sub> and, more generally, why bond lengths increase as the elements participating in the bond move further down the periodic table. Consequently, as a rule, one needs only consider valence orbitals and valence electrons when constructing molecular orbitals.

With these ideas in mind, we can draw a molecular orbital diagram for second-row elements, as shown in Figure 2.3.6. The 2s atomic orbitals have the lowest energies, and lead to the lowest energy orbitals. The 2p-atomic orbitals are degenerate, but the degeneracy is broken in bonding by their different geometries, which put electron density between the two atoms for the 2p<sub>x</sub> orbital and displaced from the axis for the 2p<sub>y</sub> and 2p<sub>z</sub> orbitals.



**Figure 2.3.6:** Molecular Orbital Diagram for  $\text{Be}_2$  and  $\text{Li}_2$ . Orbital geometries are shown on the right.

Image modified from P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019 (<https://openstax.org/details/books/chemistry-2e>).

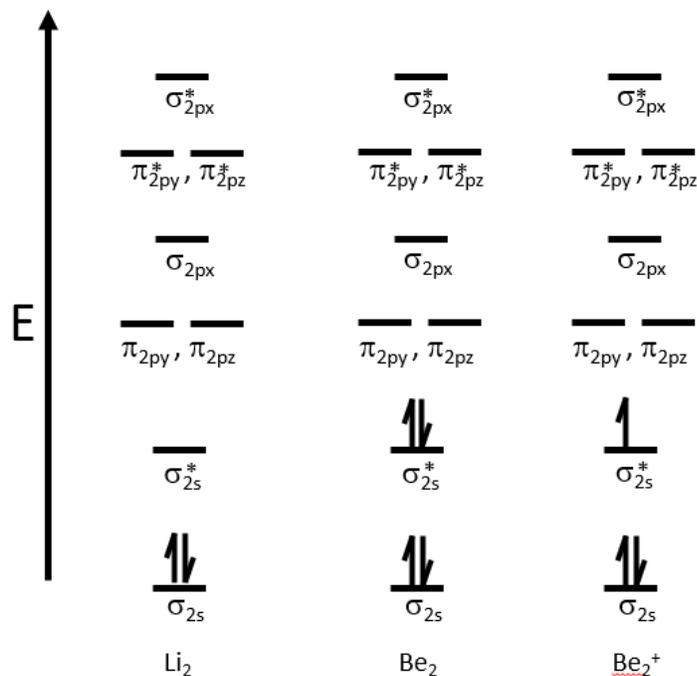
As noted above, each combination of two atomic orbitals leads to one bonding and one antibonding orbital. However, while the antibonding orbital is always higher in energy than the bonding orbital of the same type (e.g.  $\sigma_{2px}$  and  $\sigma_{2px}^*$ ), bonding orbitals from one type orbital can be higher in energy than the antibonding orbitals of another. It is intuitively tempting to fill bonding orbitals first, regardless of energy, but the filling of the orbitals must go from lowest to highest energy according to the Aufbau rules.

As an example, consider Figure 2.3.7. The lithium atom has an electron configuration of  $1s^2 2s^1$ , meaning that each lithium contributes one valence electron to the MOs. That means the  $\text{Li}_2$  MO diagram should be populated by two electrons, which should go into the lowest energy level, spin-up and spin-down according to the Aufbau rules. Be atoms have a configuration of  $1s^2 2s^2$ , so  $\text{Be}_2$  should have four valence electrons, with the second pair going spin-up and spin-down in the  $\sigma_{2s}^*$  orbital. If one makes a  $\text{Be}_2^+$  cation, one populates it with only one electron in the  $\sigma_{2s}^*$  orbital.

As we did for  $\text{H}_2$  and  $\text{He}_2$  species, we can use bond order to predict the stability of various species. The MO diagram predicts that the  $\text{Li}_2$  molecule is stable with a bond order of  $(2 \text{ bonding} - 2 \text{ antibonding})/2 = 1$ , but the  $\text{Be}_2$  molecule is unstable as its bond order  $(2 \text{ bonding} - 2 \text{ antibonding})/2 = 0$ . The  $\text{Be}_2^+$  ion has a bond order of  $(2 \text{ bonding} - 1 \text{ antibonding})/2 = 0.5$ , meaning according to MO theory it should be stable.

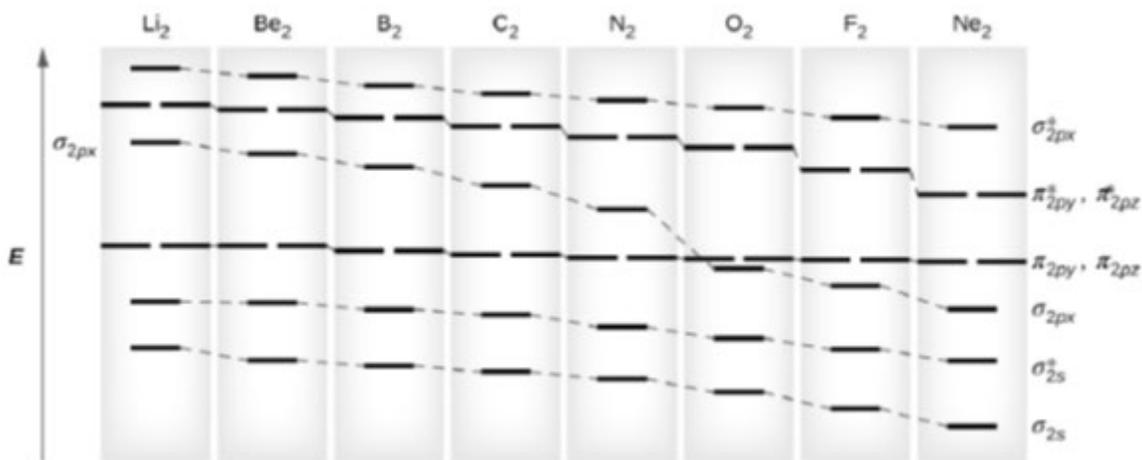
It should be noted that, in this context, “stable” does not mean “easy to make or observe.” Lithium, for example, explodes on contact with water. It is possible to create  $\text{Li}_2$  in a vacuum in carefully controlled conditions, but it will not be found in a sample kept under typical laboratory conditions. Further, MO theory is good but it is not perfect. It might be possible to create the ion, but  $\text{Be}_2^+$  it may be that MO theory’s predictions are incorrect for this ion. Higher levels of theory might also give a different answer.

**Figure 2.3.7:** Molecular Orbital Diagram for  $\text{Be}_2$  and  $\text{Li}_2$ , with electron populations shown.



This is *almost* the complete picture, but with one caveat. We stated above that atomic orbitals of different energy do not overlap, but this is not completely true. Molecular orbitals of different symmetry cannot mix, so the  $2p_z$  and  $2p_y$  (which have a symmetry defined by a plane that cuts them in half) cannot contribute to  $\sigma$ -orbitals (which have cylindrical symmetry – they can be rotated around the axis of the molecule without changing). But the  $2p_x$  and  $2s$  atomic orbitals both create orbitals of  $\sigma$ -symmetry, and to a limited extent can mix together. That means that even though the lower-lying  $\sigma_{2s}$  state is primarily composed of the  $2s$  atomic orbitals and the higher-energy  $\sigma_{2p_x}$  state is primarily composed of the  $2p_x$  orbitals, there is some  $2p_x$  in the former and some  $2s$  in the latter.

This creates an issue because the relative importance of those contributions changes depending on the number of electrons present and the identities of the elements involved. Figure 2.3.8 shows how the energies change as one moves from left to right across the second row of the periodic table. The energies of the  $\sigma_{2s}$ ,  $\sigma_{2s}^*$ ,  $\sigma_{2p_x}$  and  $\sigma_{2p_x}^*$  change relative to the energies of the pi-orbitals. The Aufbau rules still apply, but the relative energies of the different states have to be taken into account to properly implement it.



**Figure 2.3.8:** Molecular Orbital energy levels for second row elements.

From P. Flowers et al., *Chemistry 2e*, OpenStax, Houston, TX, 2019  
<https://openstax.org/details/books/chemistry-2e>.

For more complicated examples, let us consider the configurations shown for  $N_2$ ,  $O_2$ , and  $F_2$  shown in Figure 2.3.9. The filling of the orbitals follows the standard Aufbau rules, but for  $O_2$  we must remember Hund's rule: Degenerate orbitals fill with one electron per orbital, spin-aligned, until this is no longer possible. Thus, there are two unpaired electrons in  $O_2$ . This is responsible for the paramagnetism of oxygen discussed earlier, and is a success of MO theory that VB theory cannot match.

The three molecules shown in Figure 2.3.9 are known, stable gases, and it is worth looking in more detail at their bonding. The bond order for each is calculated as follows:

$$N_2: \text{bond order} = (8 \text{ bonding} - 2 \text{ antibonding})/2=3$$

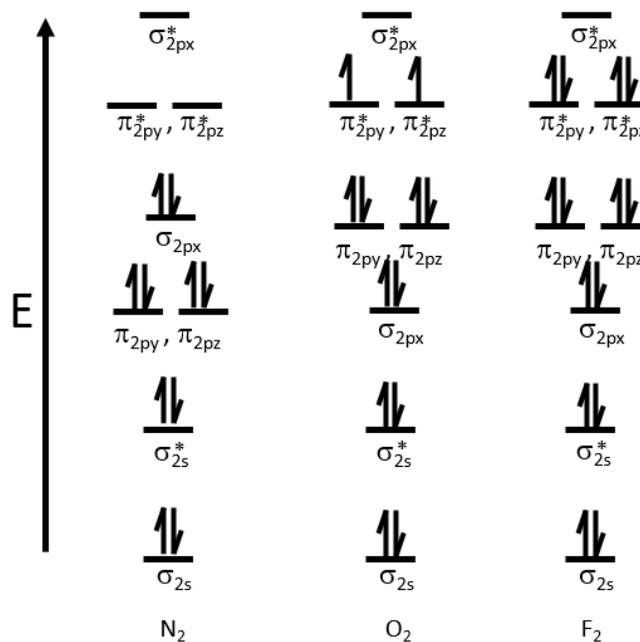
$$O_2: \text{bond order} = (8 \text{ bonding} - 4 \text{ antibonding})/2=2$$

$$F_2: \text{bond order} = (8 \text{ bonding} - 6 \text{ antibonding})/2=1$$

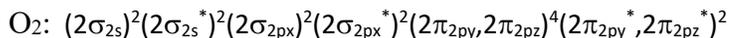
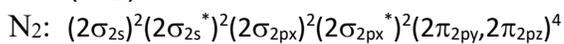
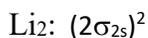
Note that Lewis structures for  $N_2$ ,  $O_2$ , and  $F_2$  indicate the existence of a triple bond, a double bond, and a single bond, respectively. In other words, Lewis structures and MO theory are consistent where they both address the same question.

But MO theory allows one to ask questions that do not have simple answers in Lewis representation. Is the  $O_2^+$  ion stable? One can answer this by removing one electron from the  $O_2$  structure shown in Figure 2.3.9 and recalculating the bond order. The result is a bond order of 2.5 for  $O_2^+$ , which implies that it is stable, and this is known to be true experimentally. As noted above, MO theory does not make perfect predictions, but it is correct more often than not and allows one to make at least educated guesses for species that cannot be described in VB theory.

**Figure 2.3.9:** Populated MO diagrams for 2<sup>nd</sup> row diatomic gases.



A last point concerns notation. We know how to indicate the electron configuration of atoms (e.g. Li:  $1s^2 2s^1$ ), and there should be something analogous for molecular orbitals. The answer is that we follow the same rules, and just use the sigma and pi orbital notation to indicate it. So, based on the configurations presented in Figures 2.3.7 and 2.3.9:



The only real difference between this notation and that used for atomic orbitals is the need to use parentheses (because the Greek letter notation is a bit more awkward) around the orbital, and the need to put degenerate orbitals (such as  $2\pi_{2py}$  and  $2\pi_{2pz}$ ) in the same parentheses.

Given that it is so difficult to build MOs for anything larger than a diatomic molecule, why is it necessary that you know Molecular Orbital Theory at this point in your studies? Because it emphasizes the idea that electrons are occupying wavefunctions, not “bonds”. This is important, because sometimes electrons can be delocalized over many atoms in a phenomenon called resonance, described in the next section.

## Section 2.4: Introduction to Resonance

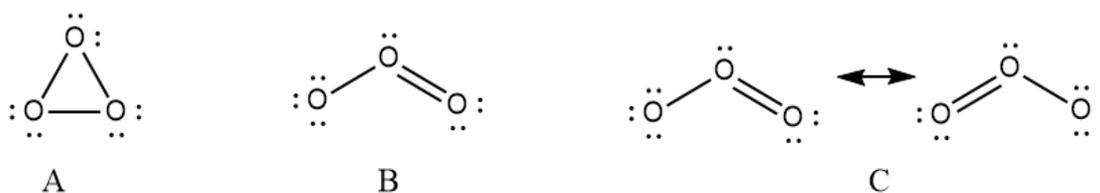
### LEARNING OBJECTIVES FOR THIS SECTION

- Understand that electrons can delocalize between more than two atoms, creating wavefunctions that do not correspond to “bonds.”
- Be able to represent delocalized electronic structures using multiple Lewis structure (“resonance structures”).
- Understand the limitations of Valence Bond Theory for describing delocalized electronic states. In particular, you should be able to distinguish between the pattern of bonding described in individual resonance states and the actual electronic character of the molecule (e.g. the difference between the behavior of benzene and its representation in Kekulé structures).
- Understand how Molecular Orbital Theory accounts for delocalized states.

Throughout this chapter, we have emphasized that the chemical bond is in fact a balance of forces. Electrons and nuclei are just particles that sometimes interact with each other in ways that create the stable conformations we call molecules. While Molecular Orbital Theory tells us that the real structure of electron wavefunctions may be more complicated, most of the time we can understand chemical bonds as resulting from pairs of electrons sitting between atomic nuclei, as described by Valence Bond Theory.

But there are situations where electrons can only be described as distributed between more than two atoms. Chemists refer to such states as delocalized, meaning they are spread out through space, and refer to such delocalization as resonance. Resonance has important implications for chemistry.

Let us start with a simple molecule: O<sub>3</sub> (ozone). You might be tempted to draw a Lewis structure for ozone that creates a triangle, with each O atom bound to both of the others. This does not occur in nature, because an equilateral triangle of this type requires bond angles of 60°, which is far lower than is allowed by chemistry (think of the allowed angles in VSEPR theory). Instead, the geometry is bent, with a central O bound to each of the other two.



**Figure 2.4.1:** Possible Lewis structures for ozone. A is incorrect, as ozone does not form an equilateral triangle. B is incorrect, because both bond lengths in ozone are known to be the same. C is the best Lewis structure representation, as it indicates delocalization of a pair of electrons.

The only way to fill the octet on all three O atoms in this bent geometry is to put a double bond on one side of the molecule or the other. Then, according to VB theory, we have two sp<sup>2</sup>-hybridized oxygens and a sp<sup>3</sup> hybridized O atoms, because two of the atoms have 3 electron domains and one has 4. But this seems arbitrary – the O atoms at each end of the molecule are identical, so why should the molecule behave as if they are different? Why should a pair of electrons “choose” to localize in a double bond on one side of the molecule rather than the other?

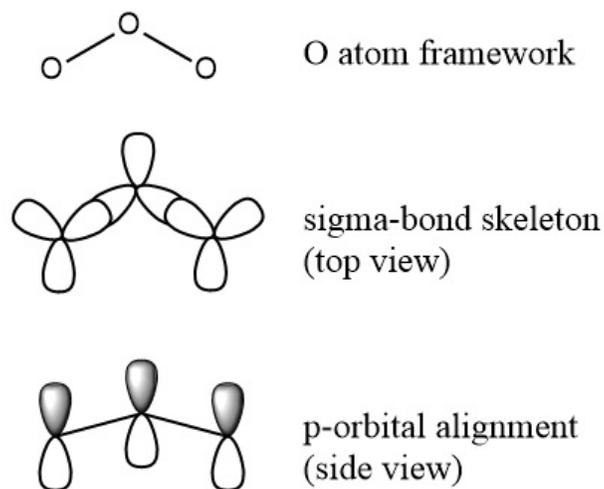
The answer is that they do not. Instead, that pair of electrons moves back and forth along all three of the oxygen atoms, and are shared between them. The ozone molecule does not contain a double bond and a single bond. It contains two single bonds and a delocalized pair of electrons that are smeared out through space in an example of resonance.

Valence Bond theory can describe resonance, but it is a bit clumsy in doing so. The distribution of electrons is represented by creating multiple Lewis structures, with a double-headed arrow between them to indicate that each structure is a partial representation of the electronic structure of the molecule. Students often try to understand resonance as if the molecule flips back and forth between the structures shown by the different Lewis structures, but this is not the case. The electrons are distributed through space in a standing wave that spans the three atoms, and their distribution does not change in time. Experiments confirm that the  $O_3$  molecule is symmetric, meaning that both O-O bond lengths are equal, which would not be true if one were a double bond and one were a single bond.

One way to view this resonance process is to view all three of the O atoms as  $sp^2$ -hybridized, meaning each has one unhybridized p-orbital. We know from the discussion of double bonds in Section 2.2 that unhybridized p-orbitals on neighboring atoms overlap and create regions of electron density that create a pi-bond. Here, the central O atom has a p-orbital that overlaps with unhybridized p-orbitals on both of the other O atoms. That central, unhybridized p-orbital does not have to choose one or the other p-orbitals on the other atoms. It overlaps with both, creating a wavefunction that spans all three atoms.

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**Figure 2.4.2:** Hybrid orbitals contributing to  $O_3$  structure. The three oxygens are taken to have  $sp^2$ -hybridization, meaning there are three unhybridized p-orbitals making up a delocalized orbital containing a pair of electrons.



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But this idea seems inconsistent with the Lewis structures drawn. After all, there is a  $sp^3$ -hybridized O atom in each of them, but the construction of this delocalized wavefunction required the contribution of an unhybridized p-orbital from each atom. The answer is simply that yes, this is clumsy (we warned you!). Participation in resonance of the type that will be described in this course requires the presence of at least one unhybridized p-orbital. If an atom contains an unhybridized p-orbital in at least one resonance form, it should be viewed as having the hybridization necessary to contribute to that resonance structure. That's a clumsy way of saying that if an atom has a  $sp^3$  hybridization in one resonance structure and a  $sp^2$  hybridization in another, you should view it as having  $sp^2$  hybridization. And if it has  $sp$ -hybridization in one and different hybridizations in others, you should view it as having  $sp$ -hybridization.

The reason for this clumsiness is that, as we noted before, VB theory assumes pairs of electrons sit between atoms. We are going to have to tolerate some awkwardness if we are going to describe resonance in a VB framework because resonance – a phenomenon that exists and needs to be described by any valid framework for chemistry – violates that assumption.

If one wishes to use Lewis structures to communicate delocalization of this type, one needs to use resonance structures. That is, rather than writing a single Lewis structure, one represents the true, delocalized structure of the electrons by writing multiple Lewis structures and placing a double-bladed arrow ( $\leftrightarrow$ ) between them. You can see an example of this for ozone in Figure 2.4.1C. This is the only time in chemistry that a double-bladed arrow of this type is used, do not confuse it with other notation you will encounter, for example, in studies of chemical equilibrium.

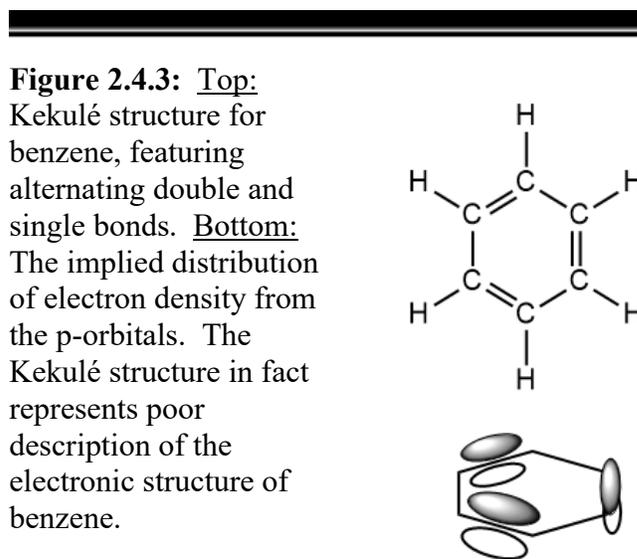
Writing good resonance structures and correctly interpreting them is actually a challenging endeavor, and is covered in detail in Chapter 3. Here, we will simply work a few more examples and focus on the principles connecting these structures to the real physics of molecules.

As a second example we consider benzene,  $C_6H_6$ , which is perhaps one of the most famous examples of resonance. If one were to try to represent a benzene ring with a single Lewis structure, it would consist of alternating double and single bonds. Each C atom would therefore have  $sp^2$ -hybridization, and thus one unhybridized p-orbital. This structure was proposed by August Kekulé in the 19<sup>th</sup> century, and is shown in Figure 2.4.3. As we discuss below, this structure is not a good description of the electronic structure of benzene.

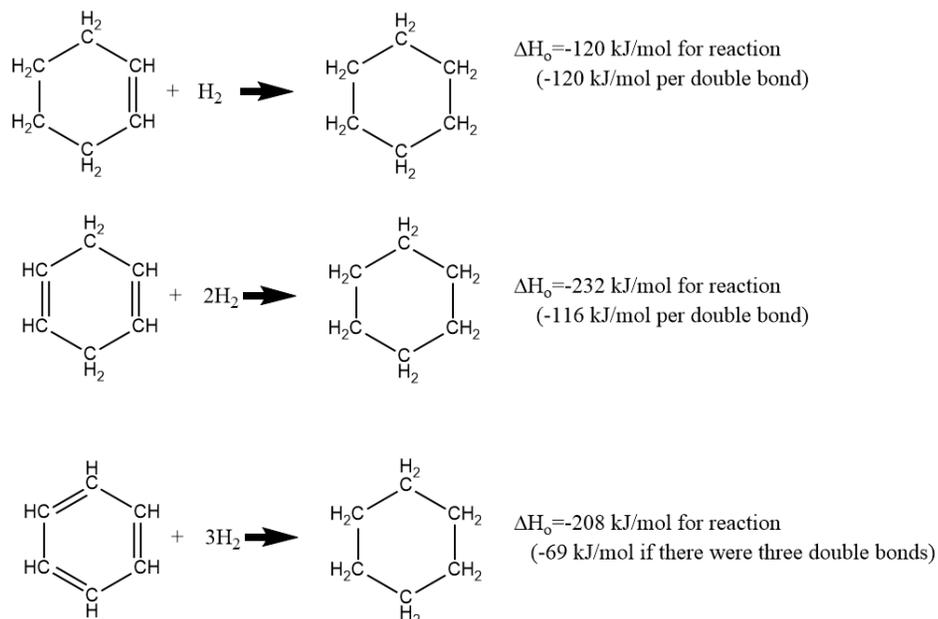
However, one can readily draw a second Lewis structure by shifting the bonds by one atom (see Figure 2.4.5). This represents a second, valid resonance structure and implies that the six electrons involved (one from each atom, in this case) are smeared out around the ring in a continuous loop rather than being localized between pairs of atoms.

Which of these structures is correct? There are several lines of evidence. First, as in the ozone example, all of the C-C bonds in the molecule are known from experiment to have the same length. And second, it is also possible to show that the C-C bond energies are different from those that would be expected from three double and three single bonds.

Consider the hydrogenation reactions shown in Figure 2.4.4. Isolated double bonds give an enthalpy of roughly -120 kJ/mol, but the enthalpies for hydrogenating benzene work out to about -69 kJ/mol for each of three imagined double bonds. The bond enthalpies are too low, meaning that resonance is acting to stabilize the molecule. This is a common theme: Where it is possible to delocalize electrons, their energy is lower than that in localized states (though this is a bit of a tautology – they wouldn't delocalize if it were unfavorable!).

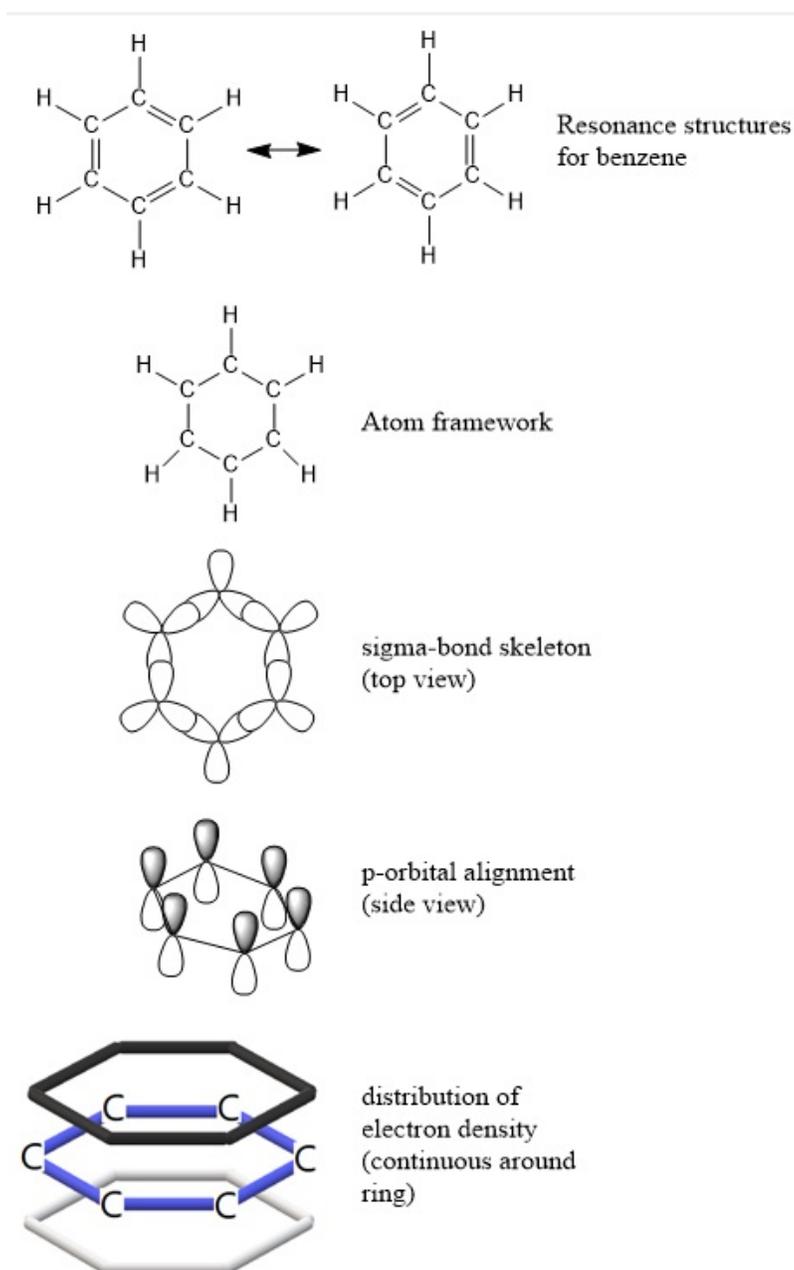


**Figure 2.4.4:** The hydrogenation reactions shown indicate that, for isolated double bonds, the heat of hydrogenation is roughly -120 kJ/mol. If one assumes benzene contains three double bonds, the heat of reaction would be -69 kJ/mol for each bond. The molecule releases less heat than it should, meaning it is more stable than the Kekulé structure would imply.

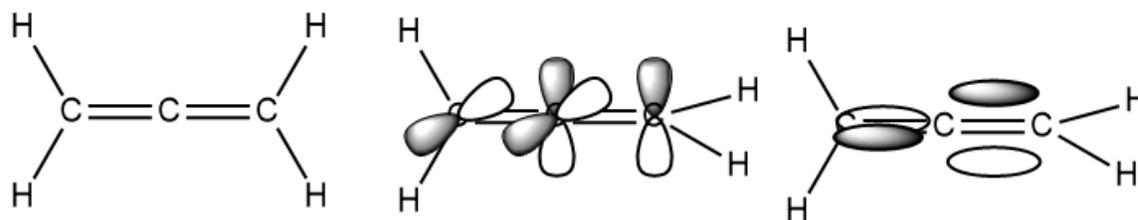


Geometry is important in resonance. In order for a molecule to support resonance, there must be 3 or more unhybridized p-orbitals that are parallel to each other and spaced no more than one bondlength away from each other. If the p-orbitals are not adjacent to each other the electrons will not delocalize; the middle structure in Figure 2.4.4 contains two isolated double bonds, and they behave almost identically with the lone double bond in the top structure.

**Figure 2.4.5:** Electronic structure of benzene. The appropriate resonance structures are drawn at the top, and the other figures schematically address the true distribution of electron density. This includes the sigma-bond skeleton, and the fact that the electrons in pi-orbitals are not isolated in alternating double bonds but rather move continuously around the ring (i.e. each is spread over six C atoms rather than shared between two).



Another case where geometry is important is where one carbon has two double bonds, as shown in Figure 2.4.6. In this case, that carbon must be sp-hybridized, meaning that its p<sub>y</sub>-orbital forms one pi bond and its p<sub>z</sub>-orbital forms another. That means the pi bonds are orientated at 90° relative to each other, preventing the overlap of parallel p-orbitals that can lead to delocalization. Thus, structures of this type do not engage in resonance (and in fact are relatively unstable and therefore uncommon in chemistry).



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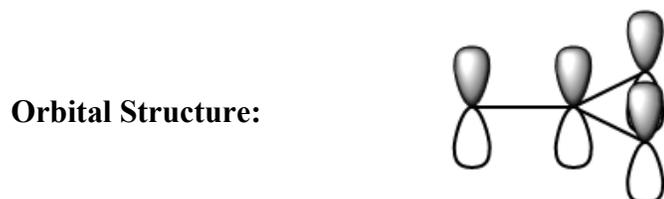
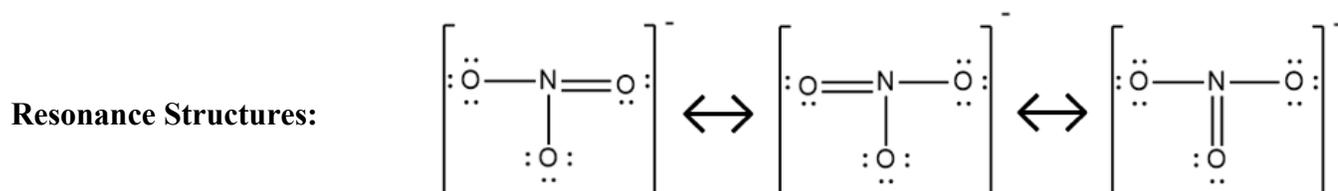
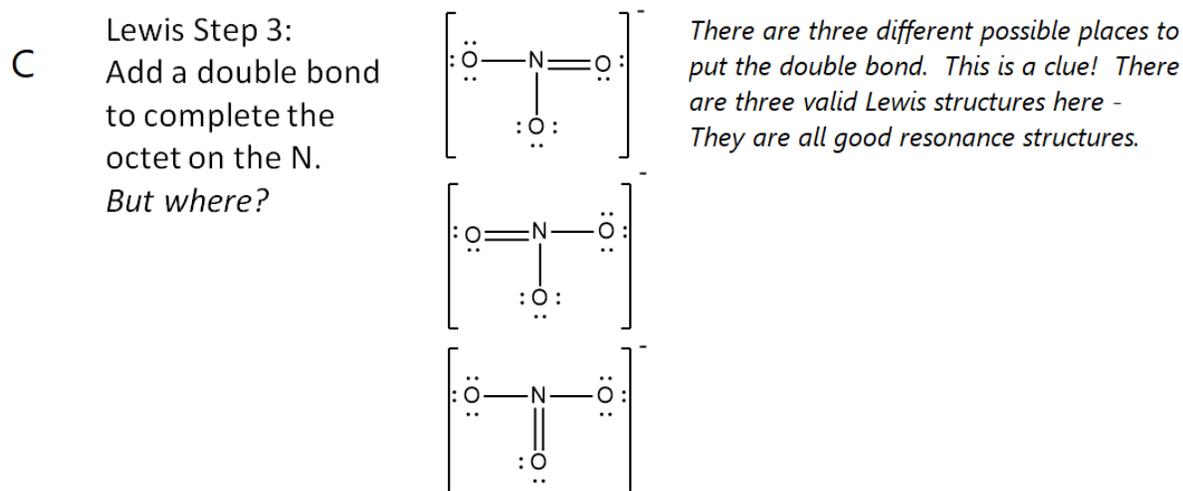
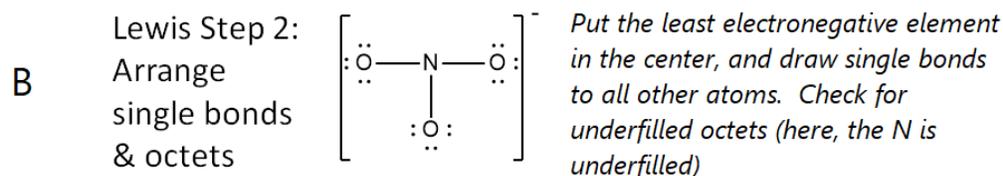
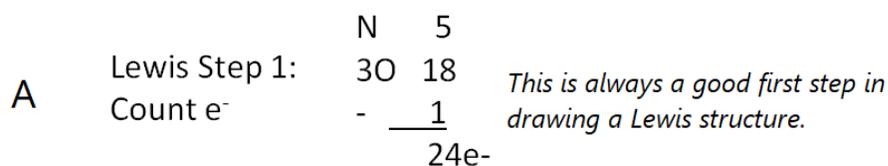
**Figure 2.4.6:** The structure of pi-bonds in systems with neighboring double bonds. The pi-bond orbitals are rotated by  $90^\circ$  relative to each other, preventing delocalization of the electrons.

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We present a relatively simple example in Figure 2.4.7 to show how one can construct resonance structures for a molecule. As with any Lewis structure involving a relatively small number of atoms, the first step is to count the number of electrons. N has 5 valence electrons, each of the three oxygens has 6 valence electrons, and the excess electron that gives the anion its -1 charge adds one more for a total of 24 electrons.

The second step is to put the least electronegative element in the center and draw single bonds to each of the others. Once that is done, distribute the electrons to the atoms in the outer ring until you either run out of electrons or fill all of the octets. Here, you will add 3 lone pairs to each O atom and complete their octets, but you will be left with an underfilled octet on the central atom.

Filling the octet requires the creation of a double bond with one of the O atoms, but now you have to make a choice. Which bond? On one level, it does not matter, because they are all the identical. But this is a clue that there is a pair of electrons can distribute themselves between the available atoms, and in fact each of the three choices represents a valid resonance structure. The result is that all four atoms are coplanar with aligned p-orbitals, and all three bonds are equivalent. This is consistent with the predictions of VSEPR theory (the N has three electron domains and is trigonal planar) and the three bonds are known to have the same length from experiments).



**Figure 2.4.7:** Construction of resonance structures for the nitrate ion, as described in the text.

Before wrapping up this chapter, let us return for a moment to benzene, as described in Figure 2.4.5 and the surrounding text, and take note of an inconsistency. We stated that there are six electrons delocalized in the pi-orbitals along the ring, but the Pauli exclusion principle says that there can only be two electrons in a given orbital. How do we account for this?

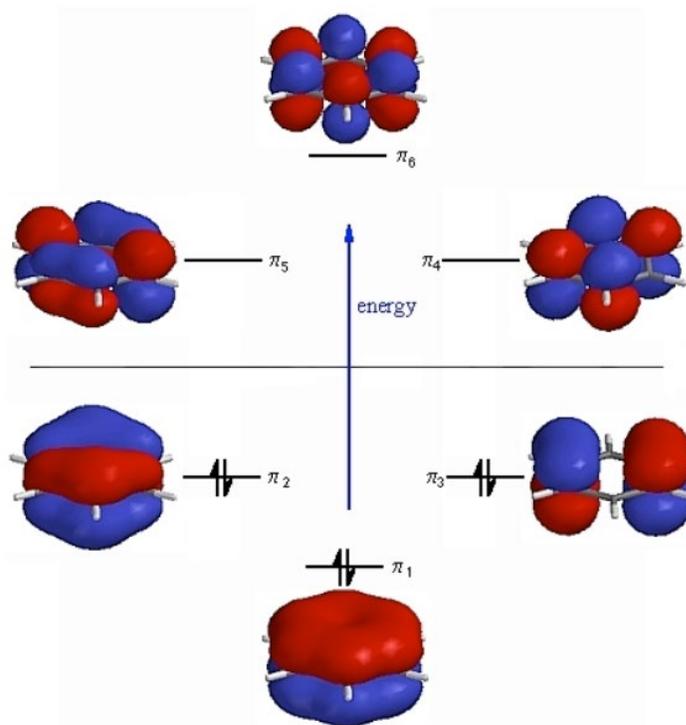
The answer is that to really understand resonance we need to make use of ideas from molecular orbital theory. Stating that the six p-orbitals combine to delocalize the electrons actually skips a step. The truth is that they combine to make a series of molecular orbitals, some bonding and some antibonding, similar to the way that atomic orbitals in diatomic molecules combine to make molecular orbitals as described in Section 2.4.3.

Diagrams of the molecular orbitals are given in Figure 2.4.8. It is not important at this stage that you understand how to construct them. But you should be aware that, where resonance appears clumsy and arbitrary in Valence Bond Theory and in Lewis structure representations, it emerges naturally in Molecular Orbital Theory. You should also try to see past the clumsiness of the Lewis structure representation and focus on the fundamental physical process: The electrons are minimizing their energies through this delocalization process in which they interact with multiple nuclei. It is only human bias that expects them to sit in a “bond,” and only the Lewis structure reliance on bonds as a concept that makes the process appear clumsy.

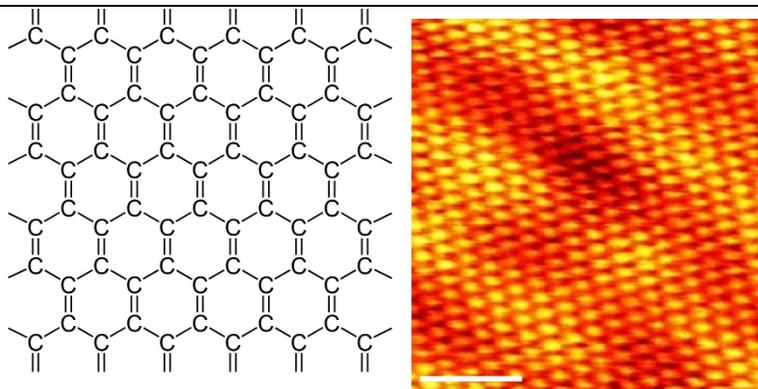
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**Figure 2.4.8:** Molecular Orbitals for Benzene. The orbitals are composed of overlapping p-orbitals. The lowest-energy state has perfect overlap with no nodes present, and electron density is simply smeared over the entire ring. The next higher two (degenerate) orbitals each have a single node. The six electrons in the pi-system sit in these bonding orbitals, with the three antibonding orbitals unoccupied when benzene is in its ground electronic state.

Image from Hanning Chen, *Lecture 14, Physical Chemistry (II)*, 2021. George Washington University website.  
[https://home.gwu.edu/~chenhanning/Lecture\\_14.pdf](https://home.gwu.edu/~chenhanning/Lecture_14.pdf) (accessed July 1, 2021).



# CHAPTER 3: Resonance Structures



Left: The structure of graphene, a solid composed of a single layer of carbon atoms arranged in alternating double and single bonds. Right: Electron Micrograph of the surface of graphene. Inset bar is 1 nm.

Left from:

Image by Yikrazuul, courtesy of Wikimedia Commons, [https://commons.wikimedia.org/wiki/File:Graphene\\_structure.svg](https://commons.wikimedia.org/wiki/File:Graphene_structure.svg), July 7, 2021.

Right modified from: Clark, K. W. et al., *Energy Gap Induced by Friedel Oscillations Manifested as Transport Asymmetry at Monolayer-Bilayer Graphene Boundaries*, *Phys. Rev. X*, **2014**, *4*, 011021. Image courtesy of Wikimedia Commons, [https://commons.wikimedia.org/wiki/File:Graphene\\_STM.png#/media/File:Graphene\\_STM.png](https://commons.wikimedia.org/wiki/File:Graphene_STM.png#/media/File:Graphene_STM.png), July 7, 2021.

I WOULD TRADE ALL MY EXPERIMENTAL WORKS FOR THE SINGLE IDEA OF THE BENZENE THEORY.

-AUGUST WILHELM VON HOFMANN

*Wilhelm von Hofmann was a 19<sup>th</sup> century chemist who laid the groundwork for much of modern chemistry. He developed novel synthetic techniques, laid the foundation for the commercial production of dyes, and introduced the idea of using models in chemistry. But, like many chemists in the 19<sup>th</sup> century, he was baffled by the structure of benzene until it was revealed by Friedrich August Kekulé in 1865.*

## BEFORE YOU BEGIN, MAKE SURE YOU KNOW

- Drawing and interpreting Lewis structures (Flowers, sec 7.3)
- Electronegativity (Flowers, sec 7.2)
- Resonance Structures and Basic Principles of Resonance (Flowers, sec 7.4 and sec 2.4 in this work)

## Section 3.1: Formal Charge

### LEARNING OBJECTIVES FOR THIS SECTION

- Be able to calculate the formal charge for an atom in a Lewis structure.
- Understand what information formal charges convey about the electronic structure of a molecule.
- Be able to compare two Lewis structures for different molecules with the same chemical formula and use formal charge arguments to identify the best structure.

The goal of this chapter is to learn how to draw resonance structures and to interpret them. Before we do this, we need a new tool called formal charge.

Formal charge is a property of an atom in a Lewis structure. It is calculated as

$$\text{Formal charge} = \# \text{ electrons of free atom} - \# \text{ electrons in lone pairs} - \frac{1}{2} (\# \text{ electrons in bonds}) \quad (3.1.1)$$

The number of electrons in the free atom refers to the number of valence electrons for the element (e.g. 4 for C, 5 for N, etc.). So, if we were to look at the structure for methanol we could calculate the formal charges on each atom as follows:

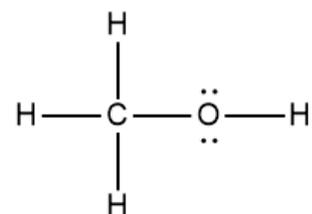
$$\text{C: FC} = 4 - 0 \text{ electrons in pairs} - \frac{1}{2} (8 \text{ bonding electrons}) = 0$$

$$\text{O: FC} = 6 - 4 \text{ electrons in pairs} - \frac{1}{2} (4 \text{ bonding electrons}) = 0$$

$$\text{H: FC} = 1 - 0 \text{ electrons in pairs} - \frac{1}{2} (2 \text{ bonding electrons}) = 0$$

H will almost always have a formal charge of zero in organic compounds, as it forms only 1 bond and never contains lone pairs. C and O in the methanol example both have 0 formal charge, which is actually relatively common for simple molecules.

**Figure 3.1.1:** Methanol Lewis structure.



Repeating the calculation for the cation shown in Figure 3.1.2, we find:

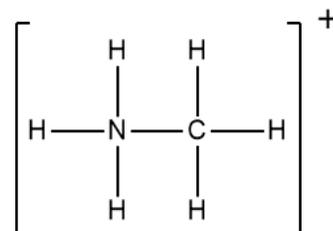
$$\text{C: FC} = 4 - 0 \text{ electrons in pairs} - \frac{1}{2} (8 \text{ bonding electrons}) = 0$$

$$\text{N: FC} = 5 - 0 \text{ electrons in pairs} - \frac{1}{2} (8 \text{ bonding electrons}) = 1$$

$$\text{H: FC} = 1 - 0 \text{ electrons in pairs} - \frac{1}{2} (2 \text{ bonding electrons}) = 0$$

Here, the calculation shows that nitrogen has a positive charge. This actually illustrates a property of formal charges, which is that *the sum of all formal charges in a molecule must sum to its total charge*. Here, the charges sum to +1, to match the charge of the ion. In methanol, they summed to zero for the neutral molecule.

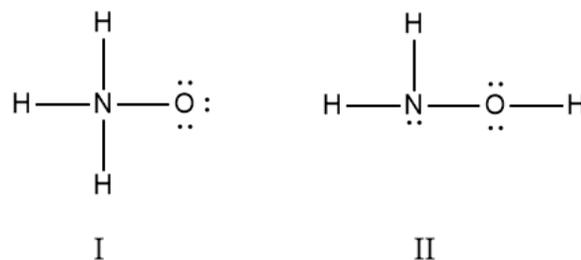
**Figure 3.1.2:** Methylammonium cation Lewis structure.



Having defined the formal charge, we should explain why it is useful. The truth is that the formal charge is an indicator for the spread of charge in the electronic structure described by a given Lewis structure. The methanol example indicates formal charge is spread relatively uniformly through the molecule, and the methylammonium suggests there is excess positive charge on the nitrogen. It does *not* mean that the nitrogen actually bears a full +1 charge. A detailed calculation of electronic structure of methylammonium would show the positive charge was distributed over multiple atoms. But a significant component of the positive charge would center on the N atom.

Formal charge can be extremely useful in understanding chemical reactions, but we will not consider that here. Instead, we will use it as a tool to compare chemical structures. For example, suppose you were told to build a molecule with the formula  $\text{NH}_3\text{O}$ . A little experimentation would reveal the two possible structures shown in Figure 3.1.3. In both cases, the octet rule is satisfied for all elements. Intuitively, it seems like II is probably the better Lewis structure, as it seems more consistent to have two bonds on O and three on N, but how to make that argument based on the physical picture?

**Figure 3.1.3:** Possible Lewis structures for  $\text{NH}_3\text{O}$ .



The answer is to look at the formal charges. Ignoring the H's (which are 0 throughout), one finds:

I:	II:
N: $FC=5-0-1/2(8)=+1$	N: $FC=5-2-1/2(6)=0$
O: $FC=6-6-1/2(2)=-1$	O: $FC=6-4-1/2(4)=0$

We can now make use of the idea that formal charges indicate charge distribution to demonstrate that II is a better description than I. Remember that opposite charges attract each other, meaning that it costs energy to separate charges of opposite sign. The formal charges on I indicate a separation of positive and negative charges, while the formal charges on II indicate a more uniform distribution of charge. This makes a convincing case that, when assembling a molecule from 3 H's, 1 N, and 1 O, structure II will be the lower-energy form and therefore the favored form.

A series of rules for identifying the "best" Lewis structure is given in Table 3.1.1. They stem from the rules for interacting charges. Rule 1 concerning minimizing charges simply reflects the fact that it costs energy to separate charges, and to force like charges to sit in the same position. Putting, say, a +2 charge on one atom requires a lot of energy to move electrons away from the atom. It costs less energy to create two +1 charges, so a Lewis structure with this configuration will be lower in energy. Rule 2 simply extends this idea to the space across bonds: Putting two +1 and charges on opposite sides of a bond costs more energy than moving them further apart.

Rule 3 simply reflects the fact that electronegativity plays a role as well, though a less significant one. More electronegative elements should in general have more negative charge (and less positive charge) than less electronegative elements.

- 
1. Formal charges should be minimized. A Lewis structure in which all formal charges are zero will be favored over those with nonzero charges. If no Lewis structure exists with zero formal charges, the structure with the lowest charges will be favored (e.g. a structure with a -1 charge on one atom will be favored over one that puts a -2 charge on one atom and a +1 on another).
  2. Lewis structures are favored if neighboring atoms have zero formal charge, or charges of opposite sign. Lewis structures are disfavored if neighboring atoms have neighboring charges of the same sign (i.e. like charges are forced to sit in close proximity).
  3. The distribution of charges should place negative charge on a more electronegative atom, and positive charges on a less electronegative atom. Use this rule only if rules 1 and 2 do not allow one to distinguish between two structures.
- 

**Table 3.1.1:** Using formal charges to rank Lewis structures

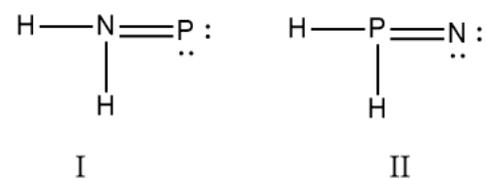
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Figure 3.14 gives us another comparison between two Lewis structures. Once again, we write the formal charges:

I	II
C: $4-4-1/2(4)=-2$	N: $5-4-1/2(4)=-1$ (atoms ordered from left to right)
N: $5-0-1/2(8)=+1$	C: $4-0-1/2(8)=0$
N: $5-4-1/2(4)=-1$	N: $5-4-1/2(4)=-1$



**Figure 3.1.6:** Possible Lewis structures for H<sub>2</sub>PN.



This example is somewhat artificial. The truth is that there is a better structure for this molecule that gives zero charges uniformly, but this is left as an exercise for the student.

## Section 3.2: Identifying Valid Resonance Structures

### LEARNING OBJECTIVES FOR THIS SECTION

- Be able to identify invalid resonance structures.

As discussed in Section 2.4, resonance is a phenomenon that is difficult to describe using Lewis structures. The only way to describe the delocalization of electrons over more than two atoms is to draw multiple Lewis structures and use a double-bladed arrow to indicate that the real electronic structure of the molecule is a combination of them. In other words, each resonance structure contains a partially correct structure for the molecule, but does not tell the whole story. Stringing these Lewis structures together will typically give the best description of the molecule that is possible within the bounds of the Lewis structure representation.

Table 3.2.1 contains rules for writing valid resonance structures. The first two – stating that the positions of the nuclei are fixed and the total number of electrons cannot change – simply reflect the fact that resonance structures must represent different distributions of electrons in the same molecule. Changing the positions of the atoms changes the identity of the molecule (see Figures 3.1.5 and 3.1.6 for examples of this), and changing the number of electrons changes the charge of the molecule or ion.

Rule three states that the octet rule (and duet rule, for H) must be obeyed. This simply reflects the fact that while there may be more than one possible Lewis structure for a molecule, each one has to obey the laws of physics. Putting more than eight electrons into the valence shell of a second-row element is extremely energetically unfavorable, and a Lewis structure that does so will not even be a partially-correct picture of the molecule. Note that third row and heavier elements can have expanded valence shells of out to 12 electrons, and nothing in the rule says an octet cannot be *underfilled* with fewer than 8 electrons. Usually such structures are not strong contributors, but they can be important for relatively unstable species such as reaction intermediates.

Rule four states that the number of unpaired electrons must be the same in all cases. This simply reflects the fact it is generally more stable to pair electrons than to leave them unpaired, so structures corresponding to an increased number of unpaired electrons will not be good descriptions of the molecule. This is another rule that will generally be most important in reactive intermediates and other short-lived species.

- 
- 
1. The positions of the nuclei must be the same in every Lewis structure.
  2. The total number of electrons must be the same in every structure, though there may be different numbers of lone pairs vs. bonds.
  3. All contributing structures must obey the duet and octet rules. Hydrogen atoms cannot have more than two electrons, and second row elements cannot have more than eight. Underfilled octets are allowed, and third row elements and higher can have expanded valence shells (i.e. up to 12 electrons).
  4. The number of unpaired electrons must be the same in all resonance structures (usually it will be zero, with all electrons are paired).

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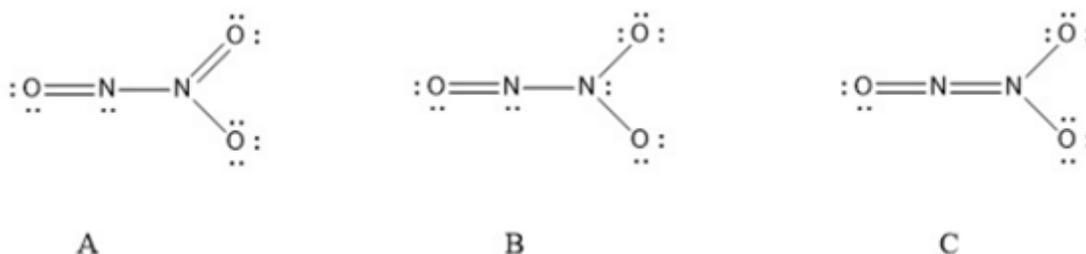
**Table 3.2.1:** Guidelines for identifying valid resonance structures.

---

A sample problem is given in Figure 3.2.1, where a series of candidate structures for  $\text{N}_2\text{O}_3$  are drawn. Which ones are valid resonance structures?

As a first step, we should probably check that all nuclei are in the correct positions. If we take the layout of structure A to be correct (O-N-N-(O)<sub>2</sub>), we can confirm that all three have the same positions for the nuclei, so none can be ruled out by Rule 1 (otherwise, they are all incorrect). Checking the number of valence electrons, we note that 2N and 3O should have a total of 28 electrons ( $2 \times 5 + 3 \times 6$ ). Structure A and Structure C both have 28 electrons, but Structure B has 30 electrons. If such a structure existed, it would have a -2 charge ( $\text{N}_2\text{O}_3^{-2}$ ), making it a different species from the molecule specified ( $\text{N}_2\text{O}_3$ ) and therefore not a valid resonance structure for the neutral molecule.

Octets are filled in all atoms in Structures A and C and there are no unpaired electrons, satisfying Rules 3 and 4, so both A and C are valid resonance structures.



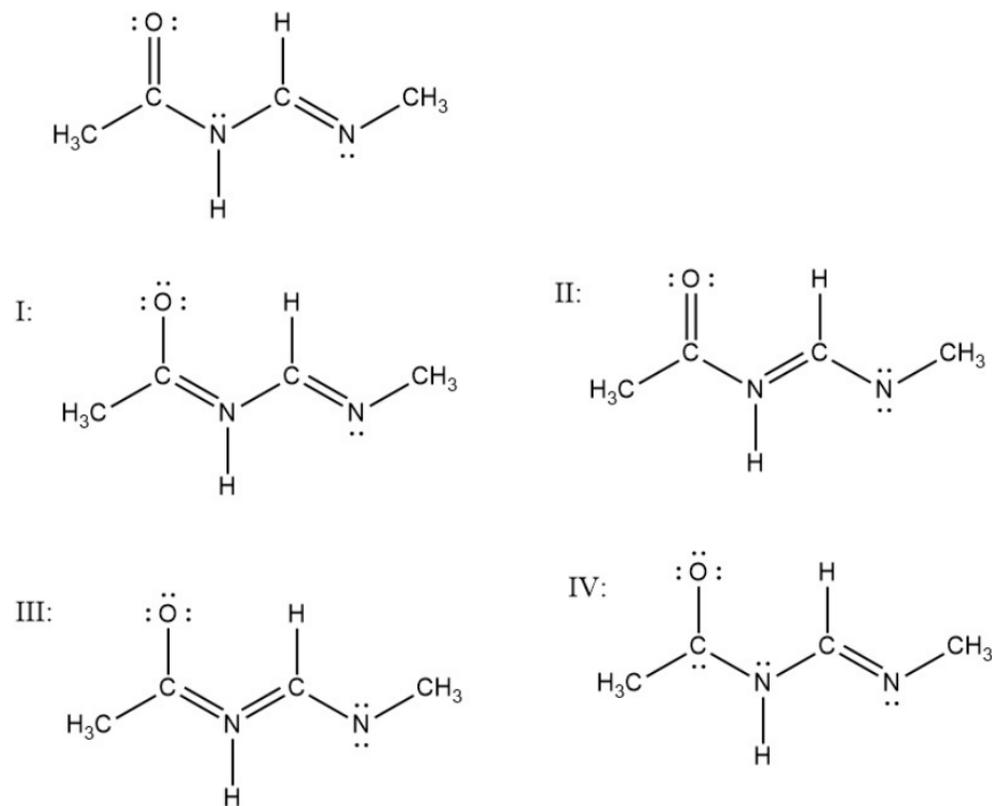
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**Figure 3.2.1:** A series of candidate resonance forms for the  $\text{N}_2\text{O}_3$  molecule. Some of these are not valid; see text for discussion.

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Figure 3.2.2 is another example for review. Here we are given one correct resonance structure and asked to identify other valid structures. Once again, we can quickly confirm that all structures have the same layout of nuclei. Therefore, Rule 1 does not eliminate any structures.

Ignoring the electrons in the C-H bonds of the two  $\text{CH}_3$  groups (which are not shown in any structure), there are 28 valence electrons in the given structure. Structures I, II, and III have 28 electrons, but Structure IV has 30 electrons and can immediately be ruled out as a valid structure. Rule 3 means we should check the octet rule for all atoms, and we immediately note that the left-hand N in Structure III has 10 electrons (in 5 bonds). This violates the rule, so we are left with I and II as valid structures. Rule 4 does not apply because the number of unpaired electrons is zero in all cases, so we can conclude that I and II are valid resonance structures.



**Figure 3.2.2:** A molecule (top) and a series of candidate resonance structures. Some of these are not valid; see text for discussion.

The ability to state with certainty that something is *not* a resonance structure is useful, but it is not sufficient. First, we have not yet learned to evaluate what these structures are telling us about the actual distribution of electrons in the molecule. Second, we do not yet know how to draw them for ourselves. The first point is the subject of Section 3.3, and the second point is the focus of Section 3.4.

## Section 3.3: Evaluating Resonance Structures

### LEARNING OBJECTIVES FOR THIS SECTION

- Be able to judge the relative importance of different resonance structures.
- Understand the physical reasons underlying the relative importance of a given resonance structure.

It is worth stating once again that the purpose of drawing resonance structures is to accurately describe the electronic structure of the molecule or ion of interest. In some cases, resonance structures are easy to interpret. For example, the three resonance structures for the  $\text{NO}_3^-$  ion given in Figure 2.4.7 indicate that a pair of electrons is shared evenly between the three oxygens. This is clear because all three resonance structures are “equivalent,” in the sense that they have one N=O double bond and two N-O single bonds. Likewise, the six electrons that are delocalized in benzene, as shown in Figure 2.4.5, are spread evenly between the six C atoms. This is confirmed by the fact that the structures each contain three single C-C bonds and 3 double C=C bonds, with their positions changed so that every C-C bond is single in one of the structures and double in the other. Crudely, one could imagine that the N-O bond in nitrate has a bond order of  $4/3$ , since the pair of delocalized electrons spends  $1/3$  of its time there, and the C-C bond order in benzene is  $3/2$ . This artificially-calculated bond order is not really a good picture of delocalization, but it does make clear that electron density is distributed evenly among the available bonds.

But how do we assess cases where Lewis structures are significantly different for different resonance structures? As we did when using formal charges to identify the best molecular structure, we can take principles based on the physics of the molecule to evaluate the relative importance of resonance structures. The rules are given in Table 3.3.1. Rule 1 just reflects the fact that underfilled octets are energetically unfavorable, so a structure that fills all octets will be favored over one that does not. Rule 2 reflects the fact electrons that are shared in bonds are generally lower in energy than lone pairs. Rules 3 and 4 are just reflections of the rules for identifying good structures based on formal charges given in Table 3.1.1. It costs energy to separate charges, and negative charges will be most favorably distributed to electronegative atoms. Rule 5 is a catchall – a resonance structure that does not meet at least one of the four previous rules has little to do with the actual distribution of electrons in the molecule and is best ignored.

- 
1. Filled Valence Shells: Structures with filled valence shells contribute more than those with one or more unfilled shells.
  2. Maximum number of covalent bonds: Structures that have the largest number of shared electrons (i.e. have the largest number of bonds) are favored. Double bonds count as two covalent bonds, and triple bonds count as three.
  3. Least separation of unlike charges: Opposite charges attract, so it costs energy to separate them. Consequently, structures that create a more uniform distribution of charge will be favored over those that distribute it.
  4. Negative charge should reside on more electronegative atoms (positive on less): Charge is drawn to atoms based on electronegativity, so these structures will be favored.
  5. Structures that do not satisfy any of Rules 1-4 should not be drawn. While the structures may be “valid” under the rules presented in Table 3.2.1, their contribution to the electronic structure is so limited that it is best ignored.

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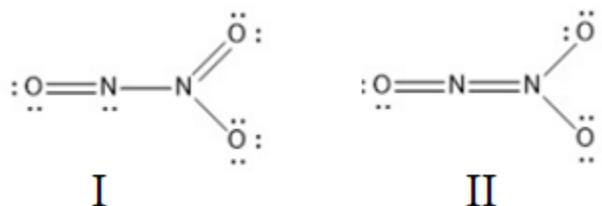
**Table 3.3.1:** Principles for ranking the importance of resonance structures.

---

Let us consider the two valid resonance structures for  $\text{N}_2\text{O}_3$  originally in Figure 3.2.1 and displayed again in Figure 3.3.1. The two structures clearly imply different distributions of electron density, with Structure I indicating a single N-N bond and Structure II implying a double bond. Likewise, Structure II implies more electron density on the right-most oxygens than is present in Structure I. Which is a better description of the molecule, and what can we learn by considering them?

Let us apply the principles from Table 3.3.1 to the structures in Figure 3.3.1. Rule 1 does not distinguish between the two structures, because all atoms have filled octets, and Rule 2 does not distinguish between because both have six covalent bonds.

**Figure 3.3.1:** Two valid resonance structures for  $\text{N}_2\text{O}_3$ .



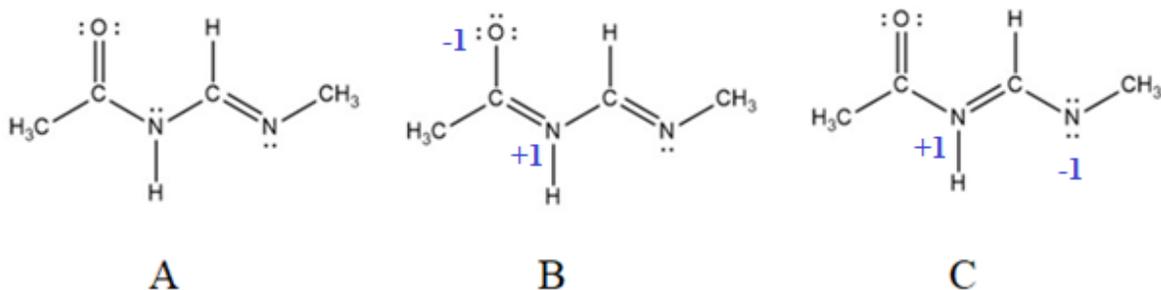
Rules 3 and 4 require knowledge of the formal charges, so we calculate them:

	I	II
O (left)	$6-4-1/2(4)=0$	$6-4-1/2(4)=0$
N (left)	$5-2-1/2(6)=0$	$5-0-1/2(8)=+1$
N (right)	$5-0-1/2(8)=+1$	$5-0-1/2(8)=+1$
O (top)	$6-4-1/2(4)=0$	$6-6-1/2(2)=-1$
O(bottom)	$6-6-1/2(2)=-1$	$6-6-1/2(2)=-1$

We can see that the formal charges in Structure I are smaller than those in Structure II, meaning that there is less separation of unlike charges. Thus, by Rule 3, Structure I is favored. We do not need to apply Rule 4, as we have our answer from Rule 3, though if we did we would not find a good basis for distinguishing between the two structures (in both cases, N atoms have a +1 charge and O atoms have a -1 charge, consistent with their relative electronegativities).

The fact that Structure I is favored does not mean that we can ignore Structure II. We should instead label Structure I as a “major” contributor and Structure II as a “minor” contributor. Electron density will be distributed in a way that looks more like Structure I than like Structure II, but the charge density across the N-N bond will still be a bit higher than would be expected for a purely single bond. More importantly, the presence of the double-bond in the minor form indicates that the p-orbitals on the two N-atoms must be aligned such that their unhybridized p-orbitals overlap. This alignment means that the molecule is planar, something that is known to be true from experiment. Thus, minor resonance structures can provide important information on chemical structure.

The two structures shown in Figure 3.3.1 do not represent the full range of possible resonance structures; we will return to this point in Section 3.4.



**Figure 3.3.2:** Three valid resonance structures for  $C_4H_8N_2O$ . Formal charges that are not zero are given in blue.

Figure 3.3.2 contains the three valid resonance structures presented Figure 3.2.2 for  $C_4H_8N_2O$ . How do we tell which is most important? And, of the three, is there also a “least” important?

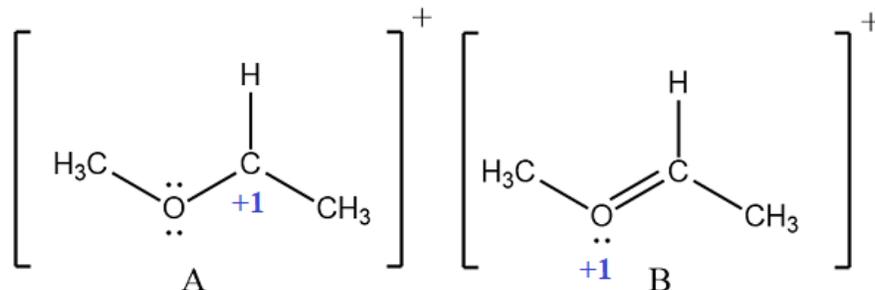
Let us apply the rules from Table 3.3.1. Rule 1 does not allow us to distinguish between the three, as all octets are filled for all atoms. Rule 2 also does not help, because there are 10 bonds shown in all cases (ignoring the hidden ones in the  $-CH_3$  groups, which do not change between structures).

We can apply Rules 3 and 4 using formal charges; nonzero formal charges are marked in blue in Figure 3.3.2. The formal charges are uniformly 0 for Structure A, while Structures B and C each have +1 and -1 formal charges on different atoms. So, Structure A will be the most important structure for the molecule.

Can we rank the remaining two structures? Applying Rule 4, we see that both Structures B and C have a +1 charge on the left-hand N, but Structure B has a -1 charge on the O atom while Structure C has a -1 charge on the right-hand N. Since O is more electronegative than N, Rule 4 rates Structure C as the least significant structure and Structure B as a “lesser” structure with significance between the other two.

What does this tell us? Well, the fact that Structure B has a negative charge on the O atom tells us there is probably some excess electron density on that atom. That could be important in determining how it will react with other compounds. Likewise, the presence of the  $N=N$  double bond in Structure C means that the molecule is likely planar, with only the H’s on the end carbons likely to be out of plane with the rest of the molecule.

**Figure 3.3.3:** Possible resonance structures for  $C_3H_7O^+$ . Nonzero formal charges are given in blue.



A third example is given in Figure 3.3.3. This species may look odd and in fact represents a relatively unstable species – ions like this might be encountered as intermediates in an organic reaction. Which resonance structure will be dominant?

Applying Rule 1, we can immediately see that Structure B will be favored by having filled valence shells on all atoms, while Structure A has an underfilled octet on one C atom. So, Structure B is favored – should Structure A be drawn at all?

Structure B has 5 shown covalent bonds, while Structure A has only four, so Rule 2 also favors Structure B. But the two are equivalent under Rule 3 (they have the same separation of charges, in this case meaning only a single +1 FC), and under Rule 4 Structure A is a better structure because it puts the +1 formal charge on the C atom. Thus, Structure A is a minor contributor and should be drawn.

The presence of Structure B indicates that the positive charge of the ion is distributed between the O and C atoms. The fact that Structure A is the major contributor indicates that, perhaps counterintuitively, the majority of the excess positive charge resides on the O atom, but based on the resonance structures there is some positive charge density on the C atom as well.

## Section 3.4: Drawing Resonance Structures

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand and be able to use push arrow notation.
- Be able to draw multiple, valid resonance structures when given a chemical structure.

Thus far, we have presented the means to judge whether a given Lewis structure is a legitimate representation of a given molecule, and how to judge the relative importance of different resonance structures when compared to each other. Examples thus far have involved comparing structures that were already drawn. Now we need to learn how to identify all of the possible resonance structures for a given molecule.

This seems like a challenging task. It is usually straightforward to draw one resonance structure for a molecule, and in most cases to draw others. But how, students often wonder, can you be sure you have drawn all of the possible resonance structures?

You can't. You can never be completely certain that you have drawn every possible Lewis structure.

The problem is that while rules for building Lewis structures are relatively simple, as are the rules for constructing resonance structures, the range of possible chemical structures is enormous. Developing a set of rules that could identify every possible Lewis structure for every possible molecule or ion would be a bit like developing a set of rules that would win every possible game of chess. There are too many variations, and no strategy can perfectly accommodate them. The only approach – for chemists and chess players alike – is to practice and to approach problems systematically.

Chemists do have one advantage over chess players: They are allowed to make bad moves. That means a good strategy is simply to write structures and check them. Usually, it is best to do this on paper rather than trying to do it in your head, where it is easy to miss complications.

One tool that is particularly useful for this is push arrow notation. This notation is used in many areas of organic chemistry, from constructing resonance structures to analyzing chemical reactions; indeed, it is a critical survival skill for organic chemistry.

Push arrow notation simply involves using a curved arrow to show where electrons move. Table 3.4.1 gives the rules for using them, which are extremely simple. They are an ideal tool for drawing resonance structures, because they do not move the nuclei and they move electrons without changing the number of electrons present. A new structure generated in this way automatically satisfies the first two rules for resonance structures given in Table 3.2.1.

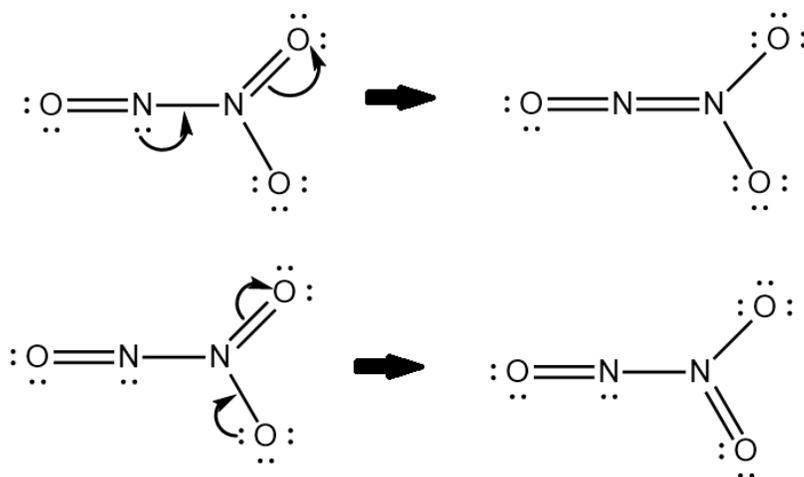
- 
1. Push arrows never move nuclei, they only move electrons.
  2. Push arrows should start either at a lone pair of electrons, a bond, or an unpaired electron (rarely). The arrow runs from the place where the electrons begin to the point where they end.
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**Table 3.4.1:** Rules for push arrow notation.

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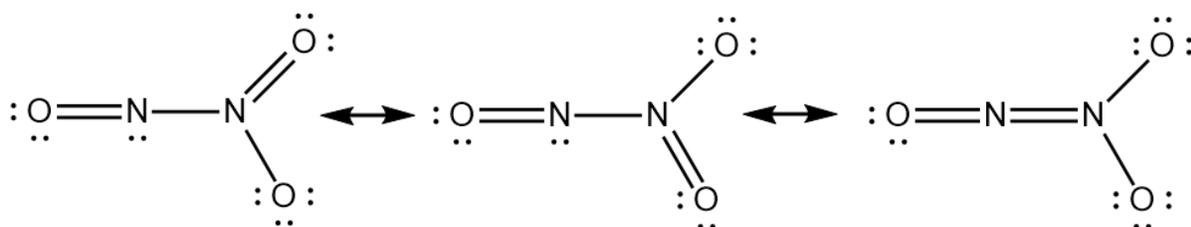
Figure 3.4.1 gives an example of push arrow notation applied to the  $\text{N}_2\text{O}_3$  structures given in Figure 3.3.1. The top line shows how the second of the two structures we had previously identified can be generated from the first. It is simply a matter of transferring the unpaired electrons into the N-N bond, and moving one pair of electrons out of the N=O double bond to make a lone pair on the O. The second move is necessary because leaving the N=O double bond in place would create an overfilled octet on the right-hand N atom.

**Figure 3.4.1:** Push arrow notation can be used to generate alternative resonance structures.



In the second line, we use two arrows to make the top N-O bond into a single bond and the bottom into a double bond. This is significant, in the same way that the nitrate structures given in Figure 2.4.7 were significant: The N-O bonds in the NO<sub>2</sub> group in N<sub>2</sub>O<sub>3</sub> both have significant double-bonding character, rather than one being a double-bond and one being single.

The final set of three resonance structures describing N<sub>2</sub>O<sub>3</sub> are given in Figure 3.4.2, with a double-bladed arrow interspersed to properly identify them. The left two structures are both “major”, and are equivalent under the rules for identifying the best resonance structure (the distribution of formal charge is the same in both cases). The right-hand structure is the minor contributor. There is no convention demanding that major vs. minor structures are drawn in a particular order.

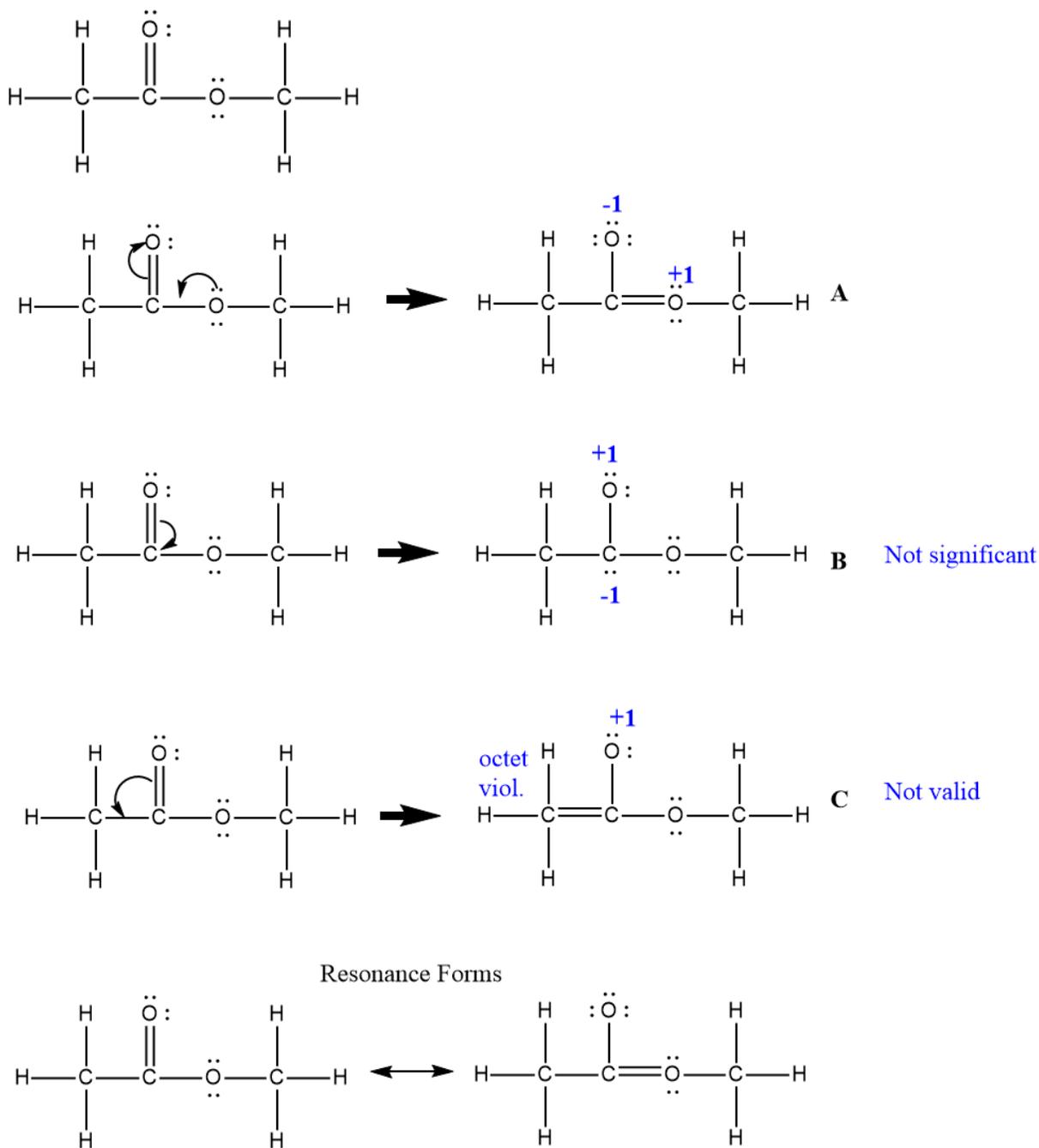


**Figure 3.4.2:** Resonance structures resulting from Figure 3.4.1.

Figure 3.4.3 contains another example. Given the structure at the top, can we identify any possible resonance structures for this molecule?

As recommended above, we attempt to construct additional candidate structures using push arrow notation. Structure A involves moving a lone pair off of the right-hand O into the C-O bond to create a double bond, and moving a pair of electrons out of the top C=O bond to create a single bond. The two moves are necessary, because just adding the electrons to the right-hand C-O bond would violate the octet rule for the C

atom (try it, it will wind up with 10 electrons in 5 bonds). The resulting structure is *valid* under the rules in Table 3.2.1 (nuclear positions and number of electrons constant, octet rule obeyed, and number of unpaired electrons still zero). But it is not clear that the resonance structure is *significant*, and the three bonds to the oxygen look a bit weird. Best to check it.



**Figure 3.4.3:** Constructing resonance structures for a sample molecule, as described in the text. Formal charges are given in blue.

First, we can see that all valence shells are filled, and the number of covalent bonds is 11, the same as in the original molecule. So it is a contributing structure and should be drawn. The formal charges in the original structure are uniformly zero, whereas there are +1 and -1 formal charges in Structure A, so Structure A will be less significant.

Structure B is also worth a look. It is *valid* (nuclear positions and number of electrons constant, octet rule not exceeded, and number of unpaired electrons still zero), but the underfilled octet on the top O is problematic. Checking against our list in Table 3.3.1, we see that valence shells are not filled (top O), the number of covalent bonds is smaller than in the original structure (10 vs. 11), it has a higher separation of charges than the zero separation of charges in the original figure, and the negative charge sits on the C atom, which is less electronegative than O. Consequently, it should not be viewed as a contributing structure and should not be drawn in the final answer.

Structure C can be quickly discarded, because it is not a valid structure. The octet on the left-most C atom is exceeded. This is something to watch out for – H atoms do not disappear, and there needs to be one bond for each.

The two valid resonance structures are drawn in the last line with the correct double-bladed arrow between them.

Another example is given in Figure 3.4.4. The structure given is a positive ion with all octets filled. Does it engage in resonance?

Thinking about the geometry of resonance discussed in Section 2.4 gives us a clue that it might. There are two double bonds with a single bond spaced between them. That means there are four p-orbitals that could be aligned to delocalize electrons. But how do we draw a resonance structure based on this?

We can try any number of strategies. But the two -CH<sub>2</sub>- groups on the left-hand side of the ring put some limits on the available structures. Remember that atoms must be in the same place in all resonance structures, so those C-H bonds must remain in place. That makes it impossible to have a resonance structure that creates a double bond with the carbons in those -CH<sub>2</sub>- groups, because that would overfill the octets on the C (try it!). But we can create a double bond between the two carbons on the right-hand side of the molecule, if we can find a way to shift electrons to make that happen.

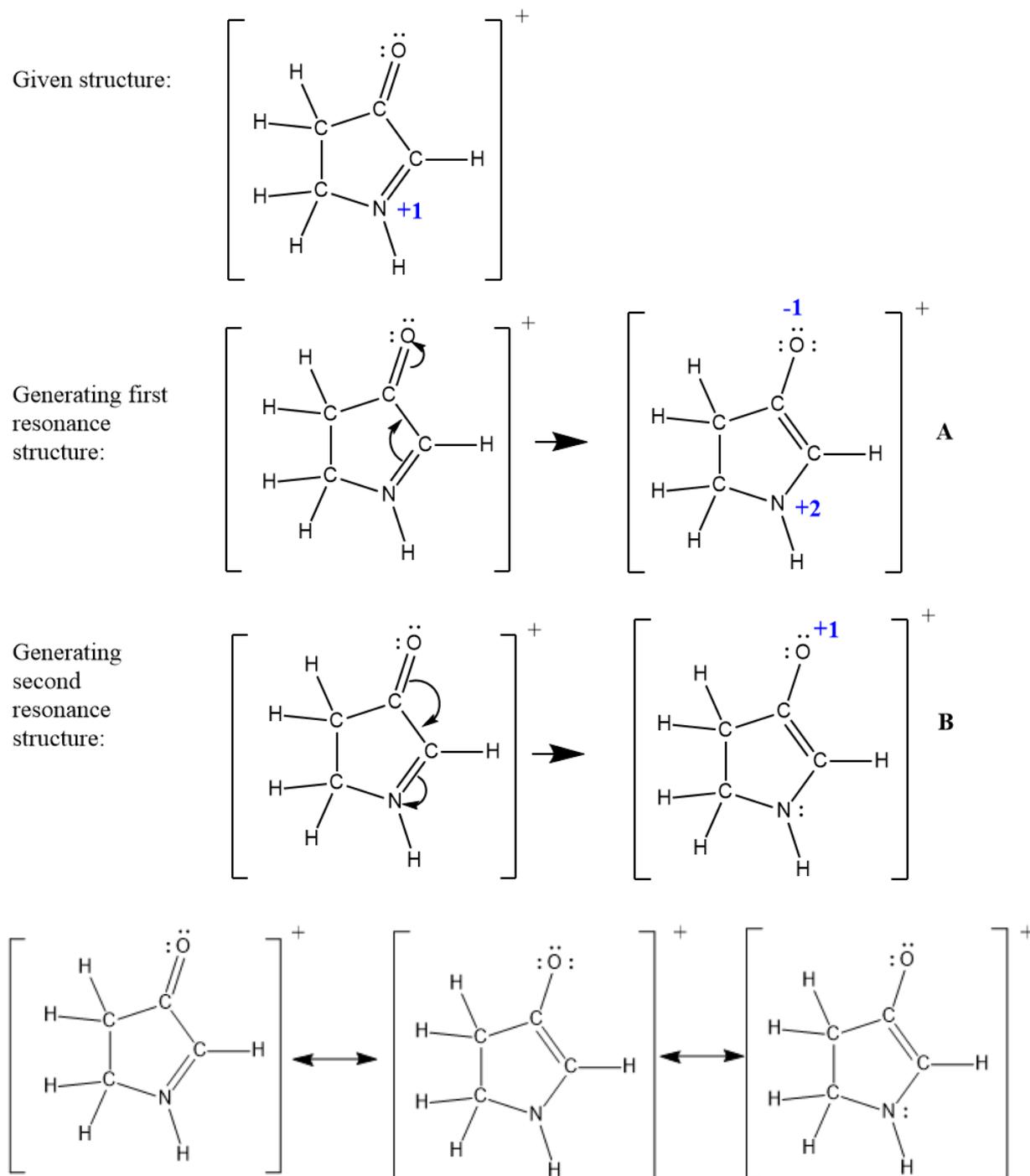
The N=C double bond in the original structure can provide a pair of electrons for the C=C bond in the new structure, so we will try that first. But creating that double bond would overfill the octet on the topmost C atom in the ring, so we cannot leave the bonds to the O atom in place. Instead, we use a second arrow to move a pair of electrons out of the C=O bond to make a lone pair on the O atom.

The new structure, labeled A, is drawn. Looking at the rules from Table 3.3.1, we see that it is a relatively poor resonance structure. It does not fill valence shells (N is underfilled) and it does not maximize the number of covalent bonds (13 vs. 14 for the original structure). Nor does it lead to the least separation of charges (compare it to the +1 charge on the N in the original structure). However, it does put the negative charge on the O, the most electronegative atom. Since it satisfies one rule, it should be drawn, but it is clearly a minor structure.

We use the arrows to generate a second structure, B, below that. Structure B suffers from the same problems as Structure A (underfilled octet on O, only 13 covalent bonds) but it does not separate charges as much as Structure A does. However, it does lead to less charge separation than Structure A, so it should be drawn and is probably more significant than Structure A. However, it puts the +1 charge on the more

electronegative atom (the O) compared to the original structure (A), so it is less significant than the original structure.

Another example is given in Figure 3.4.4. The structure given is a positive ion with all octets filled. Does it engage in resonance?



**Figure 3.4.4:** Constructing resonance structures for a sample molecule, as described in the text. Formal charges are given in blue.

Thinking about the geometry of resonance discussed in Section 2.4 gives us a clue that it might. There are two double bonds with a single bond spaced between them. That means there are four p-orbitals that could be aligned to delocalize electrons. But how do we draw a resonance structure based on this?

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The  $\text{N}=\text{C}$  double bond in the original structure can provide a pair of electrons for the  $\text{C}=\text{C}$  bond in the new structure, so we will try that first. But creating that double bond would overfill the octet on the topmost C atom in the ring, so we cannot leave the bonds to the O atom in place. Instead, we use a second arrow to move a pair of electrons out of the  $\text{C}=\text{O}$  bond to make a lone pair on the O atom.

The new structure, labeled A, is drawn. Looking at the rules from Table 3.3.1, we see that it is a relatively poor resonance structure. It does not fill valence shells (N is underfilled) and it does not maximize the number of covalent bonds (13 vs. 14 for the original structure). Nor does it lead to the least separation of charges (compare it to the +1 charge on the N in the original structure). However, it does put the negative charge on the O, the most electronegative atom. Since it satisfies one rule, it should be drawn, but it is clearly a minor structure.

We use the arrows to generate a second structure, B, below that. Structure B suffers from the same problems as Structure A (underfilled octet on O, only 13 covalent bonds) but it does not separate charges as much as Structure A does. However, it does lead to less charge separation than Structure A, so it should be drawn and is probably more significant than Structure A. However, it puts the +1 charge on the more electronegative atom (the O) compared to the original structure (A), so it is less significant than the original structure.

This completes the toolkit for understanding resonance as represented in Lewis structures. We can draw Lewis structures for the resonance forms, confirm that they are valid, and rank their relative importance as contributors to the true electronic structure of the molecule. Resonance is particularly important in understanding the behavior of two classes of organic compounds: Conjugated molecules and aromatic molecules. We look at both in the next section.

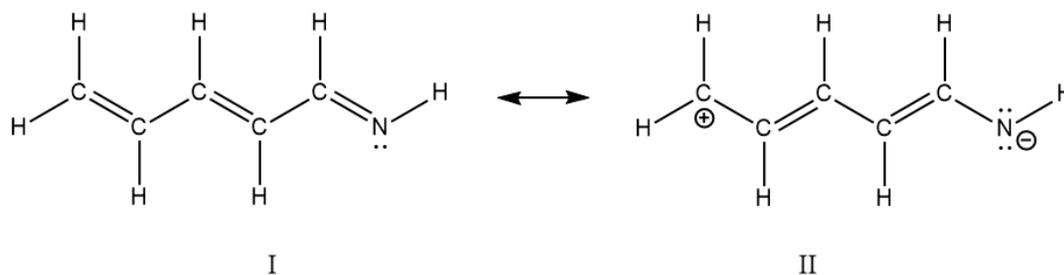
## Section 3.5: Conjugation and Aromaticity

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand what is meant by “conjugation” and “aromaticity,” and be able to identify conjugated and aromatic structures.
- Understand that some conjugated structures do not meet our criteria for having resonance structures, but nevertheless engage in resonance, as demonstrated by experiment.

As the examples above illustrate, systems with alternating double and single bonds will often engage in resonance. Such systems are referred to as conjugated, and it is a good idea to look for resonance when you encounter them.

Figure 3.5.1 is an example of this. Structure I has alternating double and single bonds, and its formal charges are uniformly zero. Structure II is valid, but not favored (underfilled octet, too few covalent bonds, a separation of charges – but the negative charge does go on the more electronegative element). While Structure II is minor, it does contribute to the structure. The molecule is planar, and electrons do delocalize over the entire chain. (Note that we have adopted the conventional “+” and “-“ notation to indicate formal charges in Lewis structures, as opposed to the blue numbering from the previous sections).



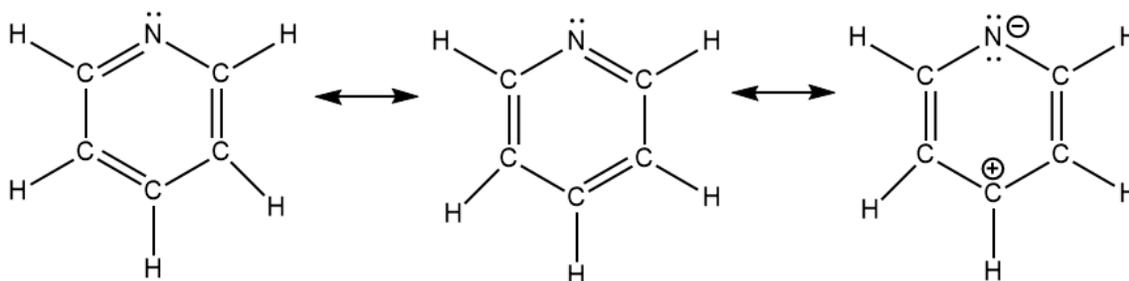
**Figure 3.5.1:** Sample resonance structures for a conjugated molecule.

The fact that there are ends to the chain works against delocalization. In order to shift the bonds in the conjugated structure, it is necessary to create formal charges at the ends and to leave an octet underfilled, as we did in Figure 3.5.1. This works against the delocalization of charge.

Compare that to the structure of benzene given in Figure 2.4.5. The two equivalent structures emerge in part because of the lack of endpoints, as the formal charges for all C atoms in the ring can remain zero.

As a more complete illustration of this phenomenon, look at the resonance structures in Figure 3.5.2. The molecule shown amounts to a ring version of the molecule in Figure 3.5.1, formed by taking a H-atom off of each end of the molecule and making it into a ring. But doing so adds a second, major resonance structure (center), as well as a minor contributor that places some excess negative charge on the N atom. The presence of the second resonance structure indicates that electrons are more completely delocalized than in the linear molecule shown in Figure 3.5.1.

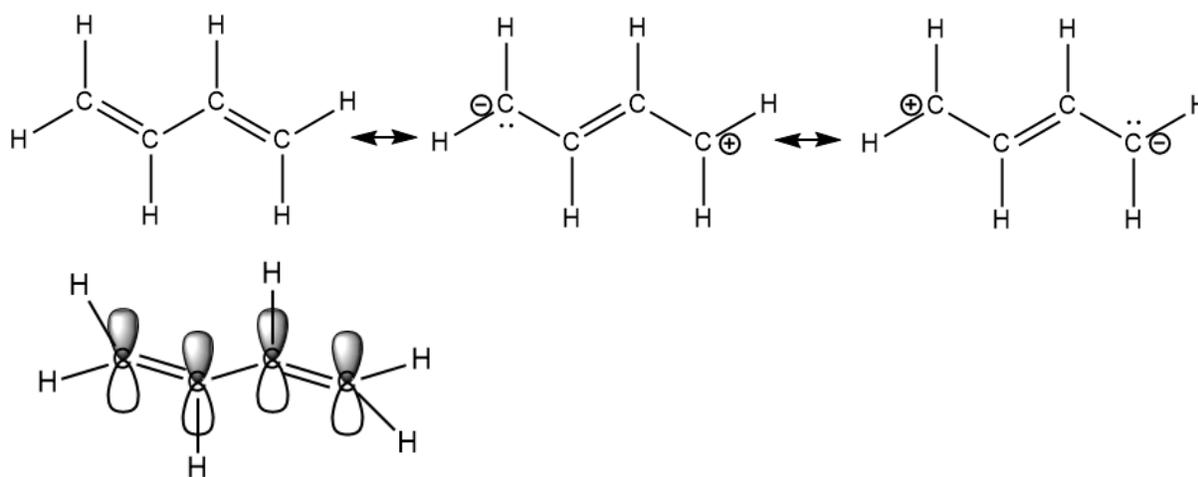
This is a general pattern and arises from real, physical effects. Atoms at the endpoints of a chain can only share electrons in one direction, while those within the chain can share them in two. This creates a broader physical space in which the electrons can delocalize, reducing their energy. Looping into a ring to eliminate the endpoints therefore tends to promote fuller delocalization than an open chain.



**Figure 3.5.2:** Sample resonance structures for an aromatic molecule.

Ring structures consisting of alternating double and single bonds are said to be aromatic, and generally display significant delocalization of electrons (the name “aromatic” is historical – having a strong aroma is not a universal property of these systems).

One more comment on conjugated systems is worth considering. Consider the molecule shown in Figure 3.5.3. Examining the second and third structures, one would conclude from our rules that they should not be drawn as resonance structures. They each have an underfilled octet on a terminal carbon, fewer covalent bonds than the left-most structure, and a separation of charges that is not supported by electronegativity. Table 3.3.1 would imply that these structures should not be drawn and that the molecule should not be considered to have any resonance structures.

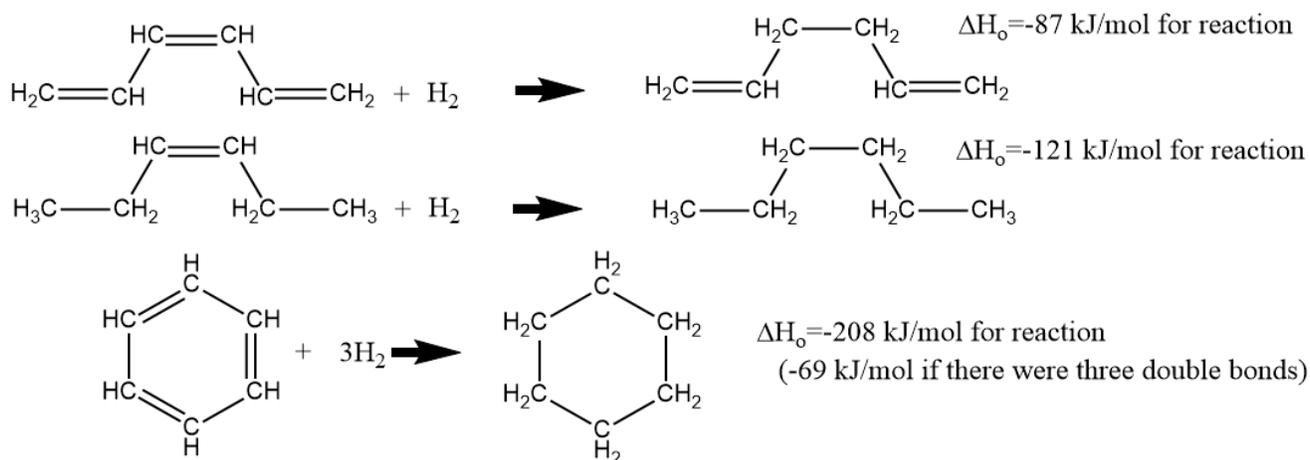


**Figure 3.5.3:** Top: A conjugated molecule with resonance structures that ought to be invalid. Bottom: Alignment of the p-orbitals in the molecule.

However, Nature does not read textbooks. This molecule has been studied experimentally and found to be planar, and to have physical and chemical properties that confirm that it engages in resonance. That makes sense when one considers the alignment of the p-orbitals shown in the bottom-half of Figure 3.5.3. The central 2 p-orbitals are aligned just as fully as the ones associated with the double-bonds drawn, so there is no reason for electrons in the orbitals to prefer one direction or the other.

The failure of the rules given in Table 3.3.1 to identify resonance in the simplest conjugated systems reflects something we warned you about in Section 2.4: Any attempt to use Lewis structures to model resonance is inherently clumsy and may be error prone. While the rules given in Table 3.3.1 are correct more often than they are wrong, some awareness of their limitations is necessary.

You will learn more about conjugated and aromatic systems when you study organic chemistry more fully. For now, simply be able to recognize a conjugated molecule as one containing a chain of alternating double- and single-bonds when drawn as a Lewis structure, and an aromatic molecule as a system containing at least one conjugated ring.



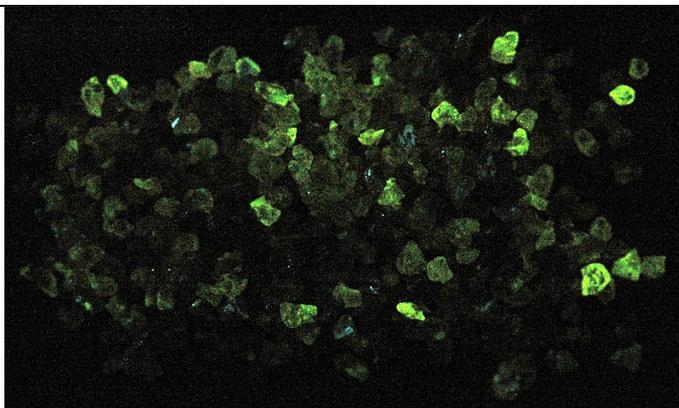
**Figure 3.5.4:** Top: Hypothetical reaction of a linear, conjugated molecule losing its central bond, and therefore breaking conjugation (heat of reaction determined by comparison of heats of reaction of different reactions).

Center: Reaction of a linear, unconjugated molecule analogous to the conjugated molecule above. The hydrogenation reaction for this molecule releases significantly more heat than that of the conjugated system, indicating that resonance stabilization is important for the molecule.

Bottom: Hydrogenation of benzene. The average heat of hydrogenation per bond has a lower magnitude than that of the linear, conjugated molecule, confirming that resonance more effectively stabilizes cyclic structures than linear ones, as discussed in the text.

# CHAPTER 4: Concepts in Organic Chemistry

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Diamonds are structures made of pure carbon. The diamonds shown above are undergoing phosphorescence, emitting green light after exposure to ultraviolet radiation.

*Image courtesy of Wikimedia Commons,  
[https://commons.wikimedia.org/wiki/  
File:Diamonds\\_phosphorescing\\_\(Zaire\)\\_\(17987449601\).jpg](https://commons.wikimedia.org/wiki/File:Diamonds_phosphorescing_(Zaire)_(17987449601).jpg),  
Accessed July 10, 2021.*

CHEMISTRY DISSOLVES  
THE GODDESS IN THE  
ALEMBIC,  
VENUS THE WHITE  
QUEEN, THE UNIVERSAL  
MATRIX,  
DOWN TO MOLECULAR  
HEXAGONS AND  
CARBON-CHAINS,  
-KATHLEEN RAINE, "THE  
HUMAN FORM DIVINE"

*This quote about chemistry, while perhaps less than flattering to the field, rightly emphasizes the central role of carbon chemistry. With its ability to form chains and its capacity for double and triple bonds, carbon's versatility is unique and it is at the center of both biology and the 21<sup>st</sup> century economy.*

## BEFORE YOU BEGIN, MAKE SURE YOU KNOW

- Orbital hybridization and pi bonding vs. sigma bonding (Chapter 2)
- Conjugation and aromaticity (Chapters 2 and 3)
- VSEPR rules and molecular geometry (Flowers, sec 7.6)
- Intermolecular Forces (Flowers, sec 10.1)

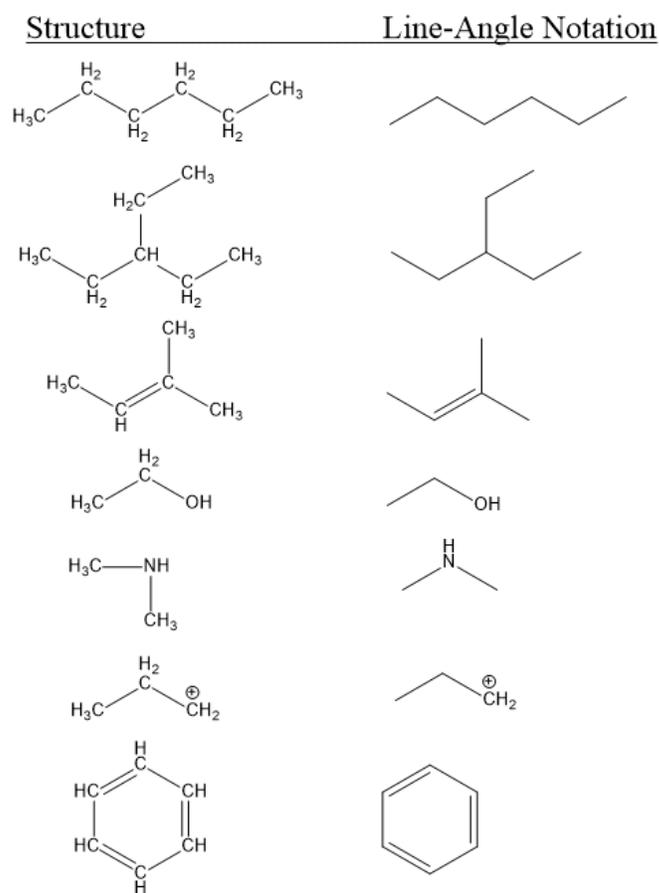
## Section 4.1: Notation

### LEARNING OBJECTIVES FOR THIS SECTION

- Be able to read line-angle notation and convert back and forth between line-angle notation and full formulas.
- Be able to read compressed formulas, and be able to convert them to other notations.
- Understand the pitfalls of working with a notation that does not include hydrogen atoms explicitly, and consider making use of prime notation to avoid those pitfalls.

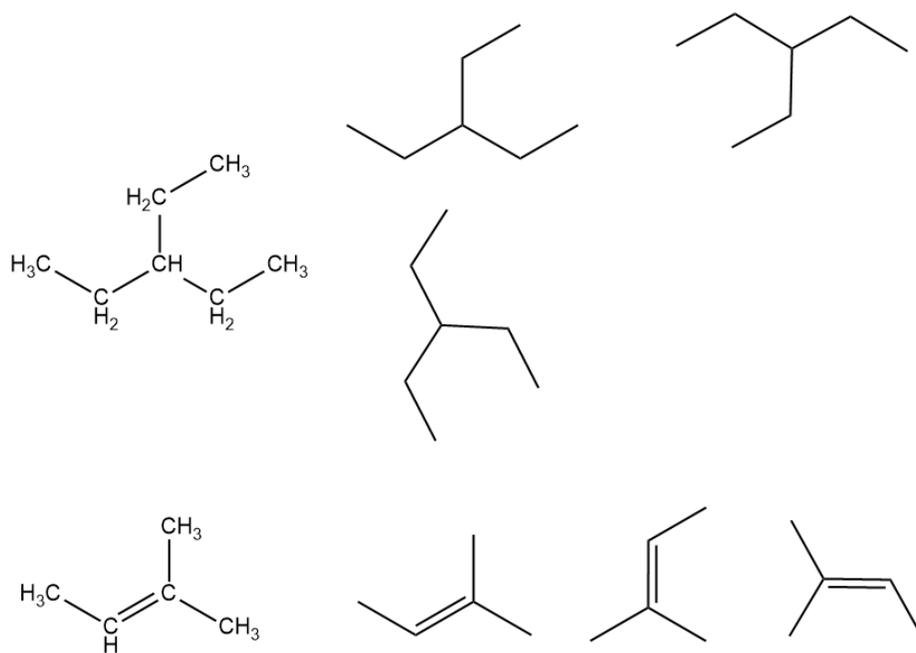
We have discussed a wide range of chemical structures in the first three chapters of this book, and by now you should have realized that an enormous variety of carbon-based compounds are possible. We have not seen long chains of other atoms such as -O-O-O-O- or -N=N-N=N- because they are unstable. N<sub>2</sub> and O<sub>2</sub> are both very stable molecules, so attempts to build longer chains will often collapse into these smaller molecules. Carbon does not form a stable C<sub>2</sub> or similar small molecule, so its hydrogen-decorated chains are relatively stable. Of course, these compounds burn in the presence of oxygen, but the activation energy is high enough for these reactions that they do not occur at room temperature (this is why you need a match to light a natural gas burner).

**Figure 4.1.1:** A series of chemical structures and their expressions in line-angle notation.



**Line-Angle Notation:** Having laid the groundwork in our discussion of chemical bonding, we are now ready to start working with carbon structures in detail. As a first order of business I must inform you that I, your humble scribe for this modest volume, am sick of writing organic structures in detail. So I am going to introduce a standard shorthand for chemistry known as line-angle notation.

The idea is simple: Large parts of organic molecules consist of chains of carbons bonded either to other carbons or to hydrogens. We do not want to bother writing the letter “C” for every carbon, so we will just draw bonds with angles between them. Anywhere two bonds join but there is no atom drawn, we will assume there is a C. Likewise, we will assume the reader understands the octet rule and knows C should have 4 bonds. So, we will simply not draw H atoms at all, and let the reader fill them in in their imagination. We do need to draw atoms other than C or H, and if C has an underfilled octet we will need to indicate that as well. And we must draw H-atoms attached to atoms other than carbon (e.g. -OH is acceptable, but -O does not indicate the presence of a H on the O). Figure 4.1.1 gives a series of chemical structures and their expressions in line-angle notation.



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**Figure 4.1.2:** A series of line-angle structures drawn at different angles. All of the line-angle structures on the right are representations of the chemical structures shown at the left.

---

**Tips and Tricks for Line-Angle Notation:** Line-angle notation can be deceptively simple. Figure 4.1.2 shows some examples of the same chemical structure rotated to different angles. It is important to become proficient enough at reading line-angle structures to quickly spot identical structures and to identify differences between them. To help develop this skill, we introduce three practices: Identifying and numbering the longest carbon chain, “flipping” the numbering, and identifying the character of the carbon. It is worthwhile investing the time in learning these skills, as the first two are central to nomenclature and the third plays an important role in the reactions of hydrocarbons.

---

### Tricks for Analyzing Line-Angle Diagrams

- Identify the longest continuous carbon chain.
  - Change the numbering of the carbon chain.
  - Identify the character (primary, secondary, etc.) of the carbon atoms.
- 

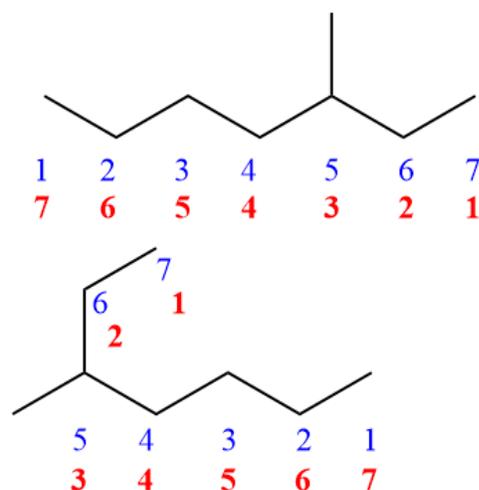
**Table 4.1.1:** A series of line-angle structures drawn at different angles. All of the line-angle structures on the right are representations of the chemical structures shown at the left.

---

Figure 4.1.3 shows two examples of numbering the longest continuous carbon chain. It is important to note places where the chain bends, as in the bottom structure, but otherwise identifying the longest chain is relatively straightforward. Likewise, once it has been identified, two possible numberings (forward and backward) are possible. This is a seemingly trivial exercise, but it is worth doing at least until you have become comfortable with complex organic structures.

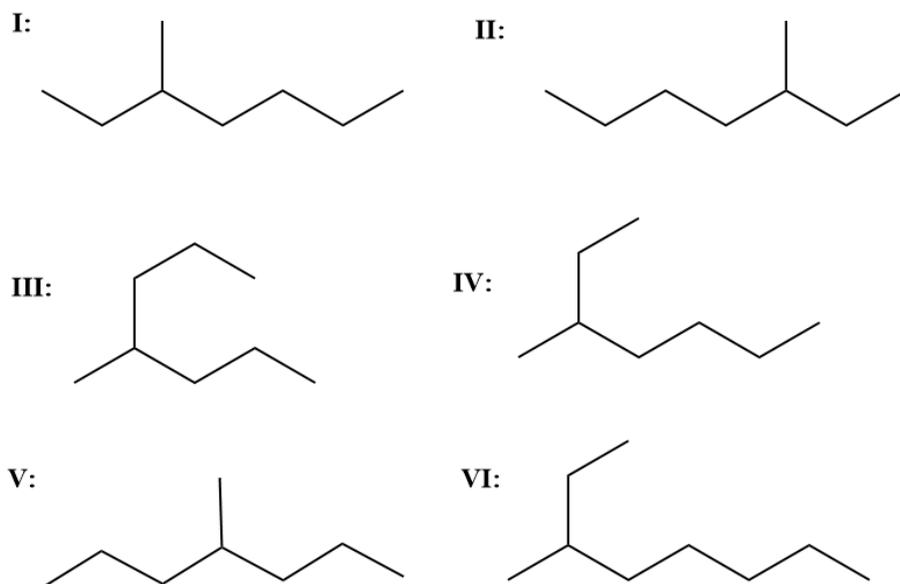
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**Figure 4.1.3:** Sample numberings of the longest carbon chain, showing two possible numbering schemes.



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Figure 4.1.4A shows a series of six structures. Some of the structures are identical, and some are different from each other. Identify which are identical, and then compare your answers to those in Figure 4.1.4B. You are strongly advised to number the chains when making this assessment.



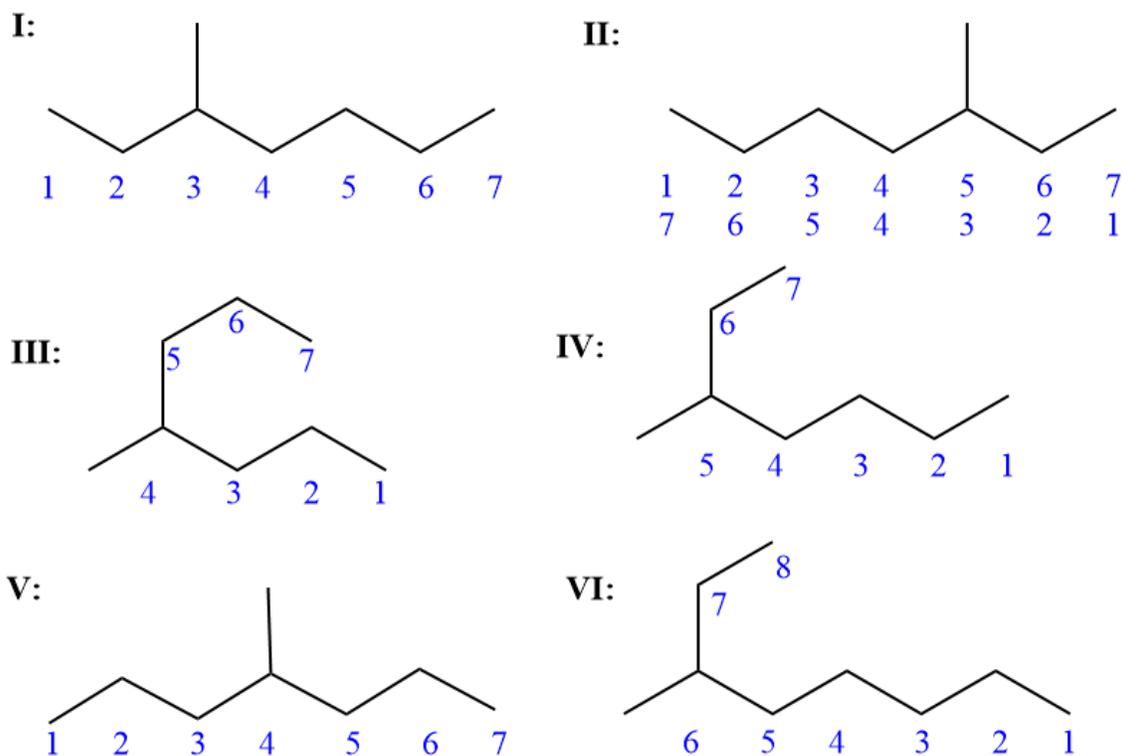

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**Figure 4.1.4A:** Which of the structures shown above are identical?

---

Figure 4.1.4B shows some possible numbering schemes, and we will reference these as we attempt to identify which molecules are identical and which are different. First, we can conclude that Structure VI is not the same as any other, as it has an 8-carbon chain while all others have only a 7-carbon chain.

Now, let us look at Structure I. It has a 7-carbon chain with a 1-carbon unit branching off of it from the third carbon. At a glance, Structure II might look different, but when the numbering is reversed it is clear that they are the same (a 1-carbon unit branching off from the third C).



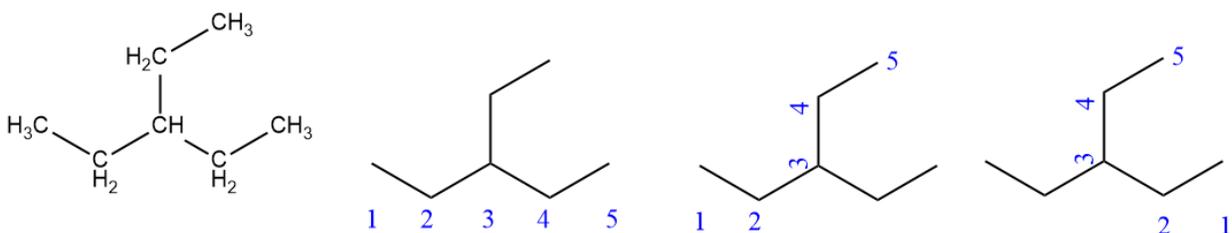
**Figure 4.1.4B:** Numberings of the longest continuous carbon chain. See text for discussion.

With both numberings printed on Structure II, we can see how to compare that structure with others. We are looking for a 7-carbon chain with a 1-carbon unit branching off from either the 3<sup>rd</sup> or the 5<sup>th</sup> carbon, depending on how we have chosen to number the chain. Structures III and V do not match this, as they have a branch from the 4<sup>th</sup> C. But Structure IV does match. So, Structures I, II, and IV are identical.

Structures III and V are the same, as both involve 1-carbon branches from the 4<sup>th</sup> carbon. And, as noted above, Structure VI is unique in the set.

**Take Note!** When we are comparing structures like this, there is no “wrong” way to number a chain. Later, we will learn about nomenclature and discover that naming the compound requires us to number the chain according to very specific conventions. But let’s not get ahead of ourselves.

Numbering the chain is a useful thing to do, and understanding that the numbering can be flipped is important. But one can encounter systems where the numbering is ambiguous in the sense that there can be more than one numbering scheme that gives the same answer. Figure 4.1.5 shows an example of this. The molecule shown has a longest chain that is five carbons long, and a two-carbon chain coming off of the 3<sup>rd</sup> carbon. And this is the result of three different possible numbering schemes, even before one considers reversing the scheme. This may seem a bit odd, but it does not pose a problem. If all three are equivalent, you can simply choose whichever scheme is most convenient to do and picture the molecule in that way.



**Figure 4.1.5:** A series of line-angle drawings identifying the longest carbon chain in each molecule. In the row, the structure is drawn the same way but appears to be numbered differently each time. In the bottom row, the structure is rotated and some sample numberings are shown.

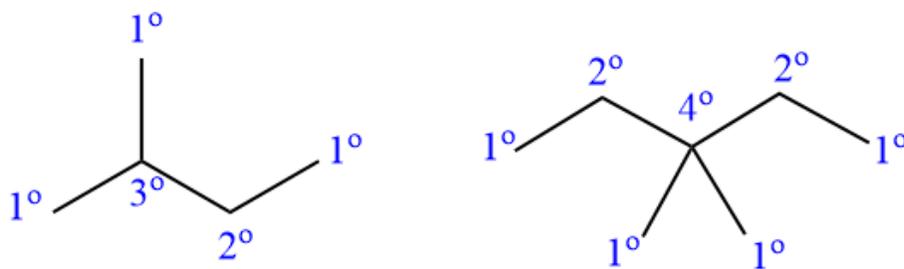
The last item in Table 4.1.1 was identifying the type of carbon atom. A common convention in chemistry is to label carbons as primary, secondary, etc. per the scheme given in Table 4.1.2. The application of the scheme is shown in Figure 4.1.6.

### Types of carbon atoms in alkanes

- A carbon is primary ( $1^\circ$ ) if it is bound to only one other carbon atom.
- A carbon is secondary ( $2^\circ$ ) if it is bound to exactly two other carbon atoms.
- A carbon is tertiary ( $3^\circ$ ) if it is bound to exactly three other carbon atoms.
- A carbon is quaternary ( $4^\circ$ ) if it is bound to exactly four other carbon atoms.

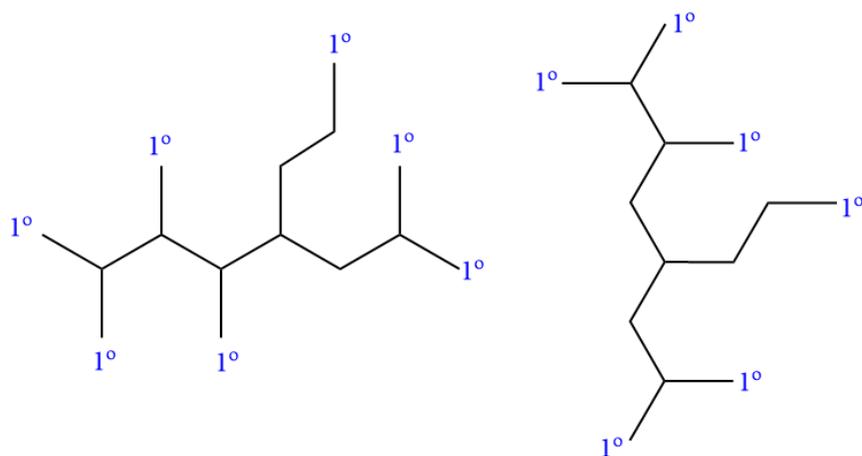
**Table 4.1.2:** Naming types of carbons in alkanes.

In terms of identifying isomers this is less definitive than identifying the longest continuous chain and its branches, and in fact it would not have been useful for the examples in Figure 4.1.4A. Structures I-V have the same number of primary, secondary, tertiary, and quaternary carbons, even though they have different structures. But Figure 4.1.7 provides an example where it could be useful as a quick check to count the number of primary carbons and save yourself the trouble of counting carbon chains.



**Figure 4.1.6:** Types of carbons in alkanes.

The conventions for identifying primary through quaternary carbons are actually more useful in other contexts. Carbons of different types undergo different chemical reactions. For that reason, hydrogens are also often referred to as primary through tertiary (think about why there would be no quaternary hydrogens).



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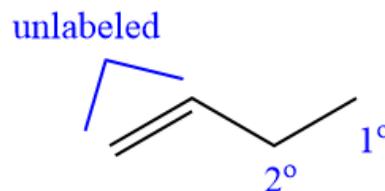
**Figure 4.1.7:** An example of how structures can be distinguished from each other by examining the types of carbons present. There are seven primary carbons in the left-hand structure, and only six in the right-hand structure.

---

The truth is that the terminology is used a bit more broadly than we will use it here. In most conventions, it can be used to describe any  $sp^3$ -hybridized carbon that is bound only to other carbons and hydrogens. So, carbons in alkenes, alkynes, and aromatics could be labeled in this scheme provided they are involved only in single bonds. An example is given in Figure 4.1.8.

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**Figure 4.1.8:** Labeling types of C atoms in a non-alkane hydrocarbon.



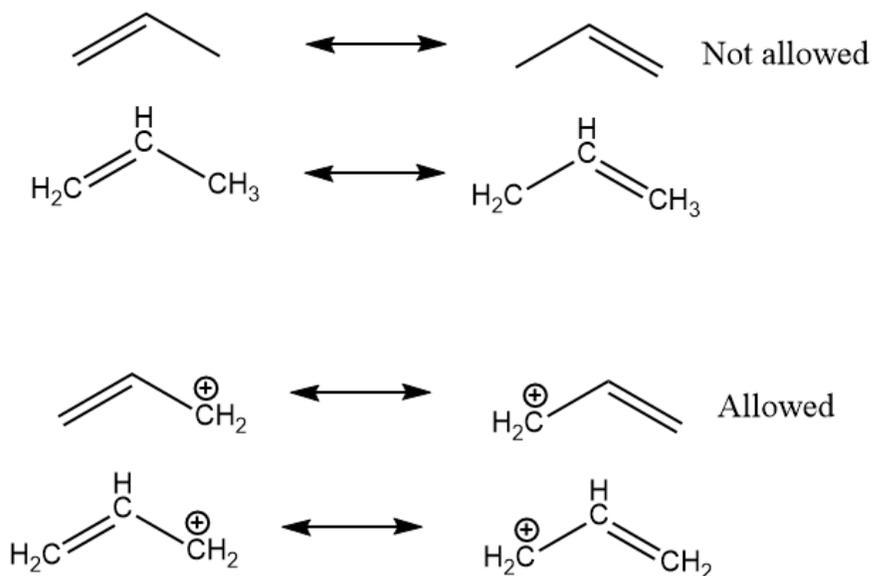
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Finally, we want to highlight one more potential pitfall of line-angle notation and suggest a workaround. This is not a “real” notation, and it would never be used to present information in a professional setting or in the final answer to a problem. But it is a useful trick for solving problems while getting used to line-angle notation.

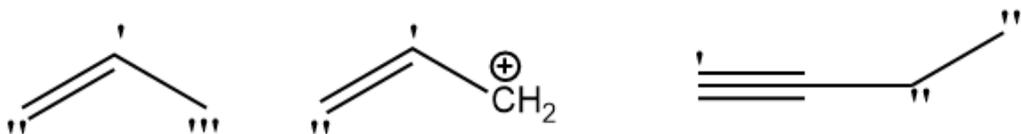
Hiding the hydrogen atoms in a line-angle structure saves a great deal of writing, but creates the risk that a reader will forget that they are there. An example is given in Figure 4.1.9, in which an invalid resonance structure is created because H atoms are overlooked in the line-angle structure.

---

**Figure 4.1.9:** Top shows an invalid resonance structure drawn based on line-angle notation (the octet on the right-most C atom is overfilled). The bottom shows a similar structure where resonance is allowed.



As a way around this, we would like to share with you the idea of prime notation. The idea is simply to use hash marks to count the number of H atoms present when using line-angle notation. Some examples are given in Figure 4.1.10. Again, this is not a formal notation and should not be used in the final answer of a question, but can be a useful guide while working through the structure, at least until you are accustomed to line-angle notation.



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**Figure 4.1.10:** Line-angle notation with prime notation to indicate the number of H atoms bound to each carbon, as described in the text.

---

**Wedge-Angle Notation:** Line-angle notation is useful for writing large structures quickly, but neither it nor conventional bonding structures give information on the geometry of a molecule. For that, we need wedge-angle notation.

Linear or planar molecules can be drawn on a page without sacrificing information about their geometry, but tetrahedral centers necessarily require the author to provide information about their structure in three-dimensions. In wedge-angle notation, this is done with three conventions:

- Bonds that lie within the plane of the page are straight, undashed lines.

- Bonds that come out of the page toward the reader are indicated with a solid wedge.
- Bonds that go into the page away from the reader are indicated with a dashed line or wedge.

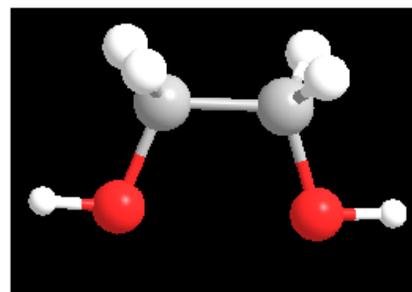
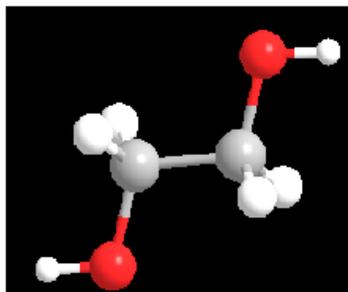
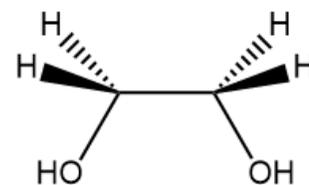
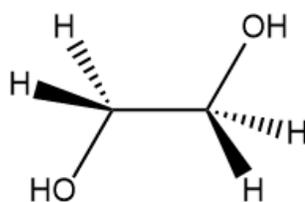
Note that, as in line-angle notation, the C atoms are implied by the connection of lines rather than the letter “C” being drawn.

An example of this representation is given in Figure 4.1.11. In this case, we show the same molecule with the molecule twisted into different geometries by rotation around the C-C bond. In one case, the -OH groups are on opposite sides of the molecule, and in the other they are on the same side. Rather than being different molecules, this is the same molecule in different conformations.

The truth is that at room temperature most molecule rotate freely around single bonds. So, if one had a sample of this compound sitting in a container, at any given moment some of the molecules would be in the first conformation and some in the second, and all of them would be changing as the C-C bond rotated in random thermal motion.

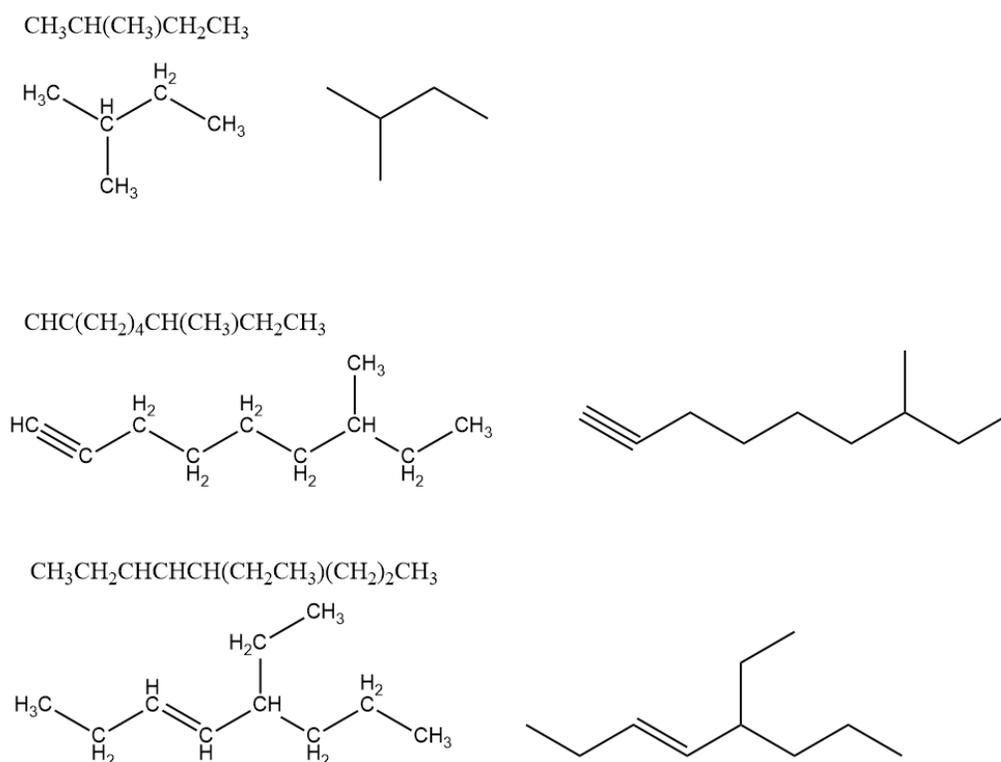
We will make some use of this notation in Section 4.3, and a great deal more use in Chapters 5 and 6. Rather than introducing it more fully now, we will expand on it as we go, but we introduce it here so we do not have to digress to introduce it later.

**Figure 4.1.11:** Wedge-angle notation and the three-dimensional structure it represents. Carbons are in dark gray, hydrogens are white, and oxygens are red. This is the same molecule, but with the groups rotated around the single bond.



**Other Notation:** Other shorthand notations are also used in chemistry. It is sometimes convenient to indicate a chemical structure within a block of text by listing groups of atoms in a line with parentheses to indicate a chain that has diverged from the main. The reader is left to infer the presence of double and triple bonds by the number of hydrogens attached to a given atom. So, for example,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  would be a straight carbon chain four atoms long, while  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$  would be a 3-carbon chain with a  $-\text{CH}_3$  group coming off the central carbon. The second C atom from the left has only one  $-\text{H}$  attached to it, because it is bonded to three other carbons (two in the chain and one branching off of it). More examples are given in Figure 4.1.12. You will also sometimes see parentheses and subscripts used to indicate long, repeating chains. For

example,  $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$  indicates a chain that is seven carbons long (-CH<sub>3</sub> groups at the end, with a chain of five -CH<sub>2</sub>- groups connecting them).




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**Figure 4.1.12:** A series of chemical structures and their expressions in line-angle notation.

---

Like line-angle notation, this does not provide the information on molecular geometry or conformation that is given in wedge-angle notation.

## Section 4.2: Hydrocarbons

### LEARNING OBJECTIVES FOR THIS SECTION

- Know the definition of a hydrocarbon, and the four sub-categories of hydrocarbons.
- Be able to identify hydrocarbons as belonging to one of the four categories.
- Understand what is meant by a saturated vs. unsaturated hydrocarbon, and be able to recognize each.

Our introduction of notation complete, we introduce the simplest class of organic compound: Hydrocarbons. These are compounds composed only of hydrogen and carbon, and so every one of them can be written with the formula  $C_xH_y$ , where  $x$  and  $y$  are some integers.

### Types of Hydrocarbons

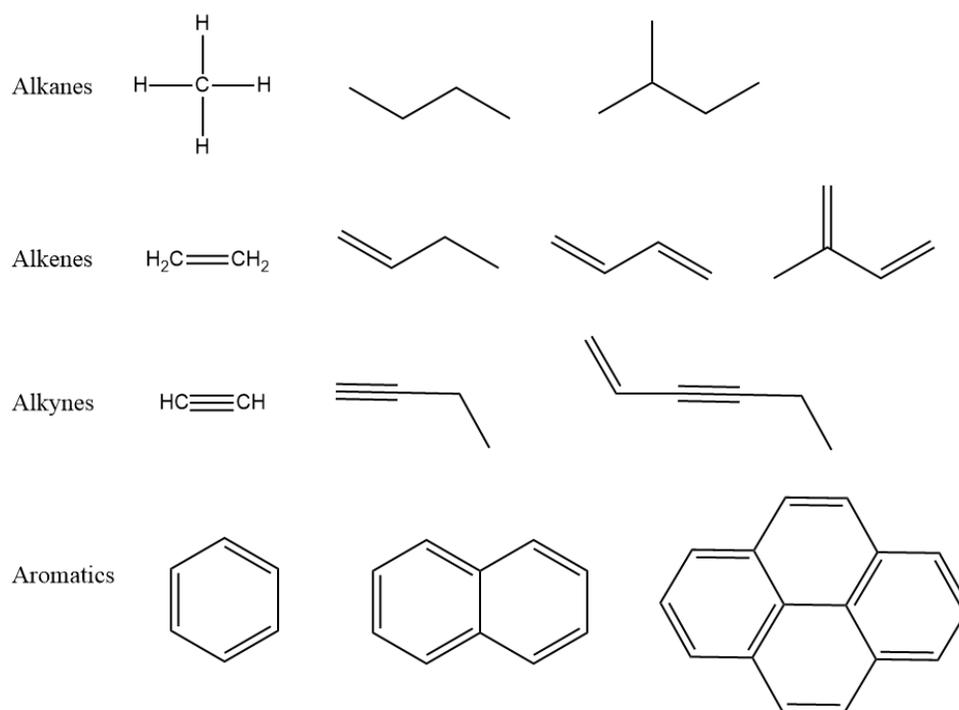
- **Alkanes:** Hydrocarbons containing only single bonds.
- **Alkenes:** Hydrocarbons containing at least one double bond, but no triple bonds. This category does not include aromatics (see below).
- **Alkynes:** Hydrocarbons containing at least one triple bond.
- **Aromatics:** Cyclic hydrocarbons with alternating double and single bonds; see Section 3.5 for a discussion of their resonance stabilization.

**Table 4.2.1:** Classes of hydrocarbons.

Even this simple category permits a bewildering range of compounds, and so we break the category down into an additional four sets of compounds listed in Table 4.2.1. The definitions are based on the presence of different types of bonds. A hydrocarbon that contains only single bonds is an alkane. If it contains at least one double bond it is an alkene; it may contain any number of single bonds, but if it contains a double bond it is an alkene. Likewise, an alkyne is a hydrocarbon that contains at least one triple bond, though it may contain double and single bonds as well. Aromatics would appear to be alkenes, but are given their own category. Some samples of each are given in Figure 4.2.1.

These divisions may seem arbitrary, but in fact they are useful. We have already seen in Section 3.5 that aromatic molecules display a particularly high degree of resonance stabilization, which affects their heat of hydrogenation. There are chemical differences between alkanes, alkenes, and alkynes that make it worthwhile to distinguish between them as well; we will find an example of this when we discuss cis-/trans-isomerization in alkenes in Section 4.3.

A useful idea is the concept of saturation. In this case, saturation refers to the hydrocarbons' ability to take in additional hydrogen atoms without breaking into smaller molecules. Aromatics, alkynes, and alkenes are unsaturated hydrocarbons, because one can add hydrogen to a double- or triple-bond and convert it into a single bond without breaking up the carbon skeleton of the compound (i.e. leaving at least a single bond between all C atoms that were connected in the original structure). Alkanes are said to be saturated hydrocarbons, meaning that they are hydrocarbons that cannot take up additional hydrogen without breaking into smaller molecules. Alkanes are sometimes said to be aliphatic, which is synonymous with saturated.



**Figure 4.2.1:** Classes of hydrocarbons.

## Section 4.3: Isomerism in Hydrocarbons

### LEARNING OBJECTIVES FOR THIS SECTION

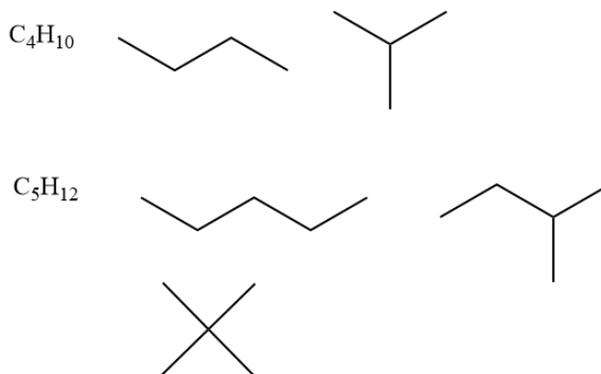
- Understand what isomers are, and be able to recognize whether two molecules are isomers.
- Understand what constitutional isomers, and be able to recognize whether two molecules are constitutional isomers.
- Understand what stereoisomers are, and how they differ from constitutional isomers.
- Understand the physical origin of cis-/trans- isomerism around double bonds, and explain why single and triple bonds do not engage in cis-/trans- isomerism.
- Be able to recognize whether a given molecule containing a double bond will engage in cis-/trans- isomerism. If it does, you should be able to identify it as being either cis- or trans-, and to draw the other isomer from the pair.
- Understand cis-/trans- isomerism in ring systems, and be able to recognize whether a given molecule containing a ring will engage in cis-/trans- isomerism. If it does, you should be able to identify it as being either cis- or trans-, and to draw the other isomer from the pair.
- Given a chemical formula for a hydrocarbon, you should be able to draw some examples of stereoisomers and constitutional isomers for that molecule.

The versatility of carbon atoms makes them a bit like childrens' blocks, in that it is possible to start with a simple set of materials and build a huge variety of structures. Chemically, this means that more than one molecule can have the same chemical formula. Different molecules with the same chemical formula are referred to as isomers.

Two examples are given in Figure 4.3.1 for alkanes. There are two possible structures with formula  $C_4H_{10}$  and three with formula  $C_5H_{12}$ . Even for acyclic (non-ring-containing) alkanes, the number of isomers increases rapidly with the number of carbons present. There are five isomers for  $C_6H_{14}$ , nine with formula  $C_7H_{16}$ , 75 with formula  $C_{10}H_{22}$ , and over 4,000 with formula  $C_{15}H_{32}$ . Further, these formulas all correspond to those of saturated hydrocarbons. As soon as one allows unsaturated structures, entirely different kinds of isomerism become possible.

We will discuss two types of isomerism: Constitutional isomerism and stereoisomerism. Constitutional isomerism is the type shown in 4.3.1, where the same combination of atoms is put together with a different arrangement of bonds. Stereoisomerism consists of molecules that have the same connectivity for the atoms – meaning that the atoms all have the same number and type of bond – but they are connected at different angles. Our first example of that, cis-/trans-isomerism, will require us to take a closer look at the nature of bonding.

**Figure 4.3.1:** Isomers with formula  $C_4H_{10}$  and  $C_5H_{12}$ .

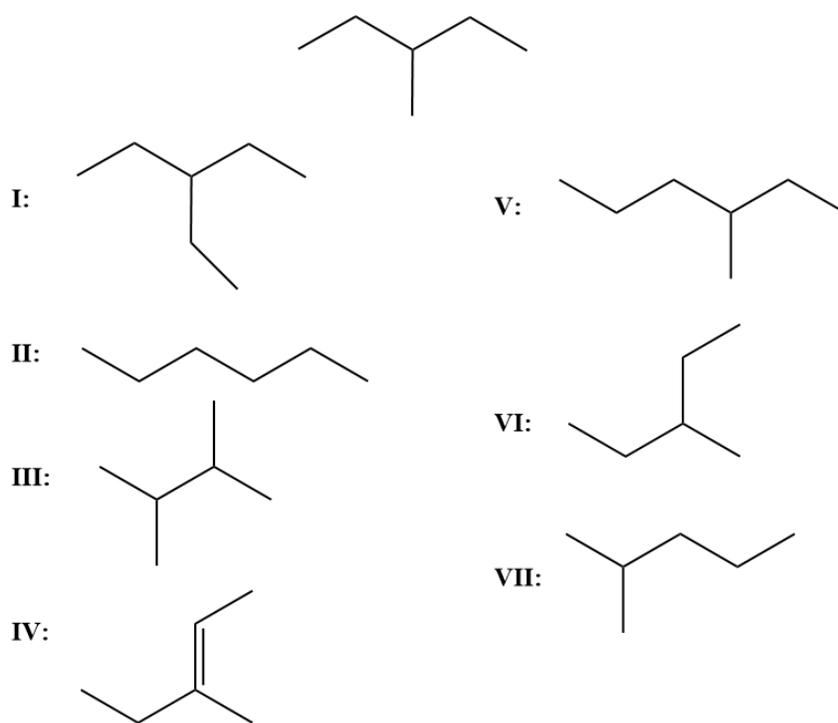


**Constitutional Isomerism:** We have already provided some examples of constitutional isomers in Figure 4.3.1.  $C_4H_{10}$  has two isomers formed by putting the same set of atoms together with a different arrangement of bonds. One has a straight chain that is four carbons long, while the other can be viewed as having a chain that is three carbon atoms long with a carbon branching off the chain at the second carbon atom.

In hindsight, it is clear that our discussion of line-angle structures in Section 4.1 also touched on the idea of isomerism. In Figure 4.1.4B, the molecule represented by Structures I, II, and IV was different from the molecule represented by Structures III and V. But both had the chemical formula  $C_8H_{18}$ .

For reasons that will become clear in the next section, acyclic alkanes are only capable of constitutional isomerism, not stereoisomerism. So we will use them as an example to demonstrate constitutional isomerism in more detail.

Look at the structures shown in Figure 4.3.2A. Try to work out which of the structures shown are isomers of the original molecule shown at the top. We will work them out together in the discussion of Figure 4.3.2B.



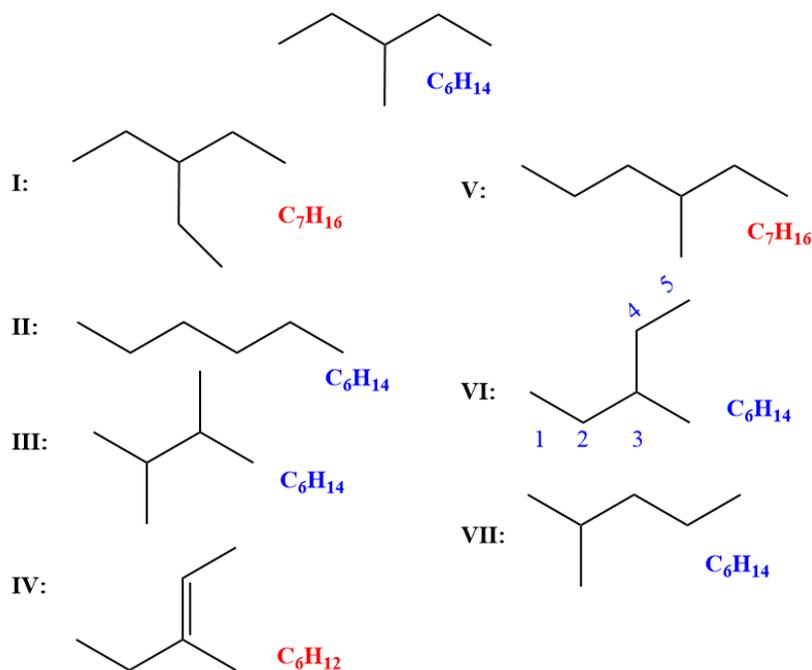
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**Figure 4.3.2A:** Which of the numbered structures are isomers of the molecule shown at the top?

---

Figure 4.3.2B offers some insight on how to identify the isomers. The first order of business is to identify which molecules have the same chemical formula as the original structure. Structures I and V have too many carbons and can immediately be ruled out. Structure IV is an alkene. It has the right number of C atoms but too few H's because forming the double-bond eliminated two of them; this is a general pattern we will discuss further below.

Of the remaining molecules, Structures II, III, and VII are isomers. Structure VI is not an isomer because it is the *same* molecule as the original. Number the C atoms as shown to see this, and compare to the original structure.



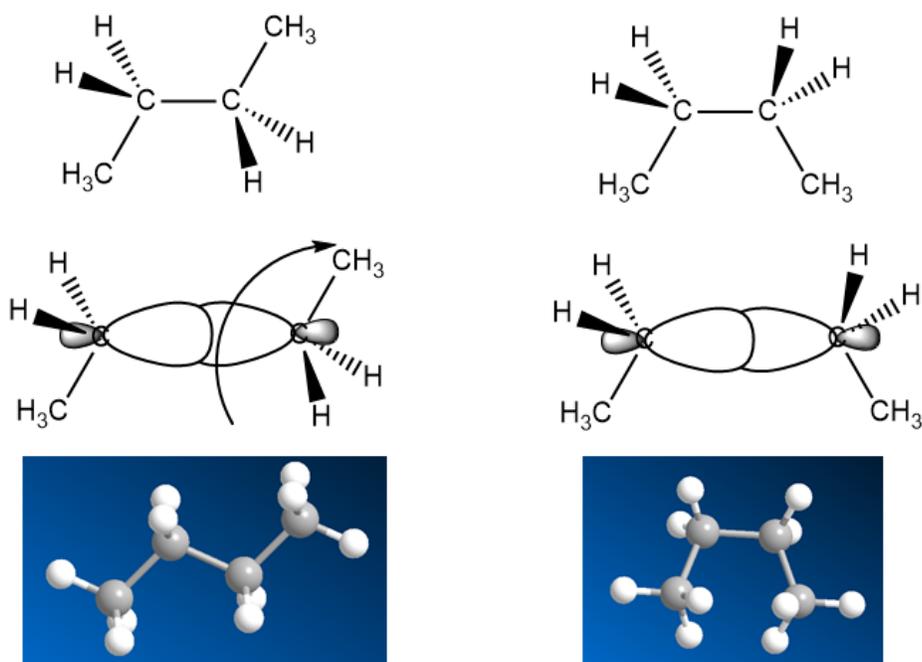
**Figure 4.3.2B:** Annotated structures for possible isomers; see text for discussion.

Once double and triple bonds are introduced, and ring structures are considered, other types of isomerization become possible. To address these, we need to consider stereoisomerism.

**Stereoisomerism I – Cis-/Trans- Character in Double Bonds:** Though it may seem counterintuitive, it is possible to have the same atoms connected by bonds in the same order but to have the atoms arranged at different angles. The simplest example of this is found in something called cis-/trans-isomerism, which has to do with the structure of double bonds.

Figure 4.3.3 presents a rehash of information originally presented in Figure 4.1.11. The wedge angle notation shows a four-carbon chain in two different conformations. This is the same molecule in different conformations. In a sample of this molecule, some would be in the first conformation and some in the second, and over time they would convert between the two.

The reason this is possible is that the sigma-bond between the carbon atoms is cylindrically symmetric, as shown in the central part of the figure. The carbon bond can twist to any angle without disrupting the overlap of the  $sp^3$ -hybrid orbitals on the two C atoms. Since the bond remains intact, the energy required for the bond to rotate is relatively small.



**Figure 4.3.3:** Three-dimensional conformations for the molecule  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ . The central part of the diagram shows the overlap of  $\text{sp}^3$ -orbitals on the neighboring C atoms that creates the sigma bond between them.

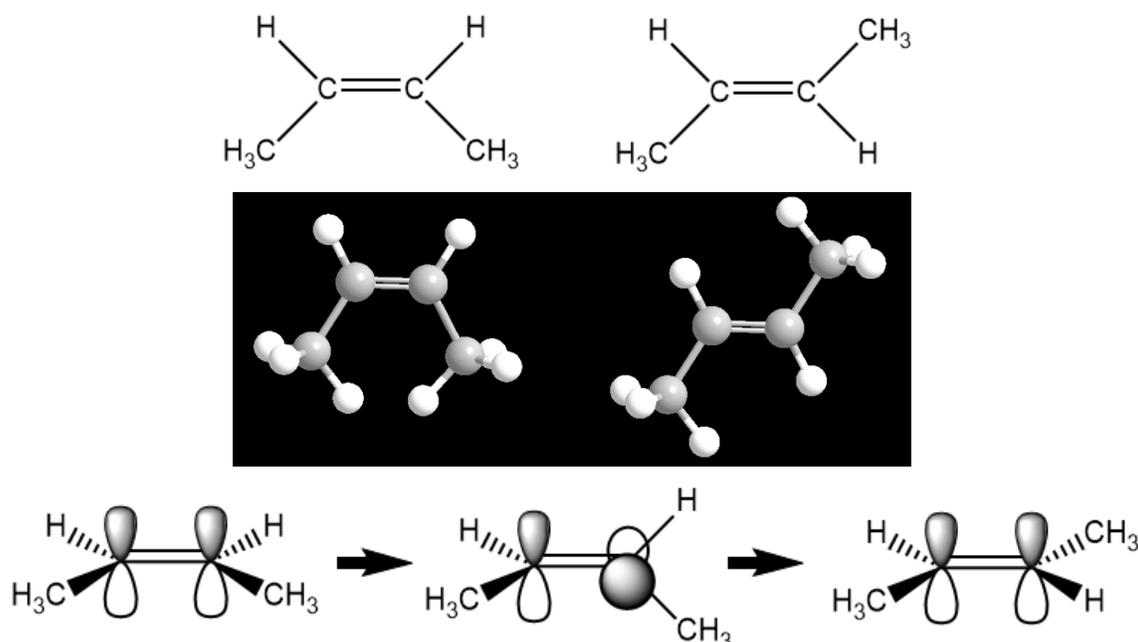
Since there is no way to control the conformation of the molecule in alkanes, the angles chosen to represent them are unimportant. Figure 4.3.4 shows two possible line-angle diagrams of the molecule shown in Figure 4.3.3. By convention, neither is taken to provide information on the conformation of the molecule. The two structures are taken to be equivalent, and it is understood that in solution they will occupy many different conformations (we will discuss conformations in more detail in Chapter 6).

**Figure 4.3.4:** Two line-angle representations of the molecules shown in Figure 4.3.3. Unlike wedge-angle notation, the line-angle representation used here is not intended to communicate information on the conformation. These two drawings communicate the same information about the molecule (that it is  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ).



The situation is different for double bonds, however, as pi-bonds are not cylindrically symmetric. Figure 4.3.5 shows two structures for the molecule  $\text{CH}_3\text{-CH=CH-CH}_3$ , the first with the  $\text{CH}_3$ -groups on the same side of the bond and the second with the  $\text{CH}_3$ -groups on opposite sides. The third line of the figure shows that the presence of the pi-bond makes rotation around the bond impossible. Remember that the pi-bond is

formed by the overlap of two p-orbitals that must be perpendicular to the sigma-bonds on the carbon (see Chapter 2). The process of rotating between the two forms brings the p-orbitals out of alignment so that the electrons can no longer be shared. In essence, this requires breaking the pi-bond, and even though the sigma bond is left intact this is more energy than will be available to the molecule even when the temperature is very high. Thus, the two forms of the molecule are viewed as separate molecules because the two forms cannot interconvert under normal circumstances.



**Figure 4.3.5:** Two- and three-dimensional representations of the molecule  $\text{CH}_3\text{-CH=CH-CH}_3$ . The third line shows how the pi bond must be broken to move from one to the other form.

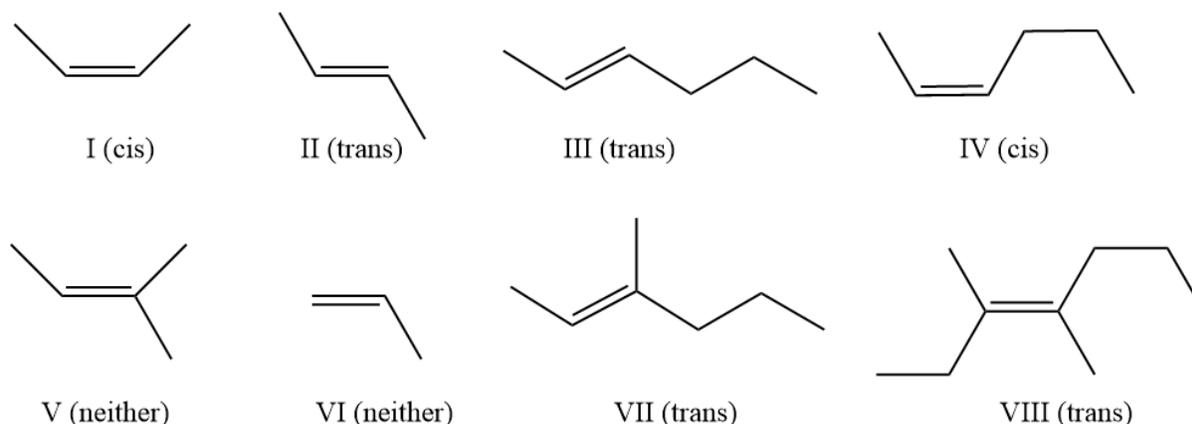
It may strike you as odd that the phase of the p-orbital (dark vs. light) seems to reverse in the process of rotation. Such a reversal of phase is allowed provided it leads to a new bond.

The barrier to rotation means that we can have molecules that are identical in every respect except for their structure across a double bond. These molecules will have the same chemical formula, so they are isomers. And every atom will have the same number and type of each bond, with only the angles being different, so these are stereoisomers, as opposed to the constitutional isomers discussed in the last section.

Isomers that are identical except for the orientation around a double bond are said to be cis-/trans-isomers. The two molecules shown in Figure 4.3.5 are examples of this type of isomer. Because the  $-\text{CH}_3$  groups are on the same side in the left-hand molecule, the molecule is said to be a cis-isomer (“cis” is a Latin prefix meaning “on this side of”). The one on the right is said to be a trans-isomer (“trans” is another Latin prefix meaning “across” or “opposite”), indicating the  $-\text{CH}_3$  groups are on opposite sides.

Figure 4.3.6 shows a series of double bond-containing molecules. Structures I and II correspond to the molecules shown in Figure 4.3.5, simply expressed in line-angle notation. Note that for single bonds the relative angles in line-angle notation do not indicate different geometries (see Figure 4.3.4), but for double-bonds they *do* indicate the geometry. Structures III and IV are

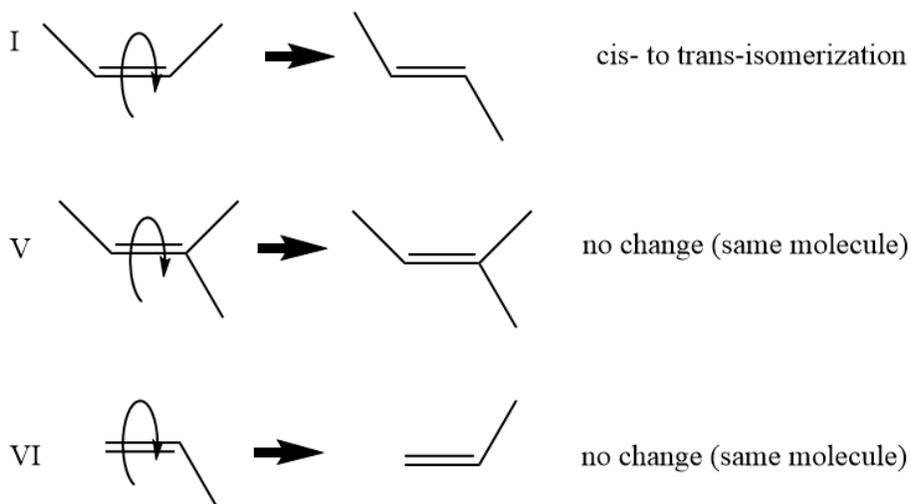
also a pair of cis-/trans- isomers; they have the same chemical formula and differ only in their orientation about the double-bond.



**Figure 4.3.6:** A series of molecules containing double bonds, with their cis-/trans-character indicated. See text for discussion.

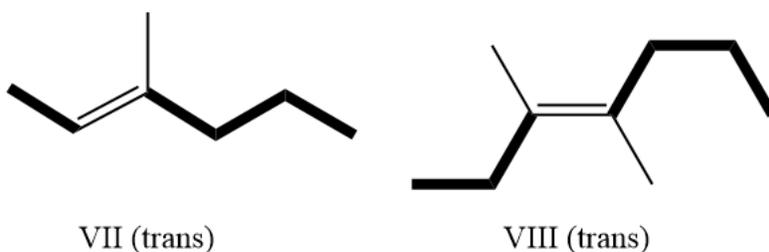
Structures V and VI each contain a double bond, but neither is a cis-/trans-isomer. To see this, look at the outcome of rotations about the double bond in Figure 4.3.6A. Rotating Structure I about its double bond gives Structure II, but rotating around the double bond for Structure V gives back the original structure. The same is true for Structure VI (the structure as drawn may look different, but you can flip the whole molecule and get back the original structure).

This does not mean that the physics work any differently for these double bonds: They are still locked into place by the overlap of the p-orbitals. But because one of the C atoms in the double bond has identical groups coming off of it (either  $-\text{CH}_3$  groups for V or  $-\text{H}$ 's for VI) the molecule does not change its structure in rotation of the bond.



**Figure 4.3.6A:** Rotation around the double bond for three structures from Figure 4.3.6. See text for discussion.

Structures VII and VIII are more complex. Rather than having just one carbon-chain on each side of the double-bond, they have two on at least one side. In a case like that, the convention is to identify the longest chain on each side and classify them as cis- or trans- based on the relationship between them. Figure 4.3.6B shows Structures VII and VIII with the longest chain on each side bolded. They are both trans-, because the longest chains on each side are on opposite sides of the molecule.



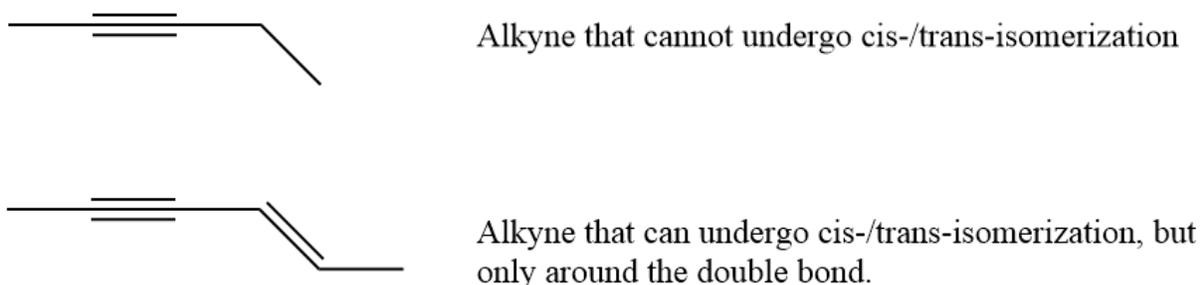
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**Figure 4.3.6B:** Structures with multiple carbon-chains on each C atom in the double bond. The longest chain on each side of the bond is bolded. See text for discussion.

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The general rule for this is actually a bit more complex than that laid out here. If the chains branch or contain atoms other than carbon, additional rules are needed to distinguish them. But for this work, the rule that the longest chain on each side determines cis-/trans- character will suffice.

As noted above, cis-/trans- isomerism of this type does not occur around single bonds because they rotate freely. Triple bonds are also not subject to cis-/trans isomerism, because they create linear structures, as shown in Figure 4.3.7. Twisting the triple bond would not change the positions of the two C atoms that neighbor the bond, so the geometry of the molecule would not change. Alkynes therefore do not undergo cis-/trans-isomerization, unless they contain a double bond.



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**Figure 4.3.7:** Structures of alkynes and their capacity for cis-/trans-isomerization.

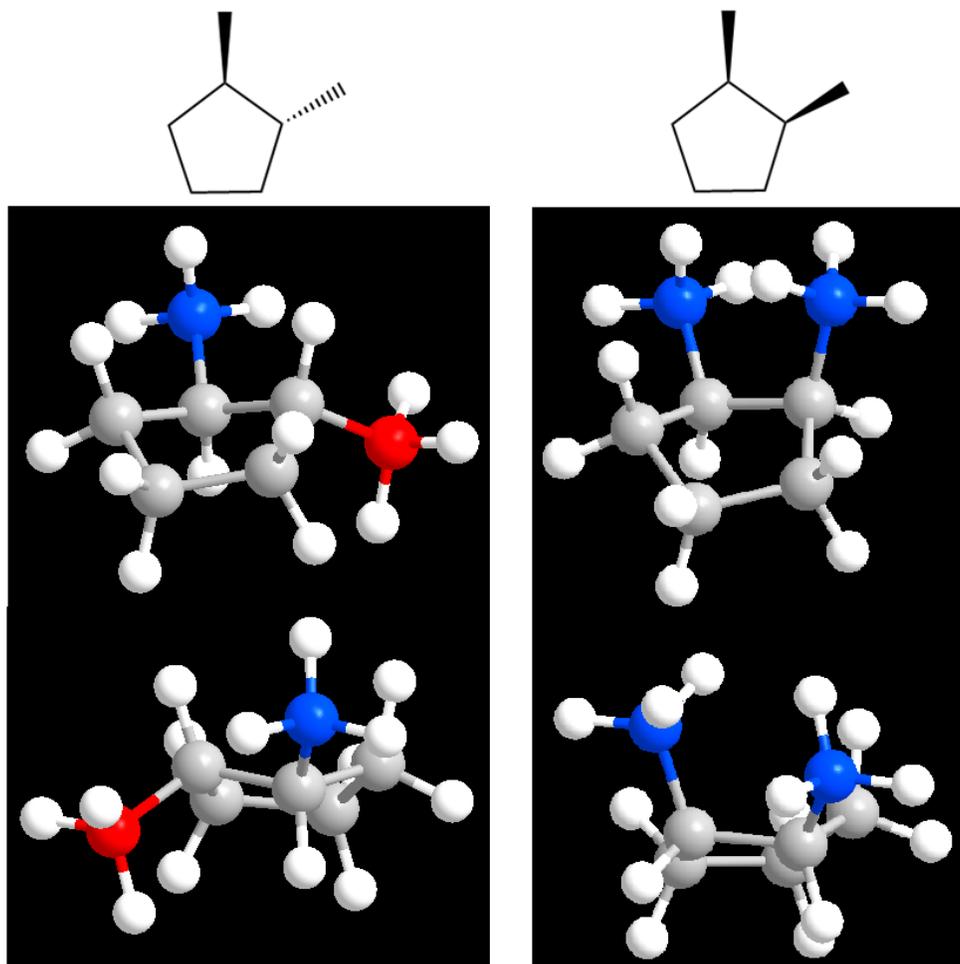
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**Stereoisomerism II – Cis-/Trans- Character in Rings:** There are actually many different kinds of stereoisomerism, and we will learn about others in later chapters. But the most straightforward extension of what we have done so far is cis-/trans-isomerism in rings.

Rings occur frequently in organic chemistry and biochemistry. We have already discussed aromatic rings, but other types of rings are also very common. The details of the geometry of rings can actually be quite complicated, and we will discuss it further when we consider the conformations of molecules in Chapter 6. But cis-/trans-isomerism in rings is fairly straightforward.

We already saw that the presence of a double bond prevents rotation, which means that if groups are arranged on opposite sides of the bond they are locked into place, creating the possibility of cis-/trans-isomerism. Ring structures also lock groups into position. While single bonds in acyclic compounds can rotate freely, atoms in rings are locked into position and cannot rotate relative to each other. It is a bit like having a ring made of ribbon and trying to twist one part of it, there is a torsional force that will resist the motion. For atomic rings this force is strong enough to prevent rotation, so groups can be trapped on opposite sides of the plane of the ring.

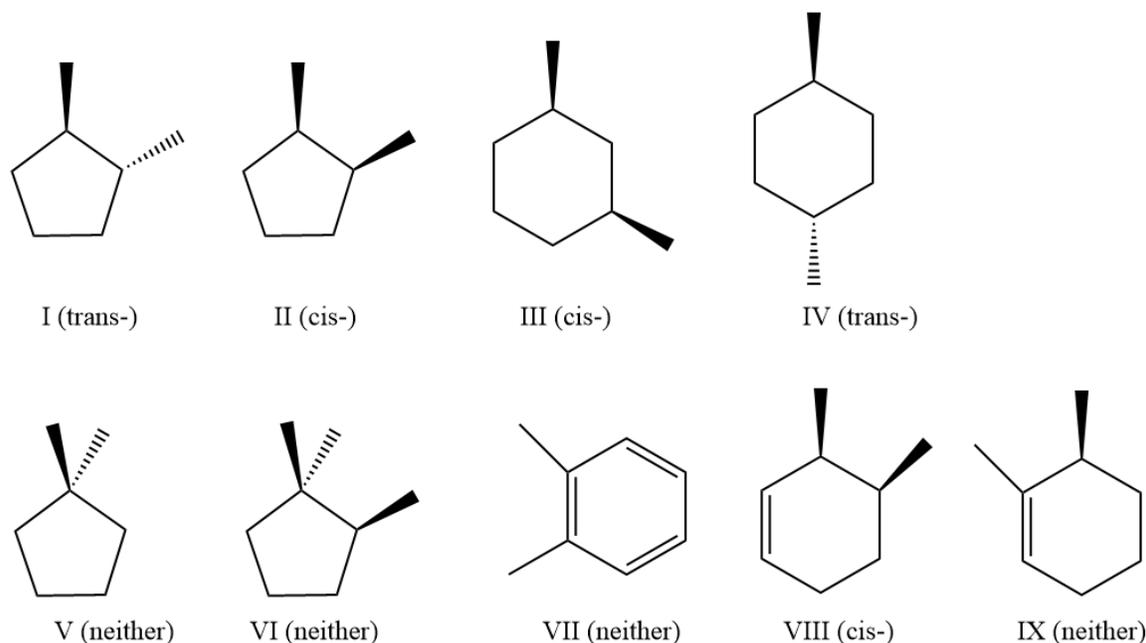
Figure 4.3.8 shows an example of this for a five-membered ring. The wedge-angle drawings show the ring in the plane of the page, with wedges indicating whether the  $-\text{CH}_3$  groups go in or out. A look at the 3-dimensional structures below it makes clear that the ring is not perfectly planar, but is puckered, a topic we will discuss further in Chapter 6. Nevertheless, it is possible to assign an approximate plane to the ring and see that the  $-\text{CH}_3$  groups are above or below it. They are locked into this configuration, making them cis- and trans-isomers.



**Figure 4.3.8:** A five-membered ring with  $\text{-CH}_3$  groups coming occurring in trans- (left) and cis- (right) configurations. The C atoms in the trans-  $\text{-CH}_3$ -groups are shown in blue and red to highlight them, with the C atoms in the cis-  $\text{-CH}_3$ -groups are both in blue.

Figure 4.3.9 shows examples of ring structures containing substituents that may be cis- or trans-. Structures I and II represent the structures given in Figure 4.3.8; they are cis-/trans- isomers of each other. Structures III and IV are six-membered rings, but these are still capable of engaging in cis- and trans- isomerism. Note that groups may be separated by more than one C-C bond and still be labeled as cis- or trans- because the ring still locks them into place.

Structure V is neither cis- nor trans- because both  $\text{-CH}_3$  groups sit on the same atom. Their relative positions are simply set by the  $\text{sp}^3$ -character of the molecule; there is no way to build an isomer that swaps one position without swapping the other. Figure VI is neither cis- nor trans- because swapping the side of the isolated  $\text{-CH}_3$  group still leaves it cis- to one  $\text{-CH}_3$  group and trans- to the other.



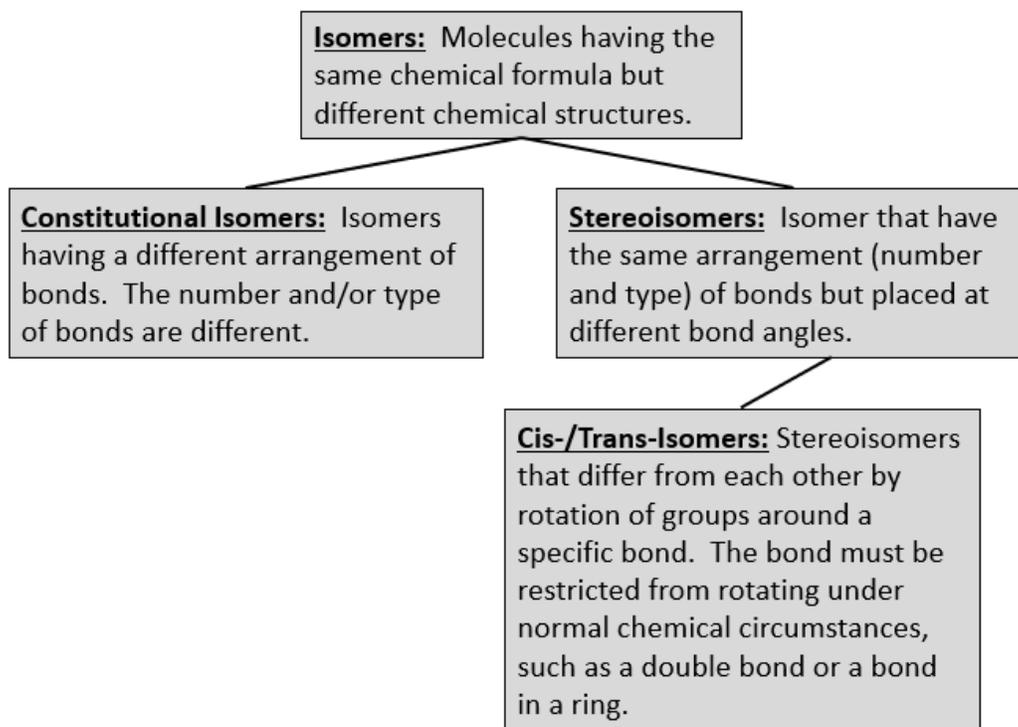
**Figure 4.3.9:** A series of structures containing rings, with their cis-/trans-character indicated. See text for discussion.

Figure VII is an interesting case. Rather than being a ring composed of single bonds, it is an aromatic ring. That means that all C atoms are  $sp^2$ -hybridized, so each bond coming out of the C atom is planar with it. The two  $-CH_3$  groups are therefore planar with each other, so cannot be regarded as cis- or trans-. Aromatic rings are not capable of cis-/trans-isomerism for exactly this reason.

Structures VIII and IX show how to deal with rings that contain double bonds but are not fully aromatic. The  $sp^3$ -hybridized C atoms can still bind two different groups, and these can be above or below the plane of the ring. If two groups are on different  $sp^3$ -hybridized carbon atoms, then cis-/trans- relationships are possible. However, if one of the groups is on a  $sp^2$ -hybridized carbon, as in Structure IX, then it is essentially in the plane of the ring and the question of cis- vs. trans- is moot.

**Putting it All Together:** As stated at the beginning of this section, carbon is capable of arranging itself in a bewildering range of patterns, and attempting to characterize them is as challenging as attempting to anticipate all of the structures that could be put together from a box of toy blocks. But a useful starting point is understanding the many ways that two molecules can have the same chemical formula but different chemical structures. This not only makes it possible to recognize isomers, but also helps the chemist understand the kinds of features that can be incorporated into a molecule.

Our work so far, summarized in Figure 4.3.10, has barely scratched the surface. But we will make use of it to explore some groups of isomers and understand their relationships.



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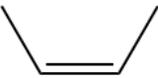
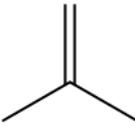
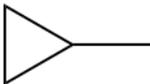
**Figure 4.3.10:** A series of structures containing rings, with their cis-/trans-character indicated. See text for discussion.

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The first thing to remember is that these molecules exist physically, can be synthesized and studied in the laboratory, and have different properties. As a simple example, consider the set of molecules with formula  $C_4H_8$  given in Figure 4.3.11. The six molecules include two cyclic structures and four acyclic structures. The boiling points for the isomers are also listed, and vary from structure to structure. In this particular case the differences are relatively small because for the most part the intermolecular forces that control the boiling point do not change much between the structures. More generally, the properties of isomers can be radically different, especially for molecules other than hydrocarbons where isomerism can change dipole moments and hydrogen-bonding characters very significantly.

It is interesting to compare the types of isomerism at play in Figure 4.3.11. Structures II and III are trans- and cis- isomers of each other; they are the same molecules given in Figure Figure 4.3.5. Structure I, however, does not engage in cis-/trans-isomerism. The end carbon of the double bond has two identical groups on it, the H's in  $=CH_2$ , so rotation around this double bond will not produce a new molecule.

**Figure 4.3.11:** A complete set of isomers with formula  $C_4H_8$ , and their boiling points.

		<u>Boiling Point</u>
I		$-6^{\circ}\text{C}$
II		$1^{\circ}\text{C}$
III		$4^{\circ}\text{C}$
IV		$-7^{\circ}\text{C}$
V		$12^{\circ}\text{C}$
VI		$0.7^{\circ}\text{C}$

In fact, Structure I is a constitutional isomer of Structures II and III; moving the double bond as shown above changes the types of groups present. Structures II and III have two  $-\text{CH}_3$  groups at the ends of its chain, while Structure I has only one. The fact is that other than II and III – which are stereoisomers of each other – all structures shown are constitutional isomers of each other.

As an aside, we point out that the cyclic structures shown are in reality very unstable, difficult to synthesize, and short-lived. We will discuss the reasons for this more generally when we discuss ring systems in Chapter 6.

To test your ability to work with isomers, draw all possible acyclic (i.e. containing no rings) isomers with the chemical formula  $C_4H_6$ .

It is always best to work through this kind of problem systematically. First, we should find one structure that matches the formula. Laying out a straight carbon chain four atoms long, we have:



(4.3.1)

Checking the formula, we see that we have 10 hydrogen atoms if the molecule is left saturated, as shown. We need a version with fewer hydrogens. By now, you should have grasped that we can lose H atoms either by adding a double bond (removing 2 H's to make room for the pi bond) or by making a ring (taking H's off the

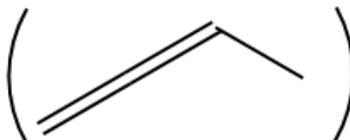
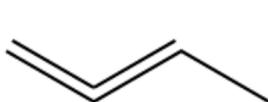
ends of the molecule and looping it around to make a sigma bond). Since we have ruled out rings, we should try a pi bond.

A new structure might be



(4.3.2)

However, this gives us the formula of  $C_4H_8$ , still too many H's. Adding another double bond:



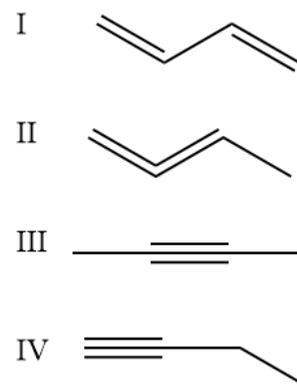
(4.3.3)

The structure on the right is the same as the one on the left, but with the geometry drawn to reflect the  $sp$ -hybridization of the C atom (i.e. the two double bonds are collinear); this is a convention that is sometimes used. Regardless, we now have the correct formula of  $C_4H_6$ .

Having obtained this, our next steps are to make systematic changes to the structure. First, we can move one of the double bonds along the chain. Second, we can replace the two double bonds with a triple bond – the number of pi bonds remains the same. The results are the four structures shown in Figure 4.3.12. It is worth stopping at this point to confirm whether the molecules shown can engage in cis-/trans-isomerization, but none can. Structures III and IV contain no double bonds, and rotation around either of the bonds in Structure I would not change the identity of the molecule.

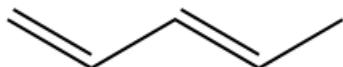
Structure II requires a closer look. The left-most double bond cannot engage in cis-/trans-isomerism, because it ends in a  $-CH_2$  group, where rotation does not lead to a change in the molecule. Rotating around the double bond in the center also does not change the molecule, because the three left-most carbons are collinear (look again at the structure given in Equation 4.3.3). This is a situation not directly covered by our prior discussion, but it is clear the collinear structure means there is no “same” or “opposite” that can be applied to the  $-CH_3$  group at the end of the molecule – so there is no cis- or trans-.

**Figure 4.3.12:** A complete set of acyclic isomers with formula  $C_4H_6$ .



A useful trick is to notice that all saturated, acyclic hydrocarbons have the formula  $C_nH_{2n+2}$ , where  $n$  is an integer. This represents a reference that can be compared with other hydrocarbons. Adding a double bond or ring structure reduces the number of H atoms by two, meaning we needed one double bond or ring to create each of the  $C_4H_8$  isomers in Figure 4.3.11, and we needed two pi bonds (because rings were disallowed) to create the structures in Figure 4.3.12.

So, if we were asked to draw isomers of  $C_5H_8$ , we could work out how many rings or double bonds we would need by comparing it against the saturated, five-carbon molecule  $C_5H_{12}$ . We recognize that  $12-8=4$  H atoms that need to be removed, meaning we need 2 pi bonds or ring structures. Thus, a structure with 5 C atoms and two double bonds should meet our needs:



(4.3.4)

It would then be a question of working through other configurations: Looking for cis-/trans- isomers (spoiler alert, this one has a cis-isomer), moving the double bonds into different relative positions, creating triple bonds and ring structures. We are not going to do this – there are more than 20 isomers for this molecule – but this serves to illustrate how one would start the process.

## Section 4.4: Nomenclature of Alkanes

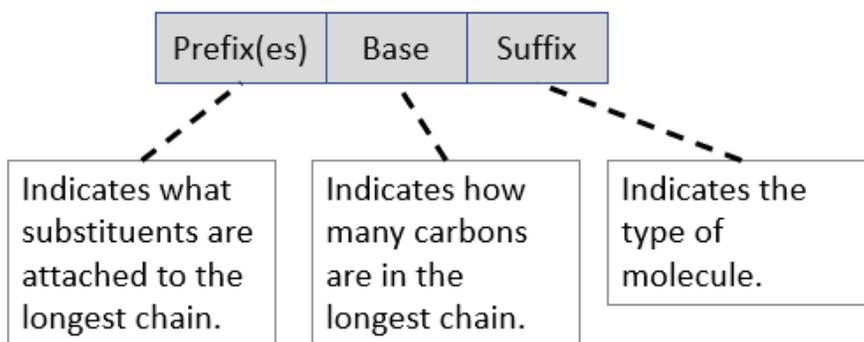
### LEARNING OBJECTIVES FOR THIS SECTION

- Understand and be able to apply the rules for naming alkanes.

Returning to our earlier analogy, carbon's ability to assemble complex structures makes working with it a bit like building with toy blocks. These simple objects that lead to a nearly infinite array of possible structures.

The practice of chemistry requires a scheme that can name *every possible molecule* that can be built in organic chemistry. This is exactly as challenging as attempting to name every structure that could be built from a box of blocks. The naming system must assign a unique name to every structure, including every possible constitutional and stereoisomer.

**Figure 4.4.1** Schematic diagram of the IUPAC nomenclature scheme.



We are going to present only a small part of the nomenclature scheme here, and explain how to name acyclic alkanes. Even this is a formidable challenge, so we must proceed systematically.

The nomenclature scheme consists of three ideas:

- 1) Identify the longest carbon chain in the molecule. The length of the chain serves as the “base” name, communicated to the reader in the root of the name.
- 2) Identify the smaller groups that are attached to this longest chain. These are referred to as substituents, and both their identity and their position on the longest chain need to be communicated to the reader. They are included in the prefix of the name.
- 3) Identify the type of compound. Here, we will only be working with alkanes, but in organic chemistry proper there are a large number of different categories of molecule. This is communicated to the reader in the suffix of the name.

This system is sometimes referred to as the IUPAC system, because it is maintained by the International Union of Pure and Applied Chemists.

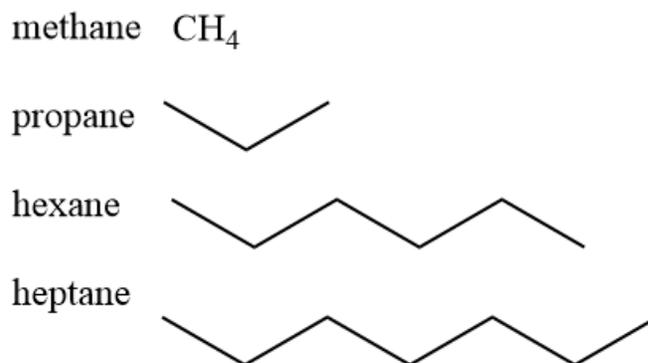
Central to the naming scheme, then, is communicating the number of carbon atoms in a given structure. The numbering scheme is given in Table of 4.4.1, and consists of a group of (mostly) roots of Latin numbers. You should memorize this table, as you are going to need it a lot.

**Take Note!** The IUPAC scheme says something about the way organic chemists think. C-H and C-C bonds are chemically relatively inert, and the chain can be viewed as a scaffolding on which more chemically relevant substituents are placed. For the alkanes we consider here, of course, all that will be present are C-H and C-C bonds, but we will discuss other substituents that occur in organic chemistry in Section 4.5.

**Table 4.4.1:** Roots for naming carbon structures containing up to 10 C atoms.

Number of Carbons	Root
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pent-
6	Hex-
7	Hept-
8	Oct-
9	Non-
10	Dec-

As a starting point, we can name some unbranched alkanes. The names of alkanes always take a “-ane” suffix, and the number of C atoms present is indicated by the roots given in Table 4.4.1. Some examples are given in Figure 4.4.2.

**Table 4.4.2:** Sample names for linear alkanes.

This is as simple as it seems, but now we need to consider how to handle more complex structures. We need to both identify the substrate and tell the reader where it is located.

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**NAMING ALKANES:**

1. Identify the longest continuous chain.
2. Identify all substituents
3. Number the chain to give the lowest possible number to a substituent.
  - A. If one numbering scheme gives a lower number than the other, it does not matter what the substituent is. Use that scheme.
  - B. If two different numbering schemes give the same lowest number, choose the numbering scheme that is first alphabetically.
4. List the substituents alphabetically
  - A. Indicate the position with a number
  - B. Indicate the number of substituents with Greek prefixes.
5. After substituents are listed, give root name, and end with “-ane” for alkanes.

*Note: When alphabetizing substituents in Rules 3B and 4, ignore the Greek prefixes from Table 4.4.4. “Ethyl” comes before “dimethyl,” because “e” comes before the “m” in methyl.*

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**Table 4.4.3:** Rules for naming alkanes.

---

The complete set of rules for naming branched alkanes is given in Table 4.4.3. Rules 1, 2, and 5 are relatively straightforward extensions of what we have already done. The rules for numbering the chain given in Rule 3 are slightly more complex, but will become clear in their use. Rule 4B mentions the need for Greek prefixes to indicate the number of a given substituent present. This could be a bit confusing – we are using prefixes within prefixes – but it is a straightforward when one realizes that “dimethyl” tells the reader “two methyl groups.” The necessary prefixes are given in Table 4.4.4; this is probably another good set to memorize.

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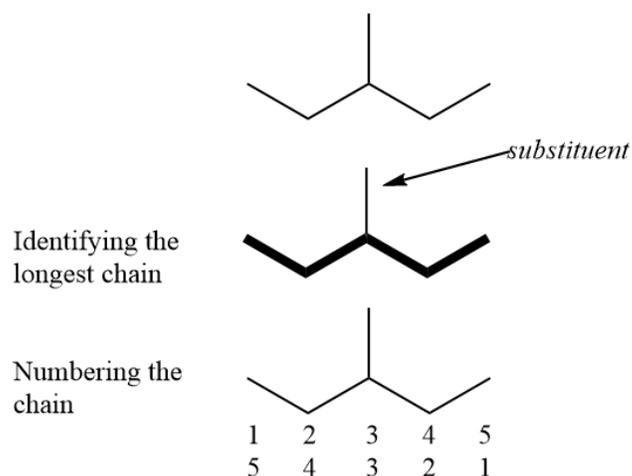
**Table 4.4.4:** Prefixes to indicate the number of substituents.

Number of Substituents	Prefix
1	<i>no prefix</i>
2	di-
3	tri-
4	tetra-
5	penta-

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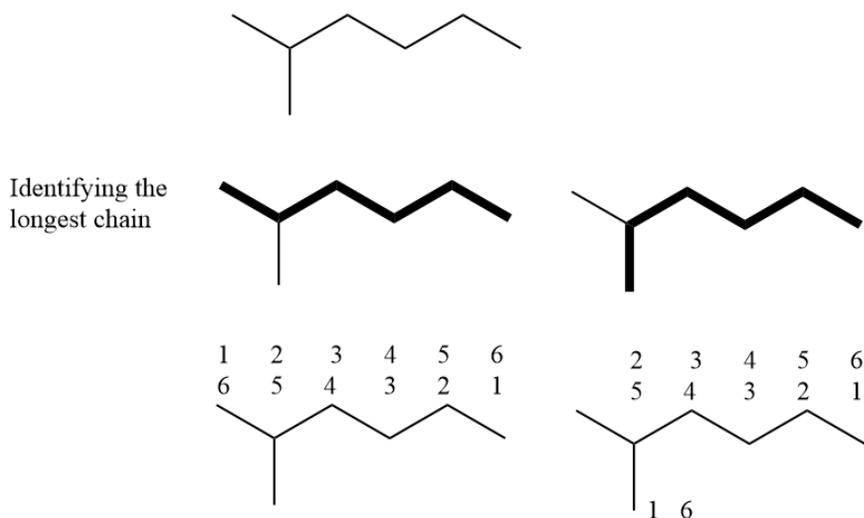
Let us apply these rules to the molecule given in Figure 4.4.3. Step 1 in Table 4.4.3 is to identify the longest continuous carbon chain, which is shown in bold in the second line of Figure 4.4.2. Next, we identify the substituents, which means every group that is not part of the main chain. In this case, that is a -CH<sub>3</sub> group. Looking at the numbering system in Table 4.4.1, the name should be based on “meth-.” In fact, the substituent is referred to as “methyl,” the -yl being added to identify it as a substituent rather than the main chain.

**Figure 4.4.2:** Steps to naming a sample alkane.



We could now write “methylpropane,” which matches the scheme given in Figure 4.4.1 (prefix-base-suffix), but this is incomplete information. We have not yet told the reader where the substituent sits, so we have to number the carbon chain. Two possible numbering schemes are given in the third line of Figure 4.4.2. Both number the C atom where the methyl group sits as “3,” so there is no ambiguity. The molecule is “3-methylpropane.”

**Figure 4.4.3:** Steps to naming a sample alkane.



Another example is shown in Figure 4.4.3. In identifying the longest chain, we seem to hit a paradox in that there are two equally long chains, both six carbons long. However, a review of the possible numbering schemes given in the next line shows that the choice does not matter. Either numbering scheme leads to a methyl group attached to what is numbered as either the 2<sup>nd</sup> or 5<sup>th</sup> carbon.

We do, however, need to choose the appropriate numbering scheme based on the rules in Table 4.4.3. Based on Rule 3, we choose a numbering scheme that puts the methyl on the 2<sup>nd</sup> carbon. So the answer is “2-methylhexane.”

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**Figure 4.4.4:** Sample alkane to name, as described in the text.

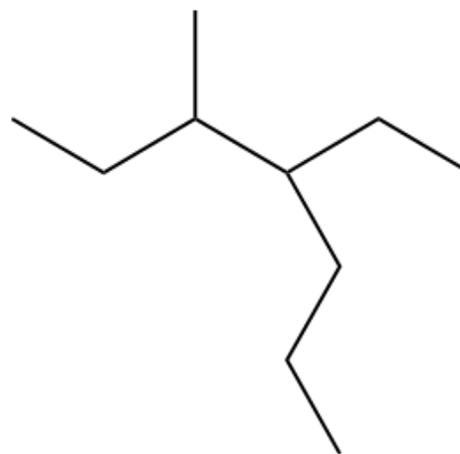


Figure 4.4.4 shows another example. Here, one may have to look twice to identify the longest chain, but it is actually seven carbons long (see Figure 4.4.4A). That means the root-name of the molecule is “heptane”.

Numbering the chain from the upper left (which will give the lowest numbers) gives a methyl at the 3<sup>rd</sup> carbon and an ethyl (2 carbons) at the 4<sup>th</sup>. So, the substituents will be identified as “3-methyl” and “4-ethyl”. But in what order should they be placed?

Rule 4 says to list the substituents alphabetically, so the name would be: “4-ethyl-3-methylheptane.”

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**Figure 4.4.4A:** Chain and numbering for molecule shown in Figure 4.4.

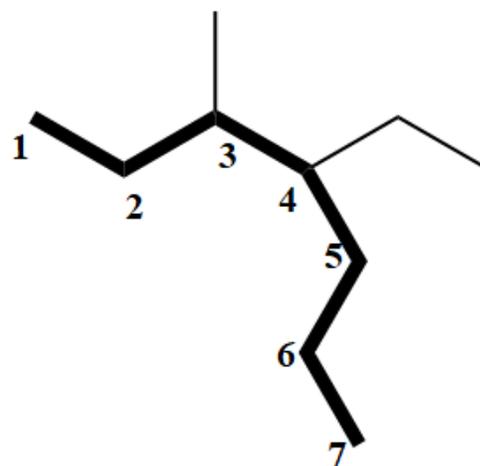
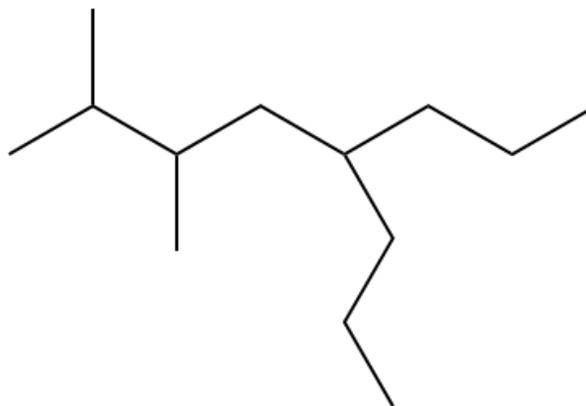


Figure 4.4.5 shows another example alkane. We start by identifying the longest chain, which will be 8 carbon atoms long (there are multiple possible choices that give 8C, but all will lead to the same name). Identifying the substituents, we have two methyl groups and one propyl group, so we will have to include the prefixes “dimethyl” and “propyl”.

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**Figure 4.4.5:** Sample alkane to name, as described in the text.



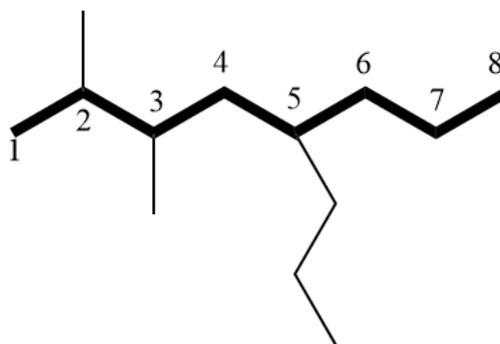
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For numbering the chain, our choices are either to start at the end that gives us a 2-methyl as the lowest-numbered substituent, or a 4-propyl. Rule 3A from Table 4.4.3 says that we should use the numbering scheme that gives us the lowest-numbered first substituent, so we want the scheme that gives us a methyl on the 2<sup>nd</sup> carbon.

We need to tell the reader that there are methyls on the 2<sup>nd</sup> and 3<sup>rd</sup> C, and a propyl group on the 5<sup>th</sup> C. So our prefixes will include, “2,3-dimethyl” and “5-propyl.” They should be listed alphabetically, *but we ignore the “di”* (see the note at the bottom of Table 4.4.3). That still means the methyl comes first, but it is important to recognize that the prefixes indicating the number of each substituent do not count in this alphabetizing scheme.

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**Figure 4.4.5A:** Sample alkane from Figure 4.4.5, possible numbering shown. There are other correct schemes, but all correct numbering schemes will same answer.



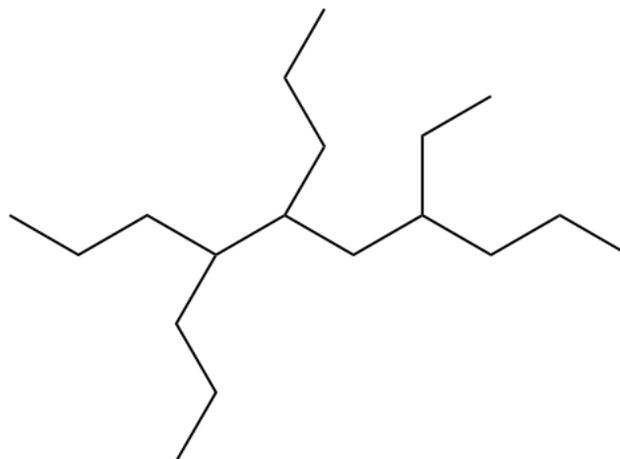
with one possible give the

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Another example is given in Figure 4.4.6. The longest chain gives 10 carbon atoms, so the root will be decane (there are two possible ways to number the chain). There are two propyl substituents (“dipropyl”) and one ethyl substituent.

---

**Figure 4.4.6:** Sample alkane to name, as described in the text.



There are two possible numberings. Going left to right gives you a propyl group on the 4<sup>th</sup> carbon, and going right to left gives you an ethyl group on the 4<sup>th</sup> carbon. Since they are tied, we break the tie with Rule 3B in Table 4.4.3. The “ethyl” comes before the “propyl” (ignore the “di-“), so our substituents are “4-ethyl” and “6,7-dimethyl”. Placed in alphabetical order, we obtain: “4-ethyl-6,7-dimethyldecane”.

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**Figure 4.4.6A:** Sample alkane from Figure 4.4.6, with one possible numbering shown. There is another correct possible scheme, but all correct numbering schemes will give the same answer.

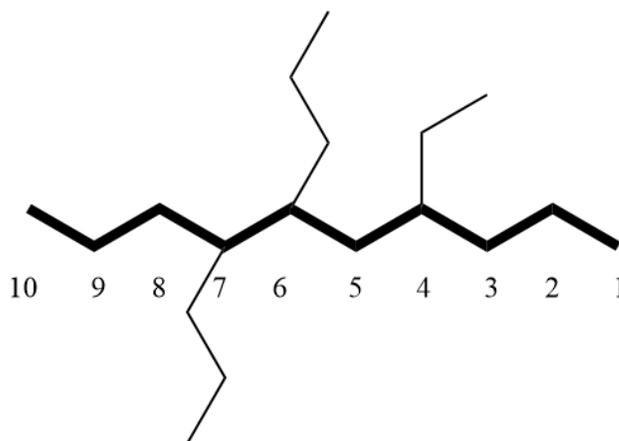
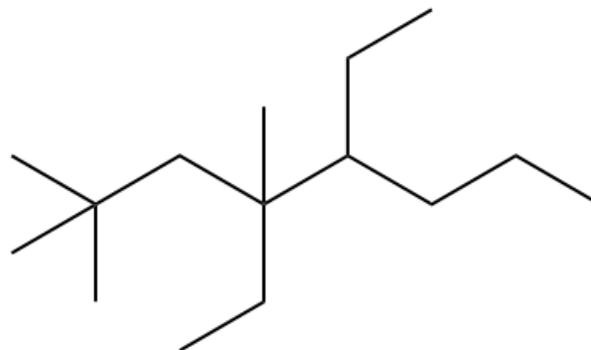


Figure 4.4.7 gives us a final example for this section. Identifying the longest chain is now slightly more complicated, but it works out to eight carbon atoms so the root is “octane”.

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**Figure 4.4.7:** Sample alkane to name, as described in the text.



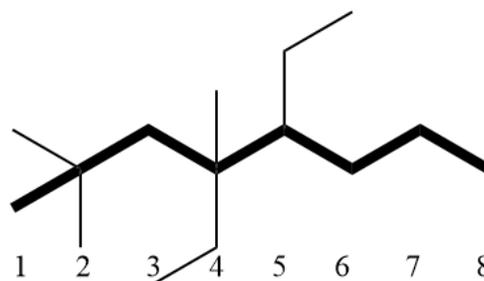
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Now we need to identify substituents. There are three methyl groups and two ethyl groups, so “trimethyl” and “diethyl” are the substituents. There is a scheme which puts the lowest-numbered groups on the 2<sup>nd</sup> carbon, so that is the scheme we should use.

We still need to tell the reader where the groups are, so the labels will be “2,2,3-trimethyl” and “4,5-diethyl”. We have multiple substituents on the same C atom, but this is an easily manageable problem. Repeating the “2” in “2,2,3-trimethyl” tells the reader there are two groups on the 2<sup>nd</sup> C atom (“2,3-trimethyl” would be incorrect because it does not tell the reader where one of the groups is). Alphabetizing ethyl before methyl, we obtain: “4,5-diethyl-2,2,3-trimethyloctane.”

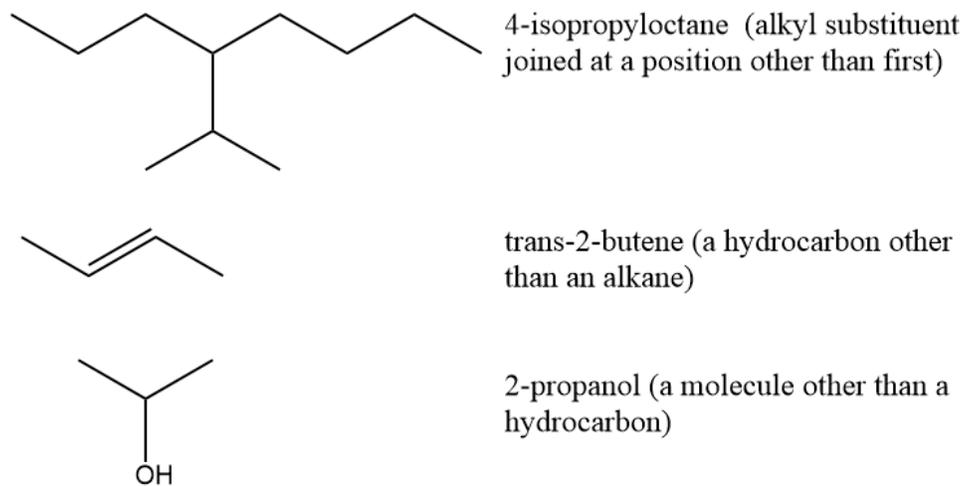
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**Figure 4.4.7A:** Sample alkane from Figure 4.4.7, with one possible numbering shown. There are other correct possible schemes, but all correct numbering schemes will give the same answer.



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As a final note, it is worth repeating that we have provided rules for naming only a very small subset of possible organic compounds. A set of molecules that do not fit our rules is given in Figure 4.4.8. But looking at these examples, you can probably get a sense of how the rules could be extended. It should also be clear that the numbering scheme we have used will remain relevant for more complex molecules. Thus, while we have only begun the process of learning nomenclature, the basic skills will remain relevant as you further your studies in other coursework.



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**Figure 4.4.8:** Some examples of organic molecules not addressed by the nomenclature scheme presented here.

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## Section 4.5: Functional Groups

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand what functional groups are, and be able to recognize common functional groups.

We mentioned in an earlier section that carbon chains are chemically relatively inert, and that organic chemists often view them as a scaffold on which other elements can be placed. Often these are other second-row elements such as nitrogen and oxygen, which can be attached to the chains to create a wide range of structures.

You should remember your discussion of intermolecular forces from first-semester chemistry. London dispersion forces are affected by the molecular weight of a molecule, which is determined in part by the length of the carbon chains. But C-C and C-H bonds are relatively nonpolar bonds, so do not contribute significantly to dipole-dipole interactions between molecules. Likewise, hydrogen bonding requires the presence of C, N, or other strongly electronegative elements (review your general chemistry textbook if you do not recall the details). Thus, the presence of elements other than carbon significantly affects the interactions between molecules and will control important physical properties such as solubility and melting/boiling points. Further, while we will not discuss reactions in much detail in this text, different elements undergo reactions that are quite different from those of carbon. Thus, the presence of elements other than C and H will be a major determinant of the behavior of a molecule.

But elements can bond in different structures, and their pattern of bonding is also important. Consequently, chemists do not talk simply about “nitrogen-containing” or “oxygen-containing” molecules, they discuss molecules as containing functional groups. Functional groups are chemical structures found in an organic molecule. In the same way that the presence of double bonds and triple bonds defined alkenes and alkynes, the presence of other structures defines other classes of compounds.

A list of functional groups is given in Table 4.5.1. This covers the most common groups and will suffice for this text, but the list is by no means exhaustive.

In a full course on organic chemistry there would be a chapter devoted to each of these groups, discussing their reactions and physical properties. Here, our goal is to help you learn to distinguish between the groups and recognize which groups are present in a given molecule. This will make it easier for you to pick up more details about them in future.

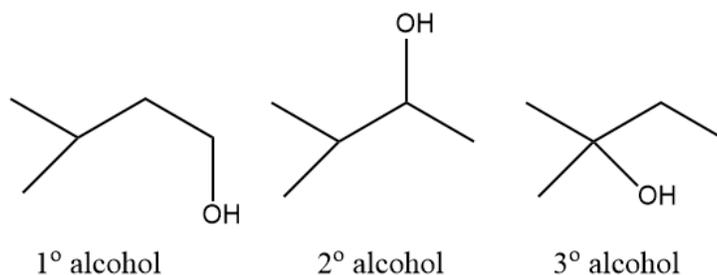
Name	Functional Group	Sample Compound
Alcohol	-OH	$\text{H}_3\text{C}-\text{CH}_2-\text{OH}$
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ \diagdown \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C} \\ \diagdown \\ \text{H} \end{array}$
Amide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ \diagdown \\ \text{N} \\   \\ \text{I} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C} \\ \diagdown \\ \text{N}-\text{H} \\   \\ \text{H} \end{array}$
Amine	$\begin{array}{c} -\text{N}- \\   \\ \text{I} \end{array}$	$\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$
Carboxylic Acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ \diagdown \\ \text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C} \\ \diagdown \\ \text{OH} \end{array}$
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1-\text{C}-\text{O}-\text{R}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{CH}_3 \end{array}$
Ether	$\text{R}_1-\text{O}-\text{R}_2$	$\text{H}_3\text{C}-\text{O}-\text{CH}_3$
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1-\text{C}-\text{R}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$

**Figure 4.5.1:** A list of common functional groups in organic chemistry. The notation “R” is commonly used in organic chemistry to denote many structures are possible. For the table above, R<sub>1</sub> and R<sub>2</sub> denote that the groups may be different or the same as each other, and may include carbon chains such as -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, etc.

**Alcohols:** Alcohols all contain the hydroxyl functional group, “-OH”. They are categorized as primary, secondary, and tertiary based on the type of carbon to which they are bound (see Section 4.1 for an explanation of 1°, 2°, and 3° carbons).

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**Figure 4.5.2:** Types of alcohols.

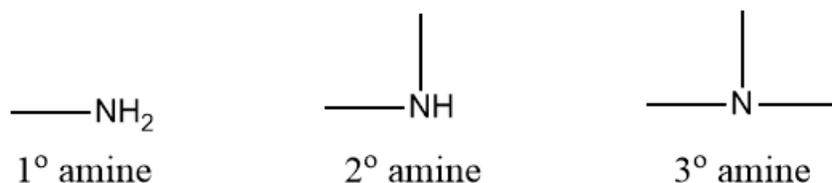


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**Aldehydes and Ketones:** Aldehydes and ketones both contain a carbonyl group, a C=O. This does *not* include the C=O structures present in amides, carboxylic acids, and esters; the presence of other non-carbon elements nearby gives them a different chemistry so they are placed in a different category. Aldehydes and ketones contain a C=O group that is isolated by at least one bond length from elements other than C and H.

Aldehydes contain a carbonyl group on a primary carbon, meaning it is at the end of a chain. Ketones contain a carbonyl group on a secondary carbon, in the middle of a chain. They receive different names because they display different chemistries. The presence of a strongly electronegative oxygen makes the -H in the -CHO group of an aldehyde more reactive than the hydrogens typically found attached to a carbon atom. So while the groups have much in common, it is important to be able to distinguish them.

**Amines:** Amines contain a nitrogen atom that is bound to one, two, or three carbon atoms. Amines are labeled as primary, secondary, or tertiary not based on the character of the carbon to which they are bound, but rather based on the number of carbon atoms to which they are bound; see Figure 4.5.3.



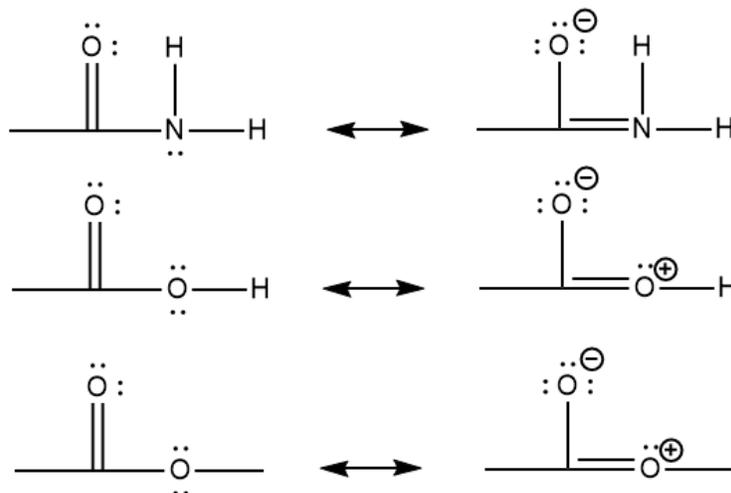
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**Figure 4.5.3:** Samples of types of amines.

Amines are distinguished from amides by the fact that they are not bound to a C=O group; we will explain this further in the discussion of amides.

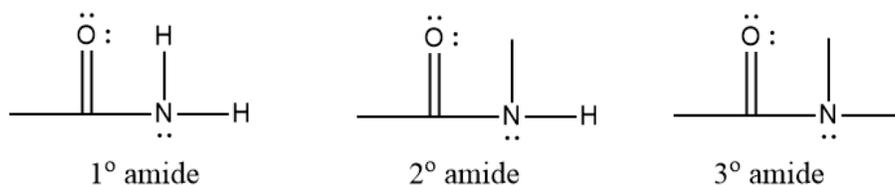
**Ethers:** Ethers are characterized by an oxygen atom bound to two other carbon atoms, neither of which is bound to an element other than C or H. You can picture an ether as a compound formed when the -CH<sub>2</sub>- group is replaced by an O atom, though chemically they can be quite different from hydrocarbons.

**Amides, Carboxylic Acids, and Esters:** These three classes of compounds are slightly confusing, in that it may not be immediately clear why amides should be distinguished from amines, or why carboxylic acids and esters should be distinguished from aldehydes and ketones. In this case, we already have enough background to understand the answer, which is that all three engage in resonance. Sample structures are shown in Figure 4.5.4. This is significant both in determining how charge is distributed in the groups and in their geometry, which in turn influences their chemical reactivity.



**Figure 4.5.4:** Resonance structures for sample amide, carboxylic acid, and ester.

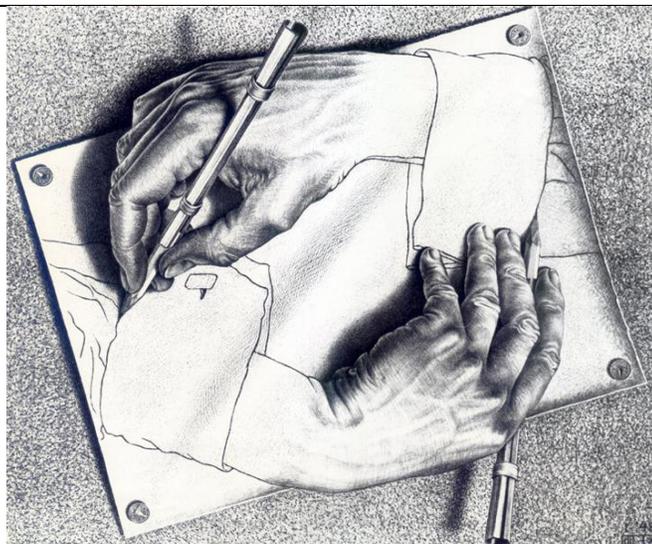
Like amines, amides can be primary, secondary, or tertiary, as shown in Figure 4.5.5.



**Figure 4.5.5:** Primary, secondary, and tertiary amides.

It may seem somewhat pointless to have gone over the functional groups in as little detail as we have. However, learning the functional groups is part of learning the alphabet of chemistry, and having it handy will make it easier to take on organic chemistry.

# CHAPTER 5: Chirality in Organic Chemistry



*Looking at the image above, you can easily identify which is the right hand and which is the left. But they are different only because one is the mirror image of the other. Molecules can also have a handedness, and just as it is awkward to use your left hand to shake a friend's right, the handedness of a molecule influences its interactions with other molecules.*

*M.C. Escher, "Drawing Hands," 1948*

*Image courtesy of WikiArt,  
<https://www.wikiart.org/en/m-c-escher/drawing-hands>, Accessed July 18, 2021.*

THE UNIVERSE IS  
ASYMMETRIC AND I AM  
PERSUADED THAT  
LIFE...IS A DIRECT  
RESULT OF THE  
ASYMMETRY OF THE  
UNIVERSE...

-LOUIS PASTEUR

*Louis Pasteur is justly celebrated for advancing the germ theory of disease, which is the basis for modern medicine. But he was also the first to discover that some molecules have a "handedness." There are molecules that are identical except that one is a mirror image of the other, just as your right hand is the mirror image of your left. His quote above – which is complicated by his use of the word "asymmetric" in a way that is not in current usage – conveys the fact that handedness not only occurs in biological systems, but is central to their chemistry.*

## BEFORE YOU BEGIN, MAKE SURE YOU KNOW

- VSEPR rules and molecular geometry (Flowers, sec 7.6)
- Wedge-angle notation (Chapter 4)
- The nature of isomers (Chapter 4)

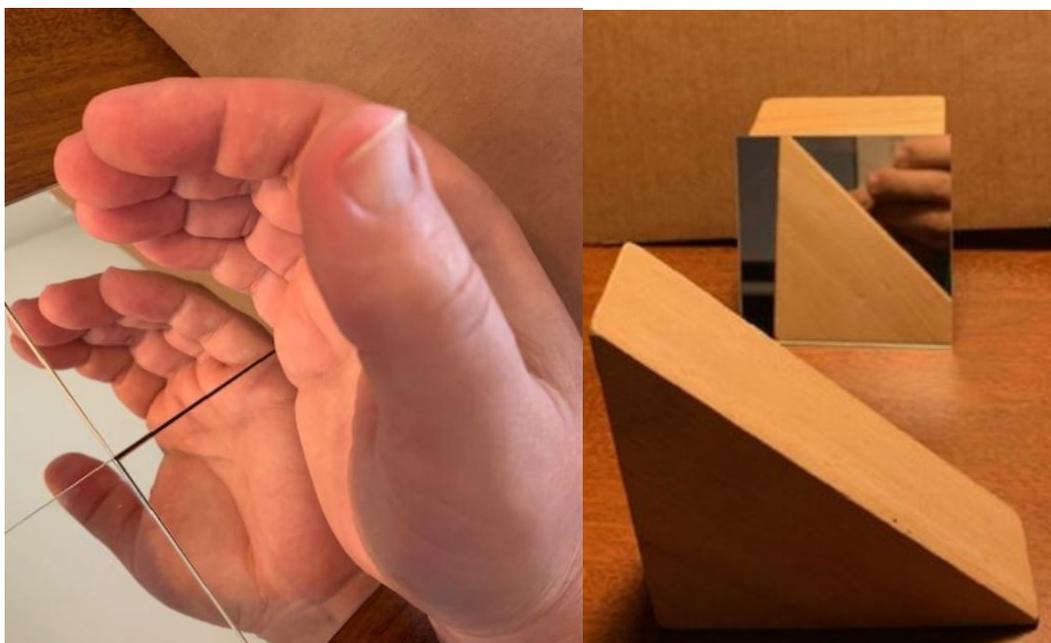
## Section 5.1: Introduction to Chirality

### LEARNING OBJECTIVES FOR THIS SECTION

- Know what is meant by the term chiral, and be able to recognize chiral objects. Be able to identify planes of symmetry and centers of symmetry and understand how they relate to the chirality of the object.
- Be able to identify tetrahedral stereocenters in molecules.
- Understand what is meant by the following terms: Enantiomer, stereocenter, diastereomer, dextrorotatory, and levorotatory.
- Understand the principles behind polarimetry and how they relate to chiral molecules.
- Be able to identify molecules that have an enantiomer, be able to recognize pairs of molecules that are enantiomers, and be able to draw the enantiomer of a given chiral molecule.

**The Concept of Chirality:** Our discussion of isomerization in Chapter 4 marks a transition from considering molecules as assemblies of bonds to thinking of them as three-dimensional objects. One of the properties that a three-dimensional object can have is chirality.

Objects that are chiral are non-superimposable (i.e. structurally different) from their mirror images. Objects that are achiral can be superimposed on their mirror image. Figure 5.1.1 shows an example of each.



**Figure 5.1.1:** Left: The right hand creates a mirror image that is a left hand. The object and the image are non-superimposable, so the hand is chiral. Right: The triangular block creates a mirror image that is identical to the original. The two objects are superimposable, so the block is achiral.

To understand what is meant by “non-superimposable,” look at your hands. The angle between your right thumb and each of your right-hand fingers is the same as the angle between your left thumb and each of your left-hand fingers. And the fingers and thumb have the same relationship with the front and back of the

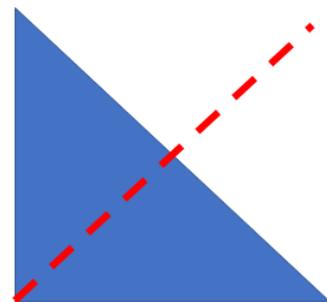
hand, being able to curl over your palm but not to bend backwards without breaking. Now lay your right hand on top of your left, so that both palms are pointing downward at the floor in front of you. Your thumbs point in opposite direction. If you try to line your hands up so your thumbs are pointing in the same direction, your palms will face in opposite directions. Your right and left hands are mirror images of each other, but have different geometries and cannot align up in a way that all of their components match.

By contrast, the triangle shown in the Figure 5.1.1 is superimposable with its mirror image (i.e. the real block is identical to the image). How is the block different?

The answer comes down to symmetry. The block has a geometric property called a plane of symmetry. A plane of symmetry is an imaginary plane that cuts the object into two equal halves, shown for the triangle in Figure 5.1.2. It is a property of geometry that objects that have a plane of symmetry are superimposable with their mirror image, and so are achiral. The wooden block in Figure 5.1.1 actually has a second plane of symmetry lengthwise (cutting lengthwise to create two triangles that are the same as the original but half as thick), but only one plane of symmetry is necessary to make an object achiral.

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**Figure 5.1.2:** A triangle with a plane of symmetry shown.



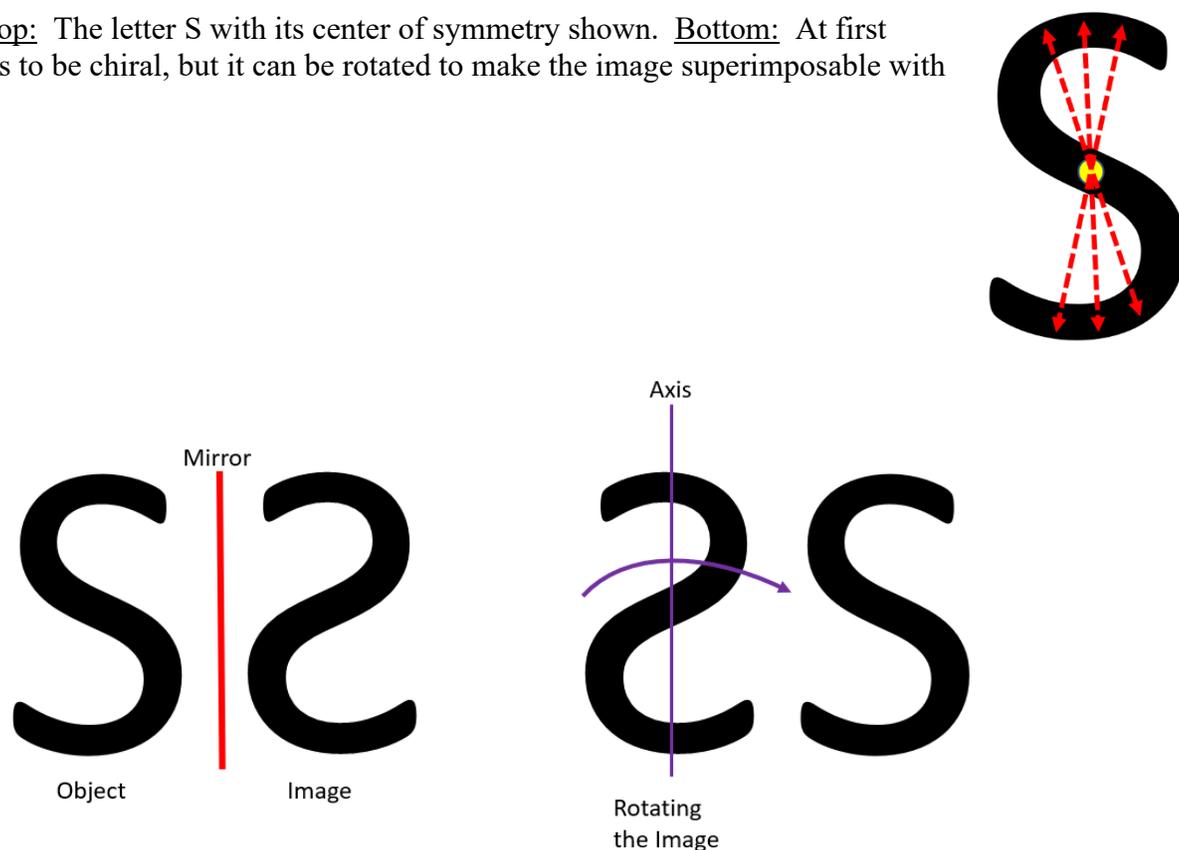
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There is a second geometric property that can make an object achiral, and that is a center of symmetry. A center of symmetry is a slightly more complicated idea than a plane of symmetry, but in essence it is a point in the molecule through which the structure can be transposed. The letter S has a center of symmetry at its midpoint, as illustrated in Figure 5.1.3. To transpose the object, pick any point in the object and draw a line to the center of symmetry.

Now continue the line through the center of symmetry, going as far away from the center as it took to get to it (i.e. if it took a distance  $d$  to get from where you started to the center of symmetry, go a distance  $d$  beyond it in the same direction). Now imagine you have moved the part of the object where you started to the new point. If in doing this transposition you end with the same object that you started with, the molecule has a center of symmetry.

If the object has a center of symmetry, you can do this for every point in the object and wind up with the same object you started with.

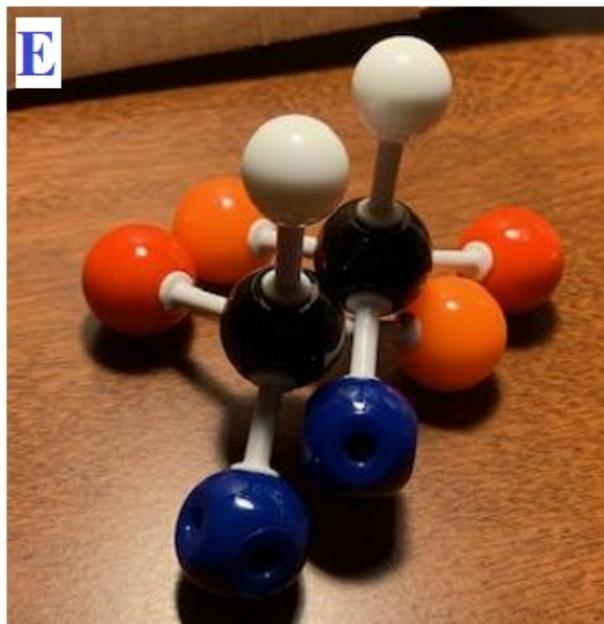
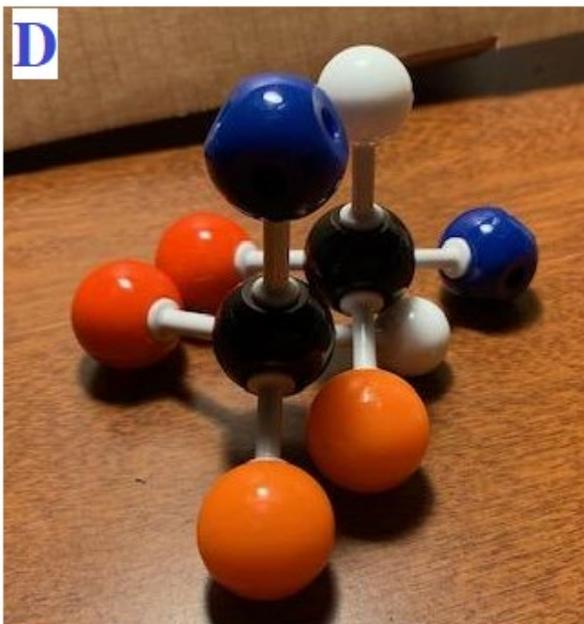
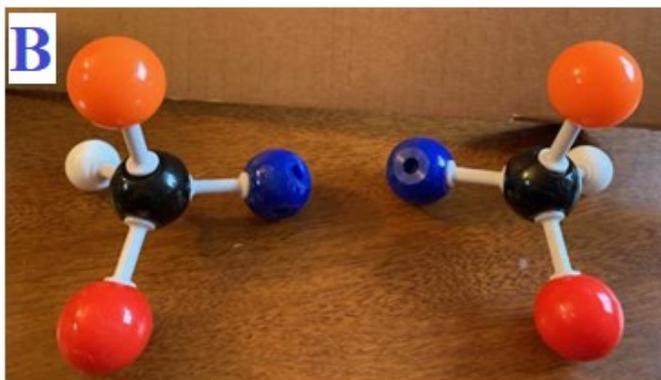
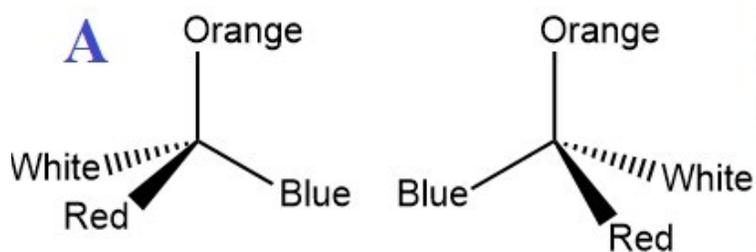
**Figure 5.1.3:** Top: The letter S with its center of symmetry shown. Bottom: At first glance S appears to be chiral, but it can be rotated to make the image superimposable with the object.



Now that we understand the basic concept of chirality, we need to consider how it applies to molecules.

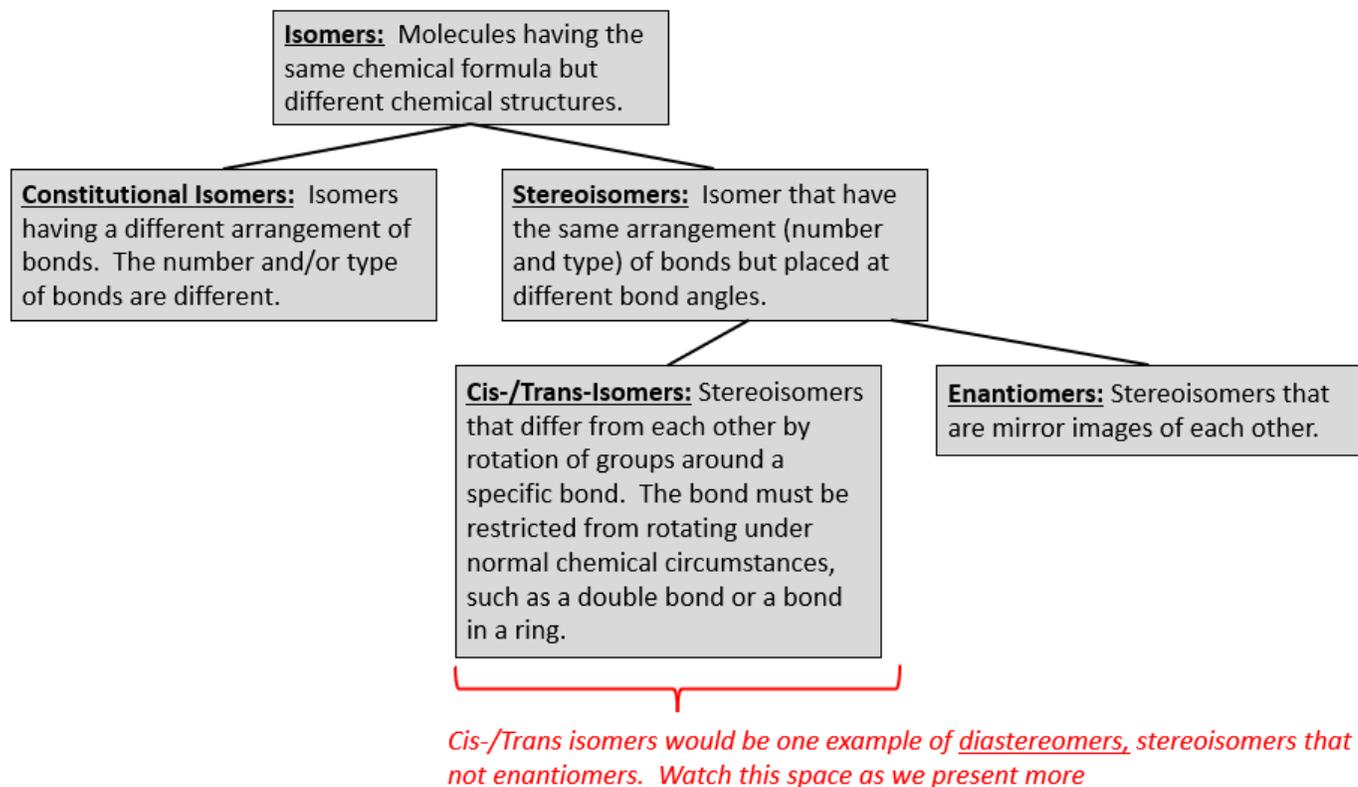
**Chirality in Tetrahedral Carbon:** Chirality manifests in many forms in chemistry and biochemistry, but by far the most common involves  $sp^3$ -hybridized (tetrahedral) carbon atoms. Figure 5.1.4 gives an example of this using molecular model kits. Tetrahedral atoms with four different substituents are chiral, meaning that there are two ways the four substituents can be attached to the center. A tetrahedral center that is chiral is referred to as a stereocenter.

**Take Note!** Trying to learn the three-dimensional thinking necessary to understand chirality is challenging. Use a model kit! If you do not have a chemical model kit, use marshmallows and toothpicks to make one. Yes, really. It is the best thing you can do for yourself. Do it!



**Figure 5.1.4:** **A:** Wedge-angle drawing depicting balls of differing color bound to a tetrahedral center. **B:** Molecular model kit depictions of the wedge angle drawings. **C:** Demonstration that the mirror image of one enantiomer is equivalent to the other enantiomer. **D,E:** The two models overlaid with each other to show that they are nonsuperimposable. The left shows that if the red and orange balls line up, the white and blue are out of alignment. And the right shows that if the white and blue line up, the red and orange are out of alignment.

Molecules that are mirror image of each other are said to be enantiomers. Like cis-/trans-isomers, enantiomers are a type of stereoisomer. Because chirality presents unique challenges in chemistry, there is a word for molecules that are stereoisomers but are not enantiomers: Diastereomers. So, cis-/trans isomers would be examples of diastereomers.



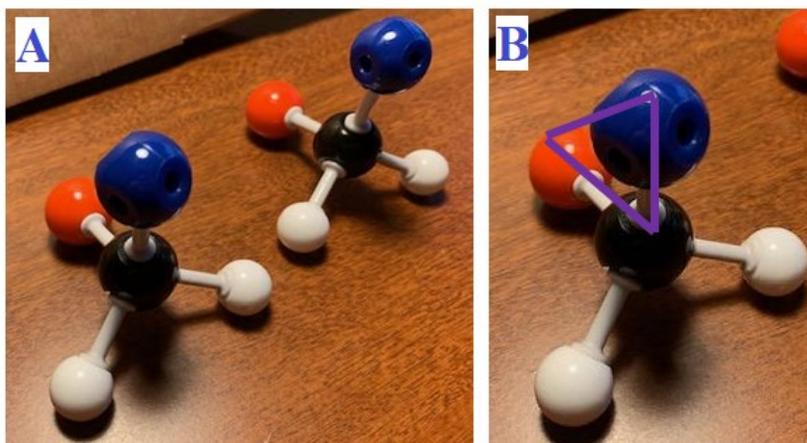
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**Figure 5.1.5:** Diagram of possible forms of isomerization.

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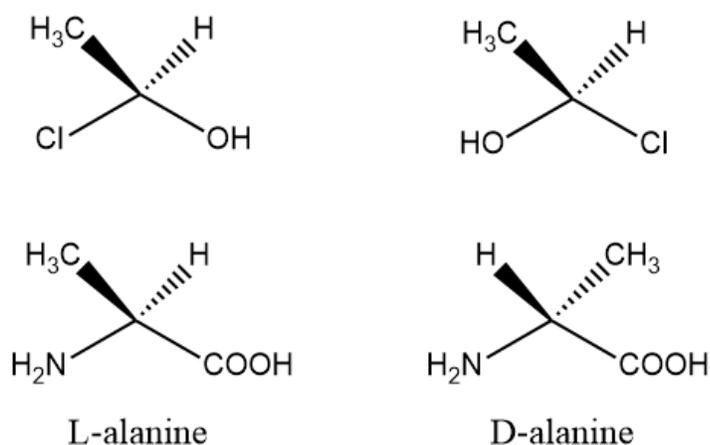
Molecules operate under the same rules for chirality as other three-dimensional objects, meaning that if they contain a plane of symmetry or a center of symmetry then they are superimposable with their mirror image (i.e. they are achiral). Figure 5.1.6 shows an example of this.

**Figure 5.1.6:** A tetrahedral carbon with two identical substituents. It possesses a plane of symmetry defined by the three atoms indicated with the purple triangle on the right-hand side, and therefore is not chiral.



Some examples of chiral chemical systems are shown in Figure 5.1.7. As indicated by the examples using colored balls above, all that is necessary to create a chiral compound is a  $sp^3$ -hybridized carbon atom with four different substituents.

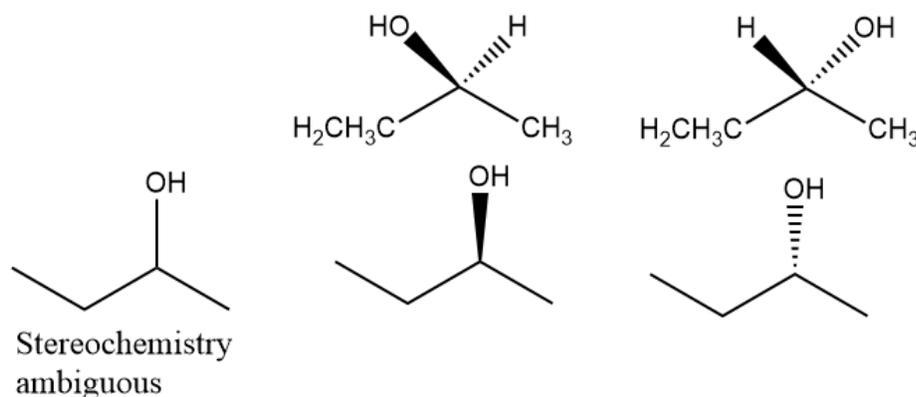
**Figure 5.1.7:** Examples of enantiomers. The figures at the top are somewhat artificial examples, but alanine is an amino acid and very common in biochemical systems (including you).



As you might expect from their similarity, enantiomers are nearly identical chemically and physically. Samples of right- and left-handed enantiomers will have the same physical properties (e.g. melting point) and identical reactivity toward other chemicals. The only exception to this occurs for reactions between chiral molecules, or when chiral molecules interacting with chiral environments such as plane-polarized light (discussed below). The enantiomeric character of molecules might be a curiosity, except that many biomolecules (among them amino acids, carbohydrates, and nucleic acids) contain chiral centers that occur in only one handedness. These centers will often interact only with one isomer of other molecules (e.g. ribosomes will not synthesize proteins from amino acids of the wrong handedness), meaning that nutrients and drugs must have the correct handedness to be metabolized by an organism. Chirality is thus critically important in biology and medicine.

Note that we needed to use wedge-angle notation to draw the molecules with their correct stereochemistry. Line-angle notation does not provide sufficient detail to indicate the chiral character of a molecule.

**Figure 5.1.8:** The line-angle drawing on the left provides enough information to identify a stereocenter (second carbon from the right) but not enough to determine its stereochemistry.



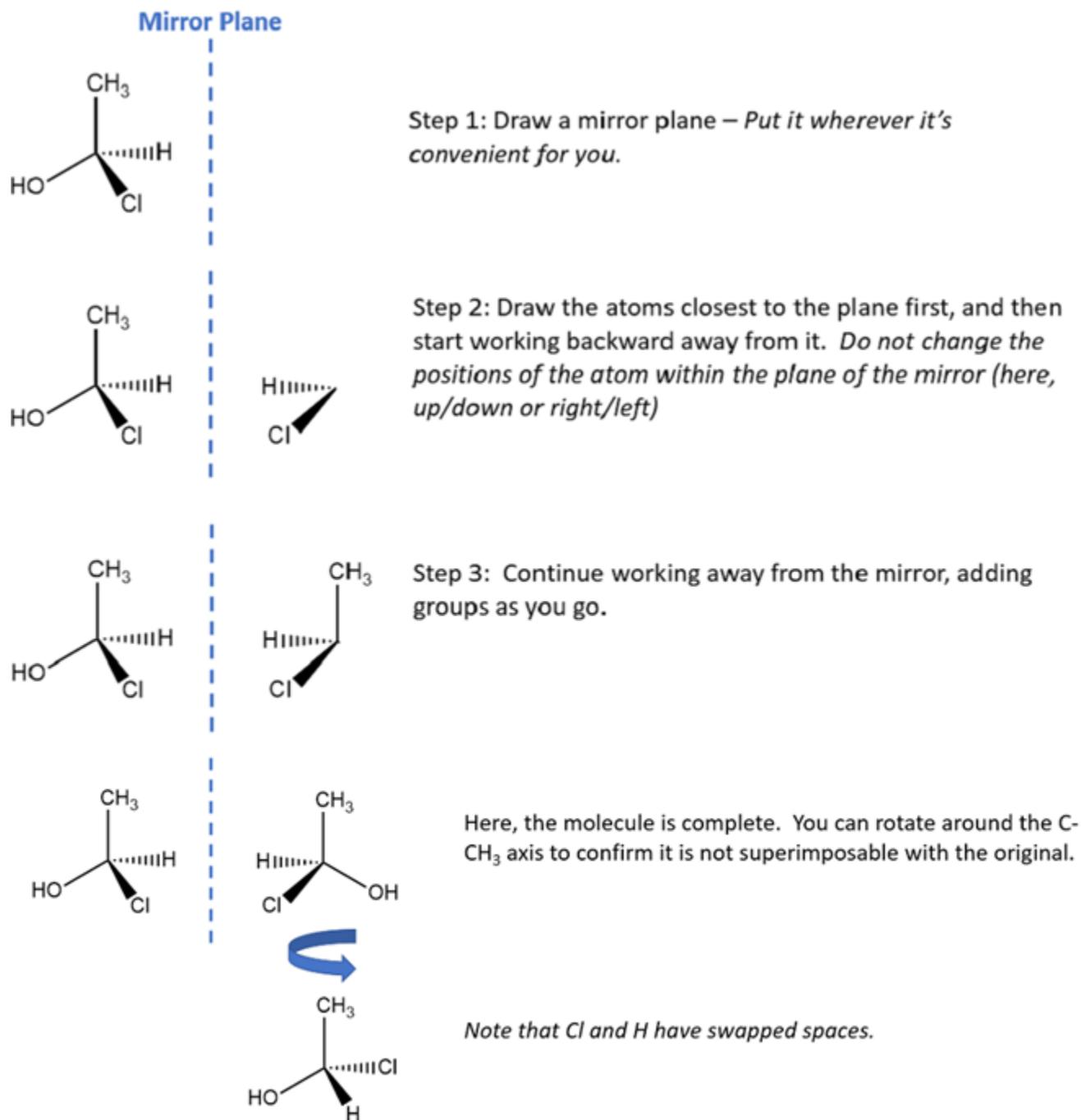
**The Mirror Plane, and Drawing Enantiomers:** It is worth taking a moment to consider how a mirror works so that we can better understand enantiomerism. If you hold your hand out in front of a mirror, the image does the same to you. Your hand – the part of you closest to the plane of the mirror – is the part of your image closer to the mirror plane. Your hand is not moved to the side, as demonstrated by the fact that you can touch the mirror plane and it appears that the image is reaching back to touch you. The fact that it appears your right hand is touching the left hand of the image seems to contradict this, but in fact it is your front and back that have switched directions, not your left and right (i.e. you are facing the mirror but your image is facing the wall behind you).

Figure 5.1.9 shows how to draw an enantiomer using the mirror plane. The key idea is to draw the mirror plane at a position next to the molecule that you find convenient (any will do) and then systematically draw the image. This is done by identifying the parts of the original that are closest to the plane of the mirror and drawing those closest to the mirror on the opposite side. It is important not to change the position of those objects in a direction that is parallel to the plane of the mirror. In the example drawn, the Cl is coming out of the page (solid wedge) and the H is going into the page (dashed wedge) in both the original and the image. Only the direction perpendicular to the mirror plane (from left to right on the page) is reversed.

The last step to rotate the figure is not really necessary, except that it makes it easier to compare the image with the original. And you will probably notice something that you likely noted in the earlier examples. When molecules are drawn in wedge-angle notation, you can create the enantiomer by swapping two (but *only* two) of the groups attached to the center. In this case, our operations amounted to swapping the positions between the H and the Cl in the original structure. Though we could have swapped the positions of the -CH<sub>3</sub> and the -OH and gotten the same molecule.

**Take Note!** Having trouble seeing all this? Don't see how the rotation is supposed to work, or how you get the same molecule by swapping -CH<sub>3</sub> and -OH as you do swapping -H and -Cl. Take out your model kit or your marshmallows and toothpicks and start building. If you don't have those, **GET THEM! SERIOUSLY! YOU REALLY NEED THEM THIS IS NOT SOMETHING YOU CAN DO WITHOUT!!!**

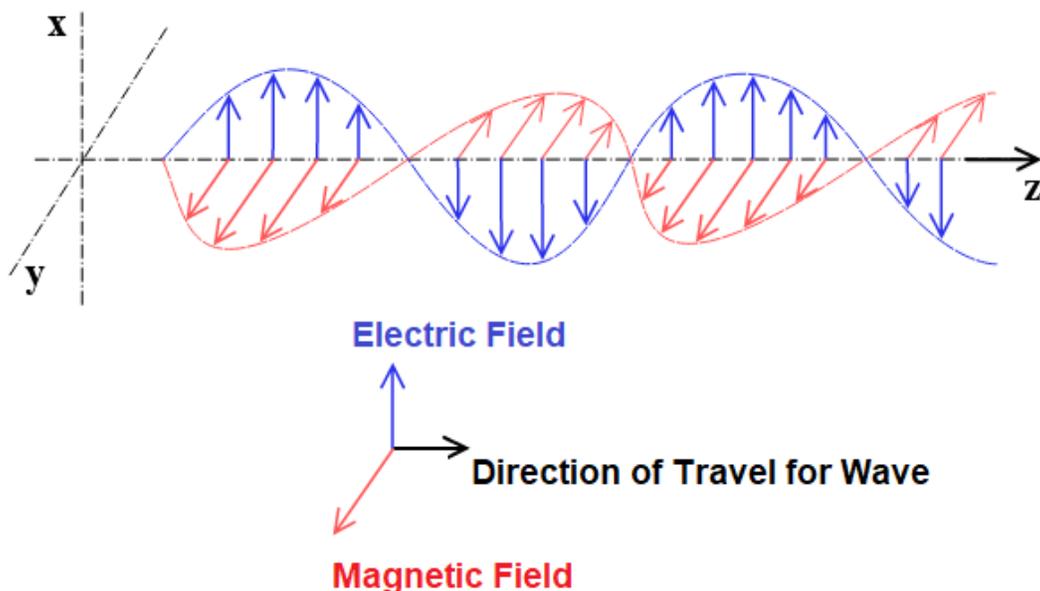
This is a general principle. In most cases, one can generate an enantiomer just by swapping two groups. But you should understand how a mirror plane works.



**Figure 5.1.9:** Steps to drawing an enantiomer using a mirror plane. The final rotation around the C-CH<sub>3</sub> axis is optional performed here to allow easier comparison between the original and its mirror image.

**Polarimetry:** Given the importance of chirality in biology, it is necessary to be able to determine whether a chiral molecule is present. This is most commonly done using a technique called polarimetry.

Light consists of waves. The amplitude of a light wave consists of an electric field and, perpendicular to that, a magnetic field; this is why light is referred to as an electromagnetic wave. While magnetic fields typically interact very weakly with molecules, electric fields interact strongly and can be changed by their interactions with matter.



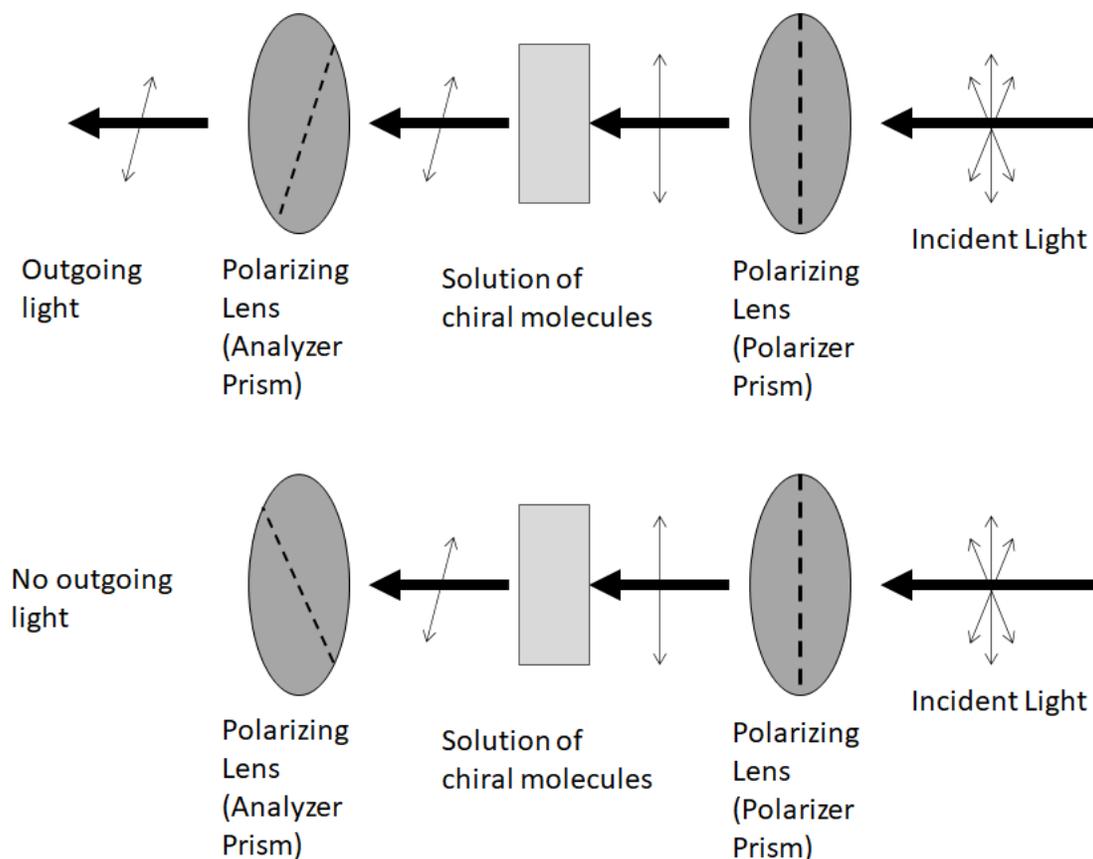
**Figure 5.1.10:** Diagram of a light wave. The electric and magnetic amplitudes of the wave are perpendicular to each other, and to the direction of travel for the wave. Modified from Wikimedia Commons, [https://commons.wikimedia.org/wiki/File:Onde\\_electromagnetique.svg](https://commons.wikimedia.org/wiki/File:Onde_electromagnetique.svg), accessed July 19, 2021.

Light emitted from a typical source, such as a fluorescent lightbulb, has no particular orientation for its amplitude, and there are oscillations in the electric field occurring at all possible angles. However, some materials have a property that lets them block all electric fields except one oriented in a preferred direction of the material. This is the principle behind polarizing lenses for sunglasses and cameras, that they reduce the intensity of incoming light by blocking out some components of the light based on their orientation. The light coming out of the polarizing lens has only one orientation for its electric field, and it is said to be plane-polarized light.

One property of chiral molecules is that they will rotate plane-polarized light. What is more, each enantiomer will rotate it in a different direction. One enantiomer will rotate the light clockwise and is said to be dextrorotatory, and the other will rotate light counter-clockwise and is said to be levorotatory.

This makes it possible to detect the presence of an enantiomer using the rotation of light measured by a device called a polarimeter. A polarimeter uses a pair of polarizing lenses to measure the rotation of light as shown in Figure 5.1.11. Unpolarized light is transmitted through the first polarizing lens to create polarized light. The light then passes through a solution containing the enantiomer. The plane polarized light will be rotated by an angle determined by the type of molecule present and its concentration.

The outgoing light passes through a second polarizing lens. When the polarizing lens is aligned with the outgoing light from the sample, the light passes through unaltered. When it is out of alignment, it is blocked. An observer can rotate the polarizing lens to determine the angle of the polarized light emitted from the sample, and comparing that to the angle of the incident light from the first polarizing lens gives the optical rotation.

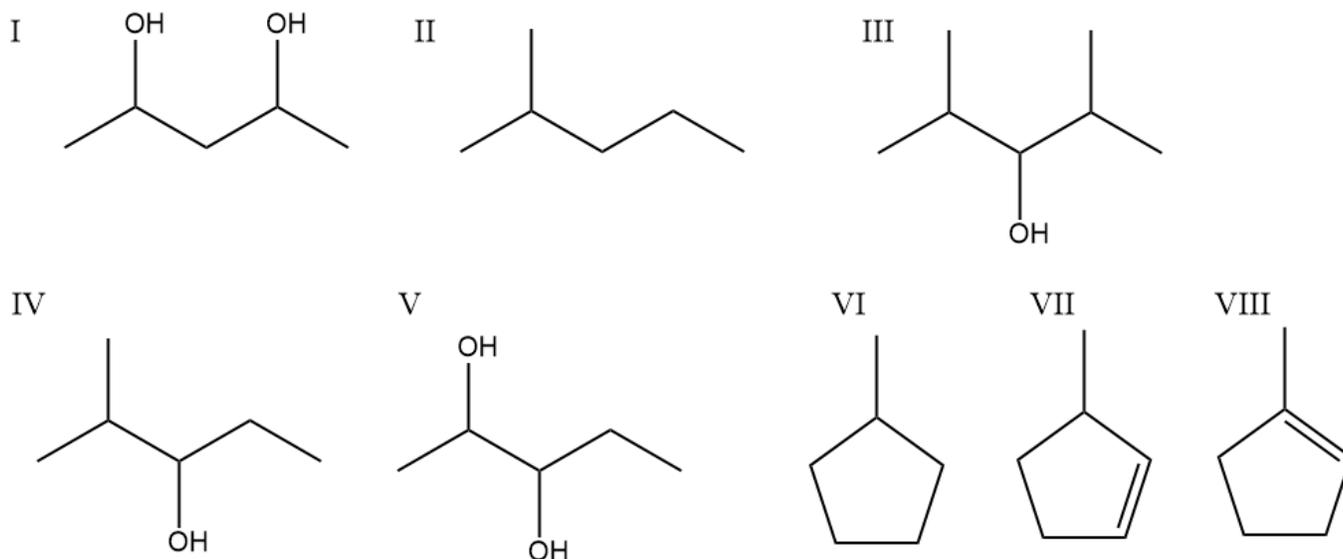


**Figure 5.1.11:** Schematic diagram of a polarimeter. The first lens creates plane-polarized light, which then passes through the sample and is rotated by an angle that depends on the identity and concentration of the chiral molecule. A second lens can be rotated to either allow passage of the rotated light or block it. The angle between the polarizing lens and the analyzing lens allows gives the angle of the rotated light.

There are complicating factors. Sometimes enantiomers can occur in mixtures, with some dextrorotatory and some levorotatory molecules in solution; this means the rotation will at least partially cancel out. Mixtures with equal concentration of each enantiomer are said to be racemic, and will not rotate light at all. Still, polarimetry is by far the simplest way to study enantiomers.

**Identifying Stereocenters:** While line-angle drawings do not communicate a specific enantiomer, it is important to be able to identify stereocenters within them as this allows one to determine whether a molecule could be chiral or not. As noted above,  $sp^3$ -hybridized carbon atoms with four different substituents (i.e. no plane of symmetry) will be stereocenters.

Examine the molecules in Figure 5.1.12 and attempt to identify the stereocenters.



**Figure 5.1.12:** Sample molecules, some of which contain one or more stereocenters. Identify the stereocenters and then read through the text to check your answer and your reasoning by comparison with Figure 5.1.12A.

The key is to look for tetrahedral centers with four different substituents. You may want to use hash marks to indicate the number of H atoms on each carbon, as described in Section 4.1, as the hydrogens must be taken into account.

For Structure I, each of the carbons bound to the two OH groups is chiral. Each C is bound to a -H, a -CH<sub>3</sub>, a -OH, and the main chain of the molecule. These are four different groups, so they are chiral centers. But, strangely, the molecule itself could have a plane of symmetry through the 3<sup>rd</sup> carbon in the chain, meaning the molecule could not be chiral. If you saw this and were confused, well-done! The truth is that a molecule that is not an enantiomer can contain chiral centers. We will return to this point in Section 5.2.

Structures II and III contain no chiral C atoms. The only candidate in Structure II would be the second carbon from the left, but that has two -CH<sub>3</sub> groups attached to it so it cannot be chiral. The same is true for the 2<sup>nd</sup> and 4<sup>th</sup> C in the chain for Structure III, so they are not chiral. The third C looks like it could be, except that each is bound to a -CH(CH<sub>3</sub>)<sub>2</sub> group. For all that this is a more complicated structure than other groups, these structures are equivalent and so the center has symmetry. That symmetry is broken in Structure IV, so the third C atom is chiral. The same reasoning makes it possible to identify the two chiral centers in Structure V.

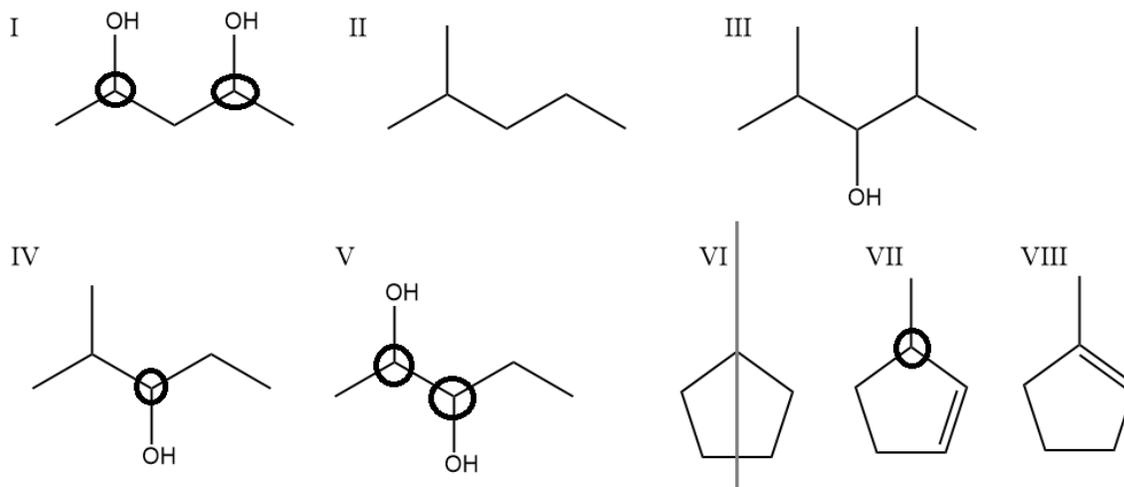
The rings in Structures VI, VII, and VIII are more challenging. The way to view the ring is to work your way outward from a candidate carbon, first looking at the neighboring atoms, and then the next neighbor, and so on until you have completed the ring.

In Structure VI, the top carbon in the ring is bound to -H, -CH<sub>3</sub>, and the two arms of the ring. Working outward in each direction, once encounters a -CH<sub>2</sub>- on both the left- and right-hand arms, so the groups are equivalent when taken that far. Working to the next, we find another -CH<sub>2</sub>-. And then we have covered all C atoms in the ring, so we have confirmed that the arms of the ring are equivalent on both sides. Thus, that topmost C is not chiral. We might have recognized that more easily by realizing that there is a plane of

symmetry that cuts the ring in half (shown in gray in Figure 5.1.12A), but it is useful to be able to treat the ring systematically.

In Structure VII, the symmetry is broken by the presence of the double bond within the ring and so that carbon is now chiral. More systematically, moving to the left one encounters a  $-\text{CH}_2-$  group while on the right one encounters  $-\text{CH}-$ , so the groups are clearly different.

The topmost C atom in Structure VIII is  $\text{sp}^2$ -hybridized, and so will not be chiral.



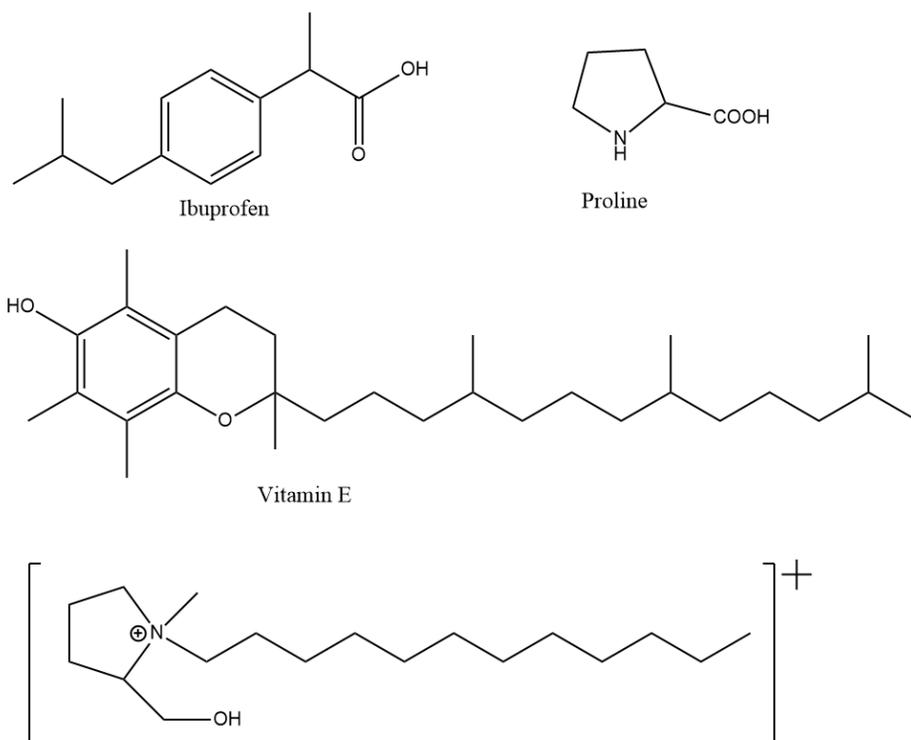
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**Figure 5.1.12A:** Chiral centers for molecules given in Figure 5.1.12. Structure VI shows a plane of symmetry for the molecule.

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A second set of molecules is given in Figure 5.1.13. See if you can identify the stereocenters in those as well.

**Figure 5.1.13:** Sample molecules, some of which contain one or more stereocenters. Identify the stereocenters and then read through the text to check your answer and your reasoning by comparison with Figure 5.1.13A.



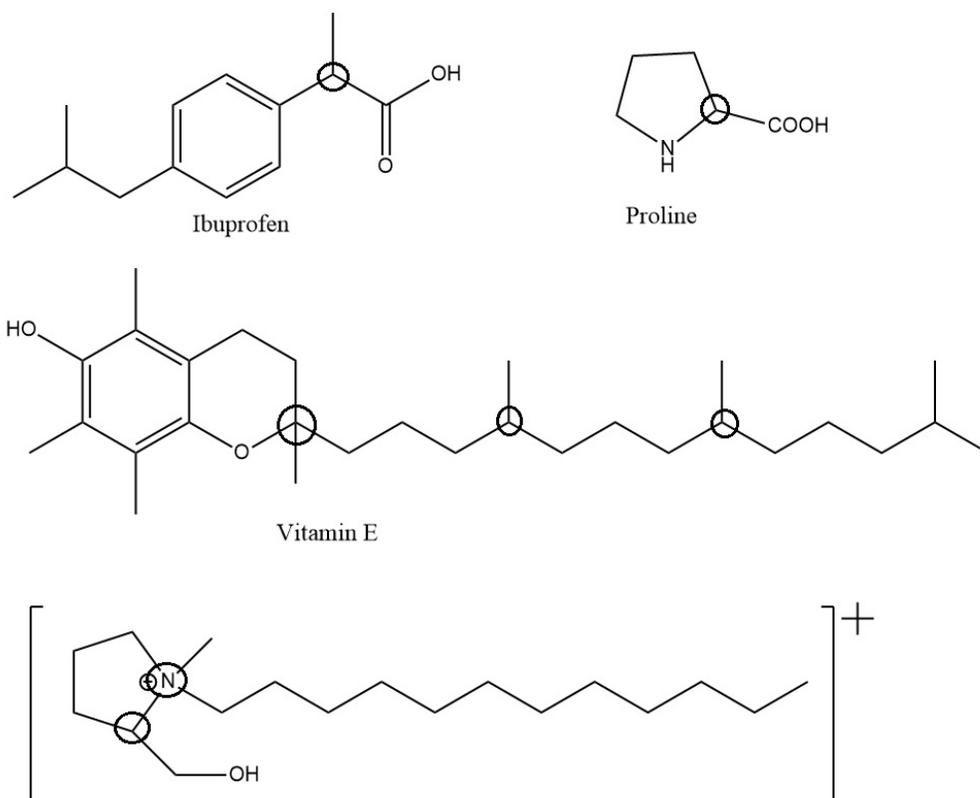
For ibuprofen, the first molecule given in Figure 5.1.13, it is easy to identify the lone stereocenter if you search systematically. The  $sp^2$ -hybridized C atoms in the ring and the carboxyl group can immediately be ruled out, and the left-hand chain has no C atoms containing 4 distinct groups. Proline is similarly straightforward, as one can quickly rule out the COOH and the three  $-CH_2-$  groups in the ring. The N atom only has 3 bonds so is not chiral, but the presence of the N breaks the ring and gives the neighboring C a chiral character.

Vitamin E is long, but again can be approached systematically. The aromatic ring and its  $-CH_3$  substituents can be ruled out, the former because they are  $sp^2$ -hybridized and the latter because they do not have enough unique groups. On the second ring and in the chain, we can rule out most C atoms because they are  $-CH_2-$  groups. The point where the long chain joins the ring is chiral because the symmetry of the ring is broken by the presence of the O. The methyl groups coming off the chain create chiral character down the line, except on the second-to-last C atom where there are two  $-CH_3$  groups.

The last molecule is actually from a recent research paper, and offers a twist. The symmetry of the ring is broken by the N-atom, so of course the carbon that is circled is chiral. But the N is chiral as well. This is possible because it is a  $sp^3$ -hybridized atom with four separate groups (the symmetry of the ring is broken by the substituent on the chiral C). This is possible because the positive charge of the ion leads to an extra bond on the N atom.

This is an unusual but not unique occurrence, and occasionally happens with phosphonium ions as well (4 groups attached to a positively-charged phosphorous). Our reason for mentioning it is not just to make you aware of these cases – though they can be useful – but to remind you that chirality is a property of geometry. It is useful to understand that a tetrahedral C atom with four unique substituents is a stereocenter, but it is essential to understand that chirality arises from geometry. As we stated at the beginning of this section, tetrahedral carbon atoms represent most cases of chirality in organic molecules, but by no means all.

**Figure 5.1.13:** Sample molecules, some of which contain one or more stereocenters. Identify the stereocenters and then read through the text to check your answer and your reasoning by comparison with Figure 5.1.13A.

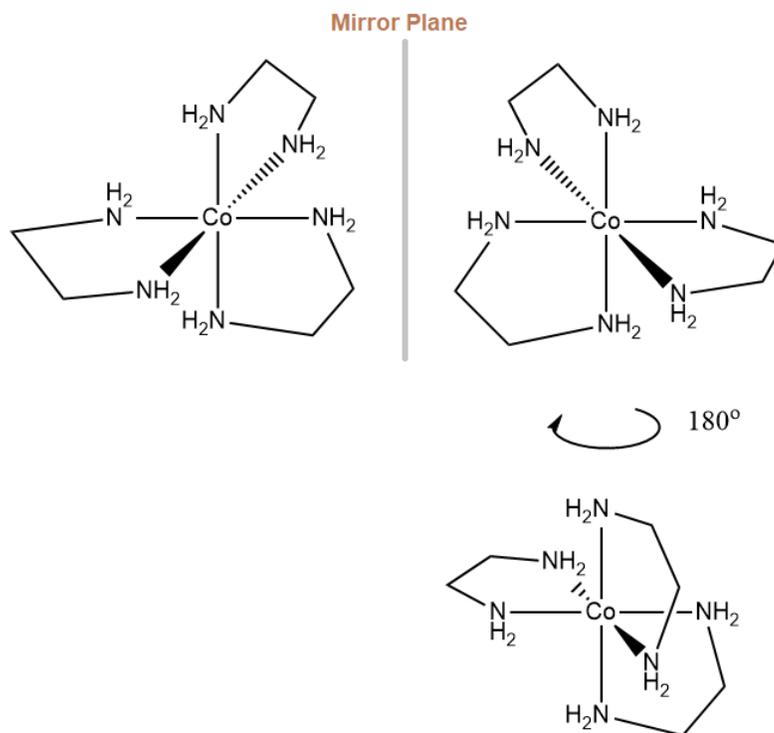


**Other Examples of Chirality:** We will mostly retain our focus on the chirality associated with  $sp^3$ -hybridized stereocenters. However, it is worth digressing to briefly consider other types of enantiomers, if only to gain a better understanding of how chirality works.

Figure 5.1.14 shows an example of a chiral metal complex that may be familiar to you from second semester general chemistry. This is actually an inorganic compound formed by coordination chemistry, which allows the metal to form coordinate bonds with pairs of electrons (in this case, on the N atoms) at six different points. The result is an octahedral compound.

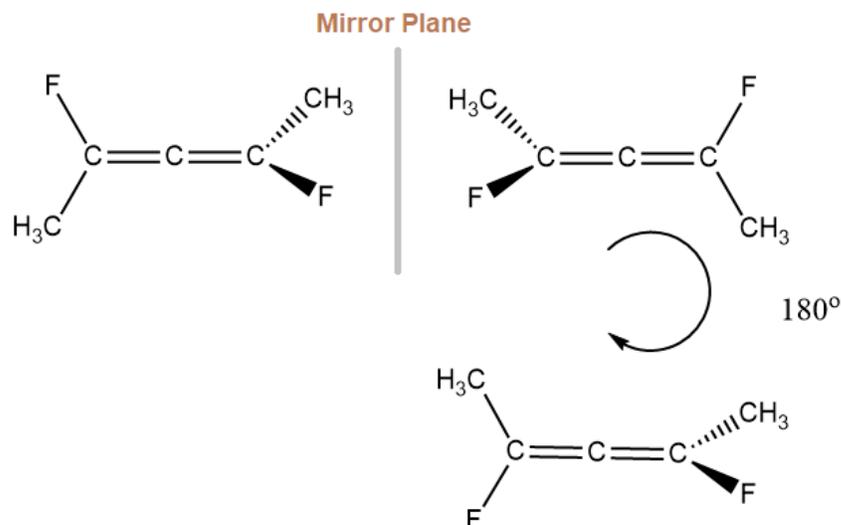
Coordination compounds are most often achiral, but when there are three bidentate ligands (i.e. molecules that bind to the metal at two different points) a chiral structure can form. Look at the mirror image shown on the right. When the mirror image is rotated, the ligand that is in the plane of the page (running from the right-hand side to the bottom site of the complex) overlaps the original structure, but the other two loops are out of position. No reorientation can superimpose the two structures; if you have trouble seeing this, you should try it with a model. **Yes, use the model!**

**Figure 5.1.14:** The  $[\text{Co}(\text{en})_3]^{2+}$  metal complex, formed from a  $\text{Co}^{2+}$  ion and three ethylene diamine ligands ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ).



This is a useful exercise, but complexes like this cannot form without the inclusion of a metal. A more relevant example for organic chemistry is shown in Figure 5.1.15. This is an organic molecule and contains no  $\text{sp}^3$ -hybridized carbon but is chiral. This is because of the geometric constraints for the  $\text{sp}$ -hybridized carbon at the center, and the distribution of groups on the  $\text{sp}^2$ -hybridized carbons. Recall that, as discussed previously,  $\text{sp}^2$ -hybridization fixes the positions of the adjoining atoms in a plane perpendicular to the unhybridized  $p$ -orbital. In this case, that means the planes defined by each of the  $\text{sp}^2$ -hybridized carbons must be at a  $90^\circ$  angle relative to each other, because the  $p$ -orbitals on the  $\text{sp}$ -hybridized carbon at the center are at  $90^\circ$ . The net result is a structure that is not superimposable with its mirror image (i.e. is chiral).

**Figure 5.1.14:** A chiral organic molecule that does not contain a chiral,  $sp^3$ -hybridized carbon. See text for discussion.



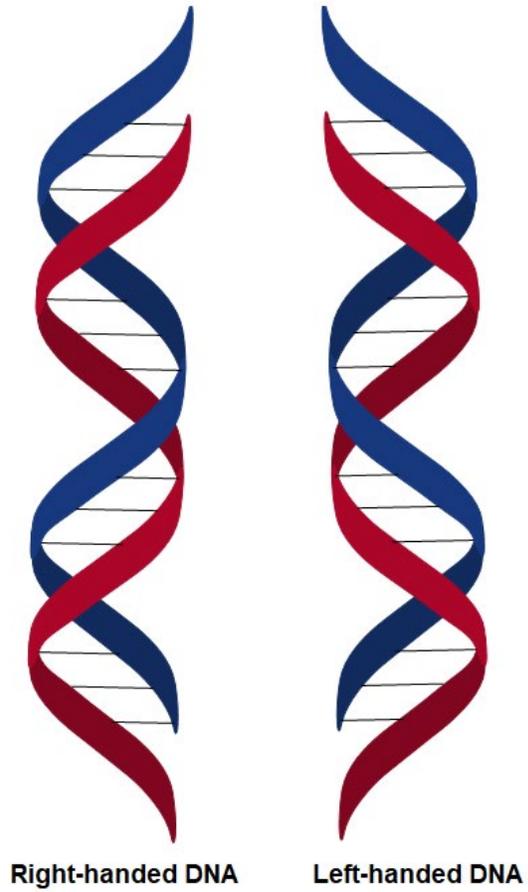
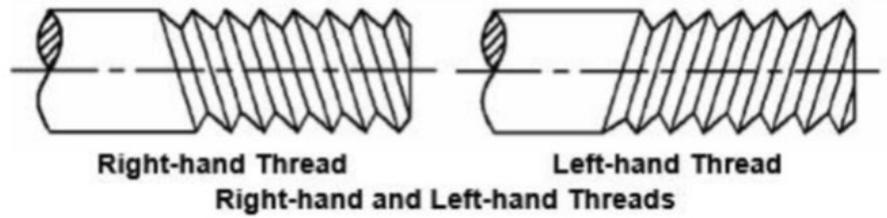
It is also important to recognize that chirality is not only a property of small molecules. Larger structures, such as biopolymers, can also have a handedness. The most famous example of this is perhaps the double-helical structure in DNA.

To see that this structure is chiral, one has to understand that a single helix is chiral. Look at the images of the screws shown in Figure 5.1.15. The pitch of the threads goes in opposite directions, which changes the direction in which the screw will “bite”. If you drive the right-handed screw with the screwdriver held in your right-hand with your thumb pointed downward, rotating the screw in the direction your fingers curl will drive it into the wood. Rotating in the opposite direction will cause it to retract. Right-handed screws are most commonly used in devices, and this handedness is the origin of the “lefty-loosey, righty-tighty” rule. The left-handed screw would follow the reverse convention.

The bottom part of Figure 5.1.15 shows a pair of DNA double helices. Lined up as they are, it is easier to see that they are mirror images of each other. Double-stranded DNA occurs in nature almost exclusively in the right-handed form. Many other biomolecules and components of biomolecules (e.g. alpha helices in proteins) also display chirality. Chirality is thus more than a quirk of the tetrahedral geometry, it is a phenomenon that appears in many contexts in chemical systems.

**Figure 5.1.15:** Top: Right-handed and left-handed screws. Bottom: Right-handed and left-handed DNA double helices.

Top figure from Shah, K.P.,  
“Fundamentals of Threaded  
Fasteners,”  
<http://www.practicalmaintenance.net>,  
accessed July 21, 2021.



## Section 5.2: Analyzing Chirality

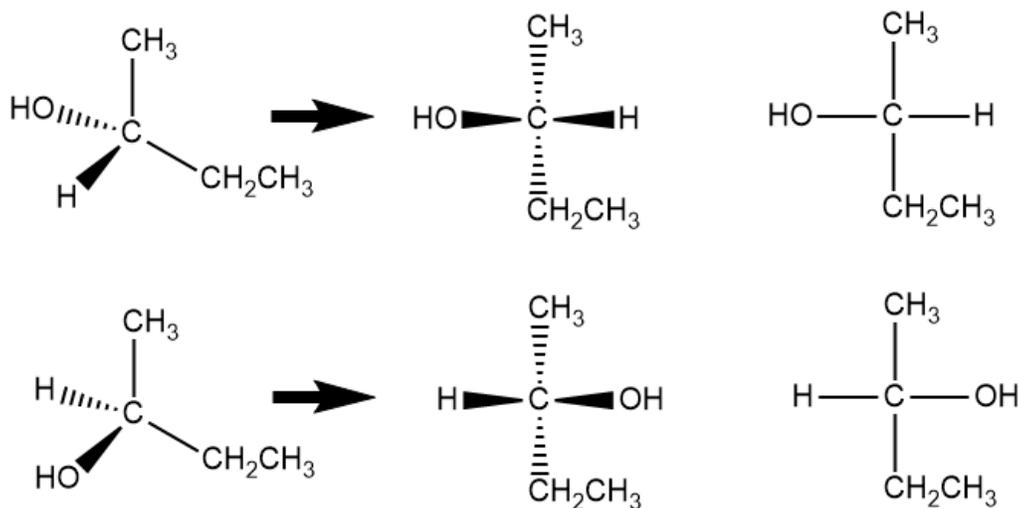
### LEARNING OBJECTIVES FOR THIS SECTION

- Be able to read a Fischer projection and express it in wedge-angle notation, and vice versa.
- Understand chirality in molecules containing two chiral centers, and be able to recognize and draw the enantiomers and diastereomers that can emerge from changes in stereochemistry.
- Know what a meso isomer is, be able to recognize one, and be able to draw one for a molecule that has one.
- Be able to recognize a stereocenter as being R or S for molecules containing one or two stereocenters. This includes knowing and being able to use the Cahn-Ingold-Prelog rules to prioritize groups.

**Fischer Projections:** As you may have noticed by now, it can be very cumbersome to draw full three-dimensional structures for every molecule containing a chiral center. A way around this is a shorthand known as a Fischer Projection.

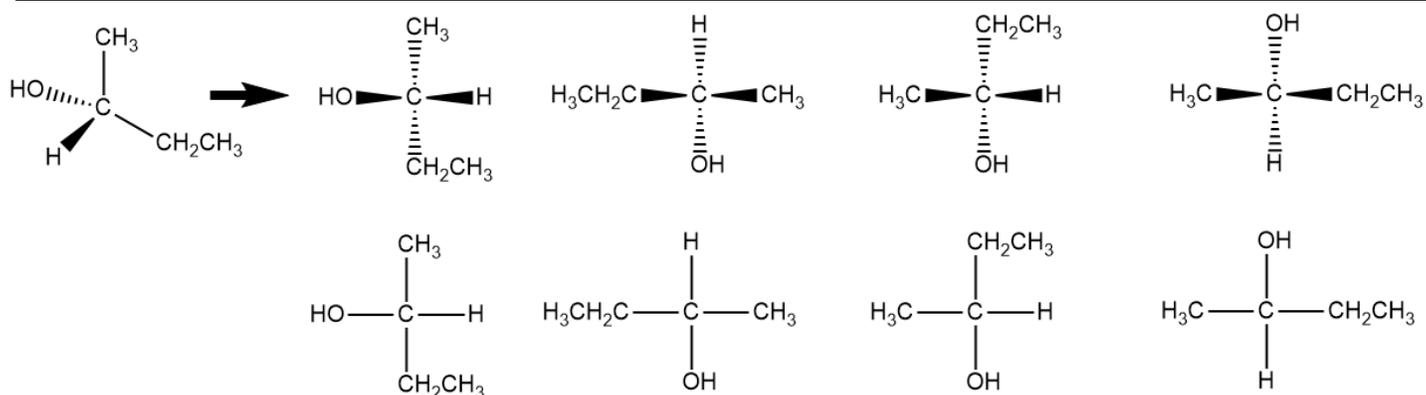
A Fischer projection capitalizes on the fact that a tetrahedron is essentially a pair of triangles rotated by  $90^\circ$  and pointed in opposite direction. Consequently, any tetrahedral stereocenter can be written with one of those triangles going into the page and the other coming out of it. Figure 5.2.1 shows how a given tetrahedral center can be rotated into such an alignment.

The Fischer projection is built around this alignment. In a Fischer projection, horizontal lines are taken to be coming out of the page (as do solid wedges) and vertical lines are taken to go into the page (as with dashed wedges). Thus, writing a Fischer projection from a wedge-angle structure requires bringing the molecule into a particular orientation.



**Figure 5.2.1:** Wedge angle representations for the enantiomers of the molecule  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ , shifted into Fischer projections.

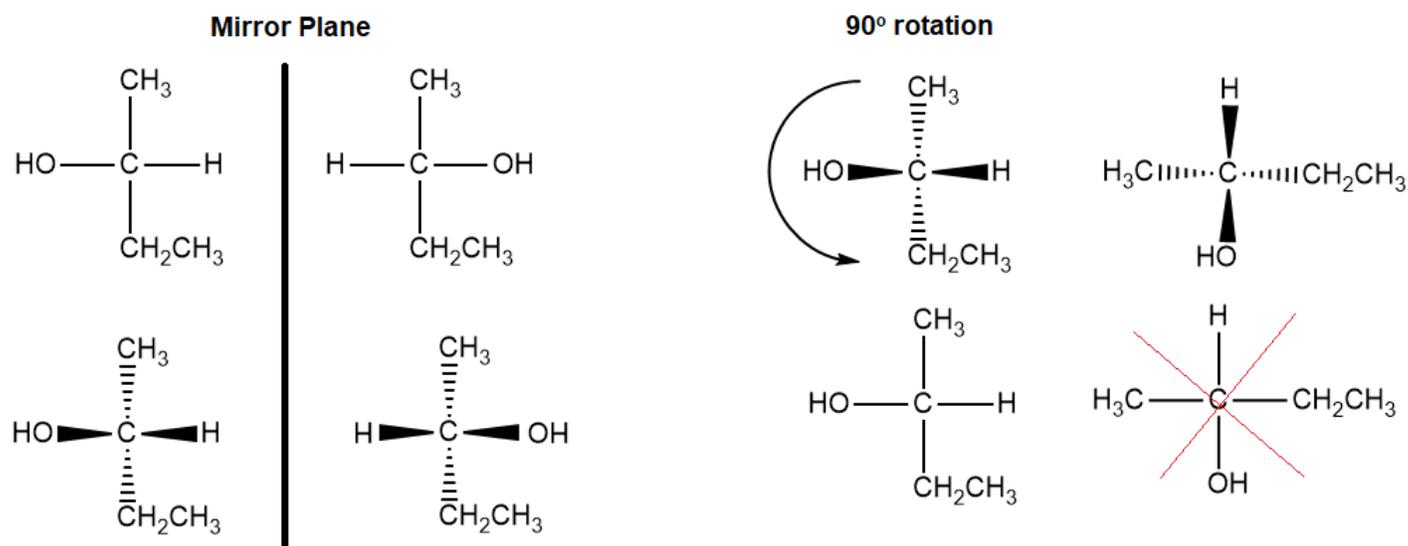
As shown in Figure 5.2.2, there are multiple Fischer projections possible for the same molecule. This is to be expected, in the same way that there can be multiple wedge angle projections for the same molecule.



**Figure 5.2.2:** Multiple Fischer projections of the same molecule.

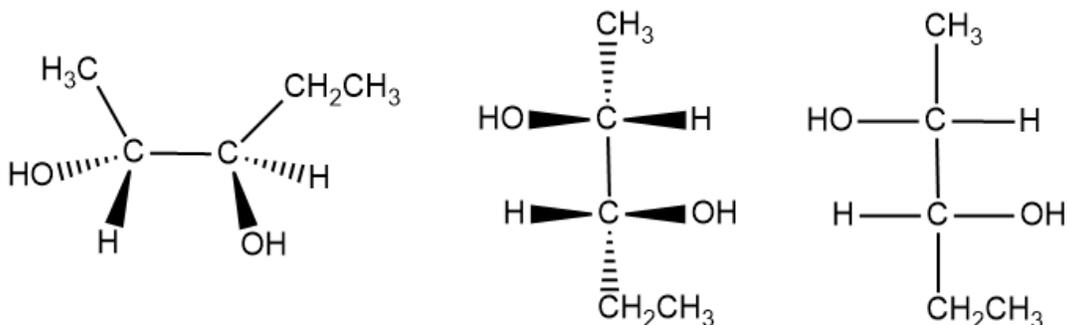
Some care must be taken in working with Fischer projections, as some operations that are intuitive in wedge-angle notation are more complicated in Fischer notation. Figure 5.2.3 shows that it is possible to use a mirror plane to generate the enantiomer of a molecule represented in a Fischer projection in the same way that it can be used for a wedge-angle projection. However, where one can simply rotate a wedge-angle projection by  $90^\circ$  and keep the same molecule, rotating a Fischer projection by  $90^\circ$  gives the wrong enantiomer. Rotating a Fischer projection by  $180^\circ$  is possible; experiment for yourself to confirm that this is true.

**Take Note!** Model kit. Seriously.



**Figure 5.2.3:** Left: Fischer projection and its mirror image, with corresponding wedge-angle representation. Reflecting through the mirror plane gives the correct enantiomer. Right: Wedge-angle rotation with a change of  $90^\circ$ ; simply rotating the Fischer projection by  $90^\circ$  gives an incorrect representation of the molecule.

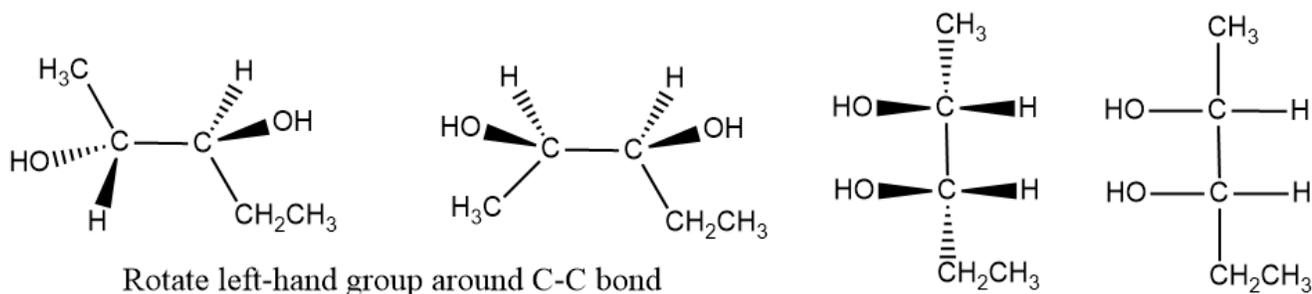
Where the Fischer projection is of greatest use is in molecules containing multiple stereocenters. An example is shown in Figure 5.2.4. The more stereocenters are present, the more time is saved by replacing wedges with straight lines.



**Figure 5.2.4:** Wedge-angle and Fischer projection of a molecule with two stereocenters.

However, it is often not quite so simple to convert wedge-angle structures into Fischer projections. Figure 5.2.5 shows a wedge-angle representation that does not neatly line up with the “up-down” angles necessary for the Fischer projection. Here, it is necessary to take advantage of the fact that single bonds can rotate without changing the identity of the molecule. Rotating around the C-C bond in the center of the molecule brings the molecule into a form where “up” and “down” wedges can be clearly distinguished and the Fischer projection drawn.

Note that there were other rotations that could have been done to bring the molecule into an appropriate form for a Fischer projection in Figure 5.2.5. Our choice was arbitrary.



**Figure 5.2.5:** Wedge-angle and Fischer projection of a molecule with two stereocenters. The left-most wedge-angle representation of the molecule does not line up with the Fischer projection and so can be modified by rotation around the C-C bond to give the second.

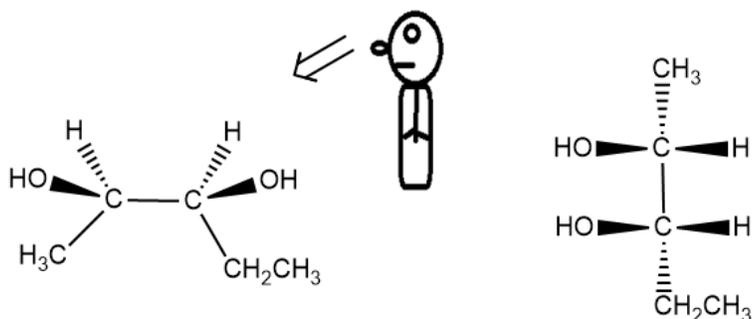
This illustrates an important point: When drawing Lewis structures or attempting to understand molecular reactions, it is often necessary to change the molecule from one conformation to another. This can be challenging to visualize, and is a skill you should work to develop. Two useful tips to guide you:

1. Remember to always rotate all groups on one side of the molecule by the same number of degrees. In Figure 5.2.5, moving from the first to the second structure required moving all three of the groups attached to the left-hand side. Bringing the CH<sub>3</sub> group into the “down” position within the plane of the page required a 180° rotation. That means that the -H and -OH groups also had to rotate by 180°.
2. Picture the person doing the visualization. Drawing an observer into the image may make it easier to visualize.

The second suggestion might seem odd, if not outright deranged, but remember that an important part of visualization is keeping track of where things sit *relative to the observer*. Consider Figure 5.2.5A, where we have drawn an observer next to the second wedge-angle projection. We want to rotate this figure so that the central C-C bond runs from the top to the bottom of the page, making it possible to write the Fischer projection. A key question is which side the substituents should sit on. Drawing the observer makes clear that both -OH groups sit on the observer's left, so should be drawn on the left after the rotation. Drawings like this are a crutch while you gain proficiency with operations of this type.

**Take Note!** Of course, if you use a model kit, you can just do the rotation.

**Figure 5.2.5A:** An observer explicitly drawn as an aid to rotating the molecule. See text for discussion.

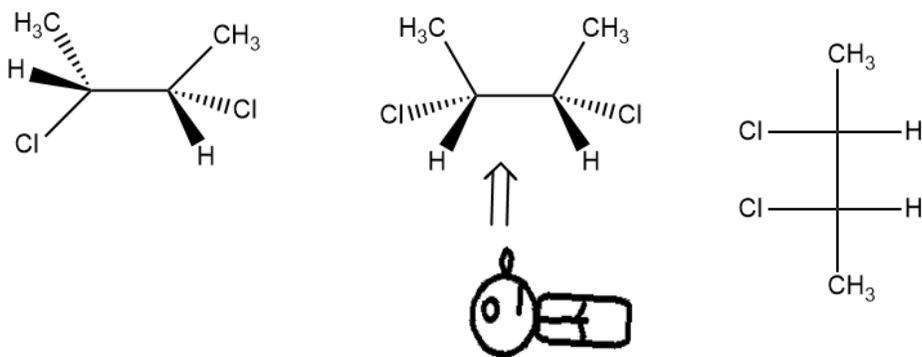


Another example of drawing in the observer is given in Figure 5.2.6. If we want to keep the CH<sub>3</sub> groups on the vertical axis (a reason we might want to do that is discussed later), then we need to rotate one of the groups by 60° relative to the other.

Here, we choose to bring the -CH<sub>3</sub> group on the left-hand C into the plane of the page. That means rotating the -H downward, though it will still come out of the page, and the -Cl atom rotates to a position behind the plane of the page.

Having gotten the two -CH<sub>3</sub> groups where we want them, we could do an additional rotation to line it up vertically with the page, though we would also need to swing it backward. But here, I have chosen instead to put the observer lying down beneath it, looking up. With the observer in place, it is easy to see that the H atoms are both on his right (coming out of the page) and the Cl atoms are both on his left. Thus, we can draw the Fischer projection directly.

**Figure 5.2.6:** Using an observer to help draw a Fischer projection. See text for discussion.



Of course, once you have become more comfortable with visualization, this type of drawing will be unnecessary. However, especially as you begin, it is absolutely critical to be systematic in your approach. It will be difficult to solve many problems in a single step – draw out intermediate structures rather than trying to picture every transformation at once. You will save yourself many mistakes.

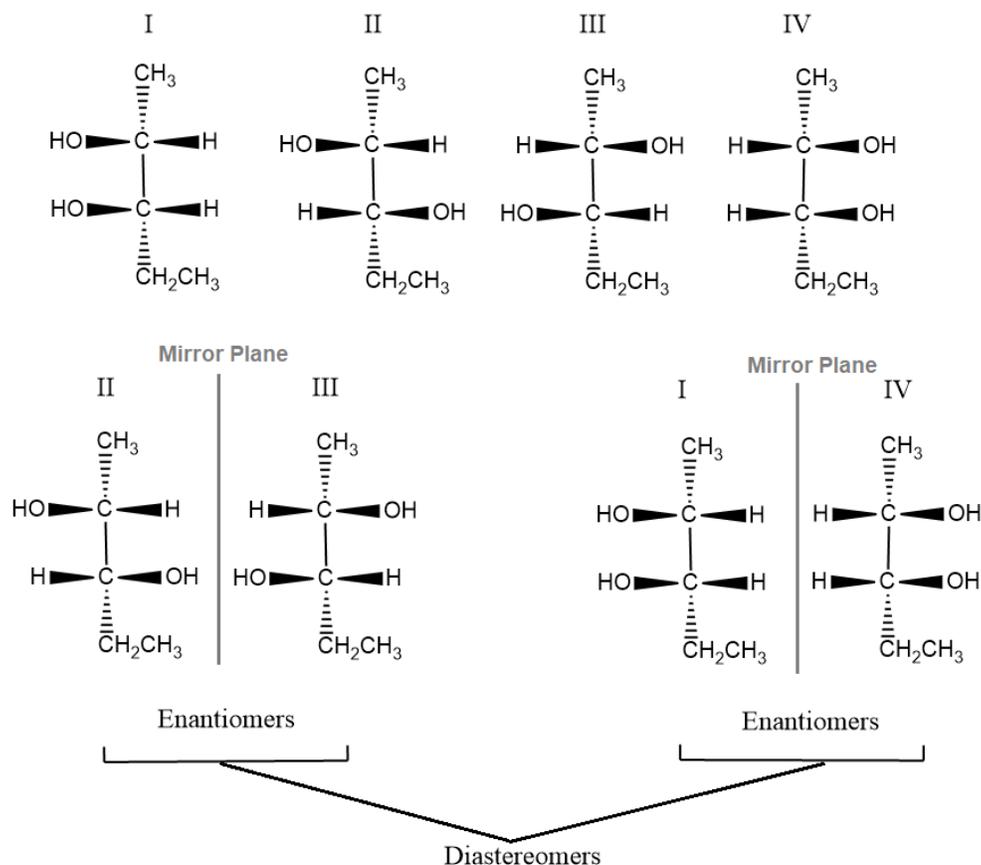
**Molecules with Multiple Stereocenters:** We have drawn some examples above that include two stereocenters, but that raises a question. No object can have more than one mirror image, which means that no molecule can have more than one enantiomer. So how does isomerism work if two chiral centers are present?

Figure 5.2.7 shows a set of four isomers based on the structure from Figure 5.2.5. Modifying each of the stereocenters by swapping the -H and -OH groups results in molecules that cannot be superimposed on each other (check this with a model if you do not see it – remember the -CH<sub>3</sub> at the top is different from the -CH<sub>2</sub>CH<sub>3</sub> at the bottom). It is easy to show that there are two pairs of enantiomers; the second line shows that Structure III is a mirror image of II, and Structure IV is a mirror image of I.

Viewed in this way, it is easy to see that I and II are not enantiomers, because the stereochemistry of one chiral center is reversed but it is identical for the other. To be a mirror image, both stereocenters must be reversed – after all, a mirror does not favor one over the other.

But what is the relationship across the pairs, say, between Structure I and Structure II? They are clearly diastereomers, differing from each other in only the angles about one stereocenter but having the same connectivity for bonds. We will also introduce a new term: Optical isomers. Optical isomers are compounds that differ from each other based on the reflection symmetry of one or more stereocenters. That means all enantiomers are optical isomers, since they have different reflection symmetry at their stereocenters. But by this definition Structures I and II are non-enantiomeric optical isomers, meaning that they are not enantiomers but they do differ by reflection symmetry at a stereocenter. The particular phrase, “non-enantiomeric optical isomers,” is not in universal use, but you should understand what it means.

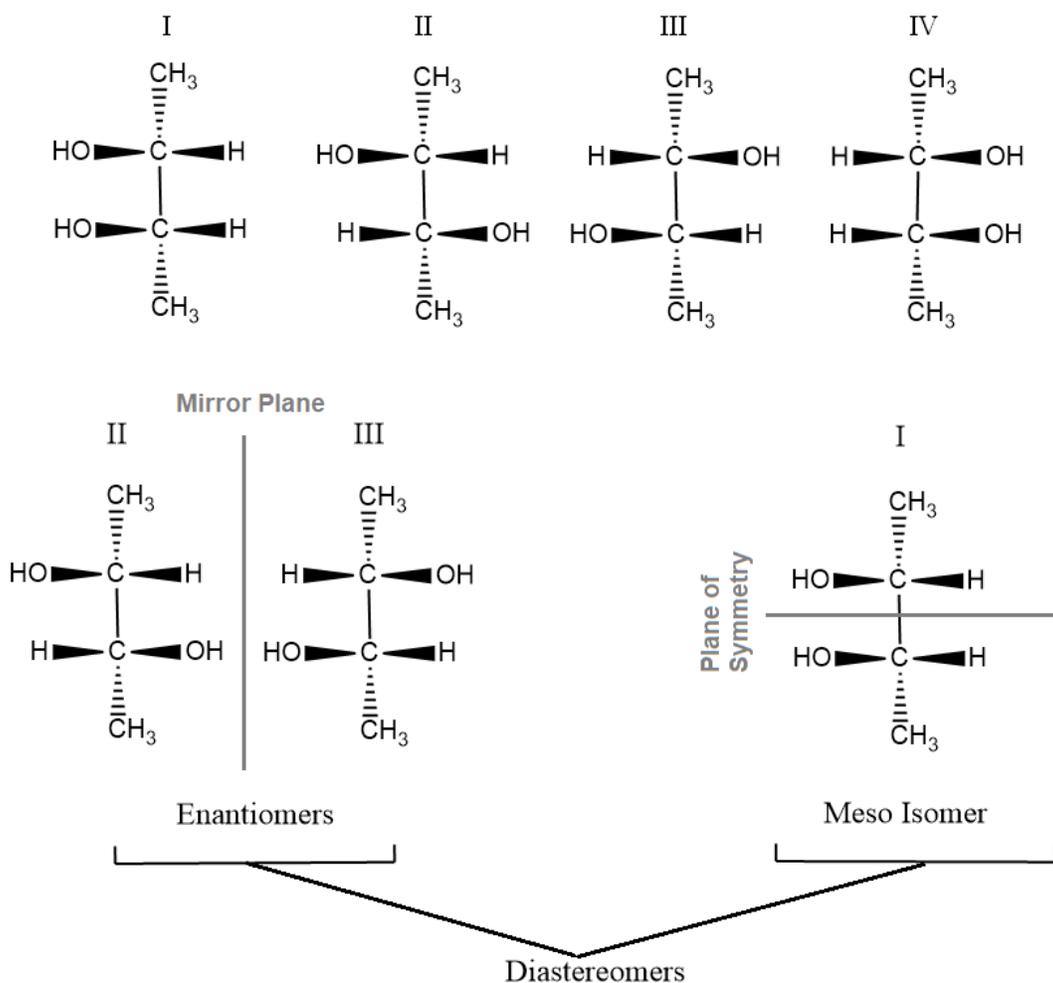
**Take Note!** Some sources define optical isomers a bit differently, and just say that the term is synonymous with enantiomers. Other sources use a definition consistent with that presented here. We use the more nuanced definition here because it is useful to be able to categorize some diastereomers as also being optical isomers.



**Figure 5.2.7:** Optical isomers for a molecule containing two stereocenters. See text for discussion.

We now need to address an odd feature of some of the molecules we have studied. You may have noticed that the molecule in Figure 5.2.6 has a plane of symmetry down the center. For that matter, we already noticed that Structure I in Figure 5.1.12 had two stereocenters but also contained a plane of symmetry. How is this possible?

The answer is that a molecule can contain chiral centers without the molecule as a whole being chiral. A molecule with two chiral centers and a plane or center of symmetry is referred to as a meso isomer. Figure 5.2.8 gives an example of this. As before, Structures II and III are mirror images of each other and are not superimposable (again, if you have trouble seeing this, use a model kit). But Structures I and IV are the same molecule. The presence of the plane of symmetry means that even though there are individual stereocenters, the molecule itself is superimposable on its mirror image and therefore achiral. Note that the molecule in Figure 5.2.8 differs from that in Figure 5.2.7 only by the replacement of the  $-\text{CH}_2\text{CH}_3$  group with the  $-\text{CH}_3$  group; that change created the plane of symmetry.



**Figure 5.2.8:** Optical isomers for a molecule containing two stereocenters and a plane of symmetry. See text for discussion.

One other point worth considering is that because single bonds rotate freely, it is possible to eliminate the plane of symmetry. This does not matter – if any conformation exists in which the molecule has a plane of symmetry or a center of symmetry, then the molecule is achiral. Also, it is often true that the same molecule in different conformations can have a plane of symmetry in one and a center of symmetry in another. Again, this is irrelevant. If it has one, it is achiral whether or not the other exists. Figure 5.2.9 shows an example of this.

**Figure 5.2.9:** The same molecule in different conformation. In the three-dimensional representation on the left, the plane of symmetry is shown. On the right, a center of symmetry is shown.

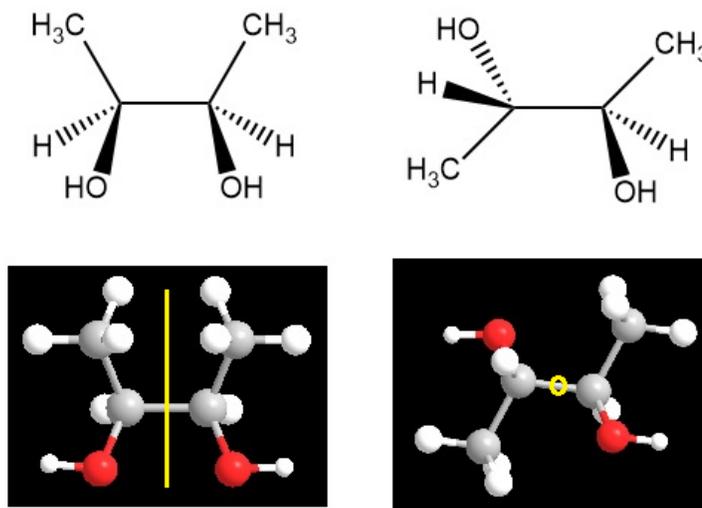
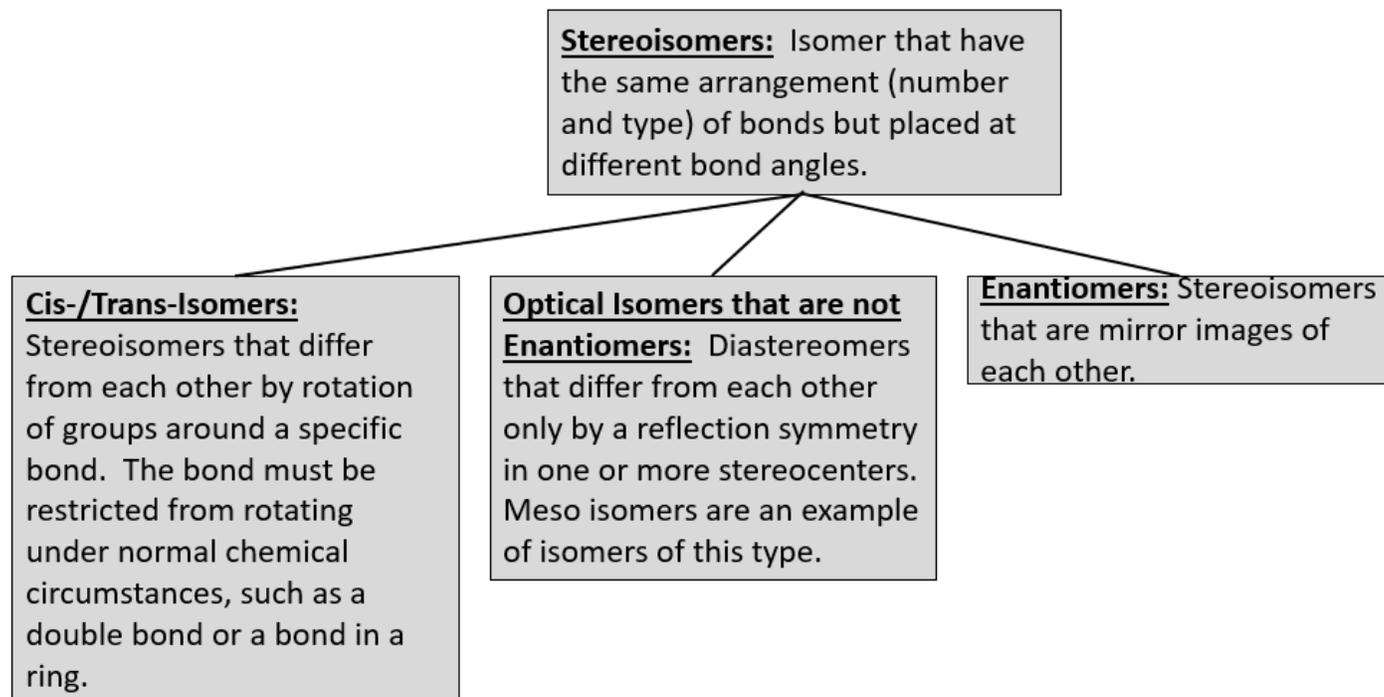


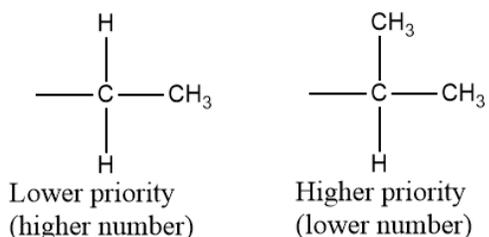
Figure 5.2.10 summarizes the types of stereoisomerism we have discussed thus far.



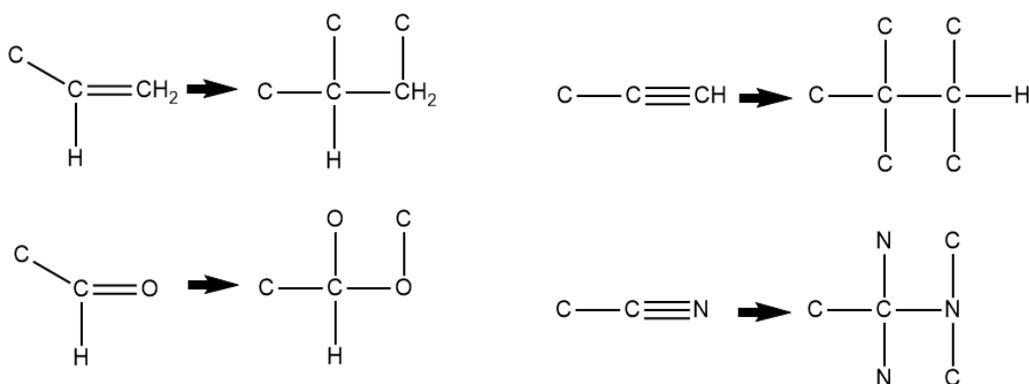
**Figure 5.2.10:** Types of stereoisomerism.

### Priority Scheme for Substituents – The Cahn, Ingold, Prelog Rules:

- 1) Look at each atom bound to the stereocenter and assign it a priority based on its atomic number. The highest atomic number is priority 1, the second highest is priority 2, etc.
- 2) If two atoms have the same atomic number, compare the atoms to which they are bound. If all of these atoms are the same, continue down the chain until you reach a point of difference.
- 3) If there are multiple atoms of the same type on two groups, the one with more of the higher-numbered atom is given the higher priority (lower number). In the example below, the  $-\text{CH}(\text{CH}_3)_2$  has a higher priority than the  $-\text{CH}_2\text{CH}_3$  group because it has two C atoms (atomic number 6, higher than H's atomic number 1) bound to it rather than just one.



- 4) Double and triple bonds should be counted as “ghost” atoms. A  $\text{C}=\text{C}$  bond counts the first carbon as if it were bonded to two other carbons. As shown in the examples below, the next atom in the chain treats the multiple bond in the same way.



### Analysis of the Stereocenter:

- 1) Number each substituent from 1 to 4 based on the Cahn-Ingold-Prelog rules (1 is highest priority, 4 is lowest).
- 2) Convert the chiral center into a rotor with the “4” group pointed into the page and the other three groups coming forward.
- 3) Check if the other three numbers are sequential when counted clockwise or counterclockwise:
  - A. If groups go clockwise by priority, it is an R group.
  - B. If groups go counterclockwise by priority, it is an S group.

---

**Table 5.2.1:** Process for identifying stereocenters as “R” or “S”. First prioritize the groups, then analyze the stereocenter as described.

---

**Labeling Stereocenters with R,S-Character:** We have covered many different aspects of chirality in this chapter, but we have left one question unanswered: How do we name different stereocenters? Specifically,

how can we identify the chirality of a stereocenter without using an attached image? In a full course on organic chemistry it would be necessary in order to name chiral compounds (though we will not do so here).

The approach is given in Table 5.2.1, and consists of two parts. The first is to assign a priority number to each substituent on the stereocenter based on its atomic number. The second is to orient the molecule so that the highest-ranking groups form a ring, and then to see whether they are ordered clockwise or counterclockwise. Clockwise and counterclockwise imply a chiral character, so the stereocenter can be characterized. The centers are labeled “R” and “S” to distinguish them.

Let us start with the molecule below:

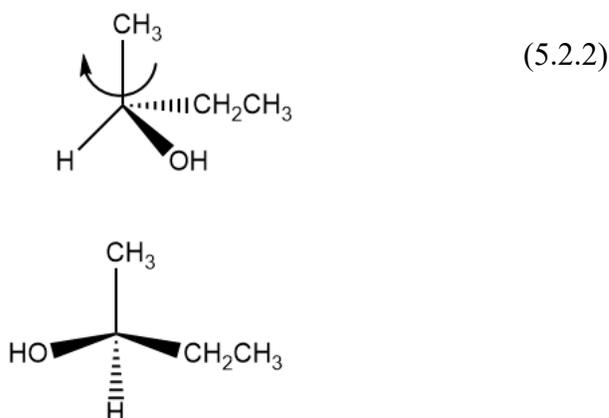


The first order of business is to prioritize each of the four groups. The atomic numbers of elements attached to the stereocenter are

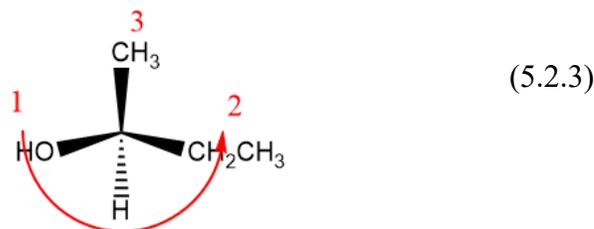
H:1                  C:6                  O:8

Clearly, O has the highest priority (1) and H has the lowest (4). We need to distinguish between the -CH<sub>3</sub> and the -CH<sub>2</sub>CH<sub>3</sub>, as both elements have atomic number 6. So we look at the next elements in the chain. For one of them there are three H's, for the other there are two H's and a C. The C atom “wins”, so -CH<sub>2</sub>CH<sub>3</sub> has priority 2 and -CH<sub>3</sub> has priority 3.

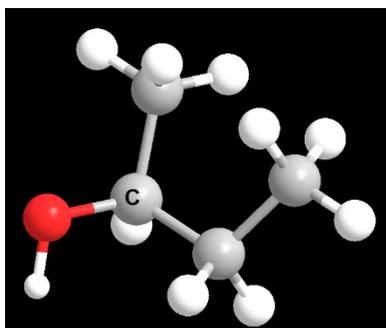
That ends the prioritization process given in the first part of Table 4.2.1. Now we need to look at the analysis scheme. We want to orient the H atom (the lowest ranking group) so that it is facing back into the page, which will mean moving the other elements to match. In this case, a simple way to do that is to rotate around the C-CH<sub>3</sub> bond by 90°:



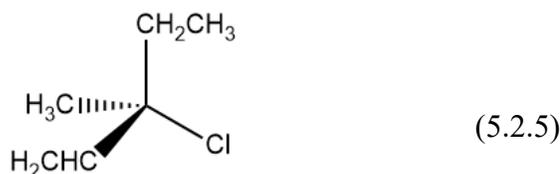
Looking at the reoriented image and numbering the groups, we can see that the order of groups (1-2-3) proceeds counterclockwise around the ring. The stereocenter is therefore labeled “S.”



To make the rotor a little easier to visualize, we provide a three-dimensional representation of the molecule in the orientation given in Equation 5.2.3. The central carbon atom is labeled C. The backward-facing H atom is just visible behind it.



Another example is given below.



Once again, our first step is to prioritize the groups. Cl is clearly priority 1, but the next three substituents have C atoms bonded to the central carbon. Using Rule 2 from the Cahn-Ingold-Prelog rules, we can see that -CH<sub>3</sub> will have the lowest priority because the other groups are bound to at least one C atom.

Comparing -CH<sub>2</sub>CH<sub>3</sub> and -CHCH<sub>2</sub>, it is necessary to recognize that the latter is unsaturated and must include a double bond (-CH=CH<sub>2</sub>). That means that the C atom is counted as being bound to two C atoms per Rule 4, which gives it a higher priority than the other group. So, -CHCH<sub>2</sub> is priority 2 and -CH<sub>2</sub>CH<sub>3</sub> is priority 3. Rotating to put the -CH<sub>3</sub> group at the back and labeling the remaining groups, we find that the groups are sequential in clockwise order, so the stereocenter has R-character.

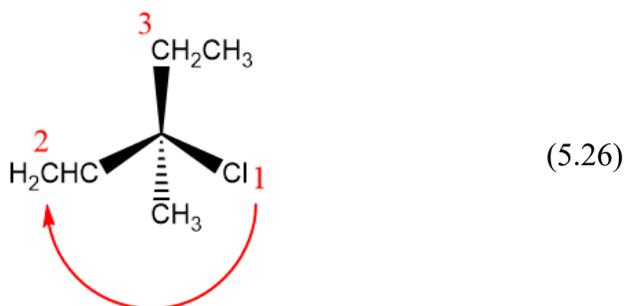
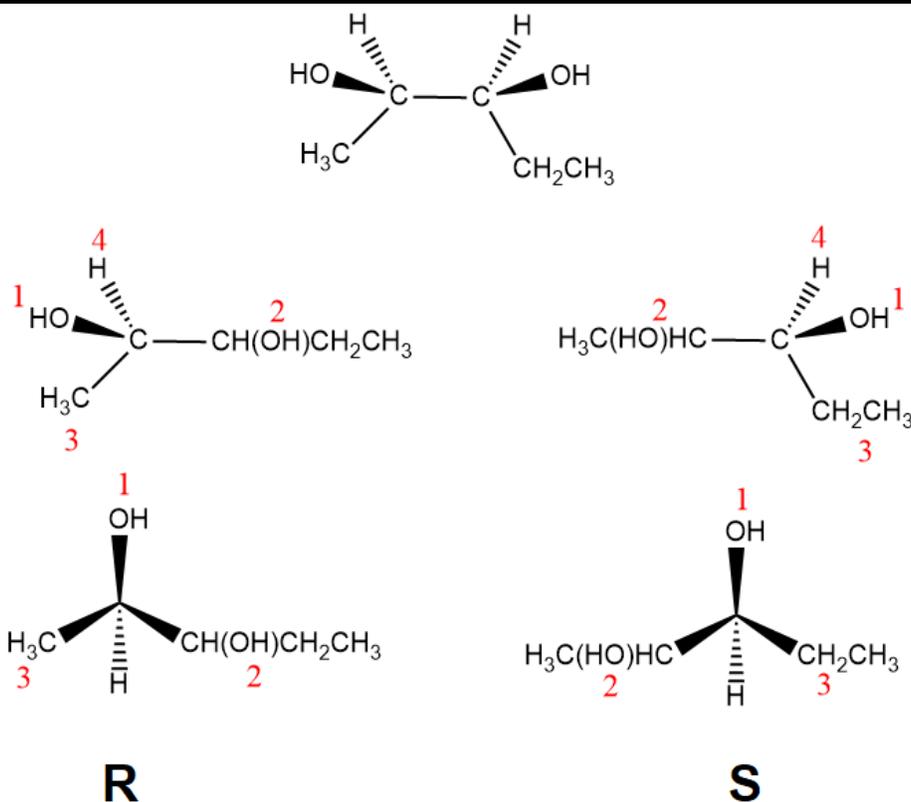


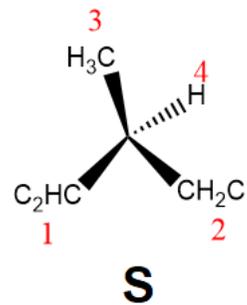
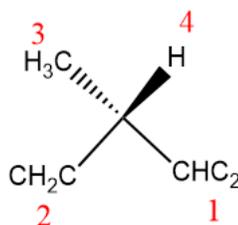
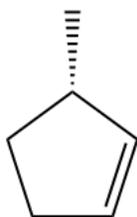
Figure 5.2.11 shows how to apply this technique when a molecule contains two stereocenters. Each stereocenter must be treated independently, so the best strategy is to write each center separately and work them out as independent problems. While the nature of the substituents of the second carbon affects the priority of the group according to the Cahn-Ingold-Prelog rules, the chiral character does not matter (note that it is not part of the CIP rules). In this case, that leads to one stereocenter having a R character and the other having a S character.



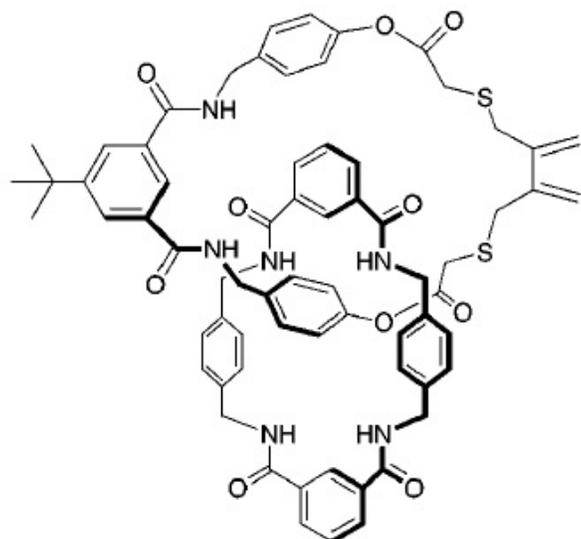
**Figure 5.2.11:** Determining the R,S-character for the stereocenters of a molecule with two chiral centers.

As a final example, let us see how to characterize the R,S character of chiral center in a ring. Figure 5.2.11 shows a wedge-angle structure that includes one chiral center. The best strategy is to rewrite the chiral center with the arms of the ring treated as separate objects, with substituents written out explicitly until they reach their first point of difference. In this case, the chiral C atom is bound to one sp<sup>3</sup>-hybridized C and one sp<sup>2</sup>-hybridized C. Treating the double bond correctly, per Rule 4 of the CIP rules, the sp<sup>2</sup>-hybridized C atom has the higher priority because it is treated as if it were bound to two C atoms, while the other is bound to only one. With the prioritization complete, the last step is to rotate the center to put the H atom into the plane of the page and view the rotor. Since the numbers are sequential in a counterclockwise direction, it has S character.

**Figure 5.2.12:** Determining the R,S-character for a stereocenter in a ring.



# CHAPTER 6: Molecular Conformations



*A pair of molecular loops interlinked with each other, and a schematic diagram showing that it is possible for the smaller loop to pass the structure on the right-hand side of the loop but not the left. While loops such as these are uncommon, the arrangement does make clear that the link between a molecule's structure and its dynamics can be very subtle.*

*Image modified from Watanabe, N., Kihara, N., and Takata, T., Change of Connectivity on Catenane Ring: Ring Expansion by Annulation-Ring Scission Sequence, *Org. Lett.* **2001**, 3, 3519-3522.*

WE LEARN THE ROPE  
OF LIFE BY UNTYING ITS  
KNOTS.

-JEAN TOOMER

*We speak of "molecular structure" as if molecules were frozen into their positions, rolling around in space while never changing their conformation. The truth is that these structures are simply average positions, and that chains of carbon insist on flopping, spinning, and twisting like ropes hung in a gale. Understanding their movements is essential to understanding their reactions.*

## BEFORE YOU BEGIN, MAKE SURE YOU KNOW

- VSEPR rules and molecular geometry (Flowers, sec 7.6)
- Wedge-angle notation (Chapter 4)
- Rotation around single bonds in hydrocarbons (Chapters 4 and 5)
- The equilibrium constant (Flowers, sec 13.2) and its relationship to free energy (Flowers, sec 16.4).

## Section 6.1: Conformations of Acyclic Alkanes

### LEARNING OBJECTIVES FOR THIS SECTION

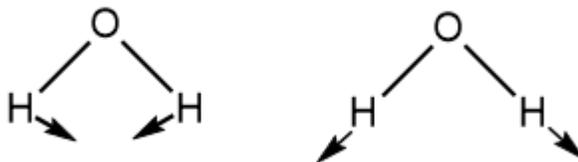
- Understand what is meant by a molecular conformation, and how it is different from an isomer.
- Know what is meant by a dihedral angle and related terms including eclipsed, staggered, anti, and gauche.
- Be able to recognize staggered, eclipsed, anti, and gauche configurations, and understand the interactions that determine their relative energies. Understand why different conformations have different energies, and be able to predict their relative energies.
- Understand what is meant by torsional strain and steric strain.
- Be able to use equilibrium theory to estimate the relative populations of different conformations at a given temperature.
- Be able to interpret and write Newman projections. Be able to convert back and forth between Newman projections and wedge-angle diagrams.

**Dihedral Angles in Alkanes:** In Chapters 4 and 5 we discussed the three-dimensional structure of molecules. When we did, we had to take into account that molecules can rotate relatively freely around sigma bonds, even though rotation is prevented by pi bonds. Here, we need to discuss molecular conformations, the different geometries a molecule can form without breaking bonds and becoming a different molecule.

At any temperature above absolute zero, molecules have an average kinetic energy proportional to their temperature. Kinetic energy is the energy of motion, and thermal energy – the energy associated with temperature – is randomly distributed into all of the different motions a molecule can perform. Some of this will involve motions back and forth or in rotating the molecule, but some can change the geometry of a molecule.

Usually, these changes are relatively small. For example, the bonds in water undergo relatively limited motions at room temperature. It costs a significant amount of energy to change the H-O-H angle and the O-H bond length, so the molecule is relatively rigid and is well-described by its average geometry. The same is true for C-C and C-H bond lengths, and for most of the angles associated with hydrocarbon chains.

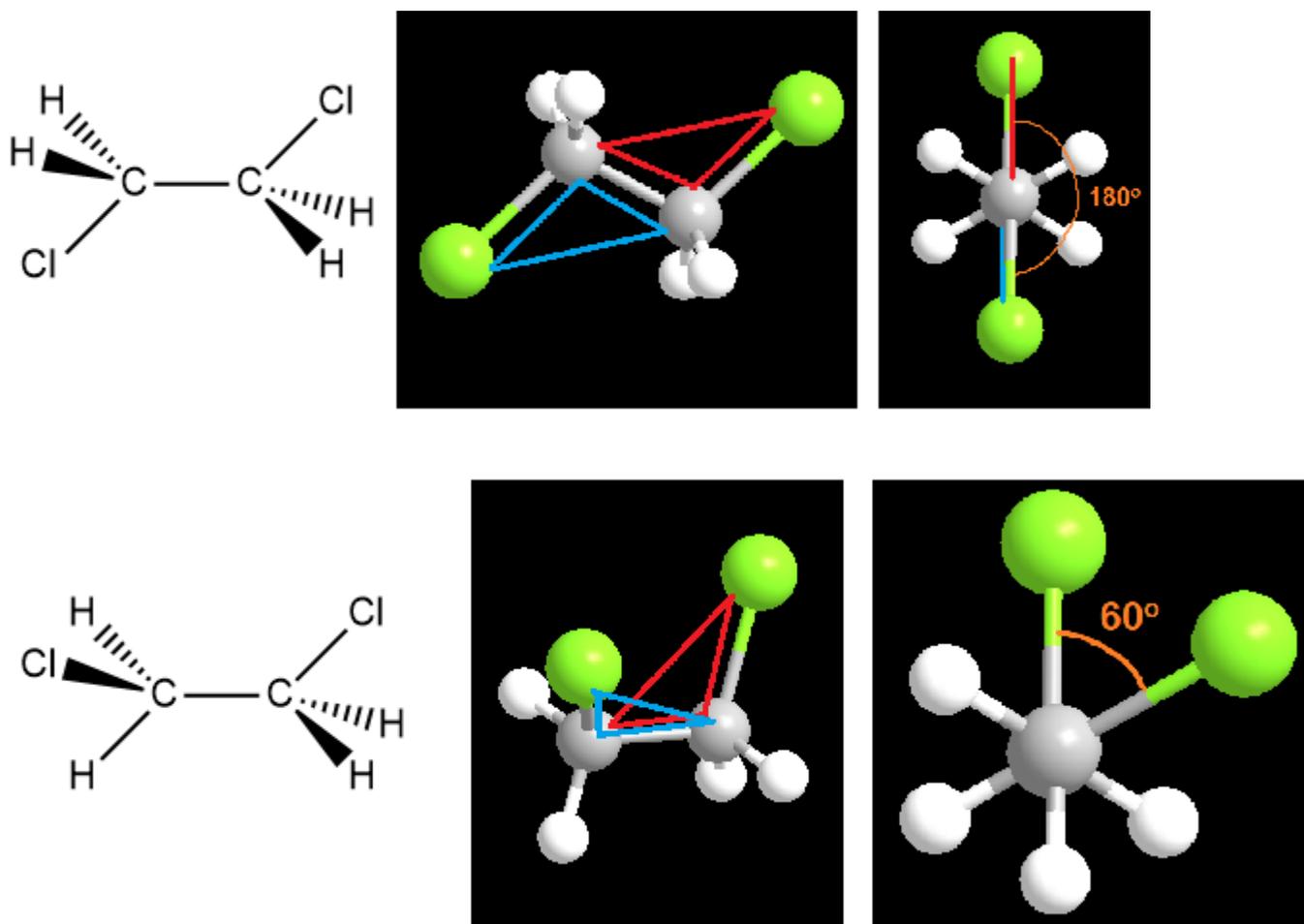
**Figure 6.1.1:** Sample bending (left) and stretching (right) motions of a water molecule.



An exception to this is the motion of dihedral angles. Dihedral angles are constructed from a group of four atoms bonded in a chain. The four atoms are broken into two groups of three atoms each, with two atoms common to both groups. Like any set of three points, each group of three atoms defines a plane. The dihedral angle is the angle between the planes.

This is a sound mathematical definition, but it does not convey the real geometric significance. Imagine looking straight down the line of the C-C bond of a molecule, standing so that the second carbon is concealed

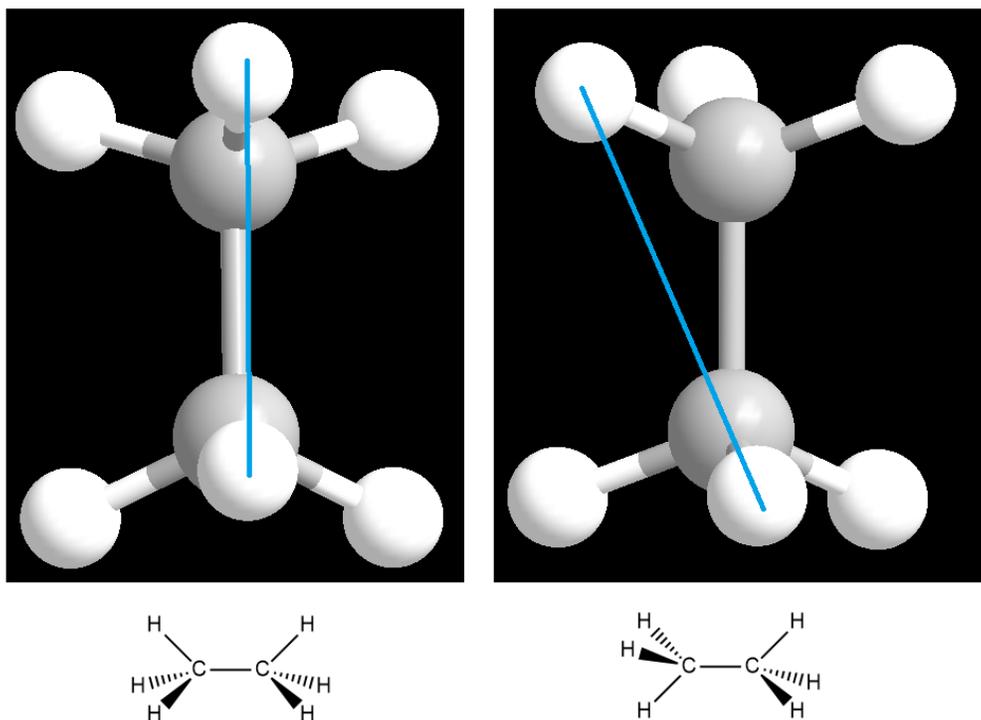
by the one nearer to you. Viewed from this angle, the dihedral angle is the angle between a group on each of the atoms. Figure 6.1.2 illustrates this. When the molecule rotates around a sigma bond, it is the dihedral angle that is changing. Motion of this type is sometimes also referred to as torsional motion.



**Figure 6.1.2:** Dihedral angles for different conformations of  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ . Central images show the planes used to define the dihedral angle between the chlorine atoms; each plane is defined by the triangle made from a set of Cl-C-C atoms. The right-most figure in each case shows an end-on view of the C-C bond where the significance of the dihedral angle – as the angle between the two Cl atoms on that axis – is more visible.

It is important to understand that changing the dihedral angle will change the energy of the molecule. To understand this, remember that bonds are clouds of electrons and electrons repel each other. Rotating around C-C bond changes the distance between the bonds on each side. As shown in Figure 6.1.3, having substituents rotated so that they are aligned with each other puts them closer together than when they are offset. Since the electron clouds repel each other, the configuration in which they are offset from each other has a lower energy.

Configurations in which the atoms on one carbon are as close as possible to those on the neighboring carbon are said to be eclipsed, and those in which they are as far apart as possible are referred to as staggered. Examples of these forms are shown in Figure 6.1.3.



**Figure 6.1.3:** Distances between H atoms on neighboring C atoms across a C-C bond in ethane. In the left (eclipsed) figure, the dihedral angle is  $0^\circ$  and the H atoms are directly across from each other. The H-H distance is therefore shorter than in the (staggered) case on the right, where the dihedral angle is  $60^\circ$ . Note that while only one H-H interaction is highlighted, each H atom interacts with multiple other H atoms across the bond.

Figure 6.1.4 shows how the energy of the ethane molecule changes as a function of dihedral angle. With three equivalent (H) groups on each carbon, there are three equivalent eclipsed configurations and three equivalent staggered configurations. The eclipsed configurations are unstable, meaning that the molecule will not remain there for long. But leaving one staggered configuration and moving to another requires 12 kJ/mol of energy, since the molecule must pass through an eclipsed configuration to rotate in this way. The average kinetic energy of a molecule at room temperature is roughly 2.5 kJ/mol, but the amount of energy in any particular motion will vary with time around this average. While the energy difference is significant, 2.5 kJ/mol is close enough to 12 kJ/mol that the molecule will undergo a torsional rotation relatively frequently.

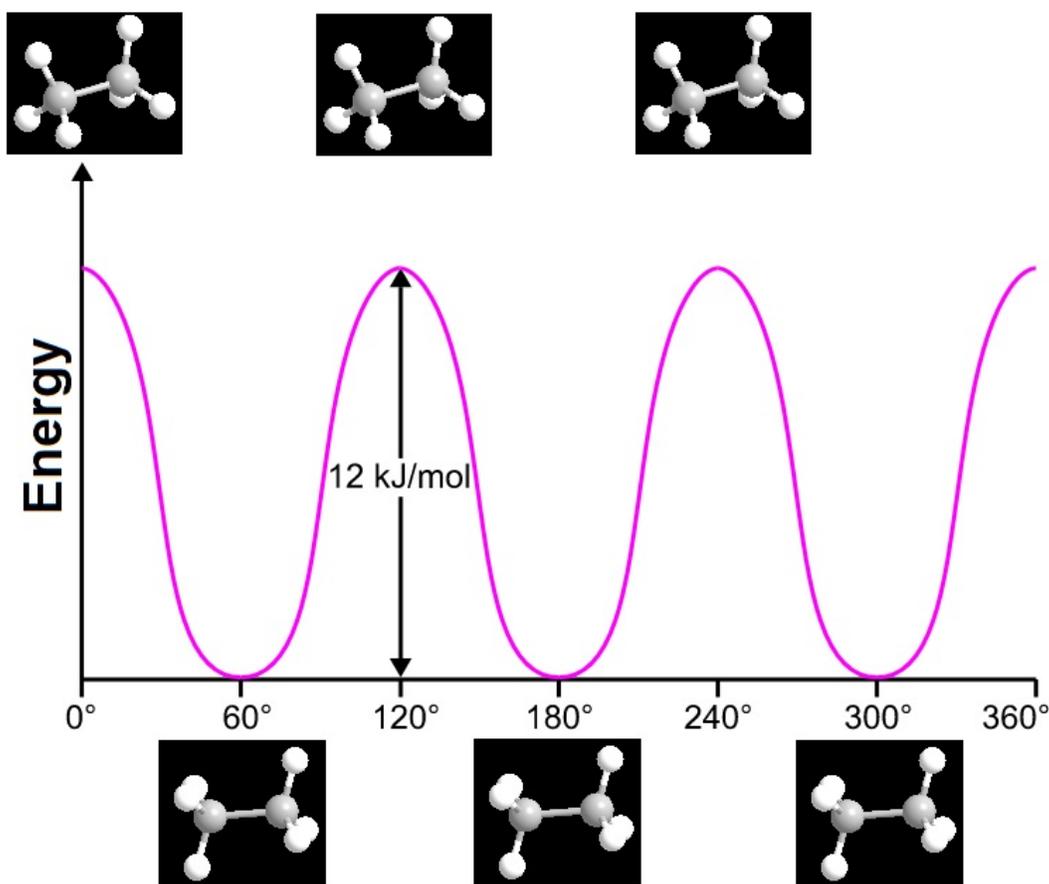
**Take Note!** Visualizing torsional motions is another challenge in organic chemistry. This is another chapter where a model kit is essential.

The energy associated with rotation around a dihedral angle is called torsional strain. As discussed, the torsional strain of the staggered conformation is lower than the torsional strain of the eclipsed conformation. Torsional strain is a specific example of a more general phenomenon called steric strain, which is the energy associated with the nonbonding interactions of

different parts of the molecule with each other. The reactivity of molecules is often influenced by steric strain, or sometimes referred to as arising from steric effects.

Looked at in this way, it may seem that the difference between conformations and isomers is arbitrary. After all, in Chapter 4 we labeled cis-/trans- configurations around double bonds as being different molecules because the barrier to their rotation was so high, but we are choosing to view eclipsed and staggered conformations as different conformations of the same molecule purely because the barrier to rotation is lower than in the cis-/trans-case. As you move on to study reactions, however, you will find that the ability to rotate around a bond can influence reaction outcomes, making the distinction useful.

On a related note, some sources refer to different conformations as conformational isomers, or conformers. We do not do so here, as the language can be confusing as it relates to isomers, but you should be aware of the terms if you encounter them elsewhere in your studies.



**Figure 6.1.4:** Relative energy as a function of C-C dihedral bond angle in ethane, with conformations shown.

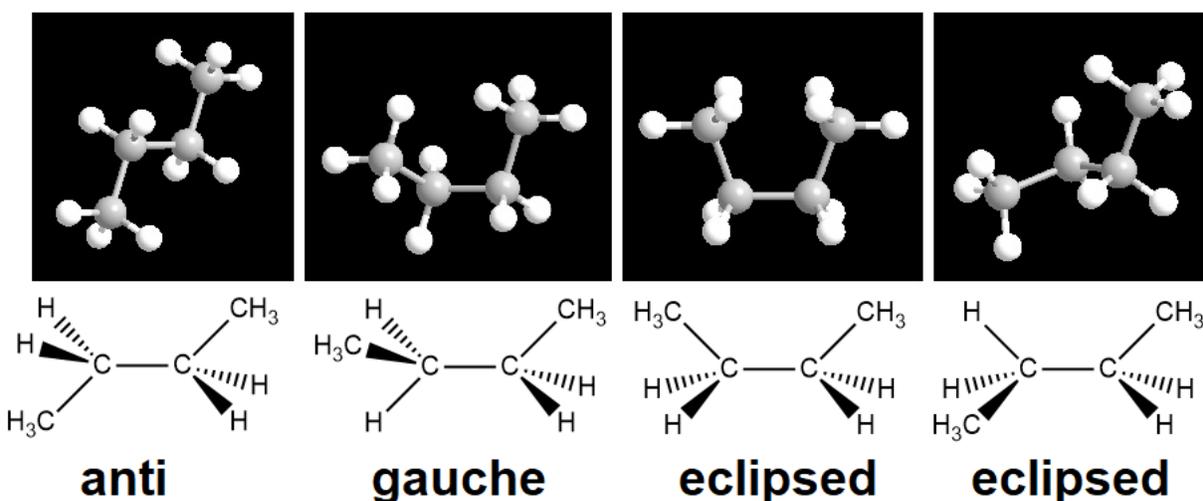
*Modified from Keminsti, accessed via Wikimedia Commons,*

*[https://commons.wikimedia.org/wiki/File:Ethane\\_conformations\\_and\\_relative\\_energies.svg](https://commons.wikimedia.org/wiki/File:Ethane_conformations_and_relative_energies.svg), accessed July 24, 2021.*

The situation can become more complex when additional types of substituents are present. Conformations of butane are shown in Figure 6.1.5. Now, instead of having three equivalent groups on each

carbon, there is one methyl group and two H's on each. There are more electrons in the  $\text{-CH}_3$  group, which means they will be more strongly repulsive than the H's that are present. Also, the C-H bonds protruding from the C mean that the substituent sweeps out more space than a single atom would and will therefore be more repulsive than the H it replaces. This changes the relative energies of different conformations, as shown in Figure 6.1.6.

Figure 6.1.5 introduces new labels for the staggered conformations: Anti and gauche. The anti conformation puts the  $\text{-CH}_3$  groups as far away from each other as possible, corresponding to a  $180^\circ$  dihedral angle. The gauche conformation is staggered, but the  $\text{-CH}_3$  groups are within  $60^\circ$  of each other. It therefore has a higher torsional energy than the anti conformation, but not as high as the eclipsed conformation.



**Figure 6.1.5:** Conformations of butane produced by torsional motion around the central C-C bond. The anti and syn conformations are both examples of staggered conformations. The two eclipsed conformations have different energies, but do not receive labels that distinguish them.

There are two different eclipsed conformations, one with the  $\text{-CH}_3$  groups directly across from each other, and the other with the methyl groups  $180^\circ$  apart. While they have different energies, neither of them gets a special name beyond “eclipsed”.

Figure 6.1.6 shows how the presence of the methyl groups affects the energies of different conformations. The gauche conformation is  $3.8 \text{ kJ/mol}$  higher than that of the anti conformation. This means that the molecule will spend more of its time in the anti than in the gauche conformation, though the fact that the difference in energy is comparable to the  $2.5 \text{ kJ/mol}$  associated with room temperature thermal energy means that both states will have a significant population. Similarly, the barriers to rotation posed by the eclipsed conformations are also different depending on whether the motion brings the two methyl groups into alignment or not. This will affect the dynamics of the molecule.

The above references “significant” populations of different conformations present at room temperature, but how can we quantify that? The answer is that transitions between different conformations obey the same

rules as chemical reactions, and come to equilibrium in the same way. In other words, the process of changing between anti and gauche conformations can be written as a chemical equation having an equilibrium constant:

$$\text{Anti} \rightleftharpoons \text{Gauche}$$

$$K = \frac{[\text{Gauche}]}{[\text{Anti}]} \quad (6.2.1)$$

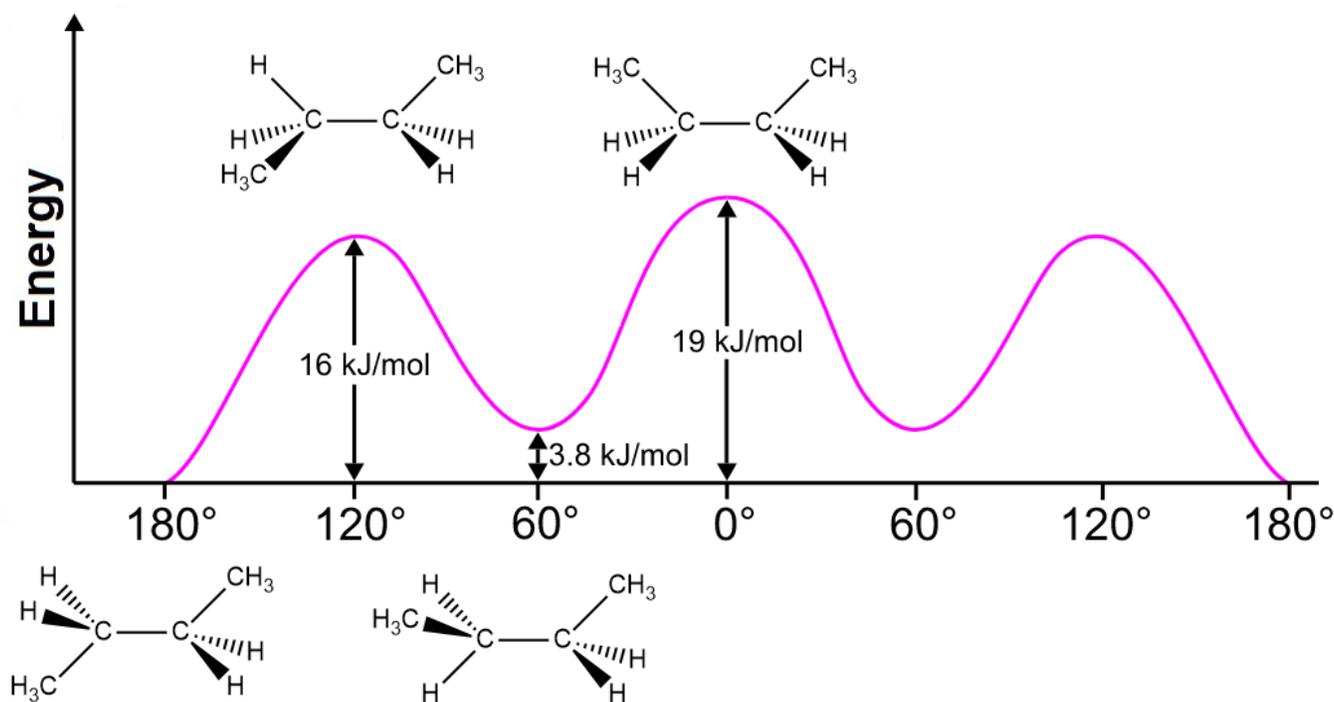
We know the energy difference between the Anti and Gauche conformations, so  $\Delta E = 3.8 \text{ kJ/mol}$  for the reaction. Remember that there is a relationship between energy and equilibrium constant:

$$K = e^{\frac{-\Delta G}{RT}} = e^{\frac{-3.8 \text{ kJ/mol}}{(0.008314 \text{ kJ/(K mol)})(298 \text{ K})}} \quad (6.2.2)$$

$$= 0.22$$

Based on this calculation, then, the population of gauche conformations is roughly 22% that of the anti.

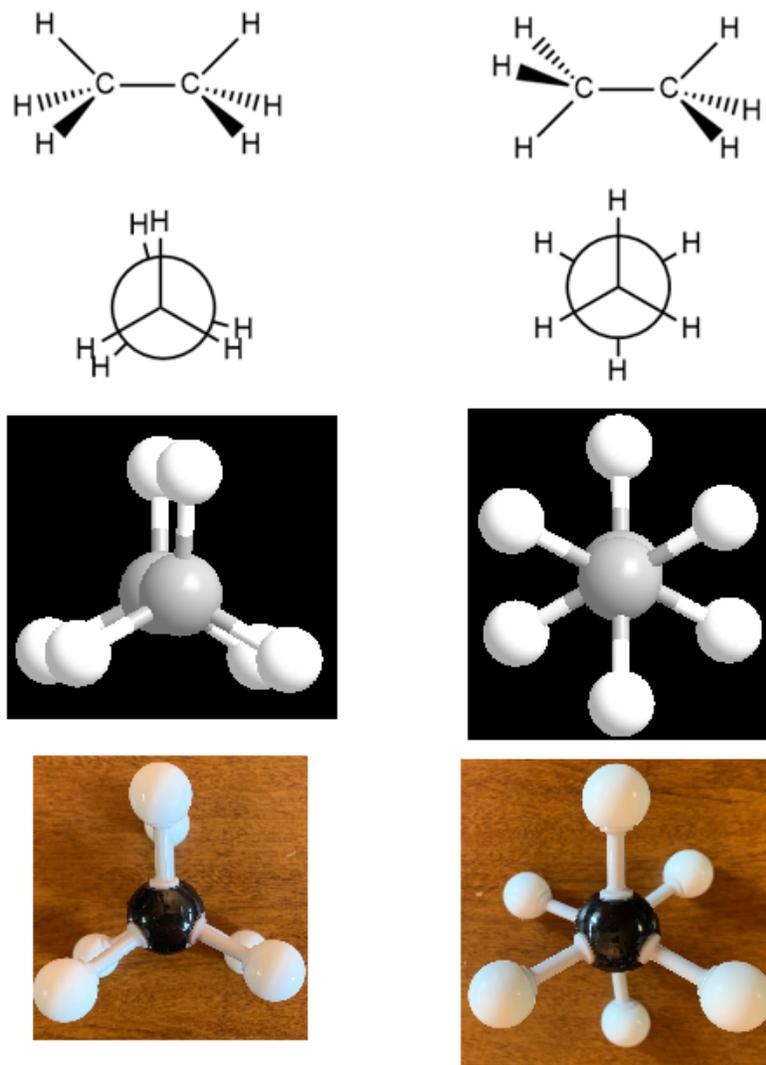
A word of caution is in order. First, we spoke of “energy” when comparing the relative energies of gauche and anti conformations, and did not specify “free energy.” In fact the number we used corresponds to internal energy, so strictly speaking should not have been used in Equation 6.2.2. This is a common problem in chemistry, where it can be easier to get internal energies from calculations than it is to get free energies, which are statistical quantities and depend partly on entropy. However, unless high accuracy is desired, internal energy is generally a good proxy for free energy (but as a student you should still understand the difference between the type of energy!).



**Figure 6.1.6:** Relative energy as a function of C-C dihedral bond angle in butane, with conformations shown. Modified from *Keminsti*, accessed via *Wikimedia Commons*, [https://commons.wikimedia.org/wiki/File:Butane\\_conformations\\_and\\_relative\\_energies.svg](https://commons.wikimedia.org/wiki/File:Butane_conformations_and_relative_energies.svg), accessed July 24, 2021.

**Newman Projections:** Before leaving the topic of dihedral angles, we must introduce a notation that makes them much easier to characterize: Newman projections. We have already seen in Figure 6.1.2 that a dihedral angle can be visualized by looking along the bond between two atoms and taking the dihedral to be the angle between different bonds on the neighboring atoms. A Newman projection is exactly this type of representation.

An example for ethane is given in Figure 6.1.7. The best way to picture the Newman projection is as if one is looking along the bond between two atoms, in this case the two carbon atoms. The nearer C atom will block the view of the second atom; this is easiest to see in the photographs of the models in Figure 6.1.7.

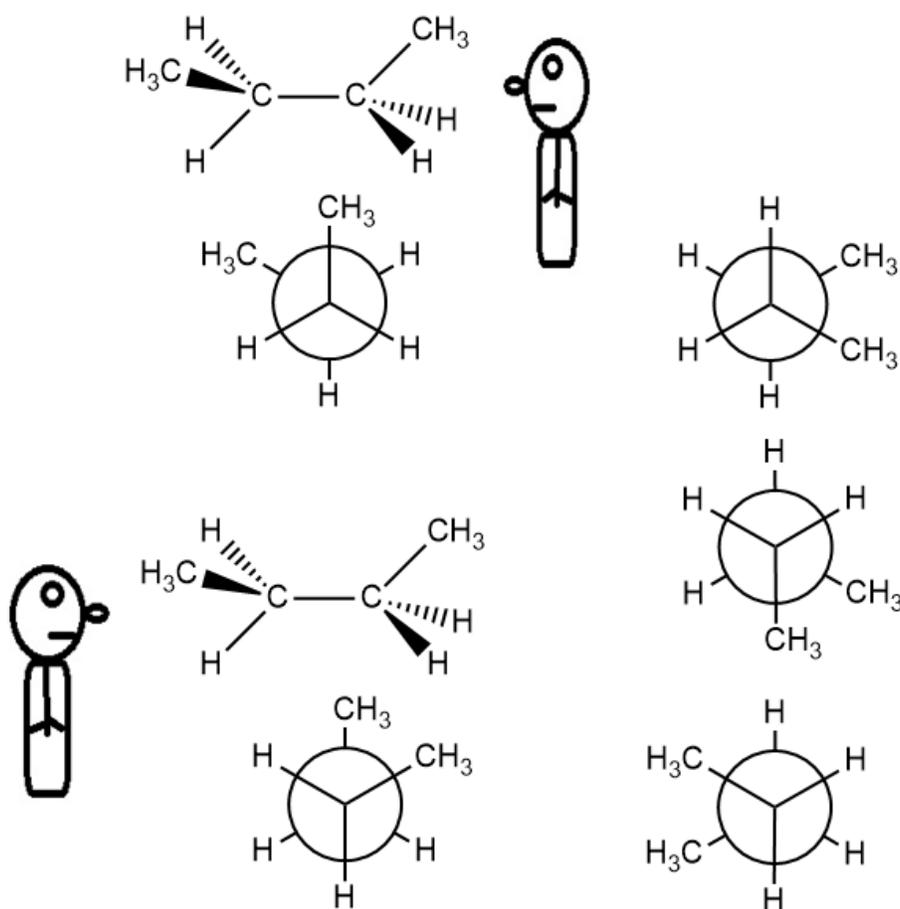


**Figure 6.1.7:** Newman projections for ethane. The eclipsed conformation is shown on the left and staggered conformation is shown on the right. Note that even though the dihedral angle is zero for the eclipsed conformation, the Newman projection shows the angles as being slightly nonzero. The reason is simply that a perfect zero angle, sited down the bond as in the Newman projection, would conceal one H behind the other (this is also the reason that the three-dimensional image in the middle row is viewed slightly askew). The models shown at the bottom make clear how this concealment works.

A key feature of the Newman projection is that three of the bonds are drawn to the center of the circle, and three are drawn to the ring. Those drawn to the center are on the nearest atom, while those drawn to the ring are on the further (concealed) atom. This is analogous to the way that, in Figure 6.1.7, one can see points where the plastic bonds attach to the nearer C atom, but the points of attachment are concealed for the farther atom.

**Take Note!** By far the best way to learn about dihedral angles is with a model kit. Hold it up and look down the bond, just as in the photos shown!

Like line-angle drawings and wedge-angle drawings, more than one Newman projection can present the same information. First, the projection can be drawn looking along the bond from either side, as shown in Figure 6.1.8. Also, only the relative angles of the groups are important in the Newman projection; the right-hand column of Figure 6.1.8 shows that one can rotate the Newman projection about the C-C axis and maintain a valid representation provided that the angles between the groups do not change.



**Figure 6.1.8:** A gauche butane configuration and some Newman projections describing it. The left column shows the same configuration viewed from different sides and the Newman projection associated with each. The right column gives several additional Newman projections, all of which are correct for the molecule shown.

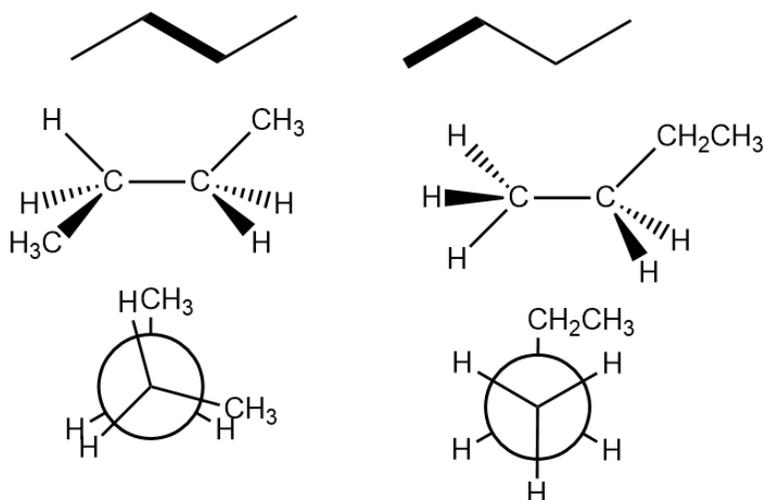
Now that we have some understanding of dihedral angles and can represent them in with Newman projections, there are a few things we should come to terms with. First, while wedge-angle notation provides

enough information to at least estimate dihedral angles, line-angle drawings do not. Given that it takes four atoms connected by three sequential bonds to define a dihedral angle, it is possible to use line-angle notation to identify where a dihedral angle will be. But line-angle drawings do not convey information about what those angles are, just as they allow identification of chiral centers but do not convey enough information to characterize the chiral center as R or S.

A second point is that many molecules will have more than one dihedral angle. Again, dihedral angles occur wherever four atoms are connected by three sequential bonds. Organic molecules can contain very long chains, and these will contain many dihedral angles. It should be clear to you by now that using wedge angle notation to represent long series of bonds is cumbersome at best. Newman projections are far easier to use, but can only depict one dihedral angle at a time, though it is possible to write multiple Newman projections for the same molecule.

Figure 6.1.9 depicts both of these problems. The bond shown is bolded in the line-angle drawing at the top of each column. A wedge-angle drawing for the relevant bond, and the corresponding Newman projection, are shown. Note that the line-angle drawing does *not* imply a specific conformation; the choices for the two other projections are arbitrary.

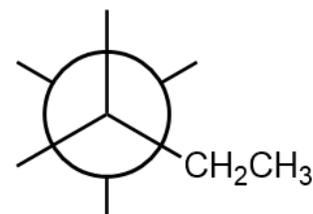
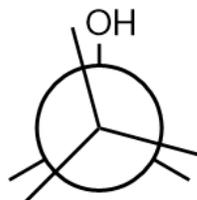
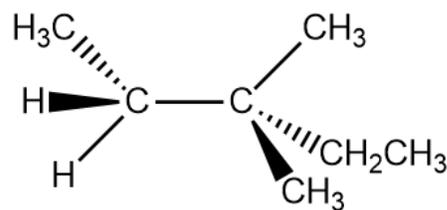
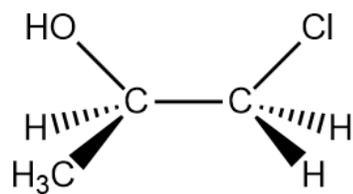
**Figure 6.1.9:** Wedge-angle drawings and Newman projections for the butane bonds indicated in bold in the line-angle drawings at the top of the column. The choices of dihedral angle are arbitrary, they are not implied by the line-angle drawings.



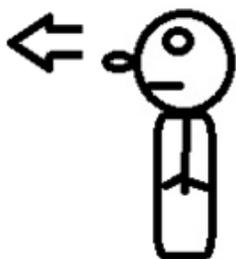
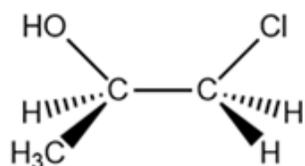
The difficulty in representing multiple dihedral angles simultaneously is more of a problem in theory than in practice. Dihedral angles are generally of greatest interest in understanding the outcomes of reactions, and these rarely depend strongly on more than one dihedral angle.

Figure 6.1.10 contains a practice exercise. Fill in the missing groups on the Newman projections to match the wedge-angle diagram shown.

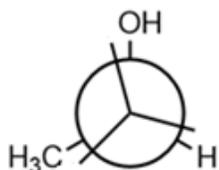
**Figure 6.1.10:** Complete the Newman projections shown to match the wedge-angle projections above.



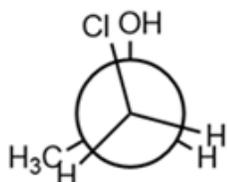
It is important to work through problems like this systematically. Figure 6.1.10A shows one way to do so. A useful exercise is imagining an observer and positioning them opposite the wedge-angle diagram in a way that can reproduce the Fischer projection. As shown in Figure 6.1.10A, this begins by recognizing whether the group in question is on the nearer C atom (as the  $-\text{CH}_2\text{CH}_3$  is in the right-hand example) or on the far C atom (as the  $-\text{OH}$  is in the left-hand example). Once that is done, it is a question of filling in blanks in a consistent manner. Positioning the observer not only helps with “near” and “far” carbons, but also with “left” and “right” sites, since the position also implies an orientation for the observer.



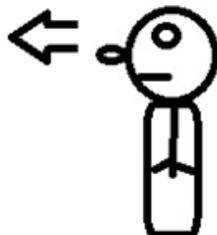
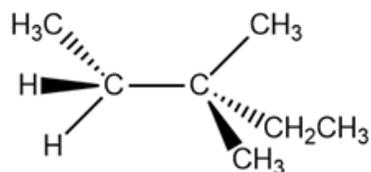
-OH is on back carbon of Newman projection, so observer must stand to right of structure



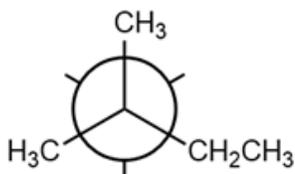
The observer is standing with left arm coming out of the page. -CH<sub>3</sub> is coming out of the page in the wedge-angle projection, so that should go on the left-hand side of the Newman projection.



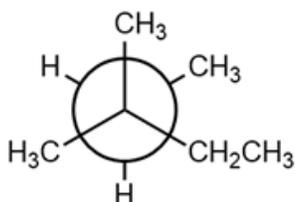
The Cl is on the top site of the front carbon, opposite the -OH group. The other sites should be filled in with H's to complete the structure.



-CH<sub>2</sub>CH<sub>3</sub> is on the forward C in the Newman projection, which means the observer is standing to the right of the wedge-angle projection. The other two groups on this C are -CH<sub>3</sub>, so they can be drawn in.



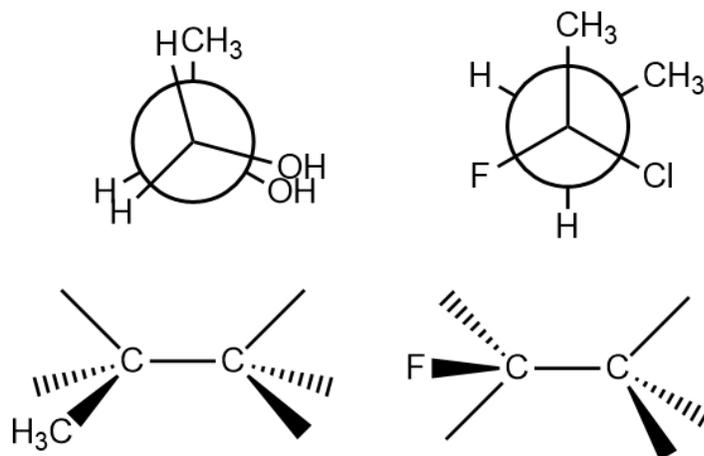
The observer is standing with their right arm going into the page, and the -CH<sub>3</sub> on the far C is going into the page. That means the -CH<sub>3</sub> group should be on the right. The other sites can be filled in with H atoms.



**Figure 6.1.10A:** Steps to constructing the Newman projections from the wedge-angle drawings.

As another example, consider Figure 6.1.11 and fill in the missing substituents on the wedge-angle diagram.

**Figure 6.1.11:** Fill in the wedge-angle projection to match the Newman projection.



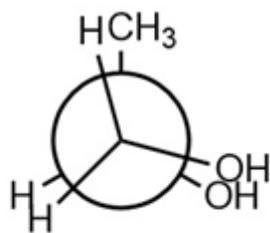
Looking at the left-hand figure, there is only one  $\text{-CH}_3$  group in the molecule. In the Newman projection it is pointing upward on the back carbon. To make the wedge-angle diagram work, we will have to take into account that it is rotated from the Newman diagram by  $120^\circ$ . On the left-hand side, the F is also out of alignment with the way that it is drawn in the Newman projection.

Figures 6.1.11A-I and 6.1.11A-II show how to approach this kind of problem on paper. It is quite challenging. But if you approach the problem with a model kit, you can do it in 3 steps:

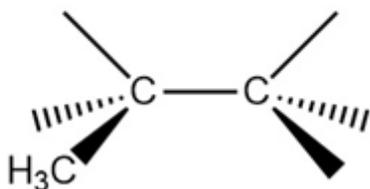
- 1) Build the wedge-angle model in either the staggered or eclipsed conformation as shown, and put the group you are given on the correct spot.
- 2) Reorient the model to match the Newman projection, so you are staring down the central bond. Add the substituents so they match.
- 3) Reorient the model so that the groups you are given match their position on your complete model. Fill in the blanks on the wedge-angle drawing.

Ultimately you may develop the facility you need to solve problems like this in your head, but the only way to build that is with experience. And the best way to build that is with a model kit.

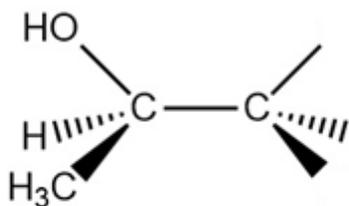
**USE A MODEL KIT!**



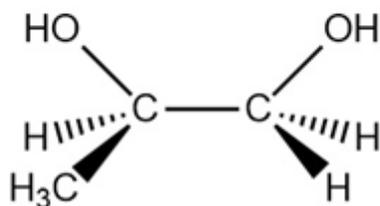
The  $\text{-CH}_3$  group is on the back C atom, which means our observer is on the right-hand side of the wedge-angle projection (further from the  $\text{-CH}_3$ ). But our observer is not standing straight up - the wedge angle projection has been rotated away from alignment with the Newman projection. We need to account for that.



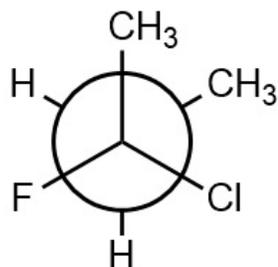
This looks weird, but it works. With the observer oriented with their feet going into the page, the observer's right is "up" on the page. The right of the  $\text{-CH}_3$  in the Newman projection is the  $\text{-OH}$ , so that goes in the top site. The H goes in the remaining back spot.



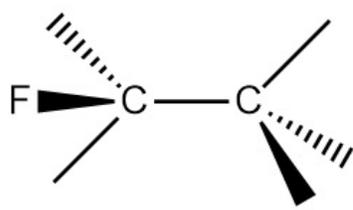
Now we just need to recognize that the  $\text{-OH}$  on the front side is opposite the  $\text{-OH}$  on the back C. The remaining sites are just H atoms.



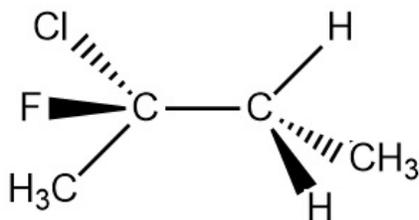
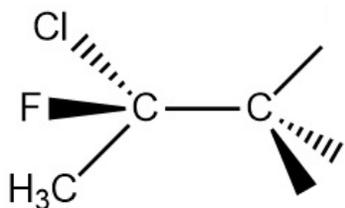
**Figure 6.1.11A-I:** Wedge-angle drawings and the corresponding Newman projection.



The F is on the nearer C atom in the Newman projection, which means the observer is to the left of the wedge-angle projection. But the F is pointed up and to the right rather than down, so we have to reorient the observer again.



When the observer is upside-down on the left side of the wedge-angle projection, their left arm is coming out of the page. This is consistent with the position of the F, which is on the left-hand side in the Newman projection. The Cl should therefore go on the observer's right (into the page) and the CH<sub>3</sub> should be at the top of the observer's view (in the plane of the page, at the bottom).



You can fill in the remaining slots by noticing that the -CH<sub>3</sub> on the far C sits between the -Cl and the -CH<sub>3</sub> on the near C atom. Then you just need to fill in the empty slots with H atoms.

**Figure 6.1.11A-II:** Wedge-angle drawings and the corresponding Newman projection.

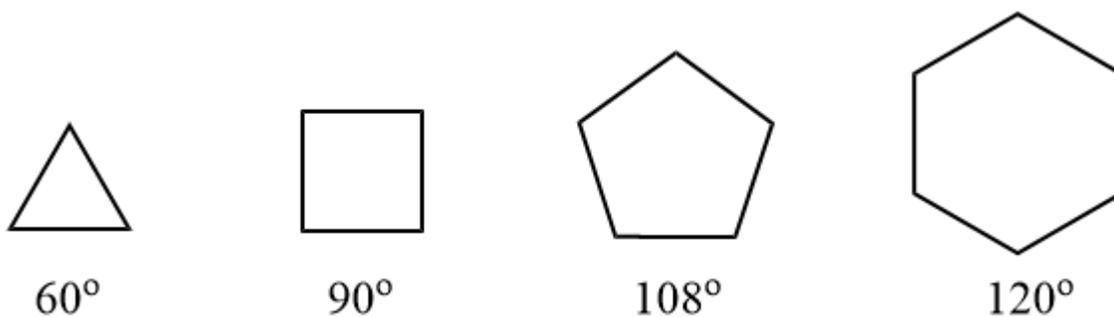
## Section 6.2: Geometry and Conformations of Cycloalkanes

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand the geometry of cycloalkanes with ring sizes from three to six carbons. Understand the role of dihedral angles and torsional strain in determining the C-C-C angles of cyclobutane and cyclopentane.
- Know what is meant by angle strain and ring strain.
- Understand and be able to recognize the chair, boat, and twist-boat conformations of cyclohexane.
- Understand the what is meant by axial and equatorial sites in a cyclohexane chair conformation, and the connection between those terms and cis-/trans- isomerism.
- Understand the nature of diaxial interactions in monosubstituted alkanes, and be able to predict which of a series of substituents would likely have the strongest diaxial interactions.

We have touched on rings frequently in this book, discussing aromatic rings in Chapters 2 and 3 and cycloalkane rings in our discussion of cis-/trans- isomers in Chapter 4 and chirality in Chapter 5. But we have not looked in detail at the skeleton of a ring. And when we do, we encounter a problem: Their internal angles seem incompatible with VESPR theory.

Planar geometric figures and their geometries are shown in Figure 6.2.1. Recall that  $sp^2$ -hybridized carbon atoms form  $120^\circ$  angles and  $sp^3$ -hybridized carbon atoms form angles at  $109.5^\circ$ . It costs considerable energy to bend bonds away from those angles, meaning that building the geometric figures shown in Figure 6.2.1 from carbon atoms would be extremely challenging. One could build a hexagonal planar aromatic ring, as the  $sp^2$ -hybridized carbon atoms are an exact match for the angle needed to create a planar hexagon. And, naively, we might think  $109.5^\circ$  is close enough to  $108^\circ$  that we could build a planar pentagon out of  $sp^3$ -hybridized carbon atoms. But the triangle and square appear inaccessible to chemistry.

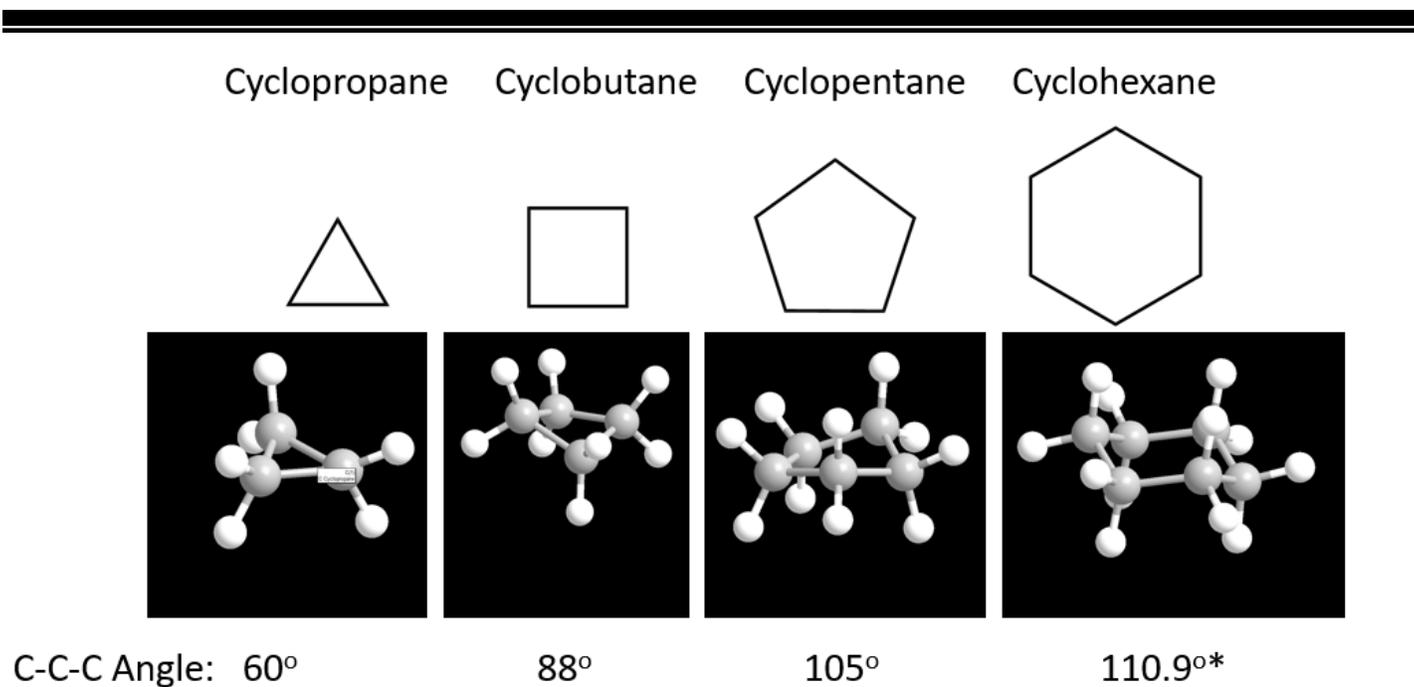


**Figure 6.2.1:** Angles for planar geometric figures with 3-6 equal sides. These are geometric figures, not line-angle drawings of compounds.

This assessment is not entirely wrong. Three- and four-membered rings do exist but are very unstable. And, as you should be aware by now, benzene and other aromatic rings are indeed planar and very stable. But five- and six-membered rings are stable and quite common because *molecules do not have to be planar*.

Figure 6.2.2 shows four cycloalkanes, their names, their three-dimensional structures, and the C-C-C angles associated with their rings. Only the cyclopropane ring has exactly the angle expected from the Euclidian geometry given in Figure 6.2.1, and that simply reflects the fact that three points define a plane. The

rings of the other molecules are puckered, taking the carbon atoms out of the plane and so eliminating the constraint implied by Figure 6.2.1.



**Figure 6.2.2:** Names, structures, and C-C-C angles for four cycloalkanes. The \* for the cyclohexane indicates that this is subject to change in different conformations of the ring (see discussion below).

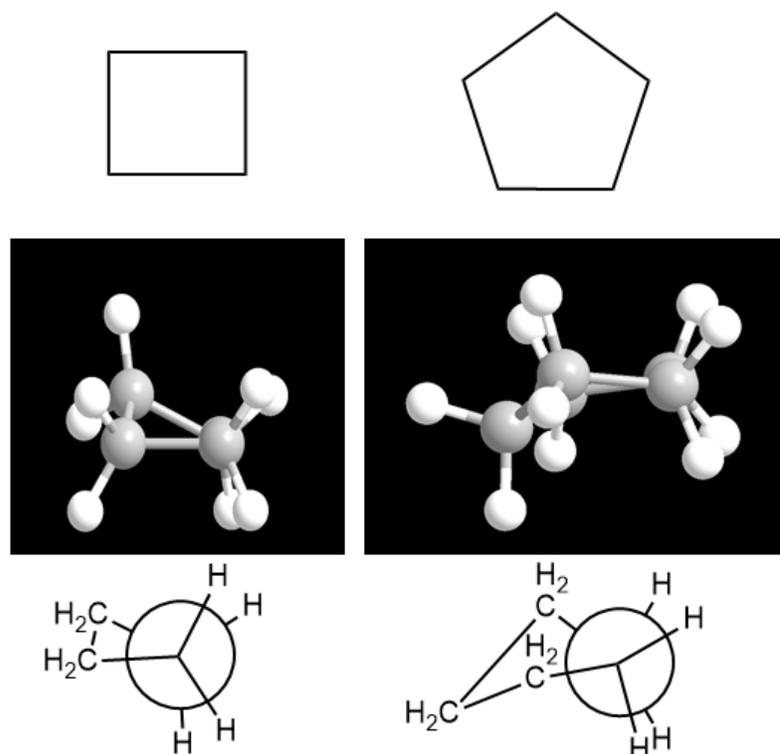
But, strangely, the angles of 88° for cyclobutane and 105° for cyclopentane seem to make matter *worse*, not better. The C atoms on both rings are  $sp^3$ -hybridized, meaning that the best angle should be near 109.5°; the distortions of the ring take the C-C-C angles away from that number rather than toward it. The reason is that the ring not only forces the molecules to have specific C-C-C angles, it also forces them to adopt eclipsed dihedral conformations for their C-H bonds.

Figure 6.2.3 shows the torsional angles associated with cyclobutane and cyclopentane. As the view along a C-C bond shows, the C-H bonds are near to being eclipsed, as are the C-C bonds leading off into the rest of the ring. Recall the significant energies associated with eclipsed geometries, as shown in Figures 6.1.4 and 6.1.6. While the puckering of the ring takes the C-C-C bond angle slightly further from its ideal value, the distortions significantly reduce the torsional energy associated with the dihedral angles. Though it is not shown, cyclopropane also has eclipsed dihedral angles around its ring.

So there are really two sources of steric strain in cyclopropane, cyclobutane, and cyclopentane. The first is the strain associated with the sub-optimal C-C-C bond angles, which are significantly distorted from the 109.5° expected for  $sp^3$ -hybridized angles. This form of steric strain is called angle strain. The second source of steric strain is the torsional strain associated with the eclipsed dihedral conformations. The distortions from planarity in cyclobutane and cyclopentane can be viewed as a tradeoff that decreases torsional strain at the price of increased angle strain.

The two forms of strain together are called small ring strain, or sometimes simply ring strain, and are characteristic of cycloalkanes with five carbons or fewer.

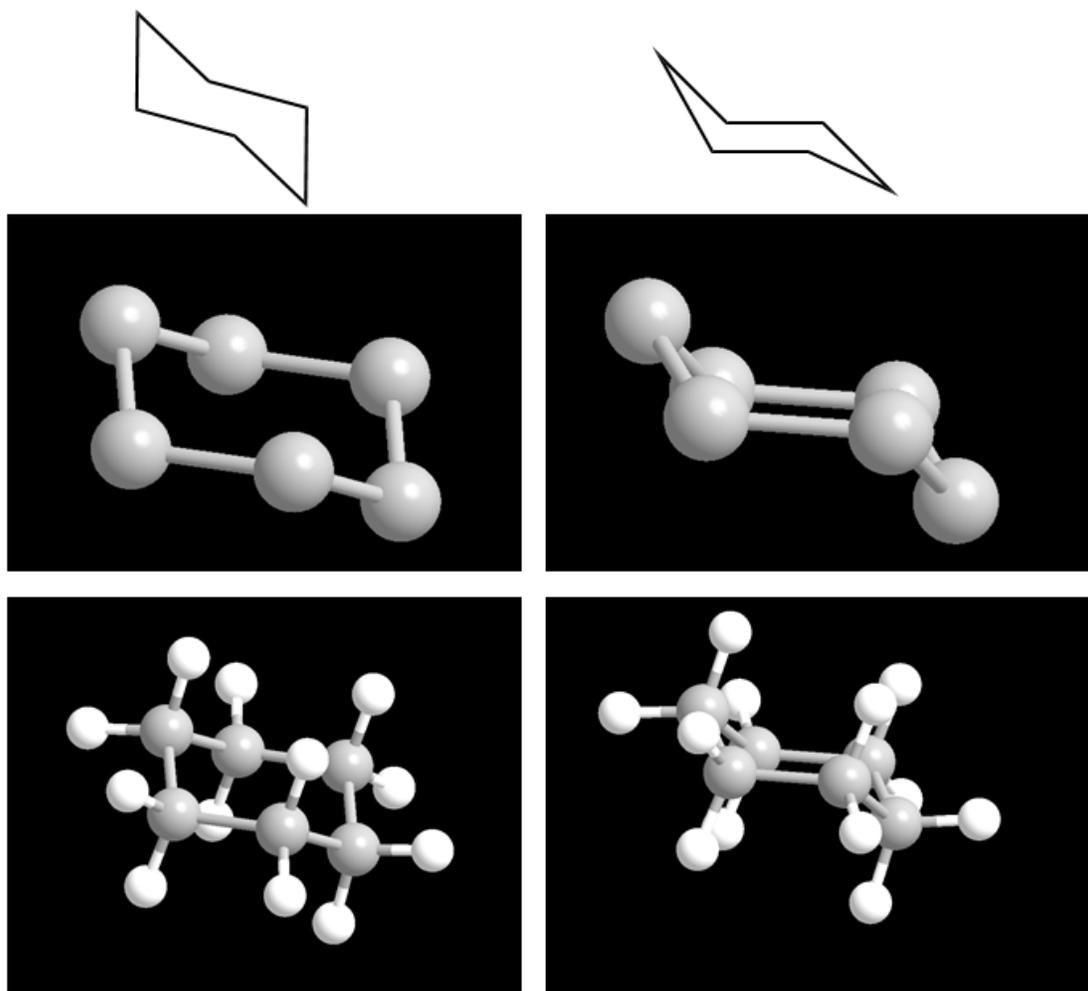
**Figure 6.2.3:** Dihedral angles for the puckered conformations of cyclobutane and cyclopentane. Both conformations have bonds that are nearly eclipsed, leading to significant torsional strain.



Cyclohexane shows more subtle and complex behavior. It does not suffer from small ring strain per se, though it does display a number of important forms of steric strain.

The first thing to recognize is that cyclohexane can exist in multiple different conformations. It is not simply a question of it puckering away from planarity, it can shift from one conformation of relative stability to another. This is similar to the way that butane possesses multiple staggered conformations at different energies, shown in Figure 6.1.6.

The most stable conformation for cyclohexane is called the chair conformation, and is shown in Figure 6.2.4. The C-C-C angle is  $110.9^\circ$ , close enough to the ideal angle for  $sp^3$ -hybridization that the angle strain is negligible. Likewise, the puckering of the ring brings the H atoms into a staggered rather than eclipsed configuration, as shown in Figure 6.2.5. So, torsional strain is minimal.



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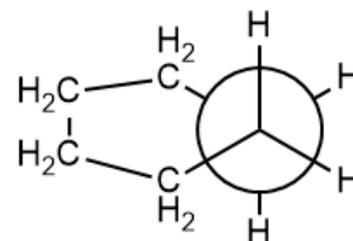
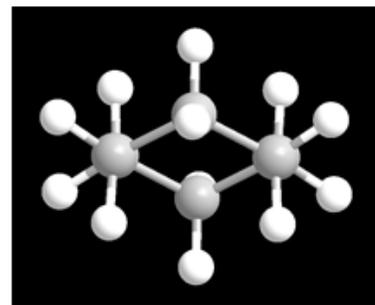
**Figure 6.2.4:** Chair conformation of cyclohexane from two different views. The left-hand view is shown slightly off-plane from the ring, and the second is shown from the side. The second row shows the carbon skeleton without H atoms in each case, and the third shows the structure with hydrogen atoms.

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The chair conformation can be visualized as four C atoms that are in the same plane, bounded at each end by one going “up” and one going “down”. This is a reasonable way to picture the molecule, but it is important to understand that the sites on the molecule are equivalent. The fact that there appear to be points going up and down is a product of how your brain resolves the image and the angle at which you have viewed it. It is possible to reorient the molecule without changing the configuration and make different “up” and “down” carbons. It is equally possible to visualize the chair conformation as a ring that zig-zags up and down as one moves around the loop. This is extremely hard to communicate with static images, and you are encouraged to build a model and explore it yourself.

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**Figure 6.2.5:** End-on view of the cyclohexane ring in the chair conformation. In this representation it is clear that the C-H and C-C bonds are staggered for cyclohexane in this conformation.

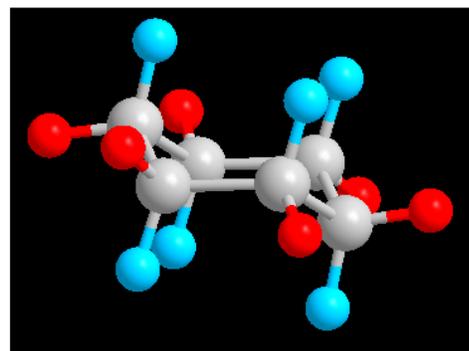
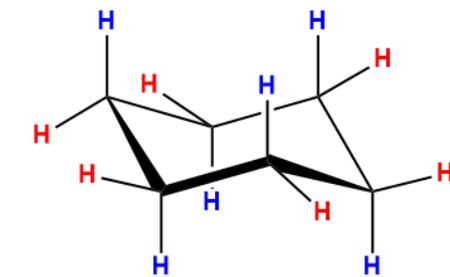


Another point of interest is that the puckering of the ring maneuvers the hydrogen atoms into configurations that are not simply “up” and “down”. As shown in Figure 6.2.6 some H atoms point outward from the ring and are labeled as equatorial, while others point parallel to the axis of the ring and are labeled as axial. There are three axial H atoms on each side of the ring.

There are multiple chair conformations of the cyclohexane ring. While they are equivalent, changing from one to another can make a different set of H atoms axial and equatorial. This is not important for unsubstituted cyclohexane, but it can make a difference if H atoms are replaced with other substituents as we will discuss below.

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**Figure 6.2.6:** Chair conformation of cyclohexane with axial hydrogen atoms shown in blue and equatorial hydrogen atoms shown in red.

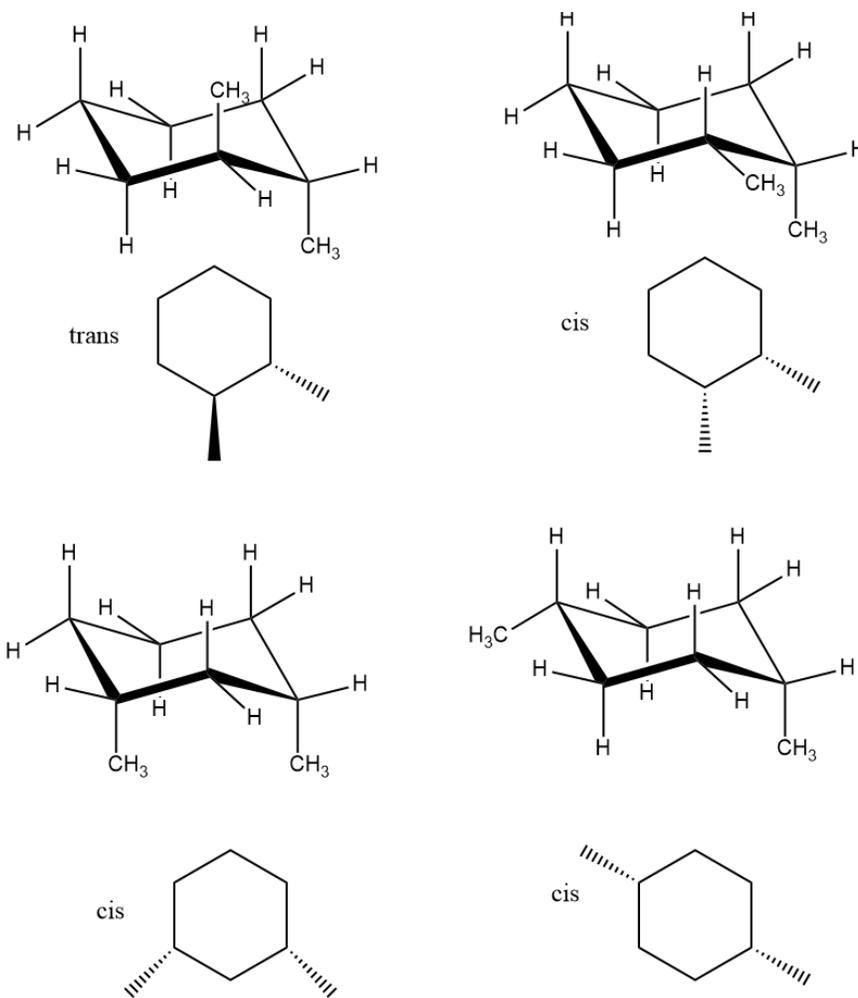


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On a related note, the differing character of the hydrogen atoms – and any substituents attached to the ring – complicates the interpretation of cis- and trans-isomers. In Chapter 4, we learned how to interpret cis- and trans- isomers corresponding to wedge-angle drawings of rings, but connecting those to the fully 3-dimensional structure of the cyclohexane ring is a more subtle problem.

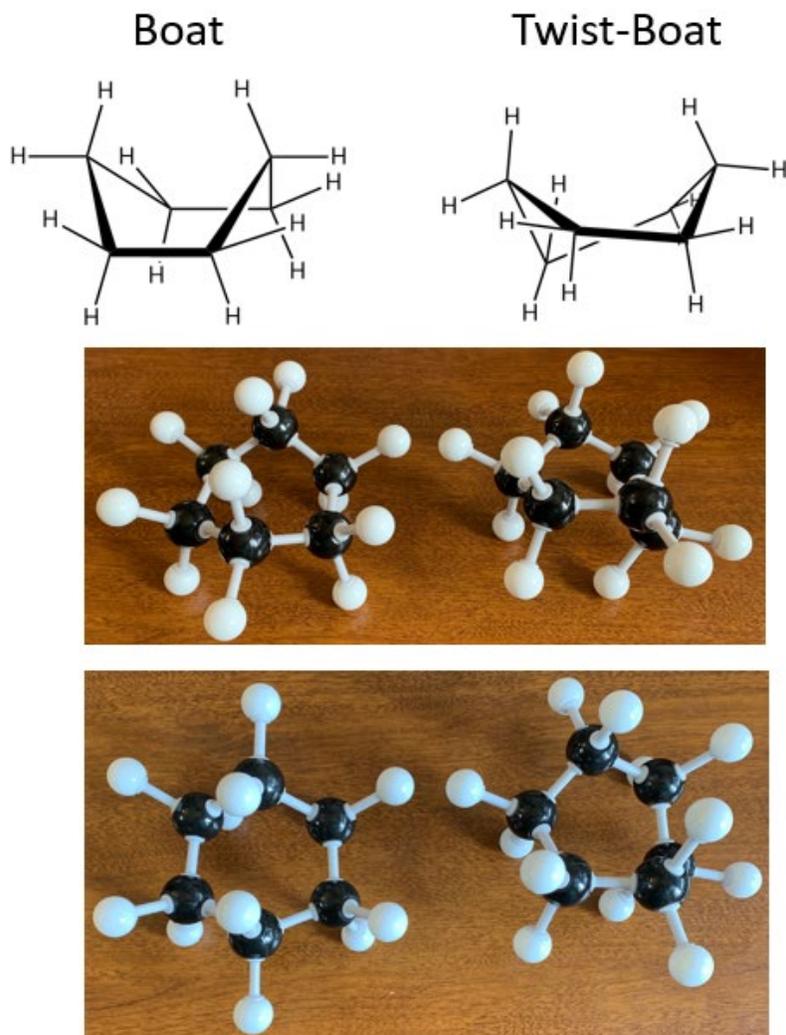
The solution is simply to choose an “up” and “down” direction (usually based on the way the molecule is drawn) and recognize that on half the carbons the axial H will be up and on the other half it will be down. On atoms where the axial H is pointed up, the equatorial H should be regarded as down; the opposite will be true in cases where the axial H is pointed down.

Having recognized that, groups that are both “down” or both “up” will be cis, and pairs of substituents in which one is up and the other down are trans. Some examples are given in Figure 6.2.7. Note that in one case, two axial methyl groups are cis, and in another two axial groups give a trans conformation. It may seem that changing the conformation could alter the cis-/trans- character of the methyl groups, but this is not the case. One can alter their axial vs. equatorial character (which depends on conformation) but one cannot alter their relative cis-/trans- positions without actually breaking and rebuilding bonds. Thus, cis-/trans- isomers do exist for cyclohexane species.



**Figure 6.2.7:** Three-dimensional line drawings and wedge-angle drawings of cyclohexane rings containing two methyl substituents. Their relative positions as cis- or trans- do not relate in a simple way to their identity as being axial or equatorial.

The chair conformation is only one of the possible conformations of cyclohexane. Two others, the boat and the twist-boat, are shown in Figure 6.2.8. The boat can be generated by changing the direction of puckering on one side of the ring so that two carbon atoms are brought into proximity over a plane formed by the four other C atoms. This configuration puts two hydrogens attached to those carbons into close proximity, and their repulsion makes the configuration unstable. The twist-boat configuration represents a twisting of the ring that moves those H atoms further from each other by breaking the planarity of those other four rings; this is illustrated in Figure 6.2.9.



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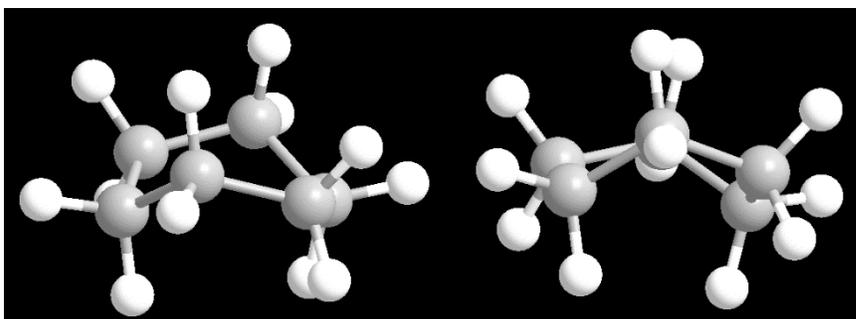
**Figure 6.2.8:** Three-dimensional line drawings and models of boat and twist-boat conformations.

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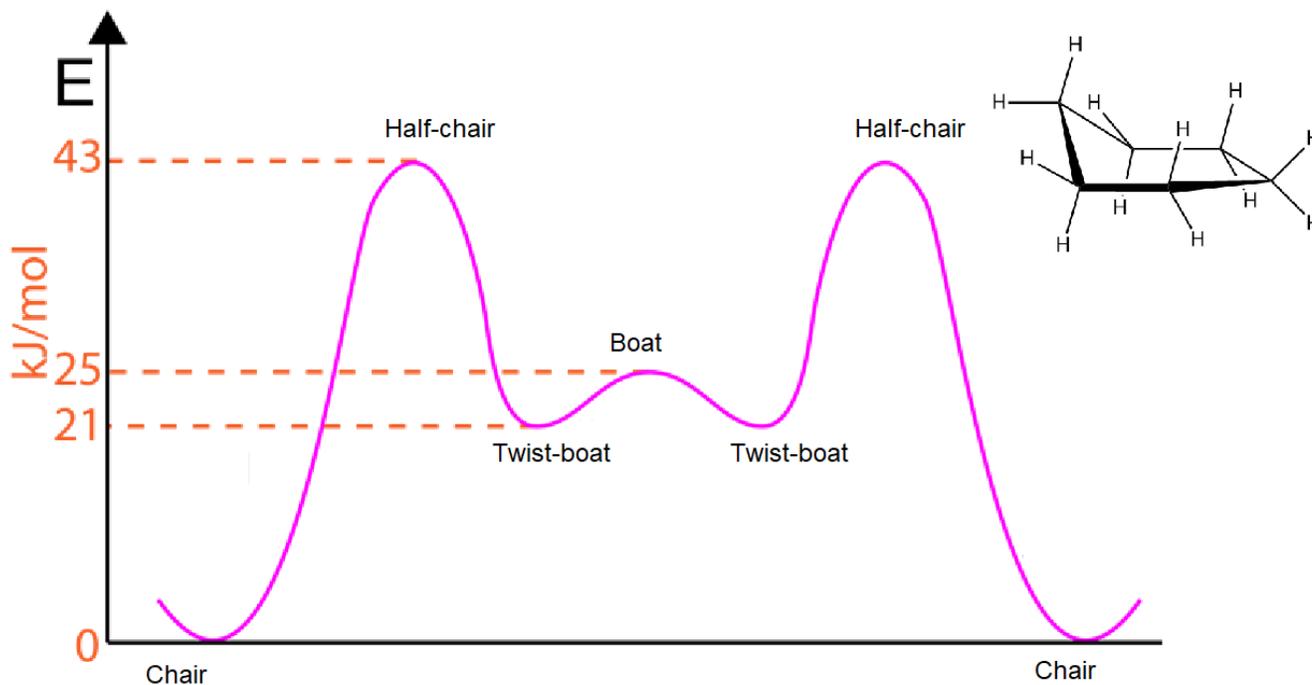
This leads to the question of energy. Again, as we saw with more simple torsional motions in the previous section, there are multiple conformations at varying energies. Figure 6.2.10 shows the relative energy of the conformations we have discussed for cyclohexane.

---

**Figure 6.2.9:** Two views of the twist-boat conformation. Note the proximity of the upright H atoms across the ring, and how the twisting of the ring moves them apart.



As with the torsional energies in the last section, the relative energies of the different conformations determine how likely the molecule is to be found in each. The twist-boat and boat energies are both significantly higher than the energy of the chair conformation, but close enough to thermal energy ( $\sim 2.5$  kJ/mol at room temperature) that there will be a significant population present at room temperature. Conversions between chair and boat conformations will be relatively slow because the molecule has to pass through the half-chair conformation, but they will happen.



**Figure 6.2.10:** Relative energies of the configurations of cyclohexane. The “half-chair” is an unstable configuration formed by swinging a point on the ring from “down” to “up”; its geometry is shown.

*Modified from Keminsti, accessed via Wikimedia Commons,*

*[https://commons.wikimedia.org/wiki/File:Cyclohexane\\_conformations\\_and\\_energies\\_with\\_hydrogens.svg](https://commons.wikimedia.org/wiki/File:Cyclohexane_conformations_and_energies_with_hydrogens.svg), accessed July 24, 2021.*

The energies of these conformations can change when other substituents are attached to the ring. Consider the methyl group attached to the ring in Figure 6.2.11. When the molecule is in a chair conformation, the  $-\text{CH}_3$  can be in either an axial or equatorial position. But notice that when the  $-\text{CH}_3$  group is in an axial position it is in close proximity to two other hydrogen atoms across the ring from it. Interactions of this type are called diaxial interactions, and they represent a type of steric interaction. When the molecule is in a chair conformation that puts the  $-\text{CH}_3$  in an equatorial position, there are diaxial interactions between the three H-atoms in the axial positions (and the three others on the other side of the molecule). But these are significantly weaker than those involving the methyl group, as the methyl group is a larger group with more electrons.

**Figure 6.2.11:** Two chair conformations of methyl-substituted cyclohexane, with three of the axial sites shown in blue. The conformations exist in equilibrium based on their energies.

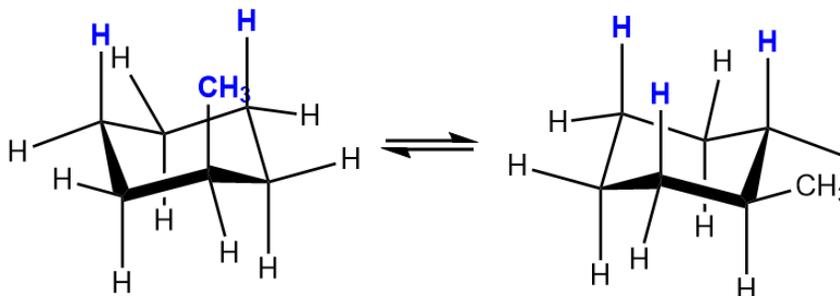
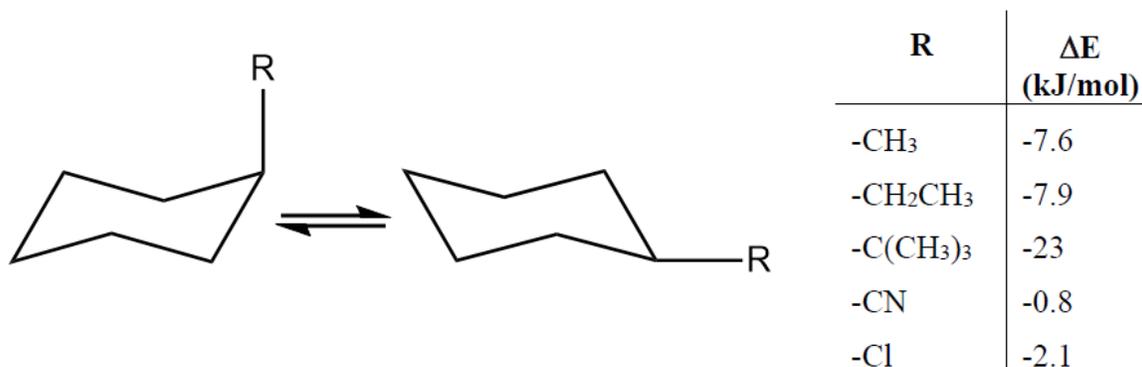


Figure 6.2.12 reports the difference in energy for various monosubstituted cyclohexanes with their substituent in axial and equatorial configurations. This is a good estimate of the strength of diaxial interactions, though other interactions around the molecule can also change the relative energies of the configurations. The key factor appears to be the “bulkiess” of the group, as the interaction strength increases greatly moving from the  $-\text{CH}_3$  to the  $-\text{C}(\text{CH}_3)_3$  groups. The linear  $-\text{CN}$  group and the monatomic  $-\text{Cl}$  group have weaker diaxial interactions, though the large atomic radius of the chlorine atom means its interactions are significant.



**Figure 6.2.12:** Energy differences for monosubstituted cycloalkanes in axial and equatorial positions. This is a rough estimate for the strength of diaxial interactions for various groups. *Data from L.G. Wade, "Organic Chemistry, 8<sup>th</sup> ed.," Pearson, 2012.*

As with the other discussions of conformation, the increased energy associated with diaxial interactions means that monosubstituted cyclohexanes will tend to remain in configurations where substituents are equatorial. You will learn in organic chemistry that this can influence reaction outcomes.

The discussion of cyclohexane and its simple derivatives is an example of the subtle behaviors associated with the flexible structures formed by carbon chains and rings. Understanding organic chemistry requires not only understanding their average position, but also recognizing the types of motion in which they can engage.

# CHAPTER 7: Acid-Base Reactions



*The reaction of vinegar and baking soda, which has powered grade school science projects for generations, is an example of acid-base chemistry.*

*Image by Katerha, courtesy of Wikimedia Commons,  
[https://commons.wikimedia.org/wiki/File:Baking\\_soda\\_and\\_vinegar.jpg](https://commons.wikimedia.org/wiki/File:Baking_soda_and_vinegar.jpg), July 28, 2021.*

THE WORLD OF CHEMICAL REACTIONS IS LIKE A STAGE, ON WHICH SCENE AFTER SCENE IS CEASELESSLY PLAYED. THE ACTORS ON IT ARE THE ELEMENTS.

-CLEMENS WINKLER

*Having discussed many aspects of chemical structure, we are now ready to explore the creation and destruction of chemical bonds. But even acid-base chemistry, perhaps the simplest class of reactions, can be a subtle process.*

## BEFORE YOU BEGIN, MAKE SURE YOU KNOW

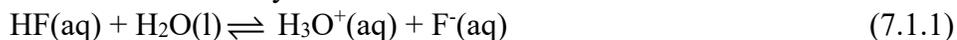
- Acid-base chemistry (Flowers, secs 14.1-14.3) and the equilibrium constant (Flowers, Chapter 13).
- Principles of Thermodynamics (Flowers, secs 5.1 and 5.3, and Chapter 16).
- Properties of logarithms (Flowers, Appendix B)
- Collision Theory and the reaction path (Flowers, sec 12.5), reaction mechanisms (Flowers, sec 12.6).
- Effective nuclear charge (Flowers, 6.5) and electronegativity (Flowers, 7.6).
- The equilibrium constant (Flowers, sec 13.2), basic thermodynamic definitions, and its relationship to free energy (Flowers, sec 16.4).

## Section 7.1: Review of Acid-Base Chemistry

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand the definitions of Arrhenius, Bronsted-Lowry, and Lewis acids and bases, and be able to use them to recognize acids and bases in reactions. Know what is meant by conjugate acids and bases and be able to recognize them in reactions.
- Understand and be able to use the curve-arrow notation to write acid/base reactions.
- Understand the definitions of  $K_a$  and  $pK_a$ , and how their values correlate with acidity. Understand how to use  $K_a$  and  $pK_a$  values to predict the equilibrium constants of reactions between acids and bases. Be able to predict whether an acid-base reaction will favor the “left” or the “right” based on the  $pK_a$ 's of reactants and products.
- Understand reaction coordinate diagrams for reactions. Know the relationships between free energy, enthalpy, and internal energy, and how each can influence a reaction. Understand the relationship between an energy diagram for a reaction coordinate and the equilibrium constant, the presence of intermediates, and the rate of reaction.

**Principles of Acid-Base Chemistry:** Let us start with some definitions of acids and bases, given in Table 7.1.1. The narrowest definition of an acid is the Arrhenius definition, which requires both that the reaction be in water and that it generate the hydrogen ion,  $H^+$ , which exists as  $H_3O^+$  when in water. An example of this might be the dissolution of hydrofluoric acid:



You should recall that HF is a weak acid, so both the molecular and ionic forms coexist in solution.

When a similar reaction is run in the vapor phase, however, it does not meet the criteria to be an Arrhenius acid-base reaction:



$NH_4F$  is an ionic compound, consisting of the  $NH_4^+$  and  $F^-$  ions. HF gave up a  $H^+$  to  $NH_3$  in a manner similar to the way that it reacted with  $H_2O$  in water. The reaction meets the conditions for the Brønsted-Lowry definition, so both Equations 7.1.1 and 7.1.2 are acid-base reactions by this definition. The expanded definition makes it easier for chemists to use the insights gained from acid-base chemistry in aqueous phase to understand reactions in other environments.

---

#### **Arrhenius:**

Arrhenius acid: A substance that dissolves in water to generate  $H^+$  (existing as  $H_3O^+$ ).

Arrhenius base: A substance that dissolves in water to generate  $OH^-$ .

#### **Brønsted-Lowry:**

Brønsted-Lowry acid: A substance that donates  $H^+$  in a reaction.

Brønsted-Lowry base: A substance that accepts  $H^+$  in a reaction.

#### **Lewis:**

Lewis acid: A substance that can accept a pair of electrons.

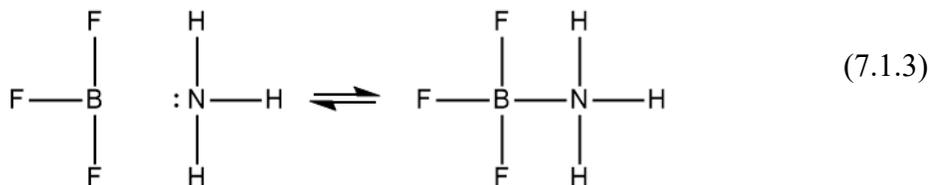
Lewis base: A substance that can donate a pair of electrons.

---

**Table 7.1.1:** Definitions of acid and base.

The Lewis definition goes further, and looks at the behavior of pairs of electrons. At a glance, this seems like an entirely different definition, but when one stops to consider the nature of  $H^+$  the definition is actually consistent with the other definitions.  $H^+$  has no electrons of its own, so it can only accept electrons; by the Lewis definition, it represents an acid in every reaction in which it participates, including Equations 7.1.1 and 7.1.2. Likewise, in each case, a lone pair of electrons is donated to the  $H^+$  (either from  $H_2O$  or  $NH_3$ ), so the bases are properly identified.

But consider the reaction shown below:



You may recall from first semester general chemistry that  $BF_3$  is an exception to the octet rule, with B having an underfilled octet. The reaction shown is different from others you may have seen before, but it does take place. In fact, it is closely analogous to Equation 7.1.2, with the neutral  $BF_3$  taking the place of  $H^+$ .  $BF_3$  accepts an electron pair and  $NH_3$  donates it, making them the Lewis acid and base, respectively.

The Lewis definition may seem esoteric, as we have so far encountered relatively few stable molecules with underfilled octets. But in fact many intermediates in chemical reactions have underfilled octets, and many metals that serve as catalysts play the role of Lewis acids.

**Take Note!** It is difficult to understand a Lewis acid-base reaction like the one given in Figure 7.1.3 without drawing the Lewis structures of the molecules involved. This should tell you that 1) You should draw the Lewis structures, and 2) Maybe Lewis' acid-base definition was just a marketing ploy for his dot structures.

Just as the definitions allow identifications of acid and base in the forward direction, they allow identification of the conjugate acid and the conjugate base. These are the acid and base if the reaction were to run in reverse. In Equation 7.1.1 one finds that  $H_3O^+$  has the potential to act as an acid and  $F^-$  to act as a base if the reaction were reversed, so  $H_3O^+$  is the conjugate acid of the (base)  $H_2O$  and  $F^-$  is the conjugate base of the (acid)  $HF$ . For an ionic compound like  $NH_4F$ , it is still possible to identify the separate ions  $NH_4^+$  as the conjugate acid of  $NH_3$  and  $F^-$  as the conjugate base of  $HF$ . However, where a covalent bond is formed, as in Equation 7.1.3, the product cannot be unambiguously identified as either conjugate acid or base and so the definition should not be applied. This situation is common for Lewis acid-base reactions, where the formation of a covalent bond frequently leads to the formation of a single product.

**Equilibrium and Acid-Base Chemistry:** Your second-semester general chemistry course committed significant time to chemical equilibrium, particularly that of acids and bases. We will provide a very brief review here, and encourage you to review on your own if you find the material unfamiliar.

As a point of notation, one often uses pH rather than  $[H^+(aq)]$ . The letter p is a shorthand for a mathematical function equal to the negative of the logarithm (base 10) of the number of interest (the  $H^+$  concentration in this case). So, for the above example:  $pH = -\log(0.00535) = 2.272$ . This may seem arbitrary, but

the use of the logarithm saves a good deal of writing scientific notation when discussing concentrations (which can range from over 1M to  $10^{-14}$  or smaller in solution).

---

*Problem:* The acid ionization constant for HF is  $K_a=6.4 \times 10^{-4}$ . What is the  $[H^+(aq)]$  in a solution prepared by adding 0.0500 moles of HF to enough water to make 1.00 L of solution?

*Solution:* Looking at Equation 7.1.1, we see that the equilibrium constant expression for the reaction is

$$K_a = [H^+(aq)][F^-(aq)]/[HF(aq)]$$

We are using  $H^+(aq)$  and  $H_3O^+(aq)$  interchangeably. Also, recall that that  $[H_2O(l)]$  does not appear in the equilibrium constant expression because the concentrations of liquids and solids do not change in reaction.

We know that before HF dissociates, the concentration should be 0.0500M. Dissociation produces 1  $H^+$  and 1  $F^-$  for every HF that breaks up, so we can use stoichiometry to place a restriction on the final concentration of each species:

	[HF(aq)] (M)	[H <sup>+</sup> (aq)] (M)	[F <sup>-</sup> (aq)] (M)
Initial	0.0500	0	0
Change	-x	+x	+x
Final	0.0500-x	x	x

Plugging known values into the equilibrium constant expression we obtain:

$$6.4 \times 10^{-4} = x^2 / (0.0500 - x)$$

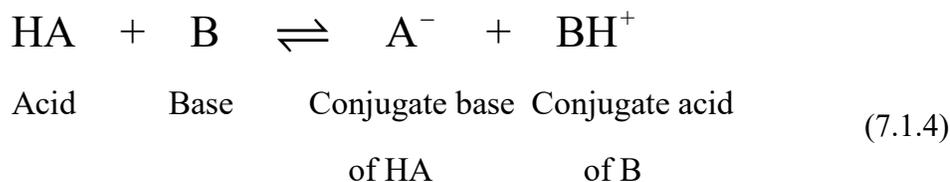
Using the quadratic equation, one obtains  $x=0.00535$ , meaning that the  $[H^+(aq)]=0.00535M$ .

---

### Example 7.1.1: Acid ionization equilibrium calculations.

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Where first-year chemistry focuses on acid-base chemistry in aqueous solution, organic chemistry will frequently apply it in solvents other than water. The prototypical reaction will then be



With the equilibrium constant expression:

$$K_{eq} = \frac{[A^-][BH^+]}{[HA][B]} \quad (7.1.5)$$

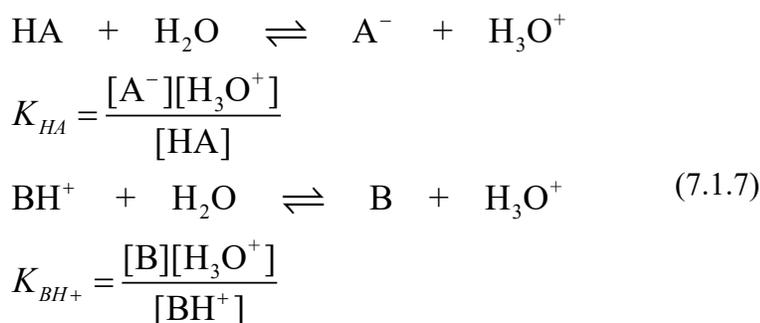
We have left out the phase (i.e. we have not specified “aq”) because we do not wish to limit the reaction to a specific environment.

The generic reaction forms in Equations 7.1.4 and 7.1.5 offer a trick. It is possible to obtain the value of  $K_{\text{eq}}$  for the reaction of acids and bases from the value of  $K_{\text{a}}$  for the dissolution of acids. Values of  $K_{\text{a}}$  are available for an enormous range of acids, so the trick makes it possible to avoid having to experimentally measure  $K_{\text{eq}}$  for every possible combination of acid and base.

For reasons that will be clear in a moment, we will multiply Equation 7.1.5 by 1. This does not change the equation, but if we express “1” as  $[\text{H}_3\text{O}^+(\text{aq})]/[\text{H}_3\text{O}^+(\text{aq})]$ , we can write:

$$K_{\text{eq}} = \frac{[\text{A}^-][\text{BH}^+]}{[\text{HA}][\text{B}]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \times \frac{[\text{BH}^+]}{[\text{B}][\text{H}_3\text{O}^+]} \quad (7.1.6)$$

This does not immediately seem like a helpful thing to do, but consider the reactions of the acid HA and the conjugate acid  $\text{BH}^+$  in aqueous solution:



We said above that we did not want to restrict ourselves to aqueous solution, but we have done so here. The values of  $K_{\text{HA}}$  and  $K_{\text{BH}^+}$  will be those reported in aqueous solution based on these expressions.

Plugging these equations back into Equation 7.1.6, we obtain

$$K_{\text{eq}} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \times \frac{[\text{BH}^+]}{[\text{B}][\text{H}_3\text{O}^+]} = \frac{K_{\text{HA}}}{K_{\text{BH}^+}} \quad (7.1.8)$$

This equation is exactly true in aqueous solution. More generally it will be *approximately* true in other solvents. This is useful not so much for quantitative predictions but for qualitative ones.  $K_{\text{HA}}$  and  $K_{\text{BH}^+}$  often differ from each other by multiple orders of magnitude, meaning  $K_{\text{eq}}$  will be much greater than or much less than 1. In a case like this, one can judge whether the reactants or products in Equation 7.1.4 will dominate based on the size of  $K_{\text{eq}}$  from Equation 7.1.8, regardless of what solvent is used. Since controlling a chemical reaction often requires knowing what species are present, this is a useful expression.

Before giving some examples of this, let us introduce a shorthand. Just as pH is often used to express  $[\text{H}^+]$ ,  $\text{p}K_{\text{a}}$  is often used to express the acid dissociation constant ( $\text{p}K_{\text{a}} = -\log(K_{\text{a}})$ ). Tables often report  $K_{\text{a}}$  values in this form. If we take the logarithm of both sides of Equation 7.1.8, we obtain

$$\begin{aligned} \log(K_{\text{eq}}) &= \log\left(\frac{K_{\text{HA}}}{K_{\text{BH}^+}}\right) \\ \log(K_{\text{eq}}) &= \log(K_{\text{HA}}) - \log(K_{\text{BH}^+}) \quad (7.1.9) \\ -\text{p}K_{\text{eq}} &= -\text{p}K_{\text{HA}} + \text{p}K_{\text{BH}^+} \\ \text{p}K_{\text{eq}} &= \text{p}K_{\text{HA}} - \text{p}K_{\text{BH}^+} \end{aligned}$$

If you are unfamiliar with the properties of logarithms you can review them in the section of the Flowers text referenced at the start of this chapter, or in a mathematics text.

Equation 7.1.9 amounts to a rewritten form of Equation 7.1.8, and can be used to predict whether a given reaction will favor reactants or products. If  $pK_{eq}$  as predicted from that equation is less than zero, then products will be favored and  $BH^+$  will be more common than HA. If  $pK_{eq}$  is greater than zero, then reactants are favored.

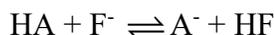
There are caveats to this. First, as noted above, these values are only approximate unless  $K_{HA}$  and  $K_{BH^+}$  are taken in the same solvent as the acid-base reaction is run. Second, while the calculation of the equilibrium constant in Equation 7.1.9 allows accurate prediction of the *equilibrium constant*, remember that it is possible to shift the equilibrium via the common ion effect. If one adds HA and B to solution in the absence of any other reagents, knowing the magnitude of the equilibrium constant is enough to predict whether reactants or products will be favored. However, if HA and B are added to a solution that already contains some concentration of  $A^-$  and/or  $BH^+$ , then the equilibrium becomes more complicated and detailed calculations are required (see the discussion of the common ion effect in the Flowers text).

Example 7.1.2 illustrates the use of Equation 7.1.9.

---

*Problem:* The  $pK_a$  for benzoic acid (a monoprotic acid) is 4.19, and the  $pK_a$  for hydrofluoric acid is 3.19. When benzoic acid is added to sodium fluoride, will the reaction favor the reactants or products?

*Solution:* We have not been told the solvent, so our solution will be approximate, but it is still worth pursuing. The fact that benzoic acid is a monoprotic acid means that we can write the equation as



Where HA is the molecular form of benzoic acid and  $A^-$  is the benzoate anion. Written in this form, we can write

$$pK_{eq} = pK_{benzoic} - pK_{HF} = 4.19 - 3.19 = 1.00$$

Since  $pK_{eq} > 0$ , the reactants are favored and there will be more HA present than HF.

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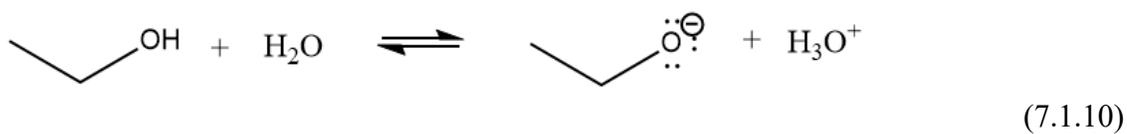
**Example 7.1.2:** Acid ionization equilibrium calculations.

---

This discussion of acid-base equilibrium is intended as a supplement to ideas that should already be familiar to you from first-year chemistry. If you are struggling, it may help to refresh your memory by reading your first-year text or the sections of the Flowers text referenced at the start of this chapter.

**Acid-Base Chemistry in Non-Aqueous Environments:** We referenced the idea above that acid-base reactions could be conducted in nonaqueous environments. We will explore that idea a little further here. While the results are not qualitatively different from those observed in aqueous environments, we will see reactions that appear different.

First, there are some species that cannot exist in water that can exist in other solvents. For example, consider the ethanoate ion, formed by the deprotonation of the hydroxyl group in ethanol:



The  $\text{pK}_a$  of ethanol is 15.9, and the  $\text{pK}_a$  of  $\text{H}_3\text{O}^+$  is  $\sim 0$  (though some texts report slightly different values as it can be difficult to define and measure). The equilibrium in Equation 7.1.10 should then be governed by

$$\text{pK}_{\text{eq}} = \text{pK}_{a,\text{ETOH}} - \text{pK}_{a,\text{H}_3\text{O}^+} = 15.9 - 0 = 15.9 \quad (7.1.11)$$

This means the equilibrium is strongly to the left, and ethanol will not dissociate in water.

Similarly, if we consider the dissociation ammonia:

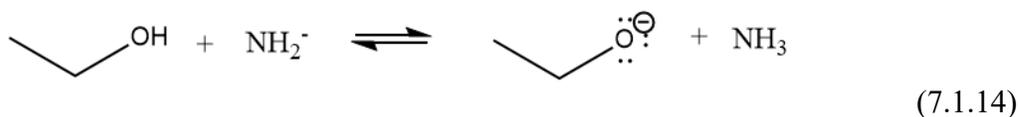


We already know this reaction will not take place, because when ammonia is added to water it acts as a base and accepts a proton from the water, not the other way around. Still, we can prove the equilibrium for this reaction will lie to the left in water by noting that the  $\text{pK}_a$  of ammonia (in solvents where it can form) is 38, so

$$\text{pK}_{\text{eq}} = \text{pK}_{a,\text{NH}_3} - \text{pK}_{a,\text{H}_3\text{O}^+} = 38 - 0 = 38 \quad (7.1.13)$$

The point is that neither the  $\text{NH}_2^-$  ion nor the ethoxide ion ( $\text{CH}_3\text{CH}_2\text{O}^-$ ) can exist in water. If either ion did emerge for some reason, the water would immediately react with it and eliminate it.

However, in organic solvents, it is possible for these species to exist. So we can imagine adding ethanol to a solution containing  $\text{NH}_2^-$  and establishing an equilibrium:



Will the ethanol or the ammonia be favored? We can answer easily:

$$\text{pK}_{\text{eq}} = \text{pK}_{a,\text{ETOH}} - \text{pK}_{a,\text{NH}_3} = 15.9 - 38 = 22.1 \quad (7.1.15)$$

The ethanol will be more common than ammonia. Again, this is not qualitatively different from acid-base reactions in aqueous phase, but it does involve species that cannot exist there and so may look very strange.

**The Reaction Path:** An important part of organic chemistry is connecting questions of energy, rate, and equilibrium to molecular structure and dynamics. A useful conceptual tool for this is a reaction coordinate. A reaction coordinate is the path along which atoms move when a reaction takes place, and it is often instructive to look at how energy changes along that path.

Before diving into that, it is worth reviewing some principles of thermodynamics. Some fundamental definitions and principles are given in Table 7.1.2. This is an impossibly brief summary, and if you find it unfamiliar you should review your first-year chemistry text.

In Chapter 6, we learned how to use the relationship between free energy and equilibrium constant to find the relative populations of different conformations of molecules in a sample. We also learned that while internal energy and free energy are different properties, it is often possible to use the internal energy as an estimate of free energy.

We can see from the relationships in Table 7.1.2 why this might be true. While the quantities are conceptually different, for reactions taking place in solution the change in volume is generally very small, meaning that enthalpy is very nearly equal to internal energy. Similarly, many reactions have relatively large enthalpies associated with the making and breaking of bonds, meaning that the changes in entropy have a relatively small effect on the reaction and the free energy is well-approximated by the enthalpy.

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### **A Brief Review of Thermodynamic Quantities:**

**Energy** (internal energy): The sum of kinetic and potential energy.

The change in energy in a reaction is often written:  $\Delta E_{rxn}^o$

**Enthalpy**: Is defined such that  $\Delta H_{rxn}^o = \Delta E_{rxn}^o - P\Delta V_{rxn}$ , where P is the pressure and  $\Delta V_{rxn}$  is the change in volume during the reaction.

Enthalpy has the property that at constant pressure and temperature,  $\Delta H_{sys} = q_p$  (the heat of the reaction)

The change in enthalpy in a reaction is often written:  $\Delta H_{rxn}^o$

**Entropy**: Loosely, a measure of the randomness of a system:  $S = k \ln(W)$ , where W is the number of ways to put a system together and k is called the Boltzmann constant ( $k = 1.38 \times 10^{-23} \text{ J/K}$ ).

The change in entropy in a reaction is often written:  $\Delta S_{rxn}^o$

**Gibbs Free Energy**: A quantity defined such that  $\Delta G_{rxn}^o = \Delta H_{rxn}^o - T\Delta S_{rxn}^o$

It is useful because it is related to the entropy of the universe:

$\Delta G_{rxn}^o = 0$ ; the entropy of the universe does not change and the reaction is reversible.

$\Delta G_{rxn}^o < 0$ ; the entropy of the universe increases in the reaction. The reaction is spontaneous, and the products will be the dominant form present at equilibrium.

$\Delta G_{rxn}^o > 0$ ; the entropy of the universe decreases in the reaction. The reaction is not spontaneous, and the reactants will be the dominant form present at equilibrium.

Recall:  $\Delta G_{rxn}^o = -RT \ln(K_{eq})$ ; this is the connection between the free energy and the equilibrium constant.

### **A Brief Review of Thermodynamic Laws:**

**First Law of Thermodynamics**: The energy of the universe remains constant in every process.

**Second Law of Thermodynamics**: The entropy of the universe always increases for spontaneous processes, and the entropy of the universe does not change for reversible processes. The entropy of the universe can never decrease.

**Third Law of Thermodynamics**: The entropy of a perfect crystal at absolute zero is zero.

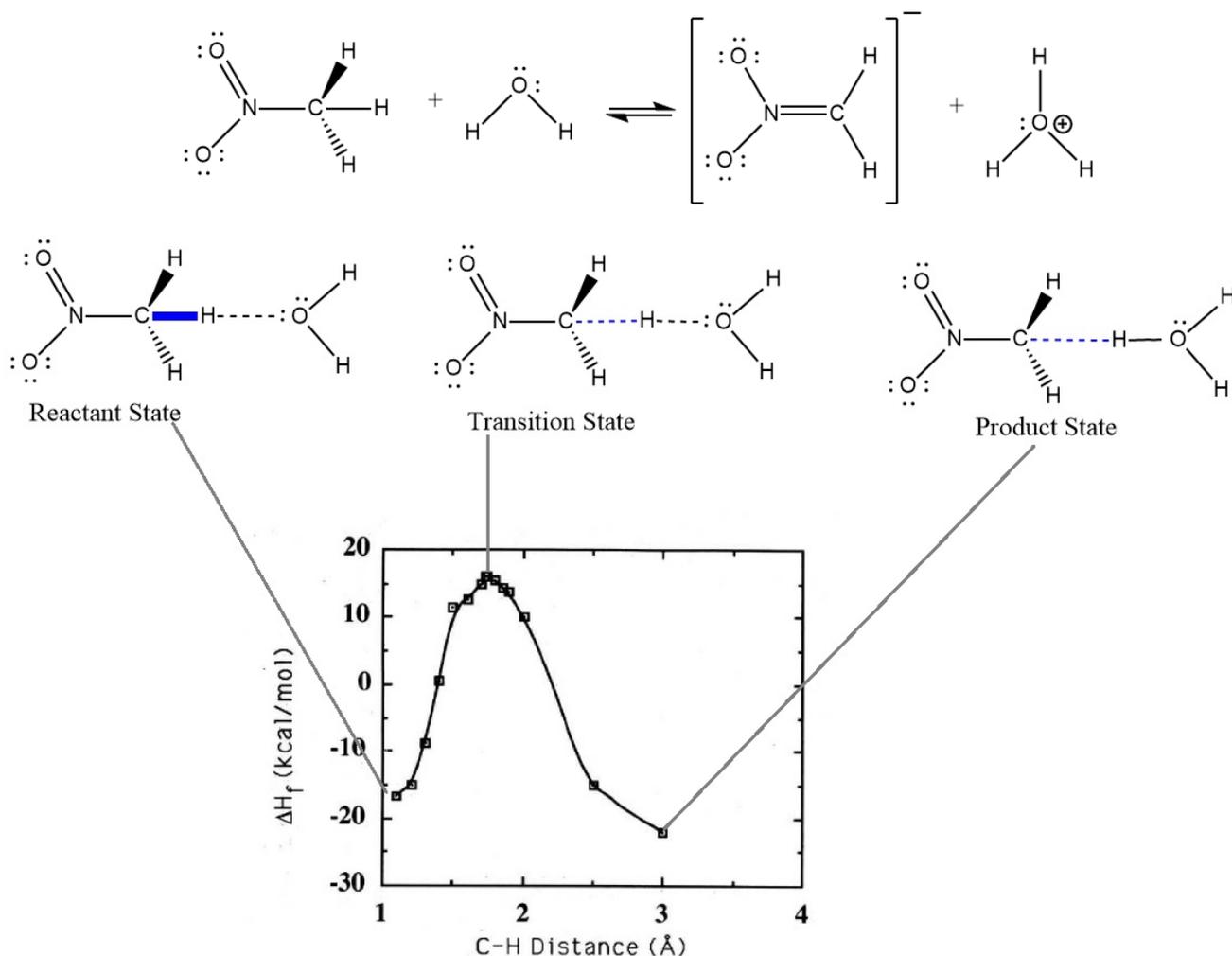
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### **Table 7.1.2: Fundamental definitions and ideas of thermodynamics.**

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It is useful to understand these approximations because the reaction path is often written in terms of the internal energy or enthalpy rather than the free energy. Reaction paths and their energies are often calculated from simulations, and entropy is a very difficult quantity to accurately compute in such calculations. Internal energies are more directly accessible.

Figure 7.1.1 shows the reaction of nitromethane with water, a classic acid-base reaction. The simplest motion one can imagine to be associated with this process is the stretching of the C-H bond. It begins with a length slightly larger than  $1\text{\AA}$  ( $1\text{\AA} = 10^{-10}\text{m}$ ), but gradually moves away from the carbon atom as it moves toward the water. The electron cloud on the oxygen is a good place for a  $\text{H}^+$  atom to sit, but the hydrogen atom is initially tied up in the C-H bond and the pair of bonding electrons is repelled by the electron cloud on the oxygen. Consequently, there is a limit as to how close the C and O atoms can get to each other, and the C-H bond has to stretch in order for the reaction to take place.



**Figure 7.1.1:** Reaction coordinate for the reaction of nitromethane with water. Top: The chemical reaction. Center: Schematic diagrams of the reactant, transition, and product states. Bottom: Enthalpy as a function of the distance between the C and H atoms in nitromethane, shown in blue in the line above.

Enthalpy plot taken from, Pietro, W. J., "Deprotonation of Nitroalkanes," *J. Chem. Ed.* **1994**, *71*, 416-420.

This stretching costs energy, as it involves increasing the C-H bond past its equilibrium bond length. Figure 7.1.1 shows the results of calculations that provide the enthalpy as a function of C-H distance, and as noted above the enthalpy is a reasonable proxy for energy or free energy. As the C-H stretches beyond its

equilibrium bond length, the enthalpy initially increases, and then begins to drop again as the H atom approaches the oxygen. Eventually, the enthalpy is lower than the value at which it started, reflecting the fact that water is a stronger base than the  $\text{CH}_2\text{NO}_2^-$  anion and the energy of the system is therefore reduced when the reaction completes.

There are several things to consider. First, while we have plotted the reaction coordinate as being simply the C-H stretch, this does not capture the full range of motion. Other bonds and angles in the molecule respond to the motion of the H atom as it moves away from the carbon atom, and if this reaction were to take place in solution the surrounding solvent molecules would move as well. Consider, for example, that as the H atom is withdrawn from the carbon, the carbon atom goes from being  $\text{sp}^3$ -hybridized to  $\text{sp}^2$ -hybridized, meaning the H-C-H angle of the remaining H atoms must change from  $\sim 109.5^\circ$  to  $\sim 120^\circ$  as the reaction progresses. The atomic motions associated with the reaction can be quite complex and difficult to characterize, even for something as seemingly simple as  $\text{H}^+$  transfer.

The second thing to consider is that this reaction, like nearly all reactions, includes a transition state, a point on the reaction path at which the energy is highest. The system must have enough energy to pass through the transition state if the reaction is going to take place. Thermal energy sloshes around randomly in molecules, and the higher the energy of the transition state the more time it will take before this random sloshing puts enough energy in the C-H motion to make the reaction possible. The energy of the transition state, referred to as the activation energy, therefore influences reaction kinetics. You may recall that the rate constant  $k_{\text{rate}}$  for a reaction is related to the activation energy  $E_a$  by the Arrhenius Equation

$$k_{\text{rate}} = A e^{-E_a/RT} \quad (7.1.16)$$

This clarifies the relationship between temperature, activation energy, and rate; you may want to review your general chemistry text if this is unfamiliar.

Based on the enthalpy plot given in Figure 7.1.1, the difference in enthalpy between the lowest enthalpy point to the left of the transition state (the reactants, roughly -17 kcal/mol) and the transition state (the peak, roughly 15 kcal/mol) is 32 kcal/mol. If we use the enthalpy to approximate the energy, this would be the activation energy for this reaction. A more generic depiction of activation energy and relative product energies is given in Figure 7.1.2.

A final point to consider is that the difference in energy between the initial and final states gives information about the equilibrium constant. Recall that, as indicated in Table 7.1.2,  $\Delta G^\circ_{\text{rxn}} = -RT \ln(K_{\text{eq}})$ . This means that if  $\Delta G^\circ_{\text{rxn}}$  is a negative number,  $K_{\text{eq}} > 0$ . The lowest-enthalpy point to the right of the transition state (the products) has an enthalpy of roughly -22 kcal/mol, meaning  $\Delta H^\circ_{\text{rxn}} = -22 \text{ kcal/mol} - (-17 \text{ kcal/mol}) = -5 \text{ kcal/mol}$ . If we use the approximation  $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}}$ , then we can estimate the equilibrium constant at room temperature to be

$$\Delta G^\circ_{\text{rxn}} = -RT \ln(K_{\text{eq}}) \quad (7.1.17)$$

$$K_{\text{eq}} = \exp[-\Delta G^\circ_{\text{rxn}}/RT]$$

$$K_{\text{eq}} = \exp[-(21 \text{ kJ/mol}) / ((8.314 \times 10^{-3} \text{ kJ/mol K}) (298 \text{ K}))]$$

$$K_{\text{eq}} = 2.1 \times 10^{-4}$$

Note that we converted from kcal/mol to kJ/mol for the calculation.

Figure 7.1.2 depicts a more generic reaction path. The specific atomic motions represented by the reaction coordinate are left unspecified, but this is often the case as they can be difficult to define. The y-axis of the plot specifies “Energy,” which should be taken to be internal energy (otherwise it should have been labeled

free energy or enthalpy). As in Figure 7.1.1, the transition state is the highest energy point on the plot and the reactants are found at the lowest energy point to the left of the transition state. Products are on the right. The activation energy is the difference in energy between the reactants and the transition state (roughly 11 kJ/mol) and the change in energy for the reaction is  $\Delta E_{\text{rxn}}^{\circ} = E_{\text{prds}}^{\circ} - E_{\text{rts}}^{\circ} = -5 \text{ kJ/mol}$  (approximately, based on the figure).

It is useful to consider how the reverse reaction might work as well. If the reaction were to run in reverse, from right to left, the change in energy for the reaction would be +5 kJ/mol and the activation energy for the reverse reaction would be 16 kJ/mol, equal to  $\Delta E_{\text{a}} + \Delta E_{\text{rxn}}^{\circ}$ .

**Figure 7.1.2:** A sample reaction coordinate, with activation energy and reaction energies shown.

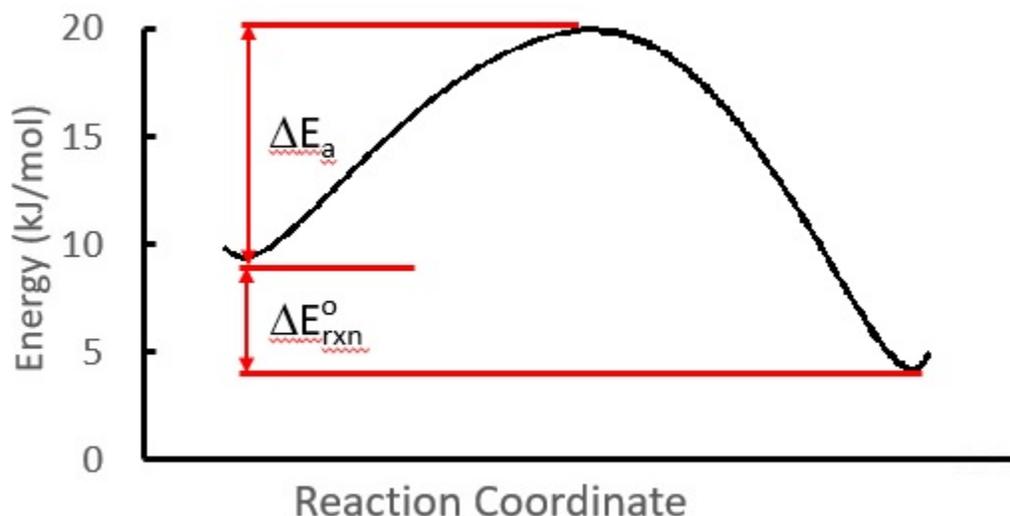
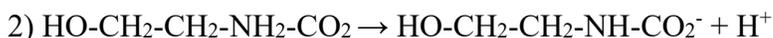
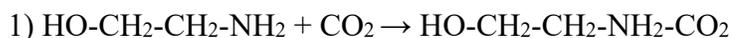


Figure 7.1.3 deals with a different case, one in which a reaction intermediate exists. You should recall from your discussion of kinetics in first-year chemistry that an intermediate is a compound that is both produced and consumed in the reaction, making it a structure that appears only in the reaction mechanism rather than a reactant or product. The data in Figure 7.1.3 are based on an article that used calculations to study the reaction shown.

The reaction includes an intermediate state in which the nitrogen is bonded to the  $\text{CO}_2$ . This state is less stable than the reactants or products, but is low enough compared to thermal energy that it will be present in solution.

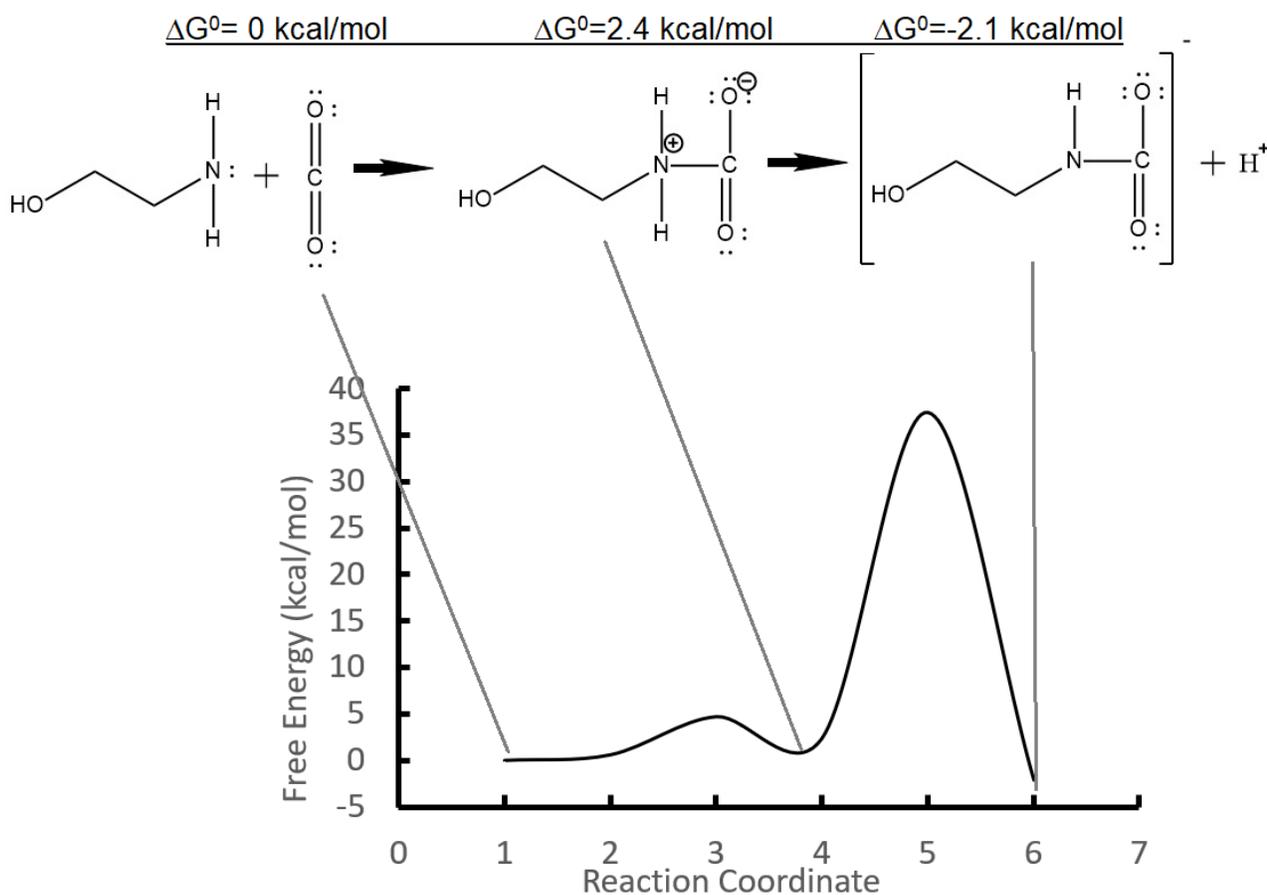
**MECHANISM:**

(7.1.18)



The first step, which forms the intermediate, represents a Lewis acid-base reaction with the  $\text{CO}_2$  acting as a Lewis acid and the ethanolamine acting as a Lewis base. The production of  $\text{H}^+$  means that the overall reaction is probably better described as a single displacement reaction rather than an acid-base reaction, though that is not important to the present discussion.

The purpose of presenting this reaction is to show how an intermediate is represented on a reaction coordinate. In order for the intermediate to have some stability, it must represent a dip (a “local minimum”) in the energy curve along the reaction coordinate. Such a dip means there are barriers to the reaction’s progress in either direction, such that it needs some minimum thermal energy to overcome one of those barriers if it is to proceed to products or revert to the reactants. It is the presence of those barriers that gives the intermediate a finite lifetime.



**Figure 7.1.3:** Reaction coordinate diagram with energies and structures of reactants, intermediate, and products indicated. Based on data from Xie, H.-B., Zhou, Y., Zhang, Y., Johnson, J. K., “Reaction Mechanism of Monoethanolamine with CO<sub>2</sub> in Aqueous Solution from Molecular Modeling,” *J. Phys. Chem.* **2010**, *114*, 11844-11852.

This creates what appear to be two different activation energies, one to enter the intermediate state and one to move on to the products. The reality is that only the largest activation energy – that between the reactant state and the highest energy point on the reaction coordinate – represents the activation energy of the overall reaction from reactants to products. The reason is simply that the random flow of energy must put enough energy into the reaction coordinate to move from the reactant state to the highest energy point in order for that reaction to take place. Other motions, which have lower energy barriers, are irrelevant.

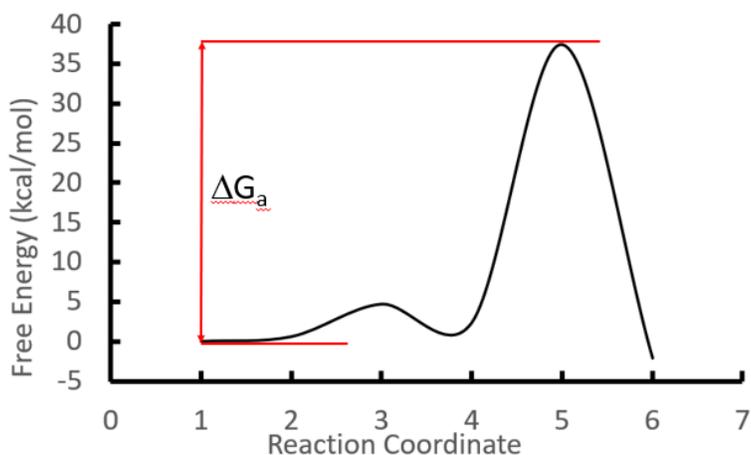
If it seems as if the presence of an intermediate should somehow give the reactants a “boost” to get over the barrier, remember that the system may slide back and forth between reactants and intermediate many, many

times. Statistically, that will not affect the time it takes enough energy to randomly accumulate in the system to overcome the barrier to reaction. A ball rolling back and forth in a tub with sloping walls does not gain more energy if one puts a speed bump of the tub, it just follows a different path.

In the reaction coordinate given, the difference in energy between the reactants and the transition state is 37 kJ/mol. Note that this is a free energy rather than an internal energy, so would only be an approximation for the  $E_a$  needed for Equation 7.1.16. But, as noted above, it is often a good approximation.

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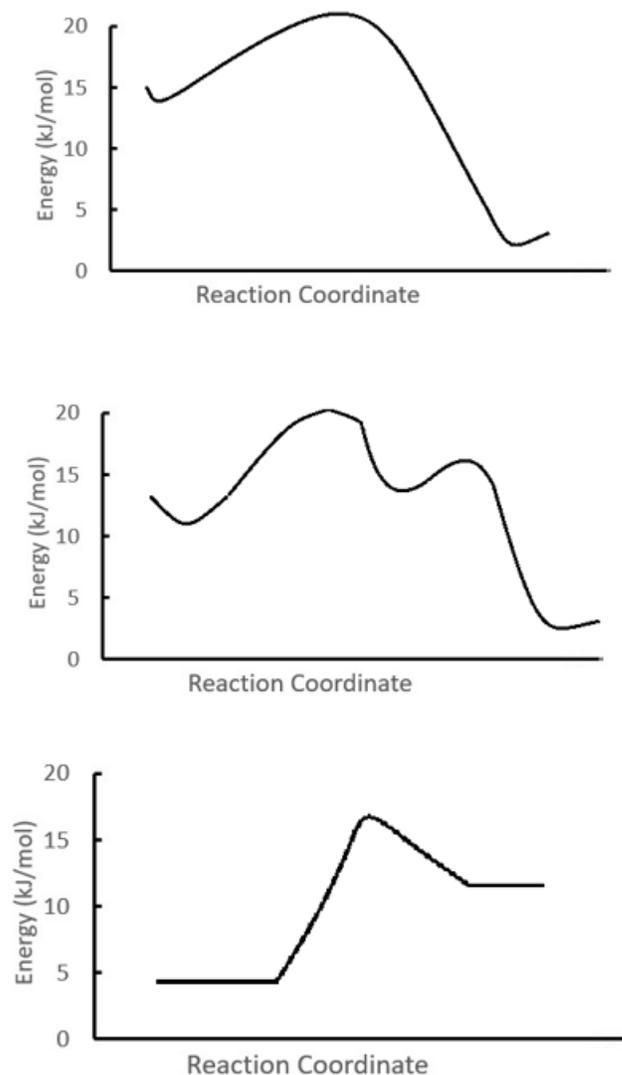
**Figure 7.1.4:** The free energy of activation in the reaction of CO<sub>2</sub> and ethanolamine



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Figure 7.1.5 shows three additional examples of reaction coordinate paths. For each one, give the activation energy of the reaction, state whether it has any intermediates, and indicate whether you believe the equilibrium constant for the reaction is greater than 1 or less than 1. The answers are indicated in Figure 7.1.5A.

**Figure 7.1.5:** Sample reaction coordinates. For each one, estimate the activation energy, state whether there is an intermediate state present, and indicate whether you believe the equilibrium constant is greater than or less than 1.



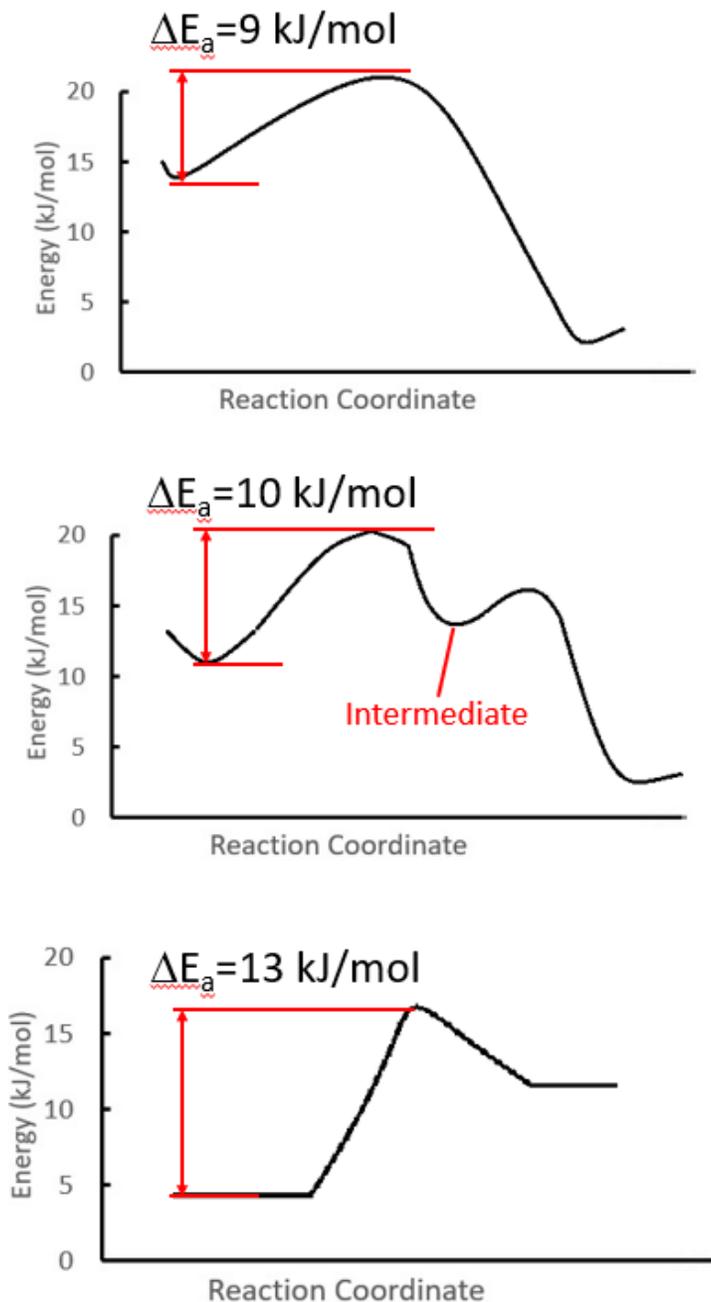
As discussed above, in each case the activation energy is the difference in energy between the reactants and the highest point on the reaction coordinate. This is shown in red on Figure 7.1.5A. Because these values are only estimated based on the image, your estimates may slightly differ from the one given; this is not cause for concern. However, if you did not recognize the measurement you needed to take to determine the activation energy, you should reread this section and/or seek assistance.

With regard to the question of an intermediate, remember that this implies a dip in the reaction coordinate, a region in which the system needs some thermal energy to escape. Only the second image has such a feature. Note that, unlike Figure 7.1.3, the intermediate is accessed after the system has passed the transition state, not before. This does not affect the fact that it is a stable position where the system will have a finite lifetime, and so it is an intermediate.

As to the final question concerning the equilibrium constant, recall the relationship given in Equation 7.1.17,  $\Delta G^0_{\text{rxn}} = -RT \ln(K_{\text{eq}})$ . This applies to free energy rather than the internal energies given in the plot, but

taking the energy as an approximation for free energy we can give our best estimate. It is a property of logarithms that  $\ln(x) > 0$  for  $x > 1$  and  $\ln(x) < 0$  for  $x < 1$ . That means that if the change in energy for the reaction is a negative number,  $\ln(K_{eq})$  must be positive and  $K_{eq} > 1$ . This is true for the first two cases, where  $K_{eq}$  should be greater than 1. In the last case, the change in energy is a positive number, meaning  $K_{eq} < 1$ . This makes sense – if the products are lower in energy than the reactants, products should be favored, and the reverse should be true if the energy of the products is higher than the energy of the reactants.

**Figure 7.1.5A:** Sample reaction coordinates, annotated to answer the questions posed.



## Section 7.2: Writing Acid-Base Reactions

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand and be able to use curved-arrow notation to write a chemical reaction.

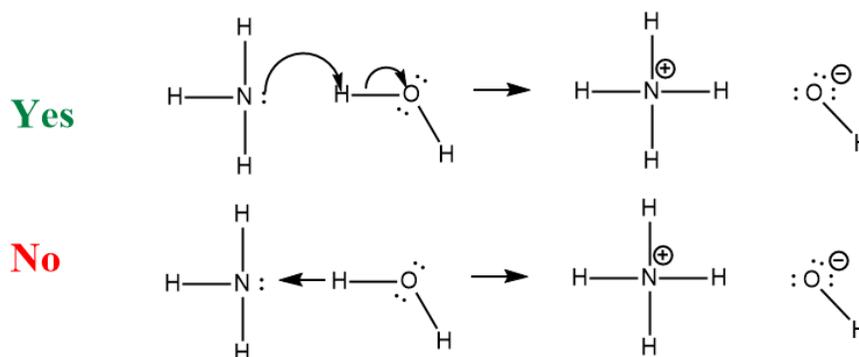
In Chapter 3, we learned how to use curved arrow notation to indicate resonance structures. Recall that arrows indicated the motion of electrons, not atoms. Chemical reactions are represented the same way by organic chemists, as tracking the flow of electrons is often far more informative than looking at the motion of nuclei. The rules for drawing curved arrows are given in Table 3.4.1, reprinted below.

1. Push arrows never move nuclei, they only move electrons.
2. Push arrows should start either at a lone pair of electrons, a bond, or an unpaired electron (rarely). The arrow runs from the place where the electrons begin to the point where they end.

**Table 3.4.1 (reprinted):** Rules for push arrow notation.

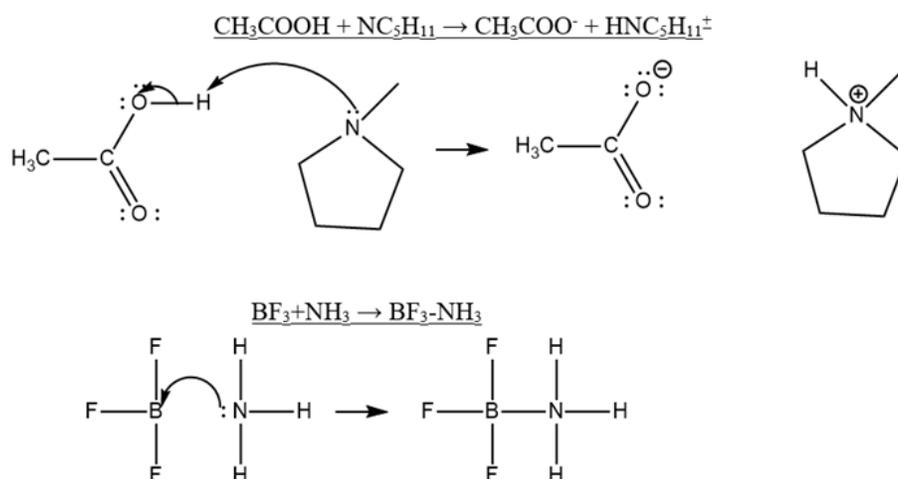
Figure 7.2.1 considers the reaction of ammonia and water, and shows how the arrows should go as well as giving an example of a common mistake. Arrows should indicate the motions of electrons, not the motion of atoms.

**Figure 7.2.1:** Reaction of ammonia and water, correctly and incorrectly expressed in curved arrow notation.



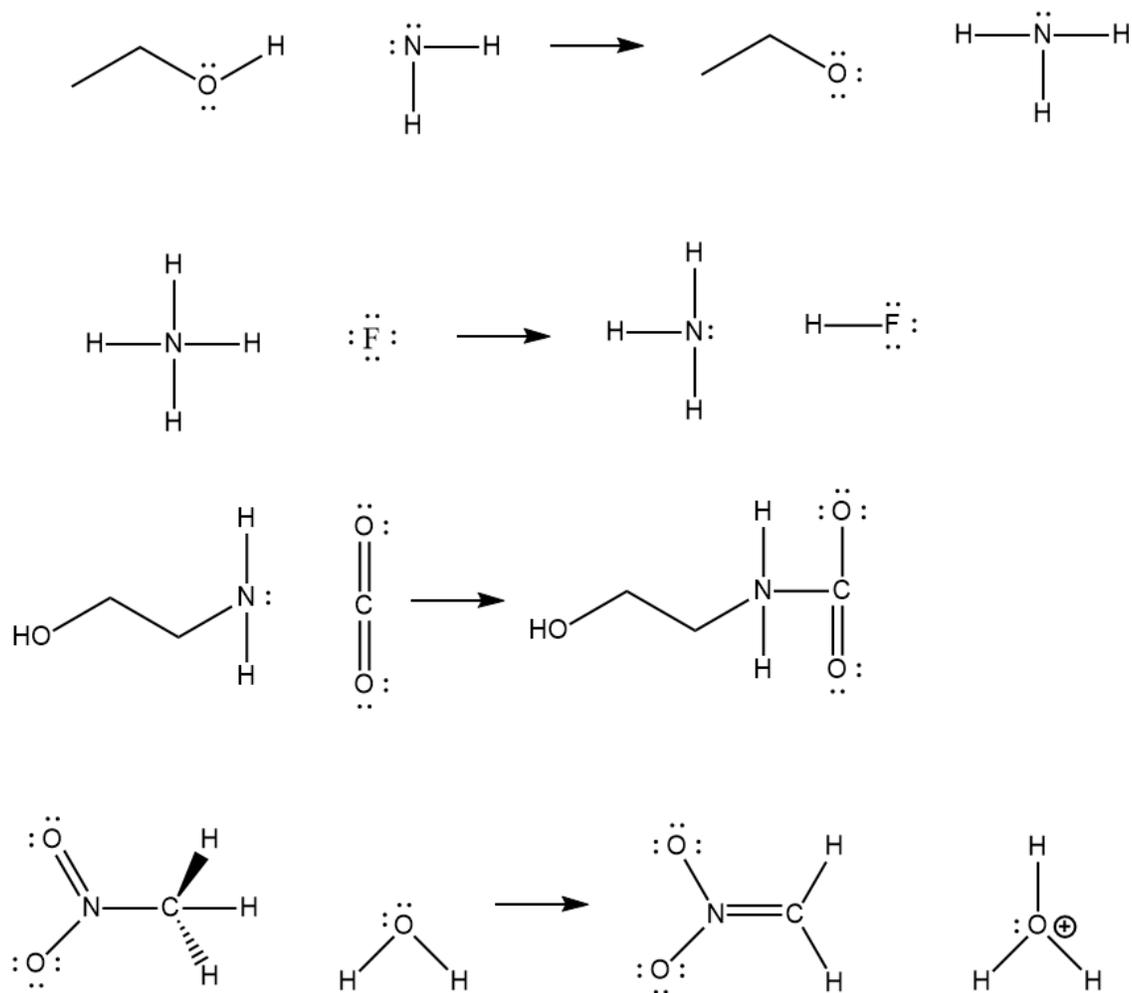
Two other examples are given in Figure 7.2.2. There are no surprises here, but you should be comfortable working with problems like those in Figure 7.2.3.

**Figure 7.2.2:** Examples of curved arrow notation.

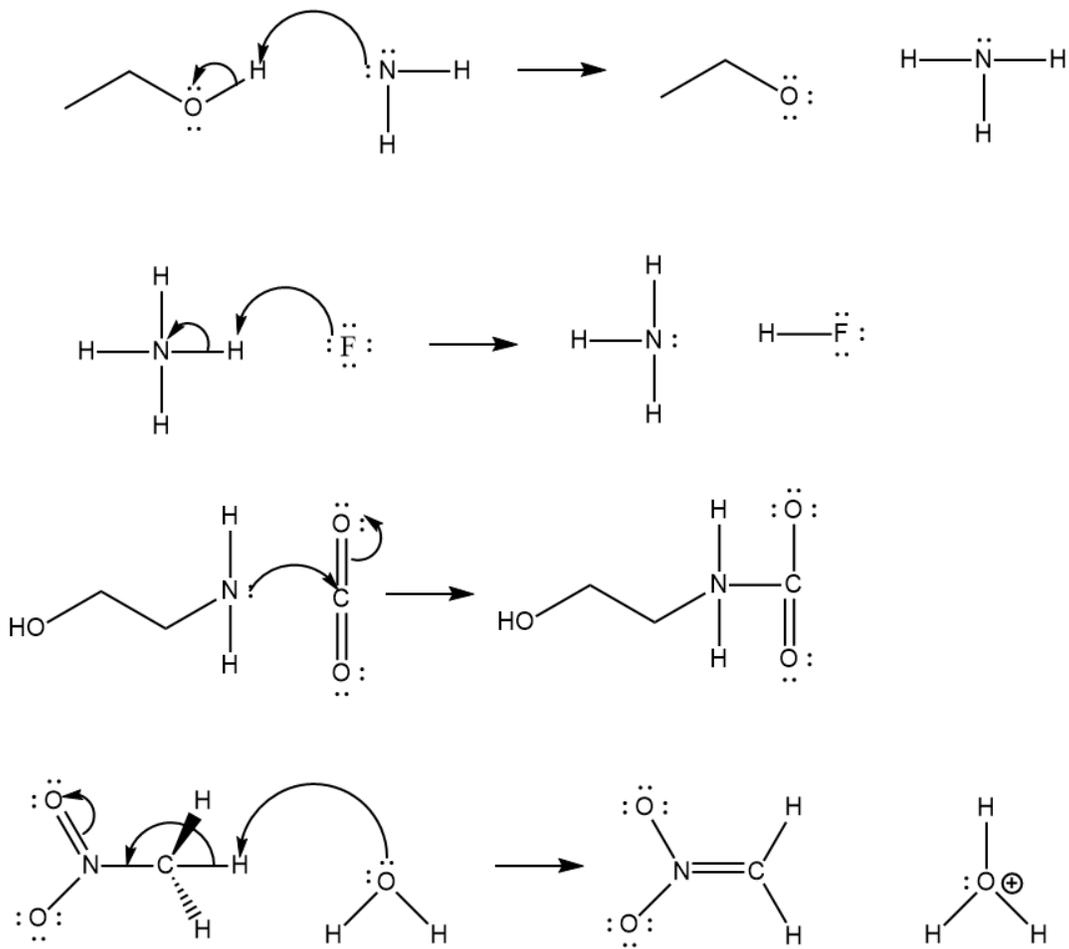


The first two cases in Figure 7.2.3 are relatively straightforward. A pair of electrons is donated from the base ( $\text{NH}_2^-$  or  $\text{F}^-$ , respectively) and a bond from the H to another element is broken, sending the electrons back to that element. The third reaction is unusual in that it requires converting a double bond to a single bond to prevent overfilling of the carbon octet, but this is allowed.

The final case involving the nitromethane is more complex, and involves a larger redistribution of electrons. With the products already written, however, you should be able to identify where the arrows go in an example like this. Remember that you do not have to just look at a specific bond. If you notice that the C-N bond becomes a double bond in the reaction, and the N-O bond becomes a single bond, you can use that information just as readily as the transfer of the  $\text{H}^+$  to work out the flow of electrons.



**Figure 7.2.3:** Some acid-base reactions. Fill in the missing arrows and compare with the answers in Figure 7.2.3A.



**Figure 7.2.3A:** Some acid-base reactions with the arrows filled in.

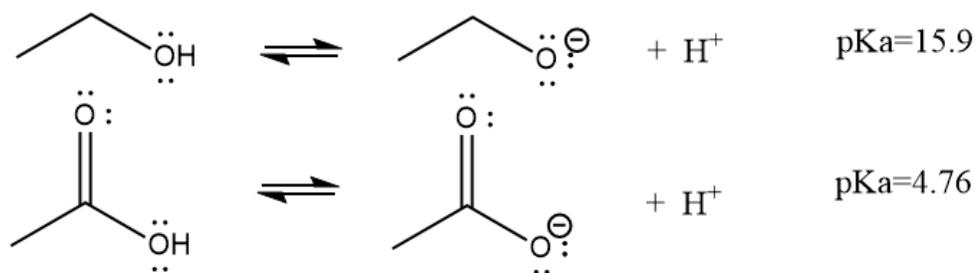
## Section 7.3: The Link Between Acidity and Chemical Structure

### LEARNING OBJECTIVES FOR THIS SECTION

- Understand how chemical structure relates to Brønsted-Lowry acidity.
- Be able to use the relationships between chemical structure and Brønsted-Lowry acidity to predict the relative acidities of two molecules for simple cases.
- If given two Brønsted-Lowry acids and their  $pK_a$  values, be able to explain why one is more acidic than the other based on their chemical structure.

In Section 7.1, we discussed how to use  $pK_a$  to compare the acidities of different molecules. But we have not addressed the question of why some molecules are stronger acids than others, or whether it might be possible to predict or explain relative acidities based on their chemical structures. Figure 7.3.1 poses this question visually – why should ethanol be so weak an acid compared to acetic acid, when their chemical structures do not at first glance appear dramatically different?

**Figure 7.3.1:** Ethanol and acetic acid dissociation reactions.



In considering this question, we will restrict ourselves to Brønsted-Lowry acids, in which the acid transfers a  $H^+$  ion. The reason is simply that the variety of Lewis acid structures is so vast that it would be difficult to say anything completely general about it.

Like all equilibria, Brønsted-Lowry acid-base reactions are controlled by free energies. There are three factors that can affect the free energies of the dissolution of an acid into ions:

- 1) The energy of splitting a neutral molecule into ions. This always costs energy, because opposite charges attract. Separating charges is always energetically unfavorable, but for reactions of the type shown in Figure 7.3.1 it is the same for both acids (i.e. a neutral molecule breaks into a pair of +1 and -1 ions). Thus, it does not explain why the two compounds should have different  $pK_a$  values.
- 2) The interaction energies of the reactants and products with the solvent. If the reaction takes place in solution, these interactions can be significantly different for different molecules and ions. As mentioned in Section 7.1,  $pK_a$  values depend on the solvent. However, solute-solvent interactions tend to be weaker than the forces associated with covalent bonding, so they are not likely to explain a case like Figure 7.3.1 where we want to understand the behavior of different molecules in the same medium.
- 3) Covalent bonding energies within the molecule. The acid and its conjugate base have different chemical structures, and the energies associated with the bonds will be very different.

It is item 3 above that is likely to be the primary determinant of acidity, and for the dissociation of a molecular acid the most important question will be how the conjugate base accommodates its negative charge.

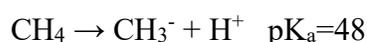
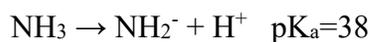
Creating a -1 anion means cramming one more electron into the molecule than the number of protons present, and because electrons repel each other there is an energetic bias against such a process. In monatomic anions (e.g. Cl<sup>-</sup>) charge can be stabilized by the quantum effects that lead to the “magic numbers” of electrons associated with the noble gas configurations. For molecular anions, other effects come into play. These are listed in Table 7.3.1, and we examine each of them in turn below.

- 1) Negative charge sits on the more electronegative atom. Electronegative atoms draw negative charge to themselves; the same factors stabilize their anions.
- 2) Negative charge sits on a larger atom. A more distributed cloud of electrons means the electrons are further away from each other on average, so electron-electron interactions are reduced.
- 3) Delocalization of negative charge through resonance. Electron resonance can stabilize anions.
- 4) Placing negative charge in an orbital with more s character. The hybridization of the atom which holds the negative charge influences electron-electron repulsion.
- 5) The Creation of Partial Positive Charge by Neighboring Electronegative Atoms. Even if the charge is not directly held on an electronegative atom, the presence of nearby electronegative atoms can create polar bonds that stabilize the presence of the charge.

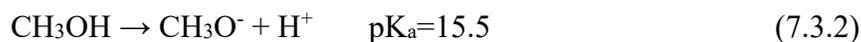
**Table 7.3.1:** Properties of a conjugate base that determine the acidity of its parent acid.

**Electronegativity of the Atom Holding the Charge:** Electronegativity is defined as the tendency of an atom in a bond to draw electrons to itself. This is why larger differences in electronegativity between bonded atoms lead to more polar bonds, and a greater accumulation of partial negative charge on the electronegative atom.

Higher electronegativity correlates with higher effective nuclear charge (review your general chemistry text if you need a refresher on this), meaning that the atom is more strongly attractive toward electrons. Another way to look at it is that if the bond is very polar, the shift in charge necessary to break it is relatively small and thus the change in energy for the formation of ions is also small. Either way, as shown in Equation 7.3.1, pK<sub>a</sub> decreases (i.e. the molecule becomes more acidic) as electronegativity increases:



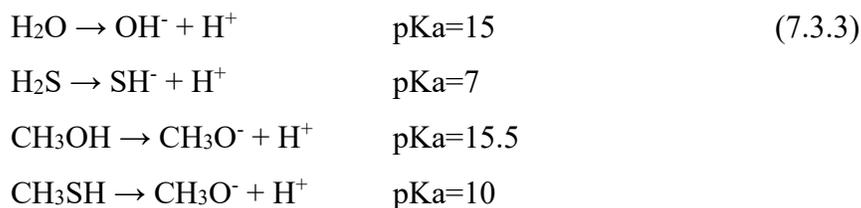
While the pK<sub>a</sub> changes when the atom is part of a larger structure than those shown in Figure 7.3.1, the trend generally remains true::



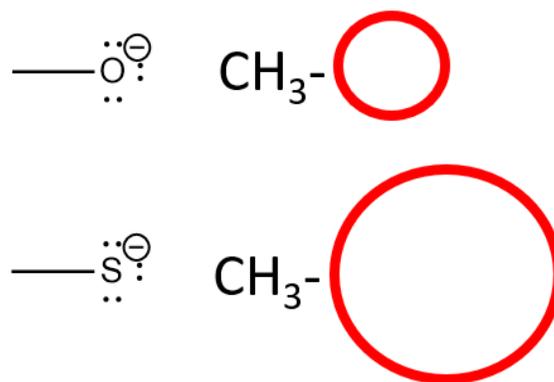
This consistency is not perfect, however. As indicated in Table 7.3.1, many other factors can influence acidity and the role of electronegativity must be balanced against them.

**Size of the Atom Holding the Charge:** Another important factor in pK<sub>a</sub> is the size of the atom holding the charge when the anion forms. Electrons repel each other, and the closer they are to each other the stronger

this repulsion becomes. Equation 7.3.3 compares the pK<sub>a</sub> values for sulfur and oxygen compounds. In each case, the sulfur compound has the lower pK<sub>a</sub> (higher acidity). This contradicts the principle that the more electronegative element should be more acidic (O has a higher electronegativity than S) but is explained by the fact that S has a larger radius.



**Figure 7.3.2:** Methoxide and methyl sulfide anions. The larger radius of the sulfur atom means that the electrons are more spread out, reducing electron-electron repulsions and making the anion more stable.



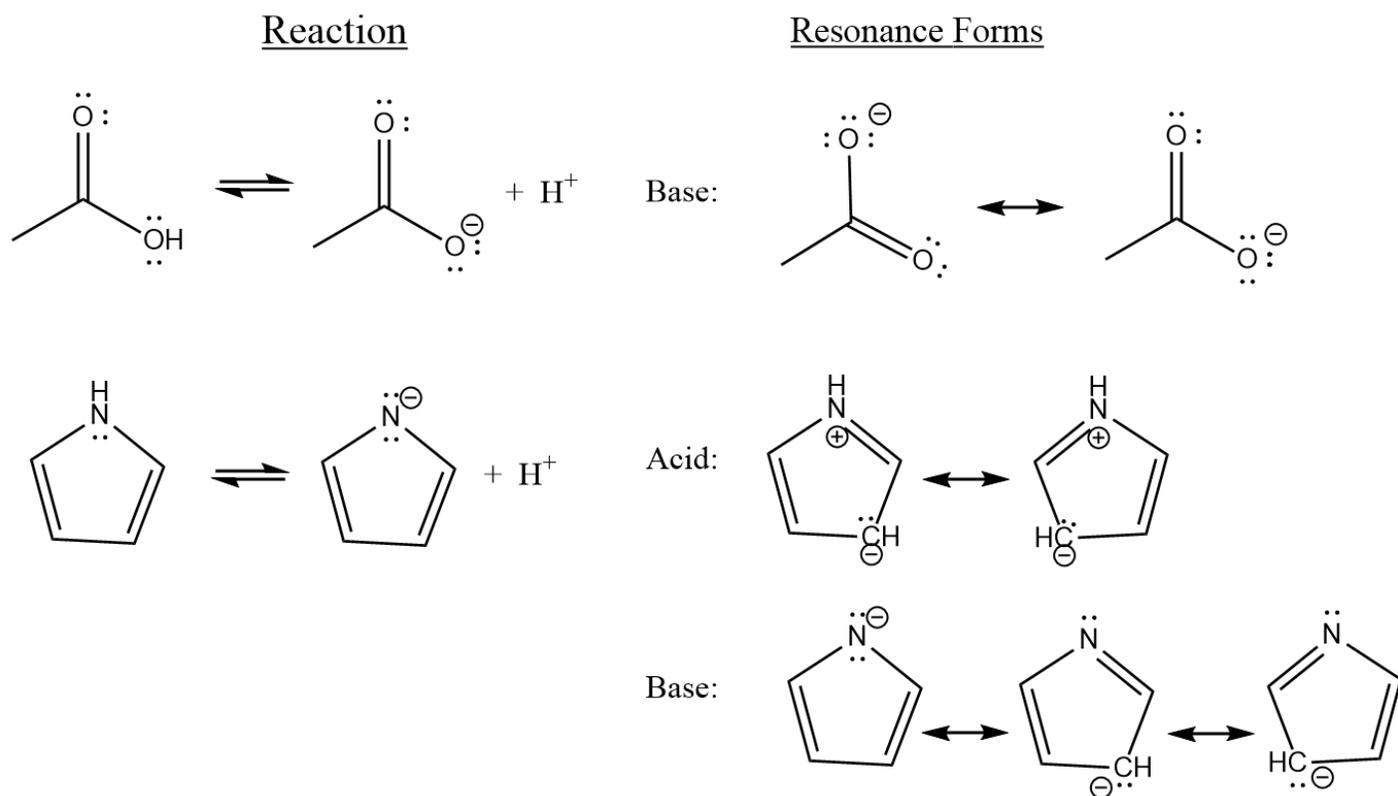
Cases like this, where different principles from Table 7.3.1 predict different relative pK<sub>a</sub> values, are relatively common. In such cases there is no way to say with certainty which will dominate. The principles are still useful, however, as there are cases in which only one rule applies or where all applicable rules predict the same outcome. Further, it can be useful to be able to use these principles to understand outcomes, as we used radius to explain the relative acidities of O and S.

**Delocalization of the Electron:** We saw in our discussion of resonance and aromaticity in Chapters 2 and 3 that the delocalization of electrons leads to more stable bonds (see Figure 2.4.4 and the surrounding discussion). In many cases, acidity is determined partly by the fact that the conjugate base engages in resonance when the parent molecule does not, or when resonance increases on dissociation.

Figure 7.3.3 shows two examples of this phenomenon. The first considers acetic acid, and gives the resonance forms of the conjugate base formed after dissociation of the acid. The anion is capable of resonance, while the molecular form of the acid is capable of little if any resonance. The emergence of resonance stabilizes the anion and leads to a relatively low pK<sub>a</sub> (high acidity). This explains most of the difference in pK<sub>a</sub> between ethanol and acetic acid highlighted in Figure 7.3.1; the ethanoate anion does not engage in resonance.

Even when resonance exists in the molecular form of the acid, the extent of resonance can increase on dissociation of the acid. The second reaction in Figure 7.3.3 illustrates this point. The molecular form of pyrrole is stabilized by resonance, but its resonance forms necessarily involve the separation of charges, thus limiting the importance of resonance. By contrast, the conjugate base delocalizes charge through three

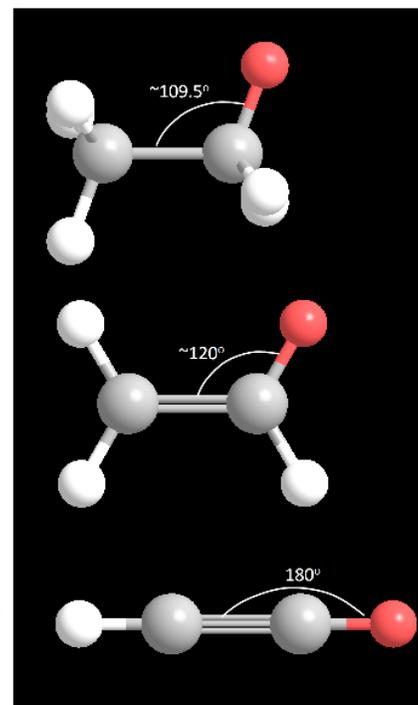
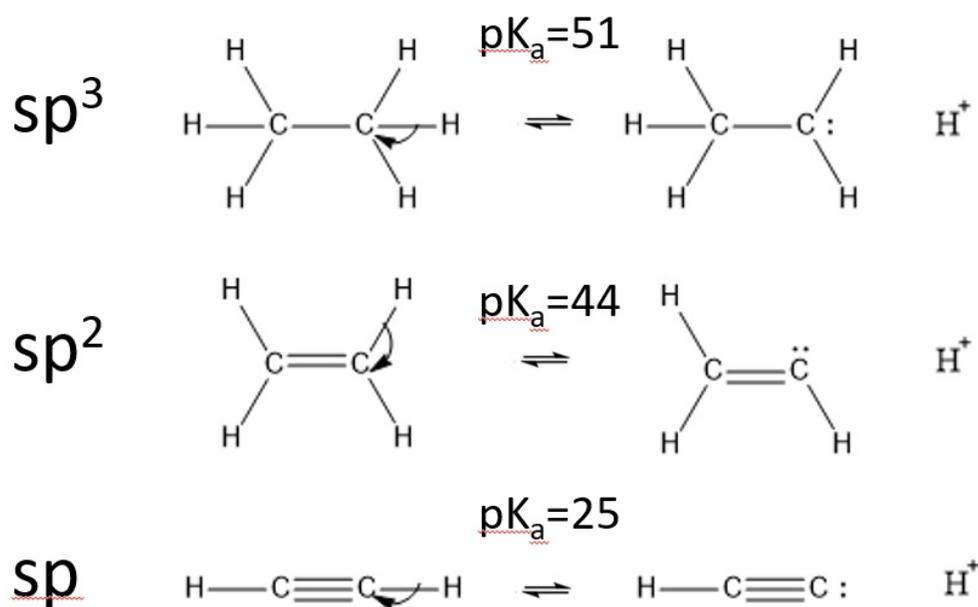
relatively good resonance structures. Thus, the degree of resonance increases on dissociation, which acts to favor the reaction. This is illustrated when one considers that the saturated analog of pyrrole, pyrrolidine ( $C_4H_8NH$ , the N-H group bound in a ring with four  $-CH_2-$  groups) has a  $pK_a$  of 35, while the resonance stabilization of pyrrole gives a  $pK_a$  of 17.5.



**Figure 7.3.3:** Some relevant resonance forms for the acid dissociation reactions of acetic acid (top) and pyrrole (bottom). Not all resonance structures are drawn, this set serves to illustrate the point. See text for discussion.

**The s Character of the Orbital:** You should recall from general chemistry that, according to the VSEPR rules, a lone pair of electrons is more repulsive than a pair of electrons in a bond, a fact that is important in predicting bond angles. The same principle is relevant to understanding acidity because when a  $H^+$  ion dissociates it leaves behind a lone pair of electrons. That pair of electrons will repel other electrons in the anion, so its position is important.

Figure 7.3.4 illustrates this principle for a series of hydrocarbons. Acidity increases as the molecule goes from ethane ( $sp^3$ -hybridization) to acetylene ( $sp$ -hybridization). This reflects the fact that the lone pair is in closest proximity to the C-C and C-H bonds for  $sp^3$ -hybridized species than at lesser hybridizations. Put differently, the greater the s-character of the hybrid orbital (i.e. the fewer hybridized p-orbitals are present), the greater the acidity.



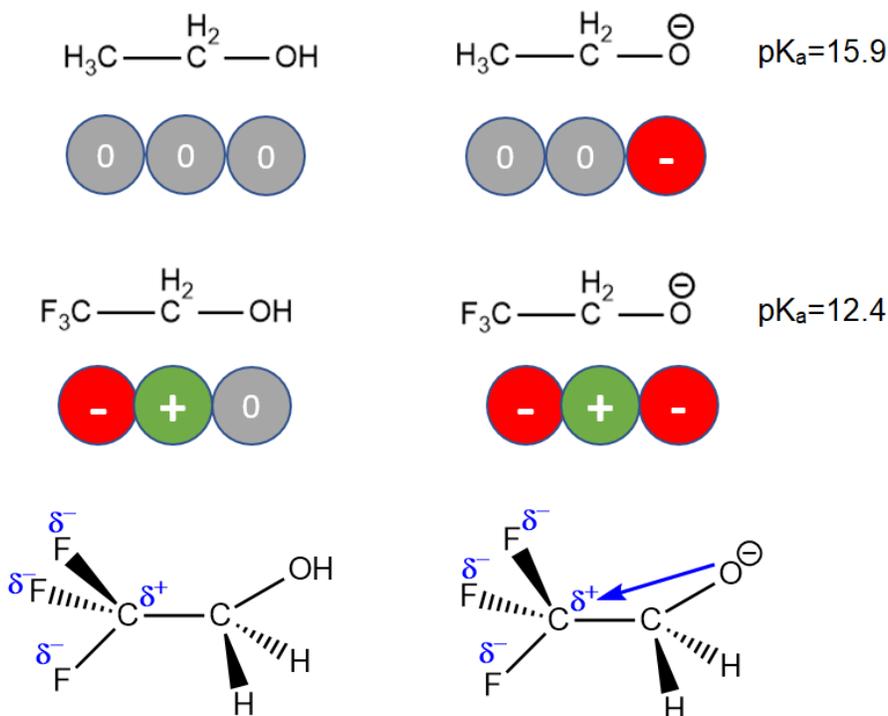
**Figure 7.3.4:** Acid dissociation constants and chemical reactions for the dissociation of  $H^+$  from a series of hydrocarbons. Right-hand column shows geometries of the figures with electron lone pairs indicated in red; they are shown as a bond and atom to indicate their position, though this is not a good representation of the details of their distribution.

**The Polarization of Sigma Bonds:** The repulsive character of the excess electron is an important factor in the energy of the anion. Rules 1), 2), and 4) from Table 7.3.1 are about finding places for the excess electron to sit that do not dramatically increase the energy of the anion. The presence of electronegative atoms is therefore important.

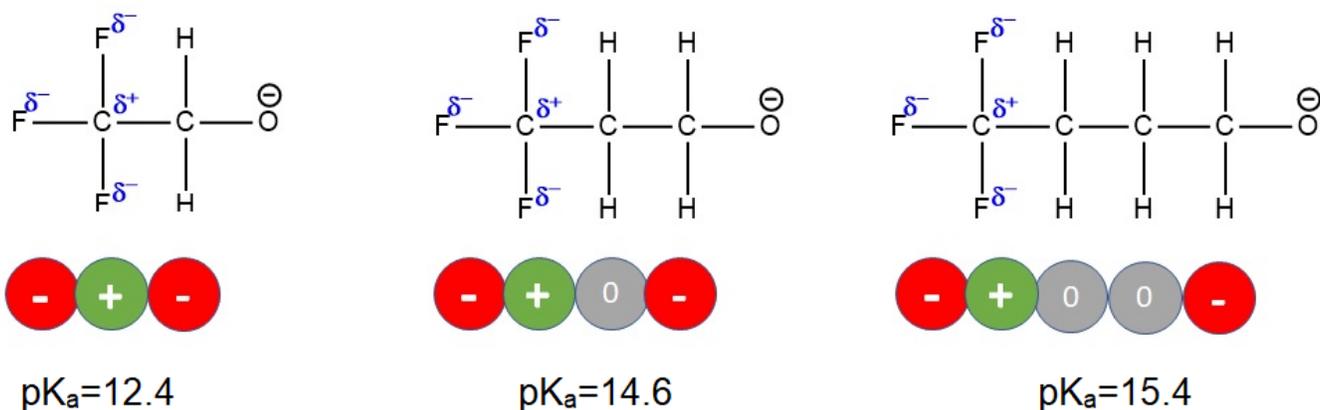
Recall that electronegative atoms create polar bonds by drawing electron density toward themselves. This is often represented as a partial negative charge on the more electronegative atom and a partial positive charge on its partner in the bond. While not equal to a full -1 or +1 charges, partial charges do change the interaction with neighboring atoms and a partial positive charge will interact favorably with an excess electron.

Figure 7.3.5 compares the  $pK_a$  of ethanol and trifluoroethanol. The trifluoroethanol is significantly more acidic. This reflects the fact that a significant partial positive charge is placed on the carbon atom to which the fluorine atoms are bound, creating a region of positive charge in the vicinity of the oxygen atom. Since positive and negative charges attract, when a negative charge is placed on the oxygen in reaction it is stabilized by the nearby partial positive charge.

**Figure 7.3.5:** Chemical structures and pK<sub>a</sub> values for ethanol and trifluoroethanol. The distribution of partial positive charge is shown schematically, and indicated in the final line. The proximity of the partial positive charge on the carbon stabilizes the negative charge on the O atom.



This effect is significant, but drops off quickly with distance. Figure 7.3.6 shows how the presence of intervening nonpolar groups reduces the acidity of the molecule. This is to be expected, as electrostatic interactions drop off rapidly with distance. In this case, only two interposing -CH<sub>2</sub>- groups are necessary to nearly nullify the effect (i.e. give a pK<sub>a</sub> nearly identical to that of ethanol).



**Figure 7.3.6:** Chemical structures and pK<sub>a</sub> values for a series of fluorinated acids. The distribution of partial positive charge is shown schematically. Acidity decreases as the fluorinated centers are displaced from the charge center.

**Inferring Acidity from Chemical Structure:** Applying these principles to predict and understand  $pK_a$  values is difficult, as many different principles can be at work in the same molecule and operate in opposite directions. We have already noted an example of this in the acidity of  $\text{CH}_3\text{OH}$  vs.  $\text{CH}_3\text{SH}$  above, where electronegativity arguments predict  $\text{CH}_3\text{OH}$  should be more acidic but size effects predict  $\text{CH}_3\text{SH}$  should be more acidic (with the latter being true in this case). This reflects the fact that chemical reactions result from a balance of forces, with more than one factor influencing outcomes and often in competition with each other. There are simple cases where only one principle is at work, or multiple principles apply but all point in the same direction. In these cases, the principles in Table 7.3.1 are generally a reliable predictor of outcomes. In other cases, where multiple rules apply in contradiction, prediction may not be possible, but the principles may still be of use in understanding the outcome.

**Figure 7.3.7:** Identify the stronger acid from the molecules shown.

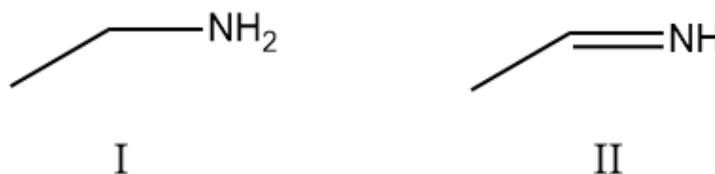


Figure 7.3.7 gives a pair of molecules, and sets challenge of identifying the stronger acid. By now, you should realize that carbon is a poor donor of hydrogen ions, and the  $\text{H}^+$  will depart the more electronegative N atom first. But in which molecule will the  $\text{H}^+$  be more prone to dissociating?

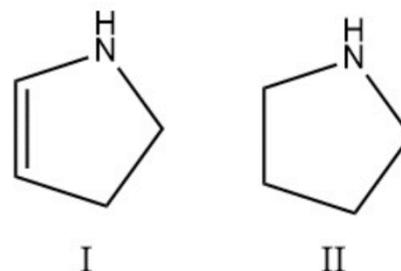
Looking at the rules in Table 7.3.1, it is clear that the first two do not apply. The H atoms are both bonded to nitrogen atoms, meaning that there is no “larger” or “more electronegative” atom. Likewise, there does not appear to any possibility of resonance in the conjugate base (you can draw out the structures and confirm for yourself), and there are no electronegative atoms in close proximity. Only rule 4 appears relevant. In Structure I, the N is  $\text{sp}^3$ -characterized, while in Structure II the N is  $\text{sp}^2$ -hybridized. Since the latter has more s-character, that is the more acidic structure.

You might be tempted to argue that Structure I should be more acidic, because there are two H atoms present and therefore the structure is twice as likely to dissociate. If one views equilibria as the result of competing rates in the forward and backward directions, this seems a reasonable argument. But you should remember that the energies involved determine rates via the activation energy, meaning that the more stable the product the higher the activation energy for the reverse direction. This is a more important determinant of kinetics, so it is better to view this kind of problem in terms of energies and base your answer on the relative energies of the anion as discussed above.

Figure 7.3.8 offers another pair of structures. Here again, Rules 1, 2, and 5 from Table 7.3.1 can be quickly ruled out as inapplicable. Rule 4 on charge delocalization seems to apply. If we look at the resonance forms for the reactant and product of Structure I ionization in Figure 7.3.8A, we see that there is little if any resonance present in the reactant form, as it involves separating unlike charges and putting positive and negative charges on atoms with the wrong order in electronegativities. The product, on the other hand, cycles excess electron density back and forth between the N and C. While the structure that puts negative charge on the C atom is less significant, it is otherwise a good resonance structure per the rules in Chapter 3. We can therefore safely predict that Rule 3 from Table 7.3.1 predicts that Structure II is the stronger acid.

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**Figure 7.3.8:** Identify the stronger acid from the molecules shown.



You might be tempted to argue that even though resonance is minimal, its existence means the N atom will have a slightly reduced s-character (as it is  $sp^2$ -hybridized in the minor resonance form). This would imply that Rule 4 should be applied as well, predicting that Structure II is the stronger acid. This is a weaker argument than the resonance argument, since it relies on such minimal resonance, but it is not incorrect. In this case, both rules imply the same outcome, so it is not necessary to judge their relative importance in any case.

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**Figure 7.3.8A:** Resonance forms related to Structure I in Figure 7.3.8; see text for discussion.

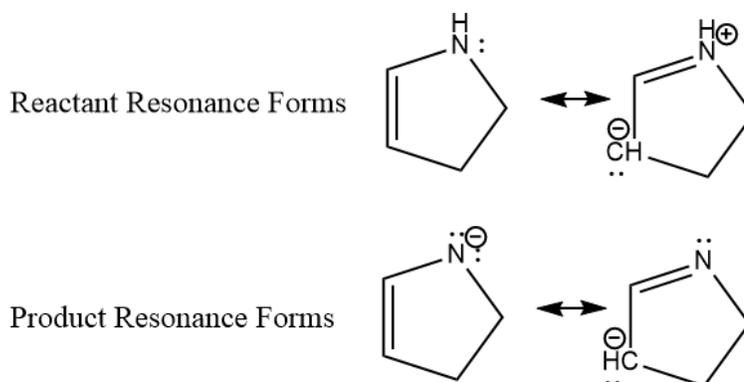
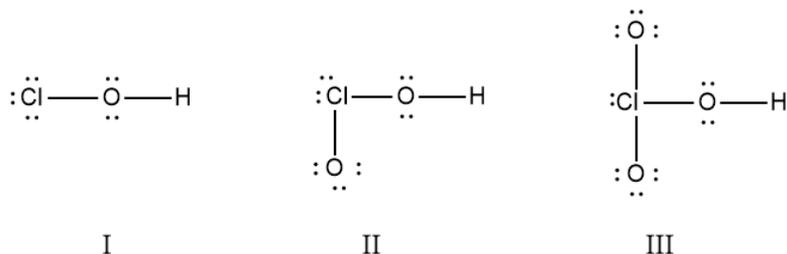


Figure 7.3.9 presents another problem, this time to choose the strongest acid from a set of three. Again, the atom is bound to the oxygen, so Rules 1 and 2 do not apply. There is no obvious possibility for resonance and all O atoms are  $sp^3$ -hybridized, so there is no basis for predicting the acidity from Rules 3 and 4. That leaves Rule 5.

Oxygen is the second most electronegative atom in the periodic table, and so it can create the kind of partial charge distribution that will stabilize an anion. That seems mostly likely to happen in Structure III, where two oxygens are present, so that should be identified as the strongest acid.

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**Figure 7.3.9:** Identify the strongest acid from the molecules shown.

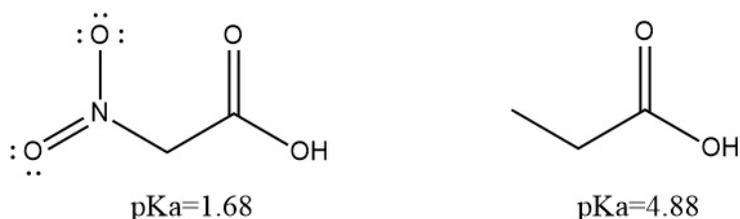


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We should also be able to use the principles we have discussed to explain the relative acidities of different molecules. Figure 7.3.10 shows two acids, and lists their pKa values. How can we explain the difference between them?

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**Figure 7.3.10:** Explain the relative acidities of the acids shown.



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You should be able to quickly realize that Rules 1 and 2 do not apply here, nor does Rule 4 as the hybridization is the same on both oxygens. Both conjugate acids are capable of resonance (similar to that shown in Figure 7.3.3 for the acetate anion), so there is no basis for distinguishing between them there. The NO<sub>2</sub> group on the left-hand structure always engages in resonance, but the available resonance structures do not change when the acid ionizes. It therefore does not influence the change in energy between reactant and product forms, and so does not influence the acidity.

However, the nitrogen is an electronegative element, and it is in close proximity to the acid. It can therefore create a partial positive charge on the neighboring carbon atom that will stabilize the anion, and so Rule 5 explains the difference.

As a preview of coming attractions, you will learn in organic chemistry that NO<sub>2</sub> is an electron withdrawing group, in this case making the N atom effectively more electronegative than it is in isolation. You can actually see why this might be true by noting that the chemical structure a +1 formal charge on the N atom. But that is a subject for complete course in organic chemistry.

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**Figure 7.3.11:** Explain the relative acidities of the acids shown.

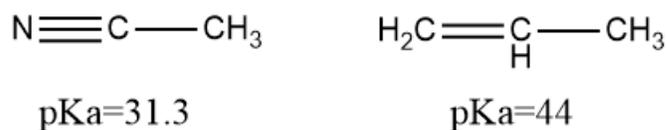
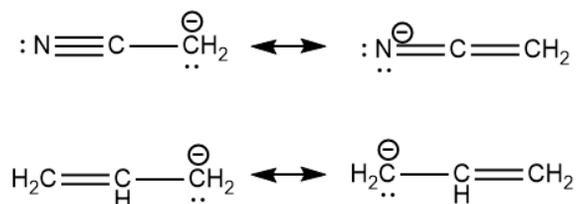


Figure 7.3.11 gives one more example, this one a bit more challenging.  $\text{CH}_3\text{-CN}$  is shown to be significantly more acidic than  $\text{CH}_3\text{-CH=CH}_2$ . An obvious first justification might be Rule 5, as the nitrogen is the most electronegative atom in either molecule. But is that a complete answer?

Both conjugate anions engage in resonance, as shown in Figure 7.3.11A. This serves to make both of them more acidic than they would otherwise be. It seems likely that the presence of resonance is a more important factor in the first structure, where the nitrogen can stabilize the negative charge, but it is difficult to be sure. It would not be wrong to include such an argument in the explanation, though it would be important to point out that both structures engage in resonance so the difference is not as significant as it might otherwise be.

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**Figure 7.3.11A:** Resonance structures of conjugate bases for the molecules in Figure 7.3.11.



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If it seems like the application of the rules from Table 7.3.1 can be complex, the answer is yes. The rules summarize a range of forces at work in acid-base reactions, and the balance between them is what determines reaction outcomes. It is therefore unsurprising that they frequently compete with each other. While they are not a perfect guide to predicting acidities, they are a useful one for understanding them.

The description of acid-base chemistry here is the first of many examples you will encounter in your studies where it is necessary to apply principles related to chemical structure to predict reaction outcomes.