ORGANIC CHEMISTRY I

Polar Covalent Bonds; Acids and Bases

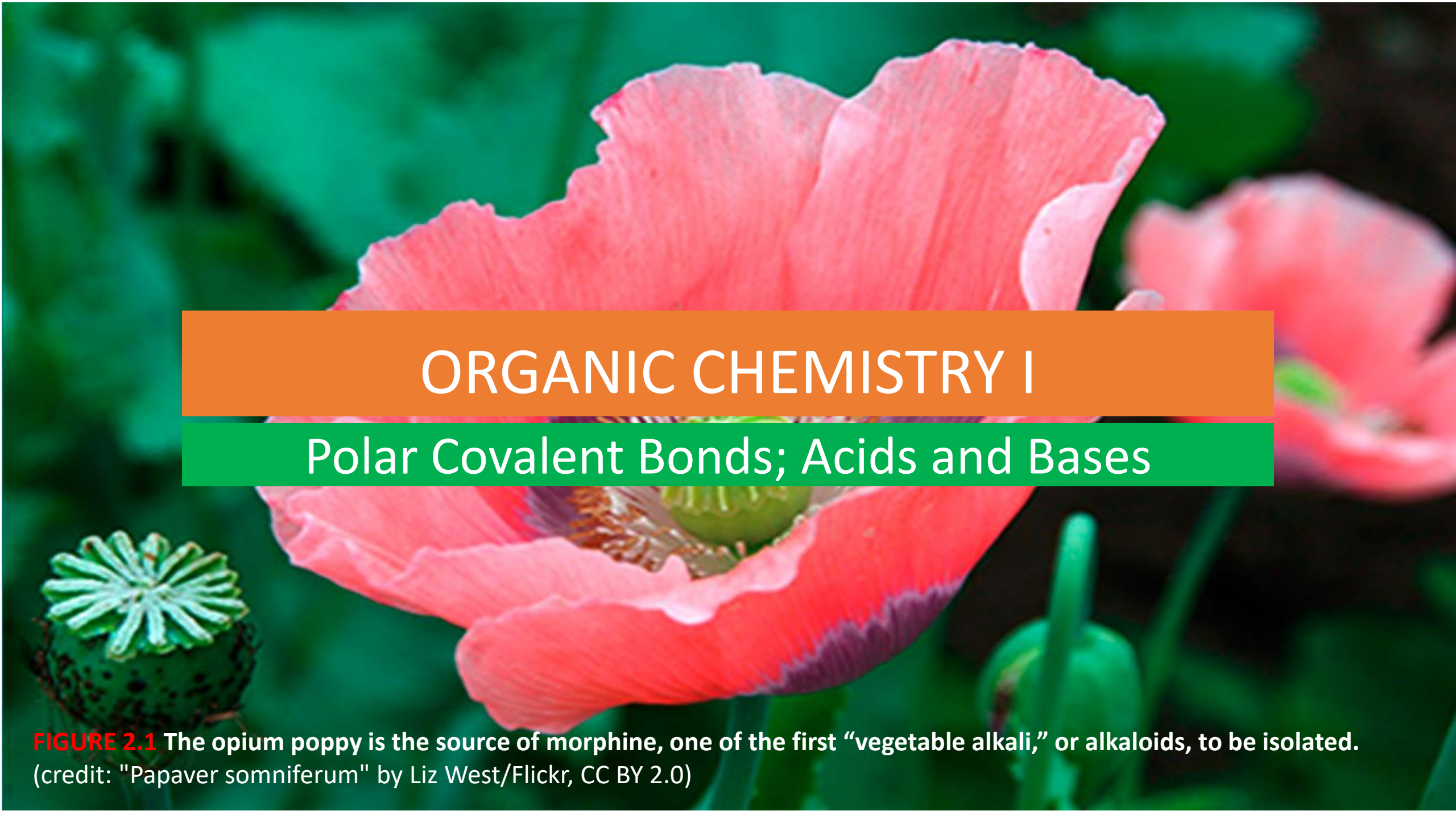


FIGURE 2.1 The opium poppy is the source of morphine, one of the first "vegetable alkali," or alkaloids, to be isolated. (credit: "Papaver somniferum" by Liz West/Flickr, CC BY 2.0)

Topic Discussion

Why This Chapter ?

1. Polar Covalent Bonds and Electronegativity;
2. Polar Covalent Bonds and Dipole Moments;
3. Formal Charges;
4. Resonance;
5. Rules for Resonance Forms;
6. Drawing Resonance Forms;
7. Acids and Bases: The Brønsted–Lowry Definition;
8. Acids and Bases Strength;
9. Predicting Acids–Bases Reactions from pKa Values;
10. Organic Acids and Organic Bases;
11. Acids and Bases: The Lewis Definition;
12. Noncovalent Interactions Between Molecules

Chemistry Matters—Alkaloids: From Cocaine to Dental Anesthetics.

Why This Chapter ?

- Understanding organic chemistry means knowing not just what happens but also why and how it happens at the molecular level.
- In this chapter, we'll look at some of the ways that chemists describe and account for chemical reactivity, thereby providing a foundation to understand the specific reactions discussed in subsequent chapters. Topics such as bond polarity, the acid–base behavior of molecules, and hydrogen-bonding are a particularly **important part of that foundation**.
- We saw in the previous chapter how covalent bonds between atoms are described, and we looked at the valence bond model, which uses hybrid orbitals to account for the observed shapes of organic molecules.
- Before going on to a systematic study of organic chemistry, however, we still need to review a few fundamental topics. **In particular**, we need to look more closely at how electrons are distributed in covalent bonds and at some of the consequences that arise when the electrons in a bond are not shared equally between atoms.

1. Polar Covalent Bonds and Electronegativity

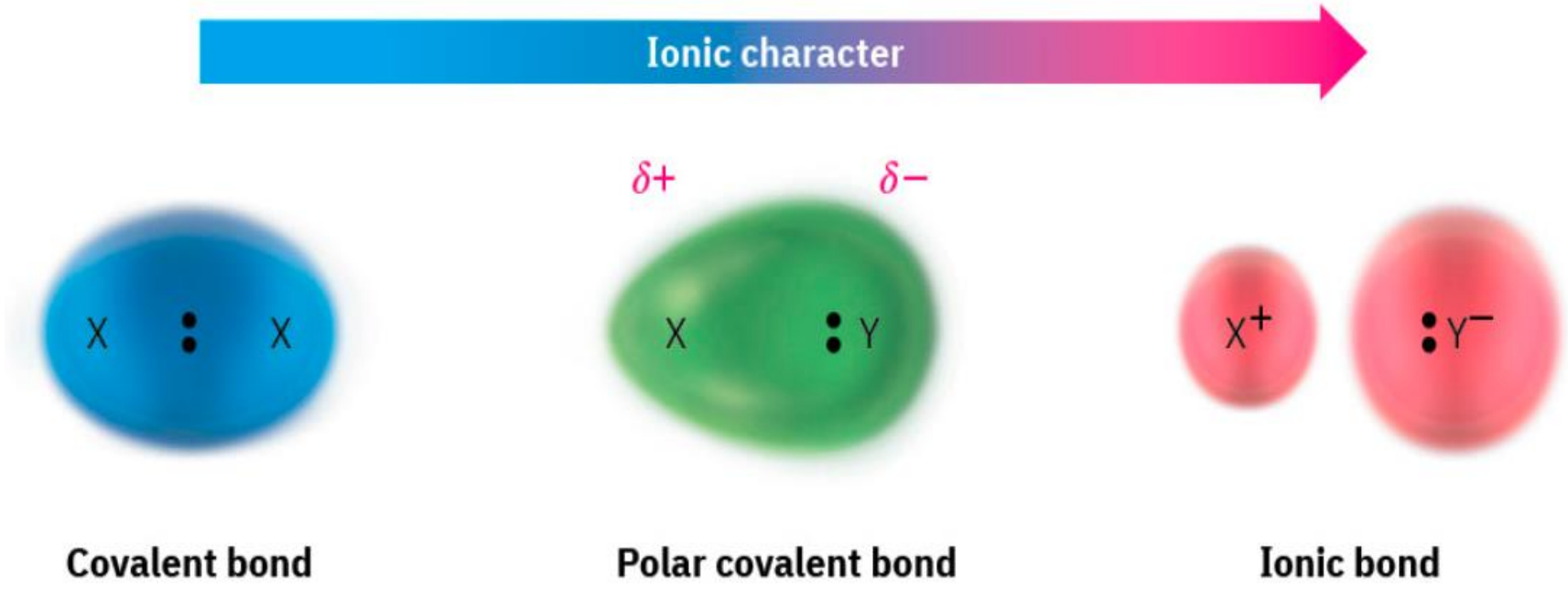


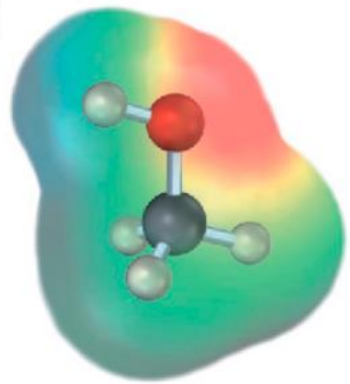
FIGURE 2.2 The continuum in bonding from covalent to ionic is a result of an unequal distribution of bonding electrons between atoms. The symbol δ (lowercase Greek letter delta) means partial charge, either partial positive (δ+) for the electron-poor atom or partial negative (δ–) for the electron-rich atom.

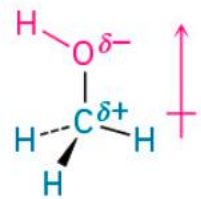
Bond polarity is due to differences in **electronegativity (EN)**, the intrinsic ability of an atom to attract the shared electrons in a covalent bond.

H 2.1																He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

FIGURE 2.3 Electronegativity values and trends. Electronegativity generally increases from left to right across the periodic table and decreases from top to bottom. The values are on an arbitrary scale, with F = 4.0 and Cs = 0.7. Elements in red are the most electronegative, those in yellow are medium, and those in green are the least electronegative.

(a)



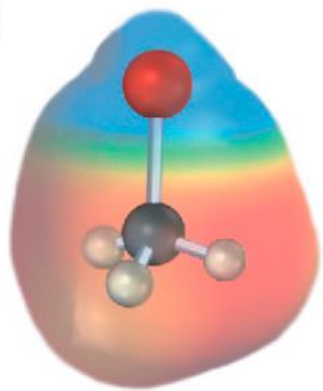


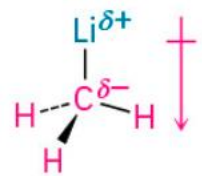
Methanol

Oxygen: EN = 3.5
Carbon: EN = 2.5

Difference = 1.0

(b)





Methyllithium

Carbon: EN = 2.5
Lithium: EN = 1.0

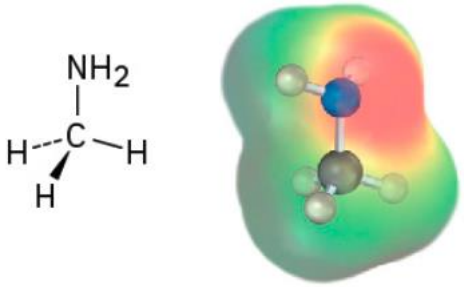
Difference = 1.5

PROBLEM 2.1
Which element in each of the following pairs is more electronegative?
(a) Li or H (b) B or Br (c) Cl or I (d) C or H

PROBLEM 2.2
Use the δ+/δ– convention to indicate the direction of expected polarity for each of the bonds indicated.
(a) H_3C–Cl (b) H_3C–NH_2 (c) H_2N–H (d) H_3C–SH (e) H_3C–MgBr (f) H_3C–F

PROBLEM 2.3 Use the electronegativity values shown in Figure2.3 to rank the following bonds from least polar to most polar: H_3C–Li, H_3C–K, H_3C–F, H_3C–MgBr, H_3C–OH

PROBLEM 2-4 Look at the following electrostatic potential map of methylamine, a substance responsible for the odor of rotting fish, and tell the direction of polarization of the C–N bond:



Methylamine

2. Polar Covalent Bonds and Dipole Moments

The **dipole moment**, μ (lowercase Greek letter mu), is defined as the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges, $\mu = Q \times r$. Dipole moments are expressed in debyes (D), where 1 D = 3.336×10^{-30} coulomb meters (C · m) in SI units. For example, the unit charge on an electron is 1.60×10^{-19} C. Thus, if one positive charge and one negative charge are separated by 100 pm (a bit less than the length of a typical covalent bond), the dipole moment is 1.60×10^{-29} C · m, or 4.80 D.

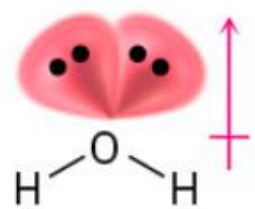
$$\mu = Q \times r$$

$$\mu = (1.60 \times 10^{-19}\ \text{C})(100 \times 10^{-12}\ \text{m})\left(\frac{1\ \text{D}}{3.336 \times 10^{-30}\ \text{C} \cdot \text{m}}\right) = 4.80\ \text{D}$$

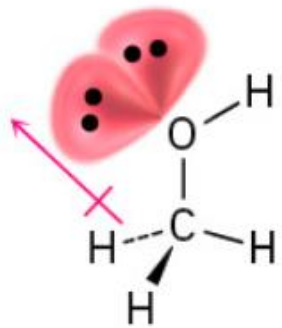
TABLE 2.1 Dipole Moments of Some Compounds

Compound	Dipole moment (D)	Compound	Dipole moment (D)
NaCl	9.00	NH_3	1.47
CH_2O	2.33	CH_3NH_2	1.31
CH_3Cl	1.87	CO_2	0
H_2O	1.85	CH_4	0
CH_3OH	1.70	CH_3CH_3	0

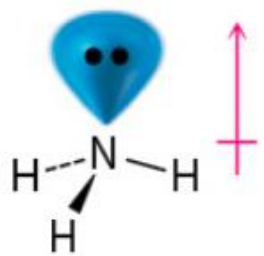
Compound	Dipole moment (D)	Compound	Dipole moment (D)
CH_3CO_2H	1.70	 Benzene	0
CH_3SH	1.52		



Water
(μ = 1.85 D)

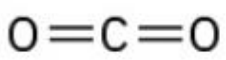


Methanol
(μ = 1.70 D)

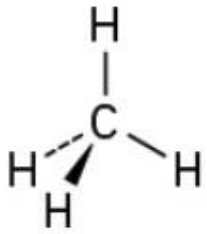


Ammonia
(μ = 1.47 D)

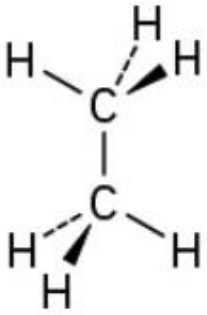
In contrast with water, methanol, and ammonia, molecules such as carbon dioxide, methane, ethane, and benzene have zero dipole moments. Because of the symmetrical structures of these molecules, the individual bond polarities and lone-pair contributions exactly cancel.



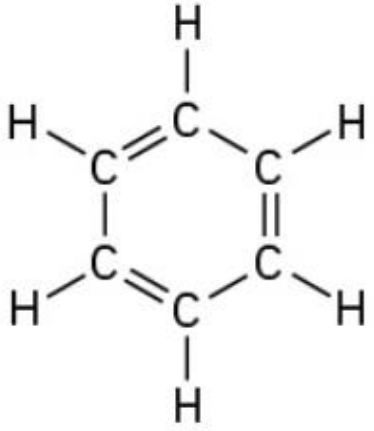
Carbon dioxide
(μ = 0)



Methane
(μ = 0)



Ethane
(μ = 0)



Benzene
(μ = 0)

WORKED EXAMPLE 2.1

Predicting the Direction of a Dipole Moment

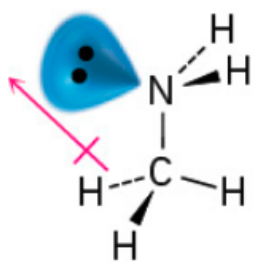
Make a three-dimensional drawing of methylamine, CH_3NH_2, and show the direction of its dipole moment (μ = 1.31).

Strategy

Look for any lone-pair electrons, and identify any atom with an electronegativity substantially different from that of carbon. (Usually, this means O, N, F, Cl, or Br.) Electron density will be displaced in the general direction of the electronegative atoms and the lone pairs.

Solution

Methylamine contains an electronegative nitrogen atom with a lone pair of electrons. The dipole moment thus points generally from $-CH_3$ toward the lone pair.



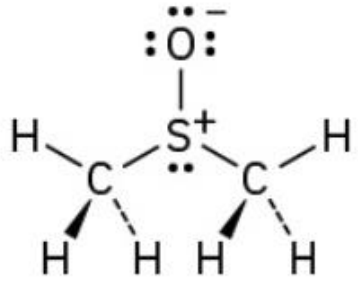
Methylamine
(μ = 1.31)

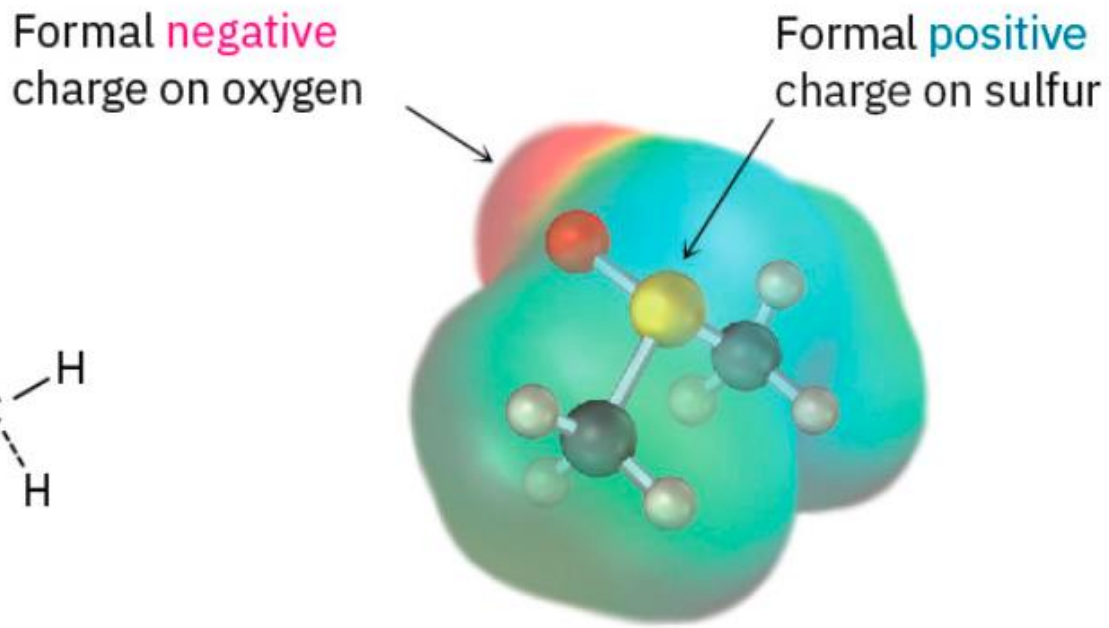
PROBLEM 2-5 Ethylene glycol, $HOCH_2CH_2OH$, may look nonpolar when drawn, but an internal hydrogen bond between the two –OH groups results in a dipole moment. Explain.

PROBLEM 2-6 Make three-dimensional drawings of the following molecules, and predict whether each has a dipole moment. If you expect a dipole moment, show its direction.

(a) $H_2C=CH_2$ (b) $CHCl_3$ (c) CH_2Cl_2 (d) $H_2C=CCl_2$

3. Formal Charges

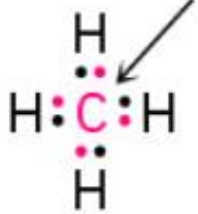




Dimethyl sulfoxide

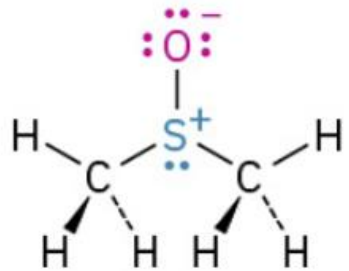
An isolated carbon atom owns 4 valence electrons.

This carbon atom also owns $\frac{8}{2}$ = 4 valence electrons.



An isolated nitrogen atom owns 5 valence electrons.

This nitrogen atom also owns $\frac{6}{2}$ + 2 = 5 valence electrons.



For sulfur:

Sulfur valence electrons	= 6
Sulfur bonding electrons	= 6
Sulfur nonbonding electrons	= 2
Formal charge = 6 − 6/2 − 2	= +1

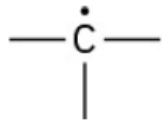
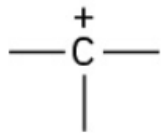
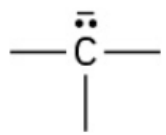
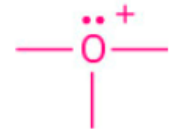
For oxygen:

Oxygen valence electrons	= 6
Oxygen bonding electrons	= 2
Oxygen nonbonding electrons	= 6
Formal charge = 6 − 2/2 − 6	= −1

$$\textbf{Formal charge} = \left(\begin{array}{c}\text{Number of}\\ \text{valence electrons}\\ \text{in free atom}\end{array}\right) - \left(\begin{array}{c}\text{Number of}\\ \text{valence electrons}\\ \text{in bonded atom}\end{array}\right)$$

$$= \left(\begin{array}{c}\text{Number of}\\ \text{valence electrons}\\ \text{in free atom}\end{array}\right) - \left(\frac{\text{Number of bonding electrons}}{2} + \begin{array}{c}\text{Number of}\\ \text{nonbonding}\\ \text{electrons}\end{array}\right)$$

TABLE 2.2 A Summary of Common Formal Charges

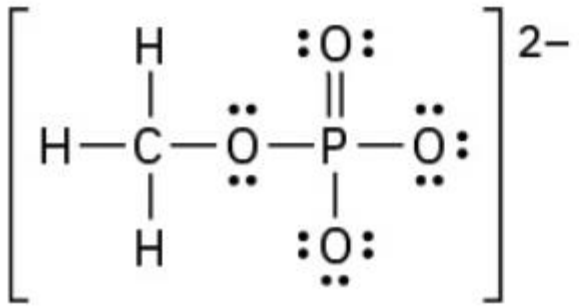
Atom	C			N		O		S		P
Structure										
Valence electrons	4	4	4	5	5	6	6	6	6	5
Number of bonds	3	3	3	4	2	3	1	3	1	4
Number of nonbonding electrons	1	0	2	0	4	2	6	2	6	0
Formal charge	0	+1	−1	+1	−1	+1	−1	+1	−1	+1

PROBLEM 2-7 Calculate formal charges for the nonhydrogen atoms in the following molecules:

(a) Diazomethane, $H_2C{=}N{=}\ddot{N}:$ **(b)** Acetonitrile oxide, $H_3C{-}C{\equiv}N{-}\ddot{O}:$

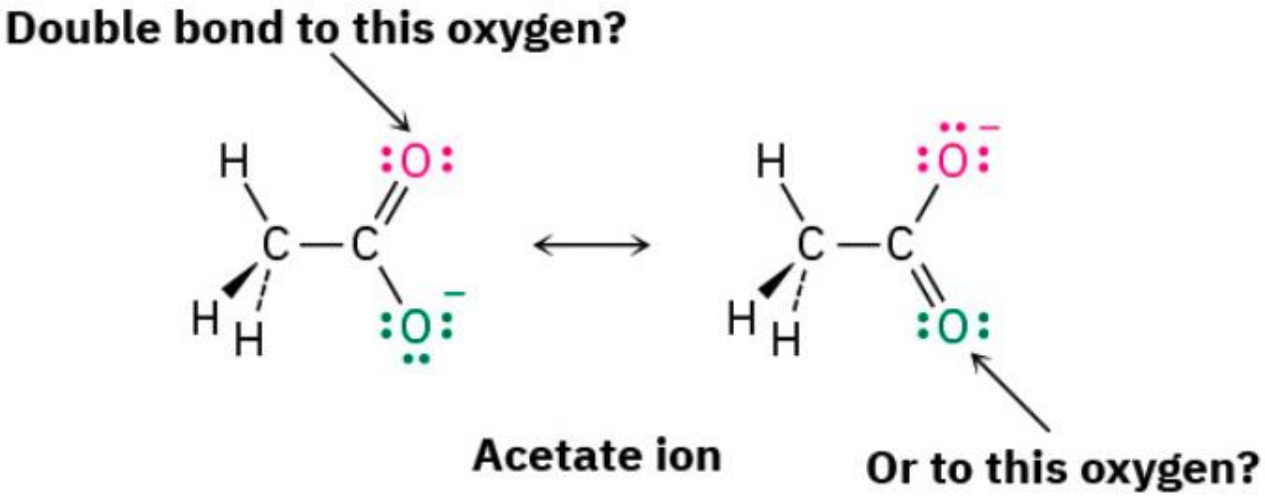
(c) Methyl isocyanide, $H_3C{-}N{\equiv}C:$

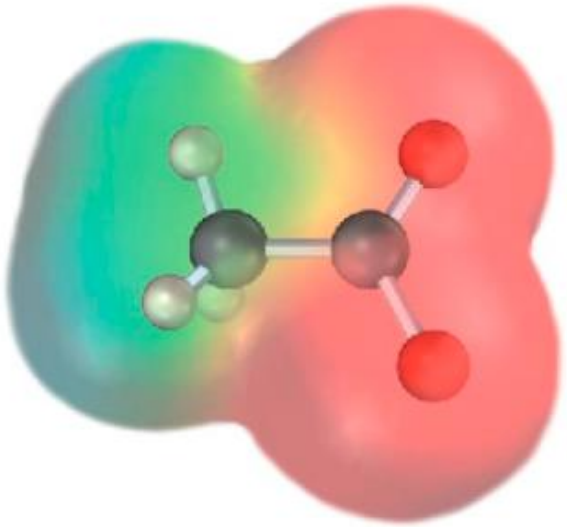
PROBLEM 2-8 Organic phosphate groups occur commonly in biological molecules. Calculate formal charges on the four O atoms in the methyl phosphate dianion.

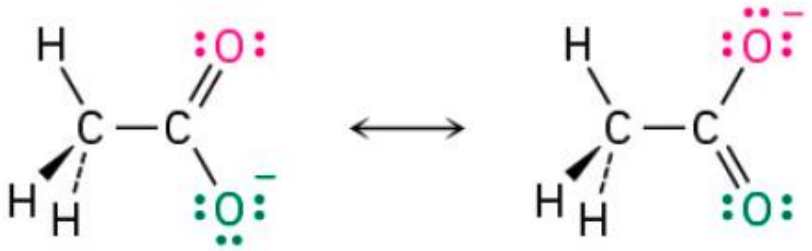


Methyl phosphate dianion

2.4 Resonance

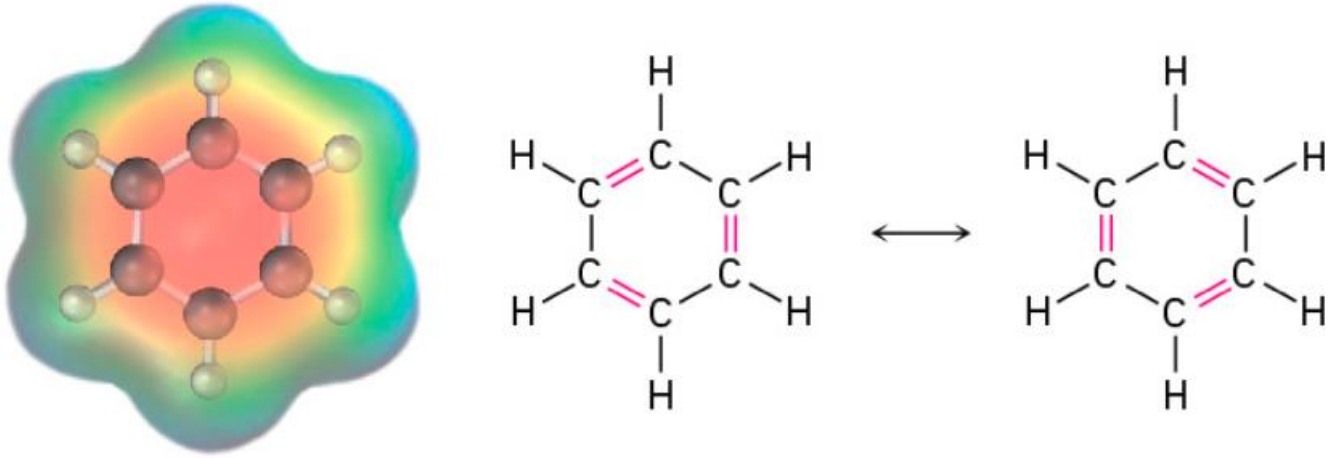






Acetate ion—two resonance forms

The two individual line-bond structures for acetate ion are called **resonance forms**, and their special resonance relationship is indicated by the double-headed arrow between them. The only difference between the two resonance forms is the placement of the π and nonbonding valence electrons. The atoms themselves occupy exactly the same place in both resonance forms, the connections between atoms are the same, and the three- dimensional shapes of the resonance forms are the same.



Benzene (two resonance forms)

2.5 Rules for Resonance Forms

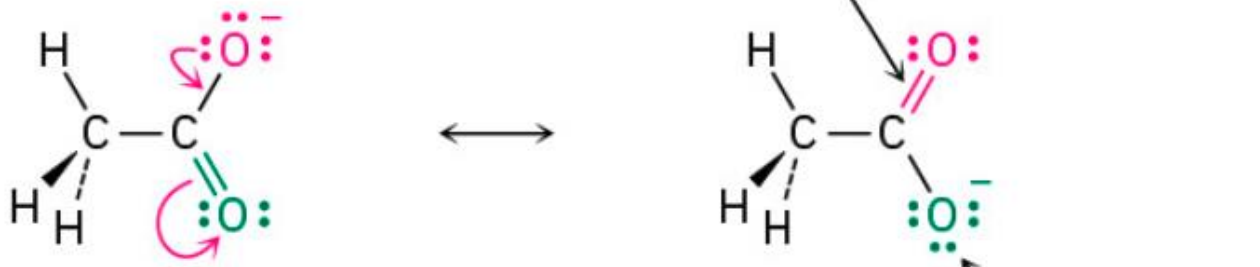
RULE 1

Individual resonance forms are imaginary, not real.

RULE 2

Resonance forms differ only in the placement of their π or nonbonding electrons.

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of a C=O bond.

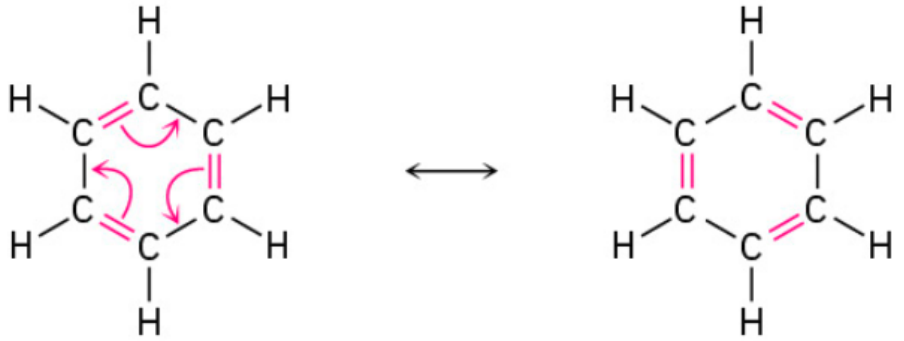


Simultaneously, two electrons from the C=O bond move onto the bottom oxygen atom to become a lone pair.

The new resonance form has a double bond here...

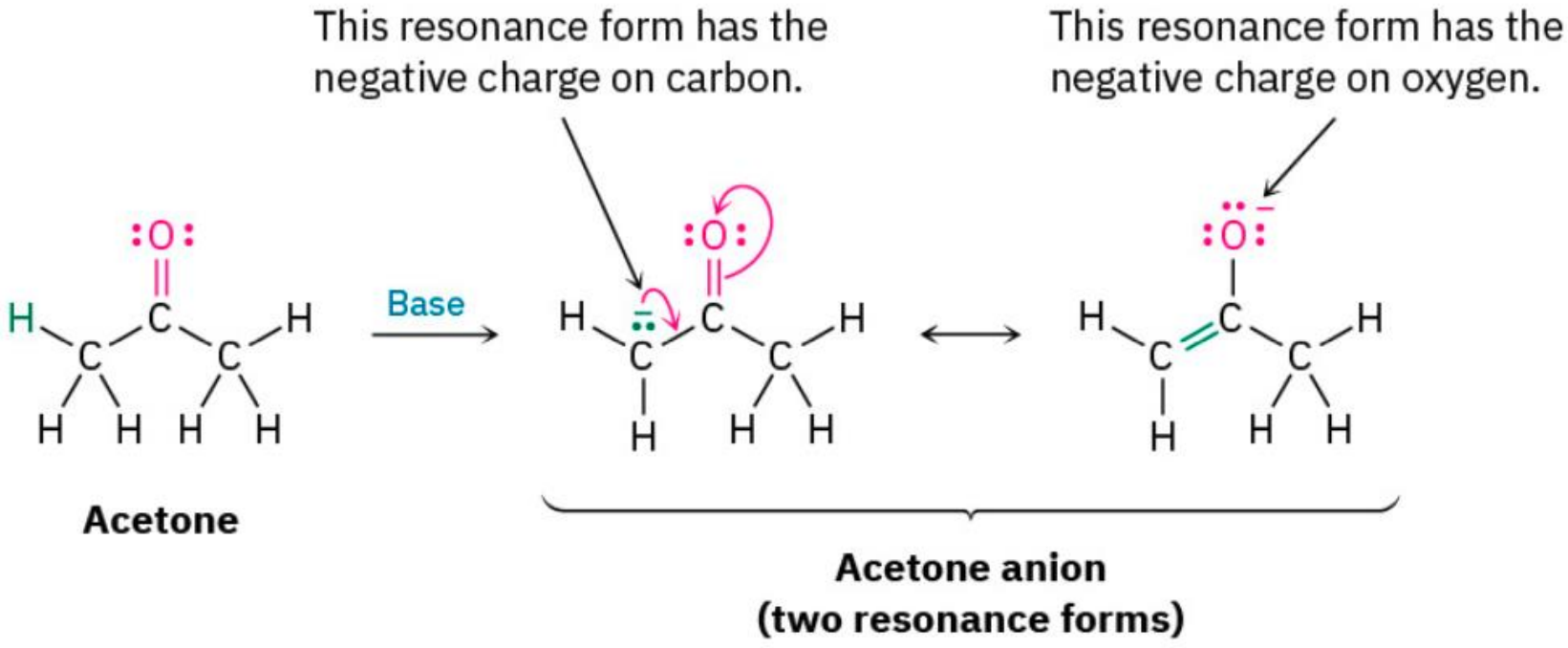
and has a lone pair of electrons here.

The situation with benzene is similar to that with acetate. The π electrons in the double bonds move, as shown with curved arrows, but the carbon and hydrogen atoms remain in place.



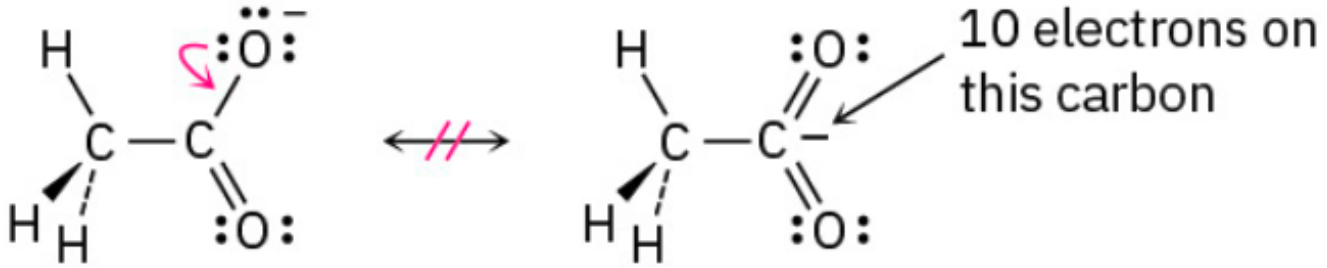
RULE 3

Different resonance fo of a substance don't h to be equivalent.



RULE 4

Resonance forms obey normal rules of valency.



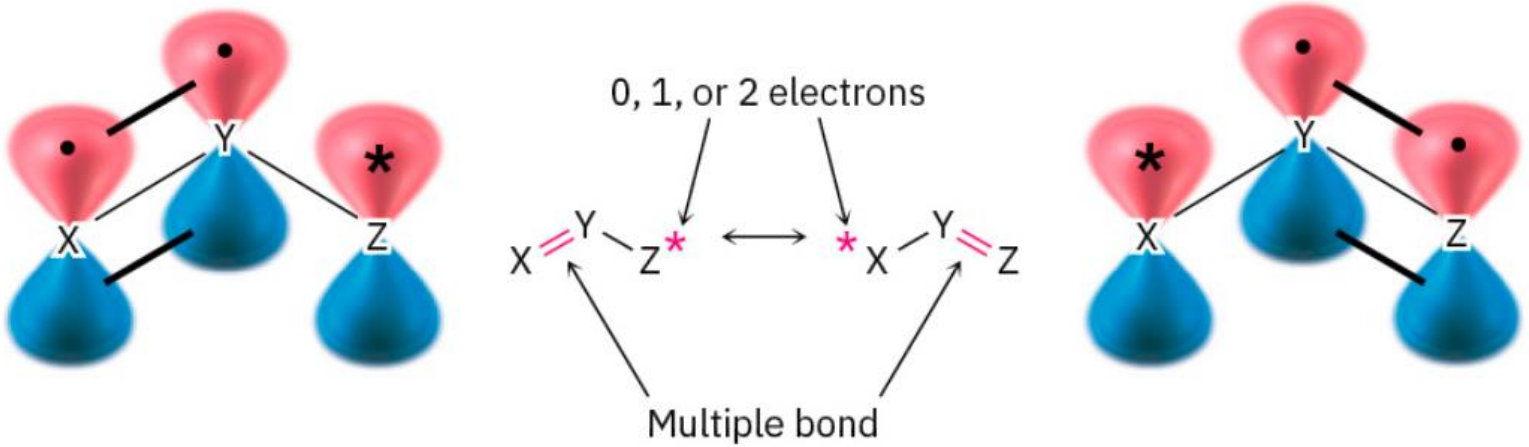
Acetate ion

Not a valid resonance form

RULE 5

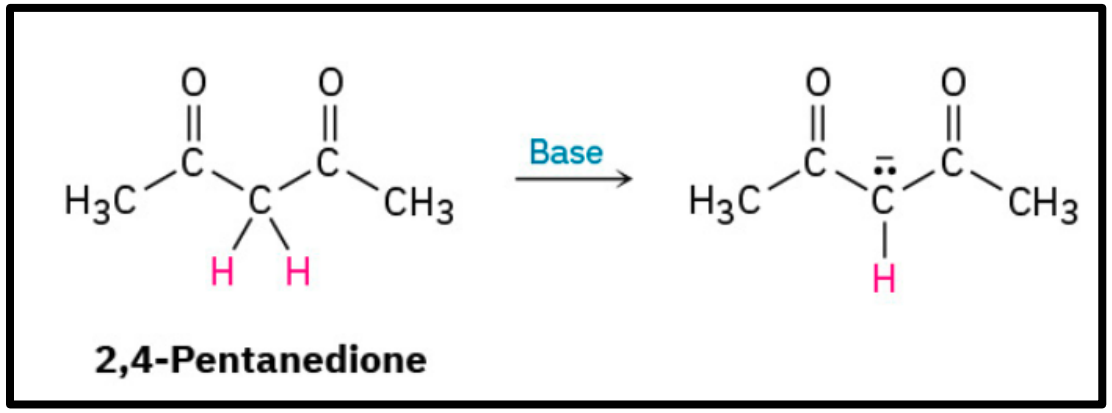
The resonance hybrid is more stable than any individual resonance form.

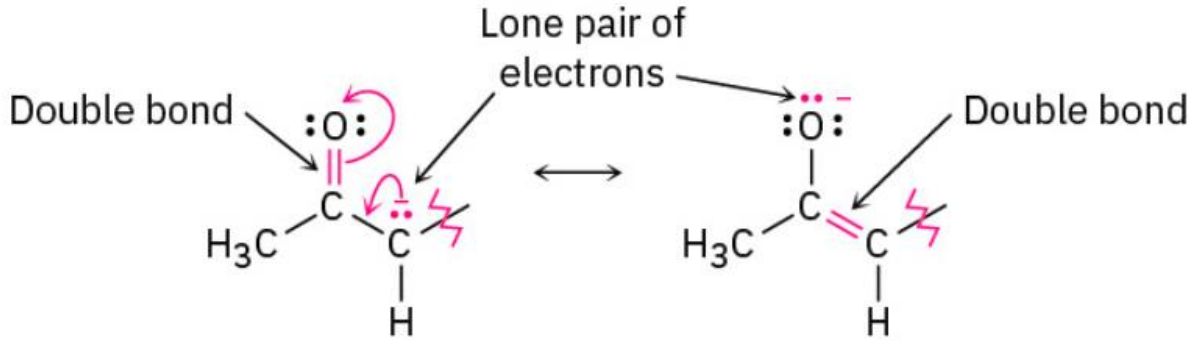
2.6 Drawing Resonance Forms

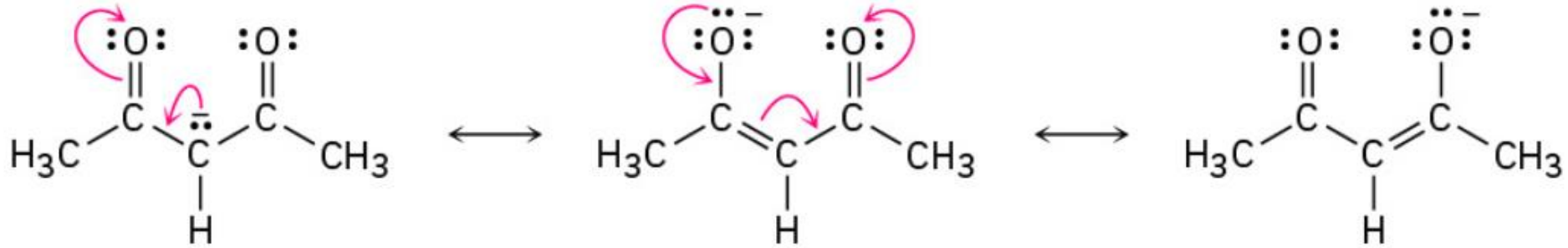


The atoms X, Y, and Z in the general structure might be C, N, O, P, S, or others, and the asterisk (*) might mean that the p orbital on atom Z is vacant, that it contains a single electron, or that it contains a lone pair of electrons. The two resonance forms differ simply by an exchange in position of the multiple bond and the asterisk from one end of the three-atom grouping to the other.

Look, for instance, at the anion produced when H^+ is removed from 2,4-pentanedione by reaction with a base. **How many resonance structures does the resultant anion have?**



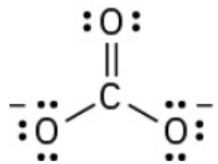




WORKED EXAMPLE 2.2

Drawing Resonance Forms for an Anion

Draw three resonance structures for the carbonate ion, CO_3^{2-}.



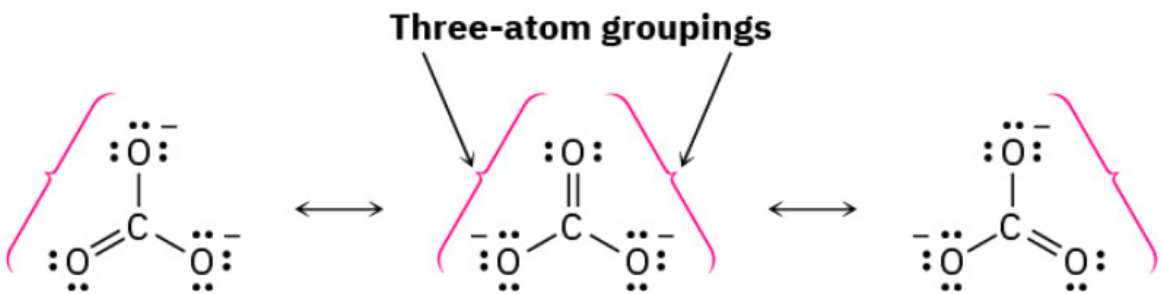
Carbonate ion

Strategy

Look for three-atom groupings that contain a multiple bond next to an atom with a *p* orbital. Then exchange the positions of the multiple bond and the electrons in the *p* orbital. In the carbonate ion, each singly bonded oxygen atom with three lone pairs and a negative charge is adjacent to the C=O double bond, giving the grouping $\ddot{O}{=}C{-}\ddot{O}:^{-}$.

Solution

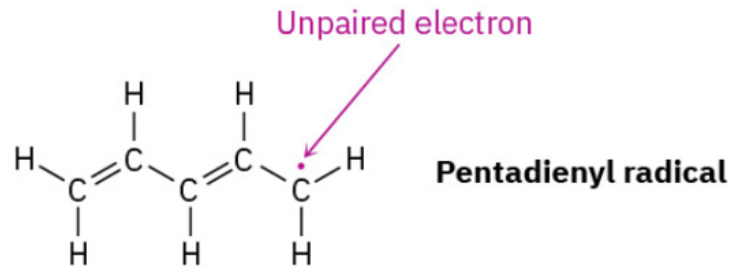
Exchanging the position of the double bond and an electron lone pair in each grouping generates three resonance structures.



WORKED EXAMPLE 2.3

Drawing Resonance Forms for a Radical

Draw three resonance forms for the pentadienyl radical, where a **radical** is a substance that contains a single, unpaired electron in one of its orbitals, denoted by a dot (·).



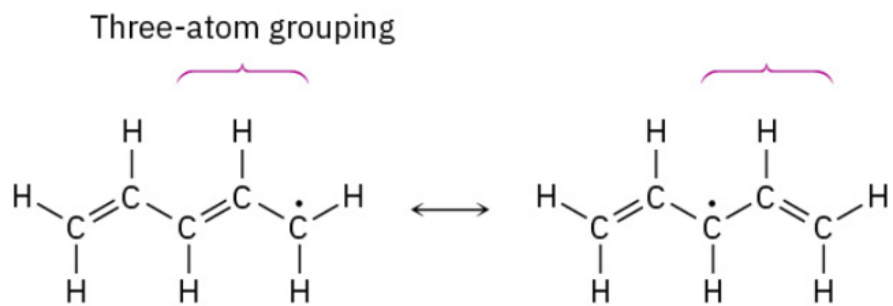
Pentadienyl radical

Strategy

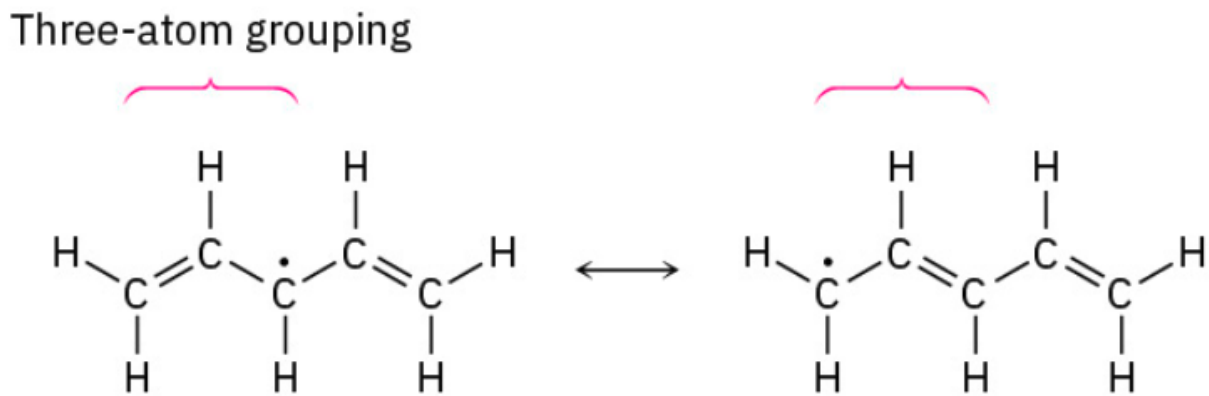
Find the three-atom groupings that contain a multiple bond next to an atom with a *p* orbital.

Solution

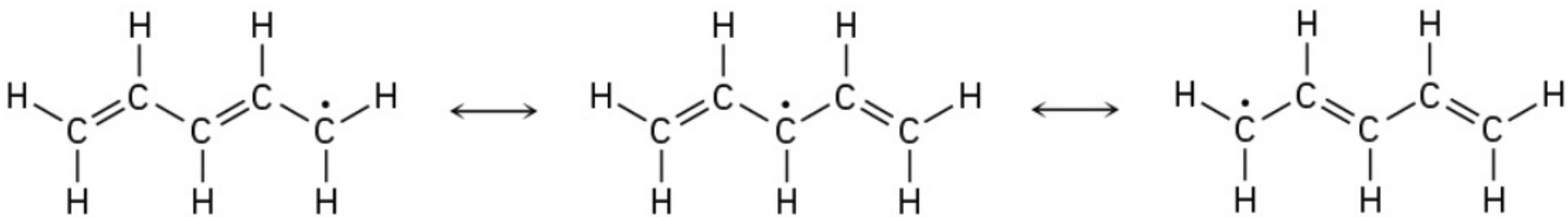
The unpaired electron is on a carbon atom next to a C=C bond, giving a typical three-atom grouping that has two resonance forms.



In the second resonance form, the unpaired electron is next to another double bond, giving another three-atom grouping and leading to another resonance form.

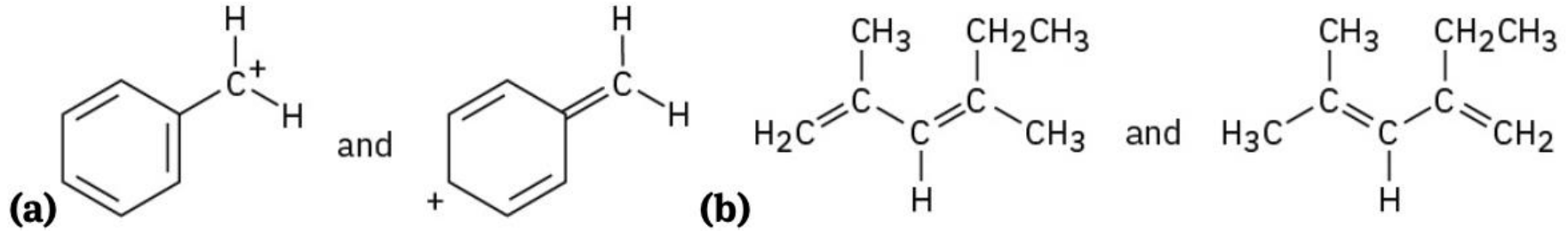


Thus, the three resonance forms for the pentadienyl radical are:



Problem 9

Which of the following pairs of structures represent resonance forms, and which do not? Explain.



Problem 2-10

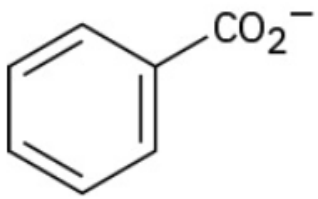
Draw the indicated number of resonance forms for each of the following substances:

(a) The methyl phosphate anion, $CH_3OPO_3^{2-}$ (3)

(b) The nitrate anion, NO_3^- (3)

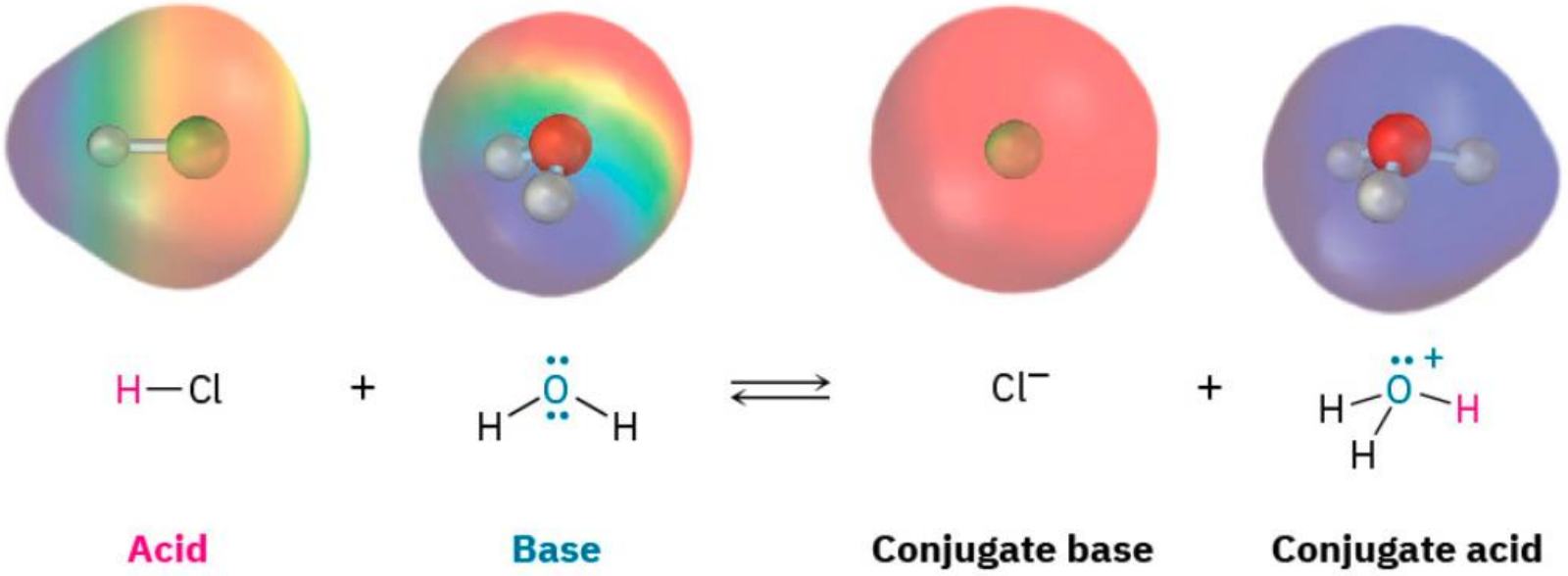
(c) The allyl cation, $H_2C{=}CH{-}CH_2^+$ (2)

(d) The benzoate anion (4)



2.7 Acids and Bases: The Brønsted–Lowry Definition

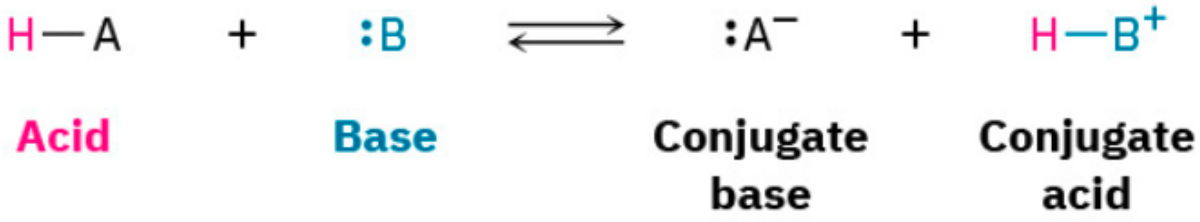
A **Brønsted–Lowry acid** is a substance that donates a hydrogen ion, H+, and a **Brønsted–Lowry base** is a substance that accepts a hydrogen ion. (The name proton is often used as a synonym for H+ because loss of the valence electron from a neutral hydrogen atom leaves only the hydrogen nucleus—a proton.)



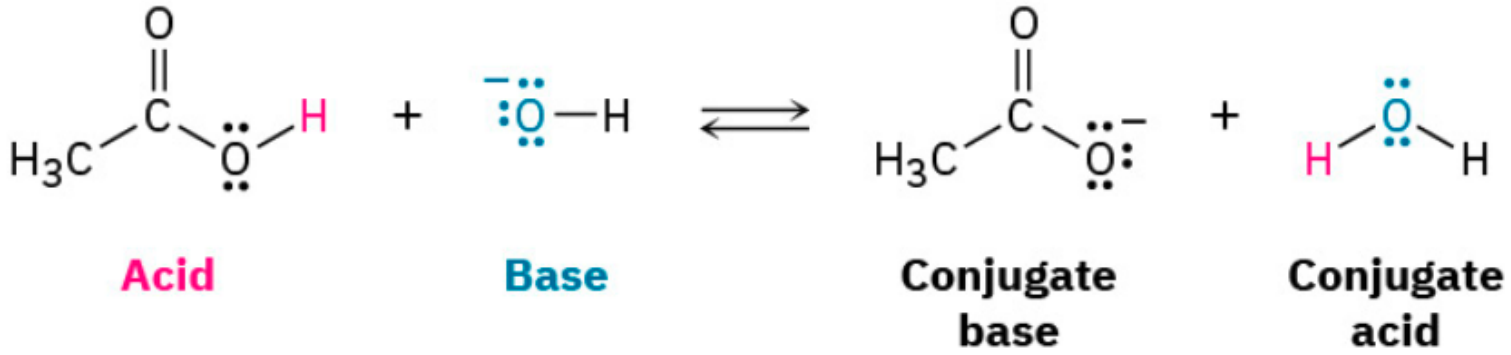
PROBLEM 2-11

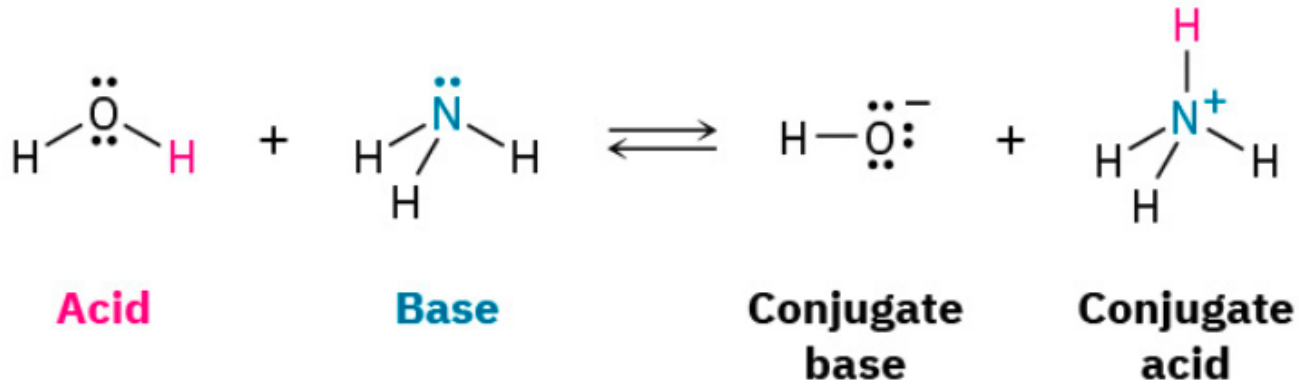
Nitric acid (HNO_3) reacts with ammonia (NH_3) to yield ammonium nitrate. Write the reaction, and identify the acid, the base, the conjugate acid product, and the conjugate base product.

In a general sense,



For example:





2.8 Acid and Base Strength

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Acid strengths are normally expressed using pKa values rather than Ka values, where the **p*Ka*** is the negative common logarithm of the Ka:

$$pK_a = -\log K_a$$

$$\underset{\text{(acid)}}{H_2O} + \underset{\text{(solvent)}}{H_2O} \rightleftharpoons OH^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{[1.0 \times 10^{-7}][1.0 \times 10^{-7}]}{[55.4]} = 1.8 \times 10^{-16}$$

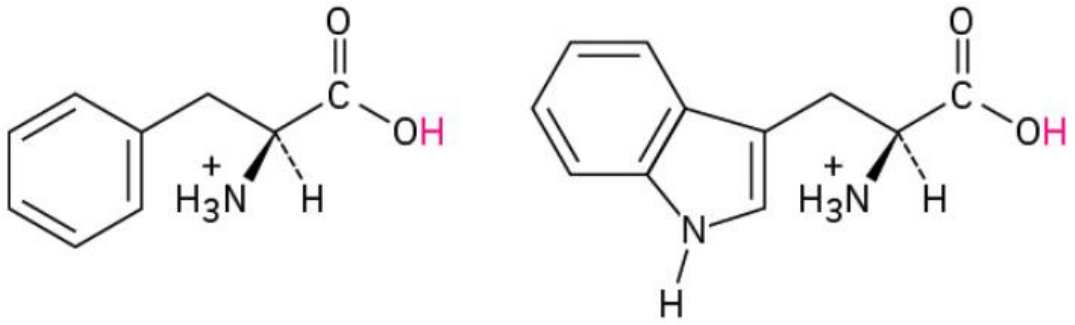
$$pK_a = 15.74$$

TABLE 2.3 Relative Strengths of Some Common Acids and Their Conjugate Bases

	Acid	Name	pK_a	Conjugate base	Name	
Weaker acid	CH_3CH_2OH	Ethanol	16.00	$CH_3CH_2O^-$	Ethoxide ion	Stronger base
	H_2O	Water	15.74	HO^-	Hydroxide ion	
	HCN	Hydrocyanic acid	9.31	CN^-	Cyanide ion	
	$H_2PO_4^-$	Dihydrogen phosphate ion	7.21	HPO_4^{2-}	Hydrogen phosphate ion	
	CH_3CO_2H	Acetic acid	4.76	$CH_3CO_2^-$	Acetate ion	
	H_3PO_4	Phosphoric acid	2.16	$H_2PO_4^-$	Dihydrogen phosphate ion	
	HNO_3	Nitric acid	–1.3	NO_3^-	Nitrate ion	
Stronger acid	HCl	Hydrochloric acid	–7.0	Cl^-	Chloride ion	Weaker base

PROBLEM 2-12

The amino acid phenyl alanine has pKa=1.83, and tryptophan has pKa=2.83. Which is the stronger acid?



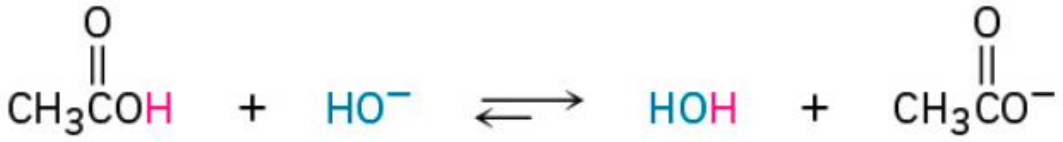
Phenylalanine
(pK_a = 1.83)

Tryptophan
(pK_a = 2.83)

PROBLEM 1-13 Amide ion, H_2N^-, is a much stronger base than hydroxide ion, HO^-. Which is the stronger acid, NH_3 or H_2O? Explain.

2.9 Predicting Acid–Base Reactions from pKa Values

Acetic acid ($pK_a = 4.76$) + **Hydroxide ion** ⇌ **Acetate ion** + **Water** ($pK_a = 15.74$)

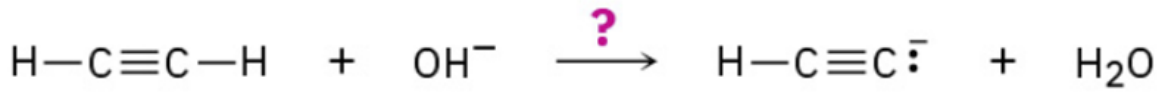


Stronger acid + **Stronger base** ⇌ **Weaker acid** + **Weaker base**

WORKED EXAMPLE 2.4

Predicting Acid Strengths from pK_a Values

Water has pK_a = 15.74, and acetylene has pK_a = 25. Which is the stronger acid? Does hydroxide ion react to a significant extent with acetylene?



Acetylene

Strategy

In comparing two acids, the one with the lower pK_a is stronger. Thus, water is a stronger acid than acetylene and gives up H^+ more easily.

Solution

Because water is a stronger acid and gives up H^+ more easily than acetylene, the HO^- ion must have less affinity for H^+ than the $HC{\equiv}C{:}^-$ ion. In other words, the anion of acetylene is a stronger base than hydroxide ion, and the reaction will not proceed significantly as written.

WORKED EXAMPLE 2.5

Calculating K_a from pK_a

According to the data in TABLE 2.3, acetic acid has pK_a = 4.76. What is its K_a?

Strategy

Since pK_a is the negative logarithm of K_a, it's necessary to use a calculator with an ANTILOG or INV LOG function. Enter the value of the pK_a (4.76), change the sign (–4.76), and then find the antilog (1.74×10^{-5}).

Solution

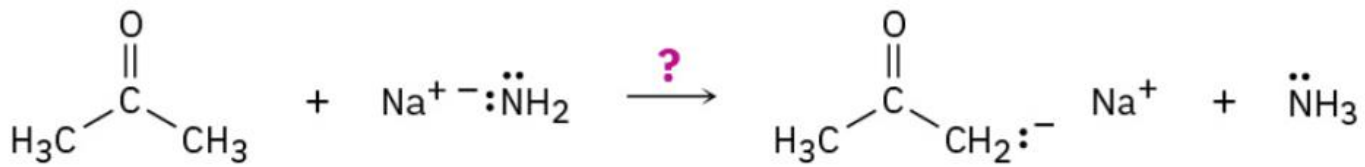
$K_a = 1.74 \times 10^{-5}$.

PROBLEM 2-14 Will either of the following reactions take place to a significant extent as written, according to the data in Table 2.3?

(a) $HCN + CH_3CO_2^- Na^+ \xrightarrow{?} Na^+ {}^-CN + CH_3CO_2H$

(b) $CH_3CH_2OH + Na^+ {}^-CN \xrightarrow{?} CH_3CH_2O^- Na^+ + HCN$

PROBLEM 2-15 Ammonia, NH_3, has $pK_a \approx 36$, and acetone has $pK_a \approx 19$. Will the following reaction take place to a significant extent?

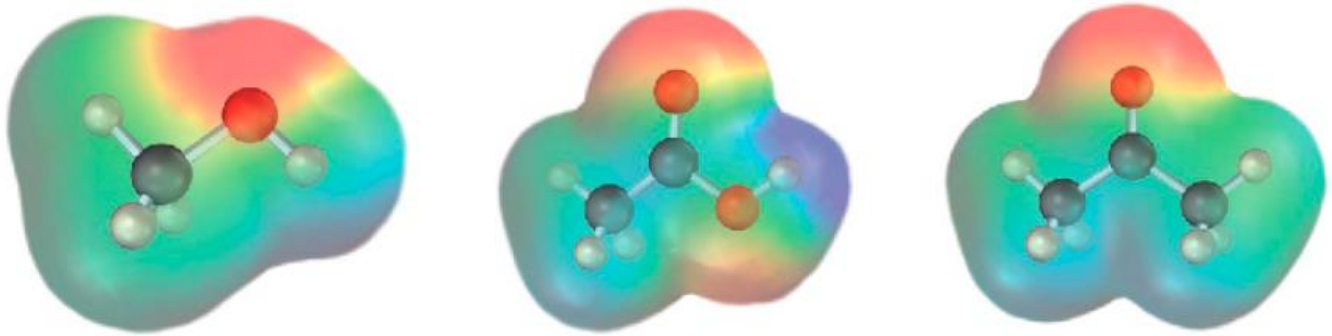


Acetone

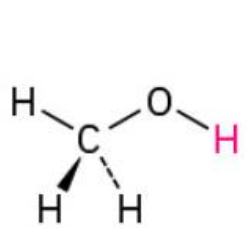
PROBLEM 2-16 What is the K_a of HCN if its $pK_a = 9.31$?

2.10 Organic Acids and Organic Bases

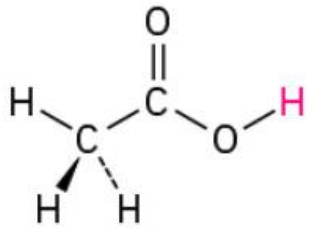
Organic acids are characterized by the presence of a positively polarized hydrogen atom (blue in electrostatic potential maps) and are of two main kinds: acids such as methanol and acetic acid that contain a hydrogen atom bonded to an electronegative oxygen atom (O–H) and those such as acetone (**Section 2.5**) that contain a hydrogen atom bonded to a carbon atom next to a C=O bond (O=C-C).



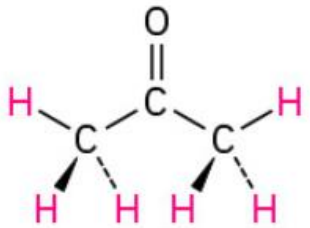
Some organic acids



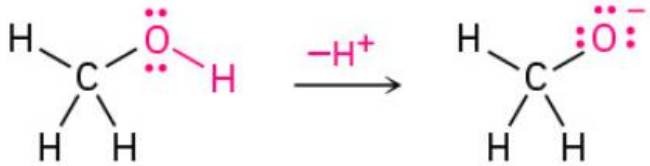
Methanol
($pK_a = 15.54$)



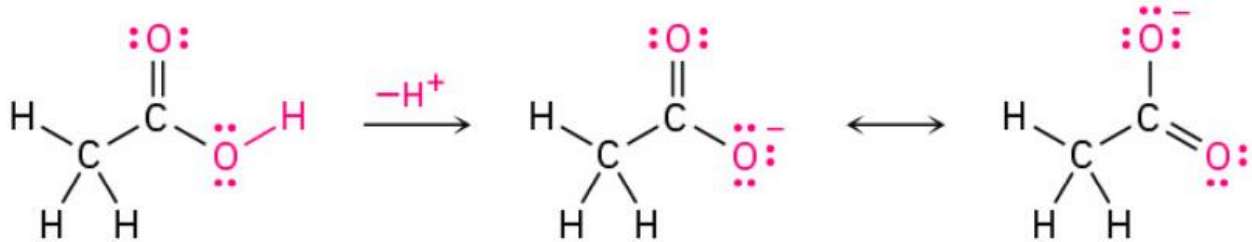
Acetic acid
($pK_a = 4.76$)



Acetone
($pK_a = 19.3$)

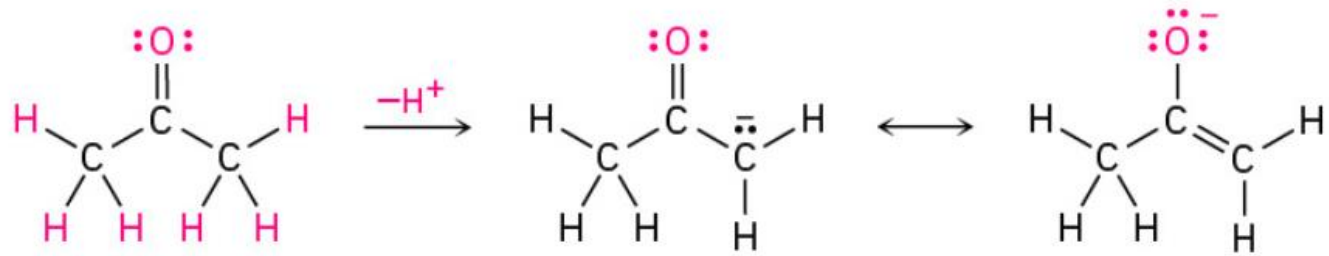


Anion is stabilized by having negative charge on a highly electronegative atom.



Anion is stabilized both by having negative charge on a highly electronegative atom and by resonance.

The acidity of acetone and other compounds with C=O bonds is due to the fact that the conjugate base resulting from loss of H^+ is stabilized by resonance. In addition, one of the resonance forms stabilizes the negative charge by placing it on an electronegative oxygen atom.



Anion is stabilized both by resonance and by having negative charge on a highly electronegative atom.

Electrostatic potential maps of the conjugate bases from methanol, acetic acid, and acetone are shown in **FIGURE 2.5**. As you might expect, all three show a substantial amount of negative charge (red) on oxygen.

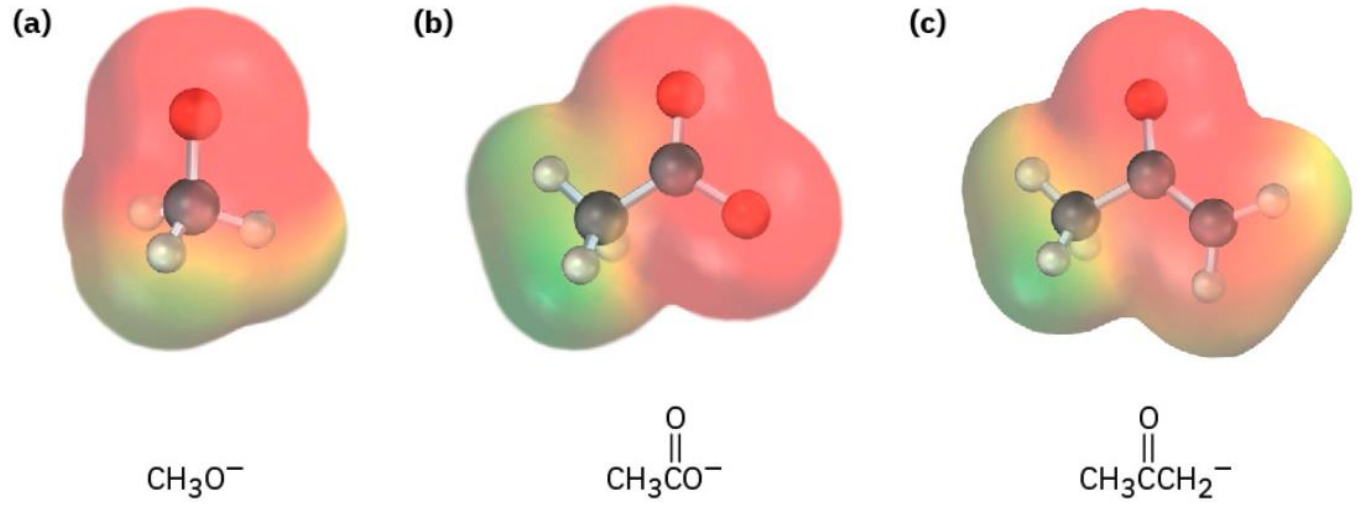
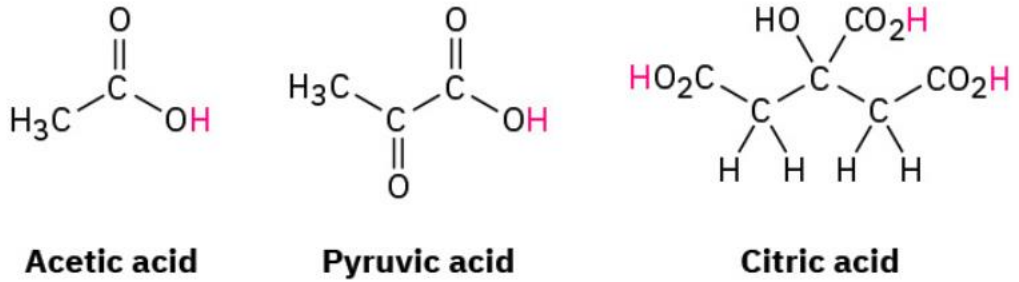
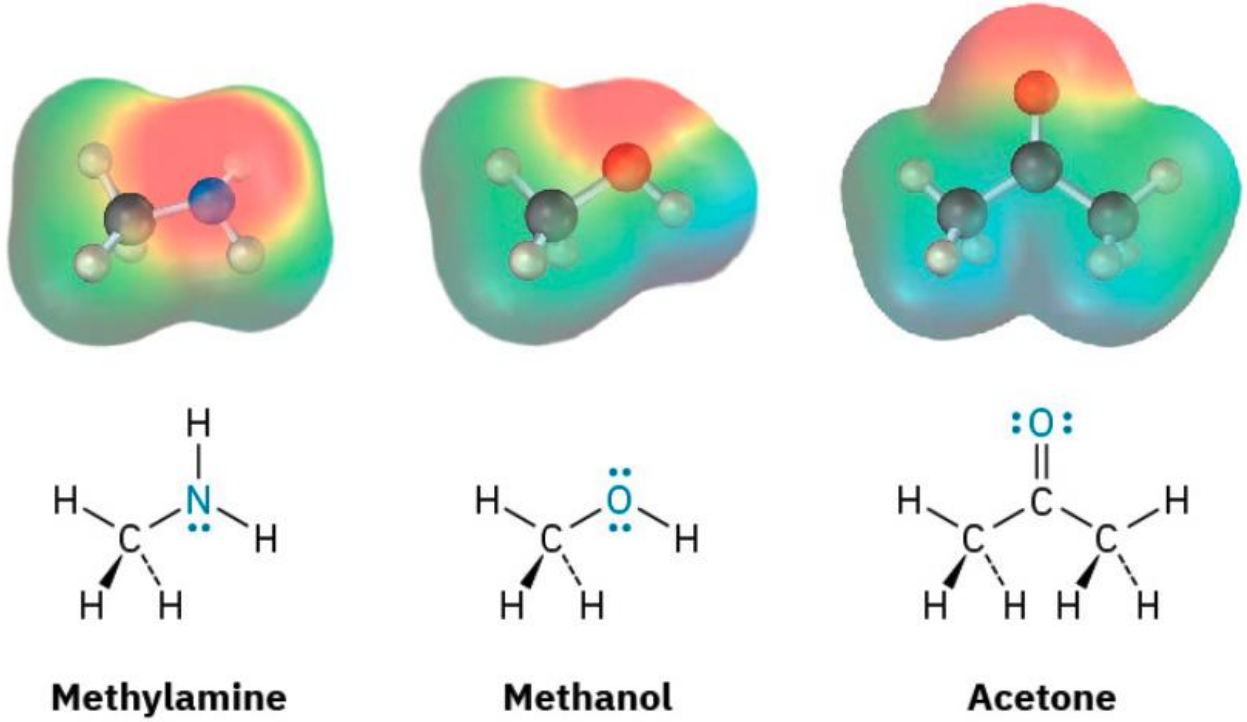


FIGURE 2.5 Electrostatic potential maps of the conjugate bases of (a) methanol, (b) acetic acid, and (c) acetone. The electronegative oxygen atoms stabilize the negative charge in all three.



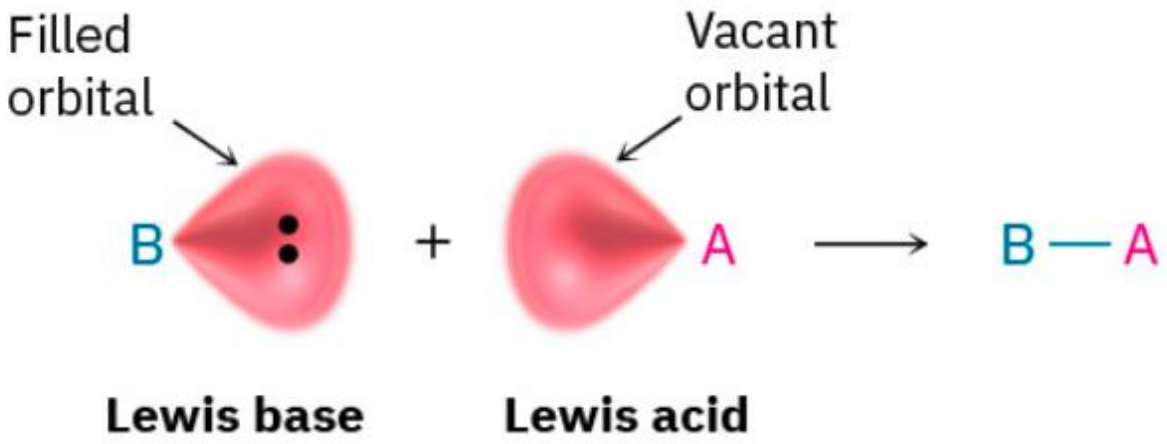
Organic Bases

Organic bases are characterized by the presence of an atom (reddish in electrostatic potential maps) with a lone pair of electrons that can bond to H+. Nitrogen-containing compounds such as methylamine are the most common organic bases and are involved in almost all metabolic pathways, but oxygen-containing compounds can also act as bases when reacting with a sufficiently strong acid.



2.11 Acids and Bases: The Lewis Definition

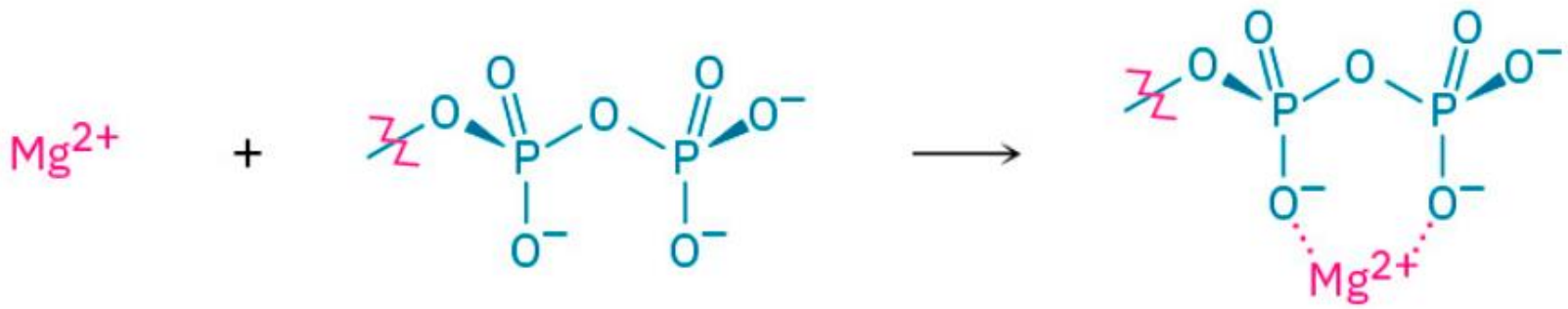
The Lewis definition of acids and bases is more encompassing than the Brønsted–Lowry definition because it's not limited to substances that donate or accept just protons. A **Lewis acid** is a substance that accepts an electron pair, and a **Lewis base** is a substance that donates an electron pair. The donated electron pair is shared between the acid and the base in a covalent bond.



Lewis Acids and the Curved Arrow Formalism

The fact that a Lewis acid is able to accept an electron pair means that it must have either a vacant, low-energy orbital or a polar bond to hydrogen so that it can donate H^+ (which has an empty 1s orbital).

Thus, the Lewis definition of acidity includes many species in addition to H^+. For example, various metal cations, such as $Mg^{2+,}$ are Lewis acids because they accept a pair of electrons when they form a bond to a base.



Lewis acid **Lewis base (an organodiphosphate ion)** **Acid–base complex**

In the same way, compounds of group 3A elements, such as BF_3 and $AlCl_3$, are Lewis acids because they have

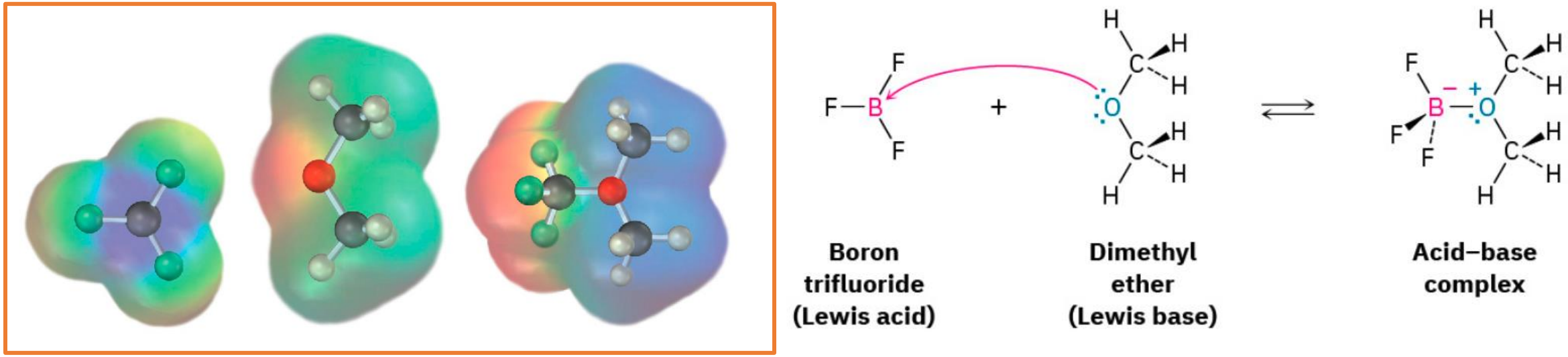
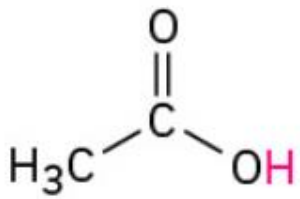


FIGURE 2.6 The reaction of boron trifluoride, a Lewis acid, with dimethyl ether, a Lewis base. The Lewis acid accepts a pair of electrons, and the Lewis base donates a pair of nonbonding electrons. Note how the movement of electrons from the Lewis base to the Lewis acid is indicated by a curved arrow. Note also how, in electrostatic potential maps, the boron becomes more negative (red) after reaction because it has gained electrons and the oxygen atom becomes more positive (blue) because it has donated electrons.

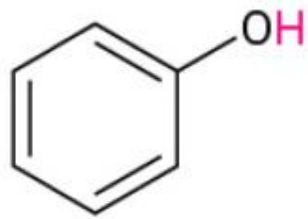
Some Lewis acids

Some neutral proton donors:

H_2O HCl HBr HNO_3 H_2SO_4



A carboxylic acid



A phenol

CH_3CH_2OH

An alcohol

Some cations:

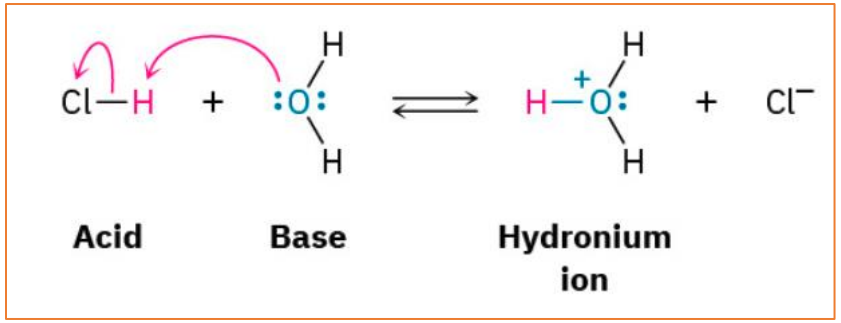
Li^+ Mg^{2+}

Some metal compounds:

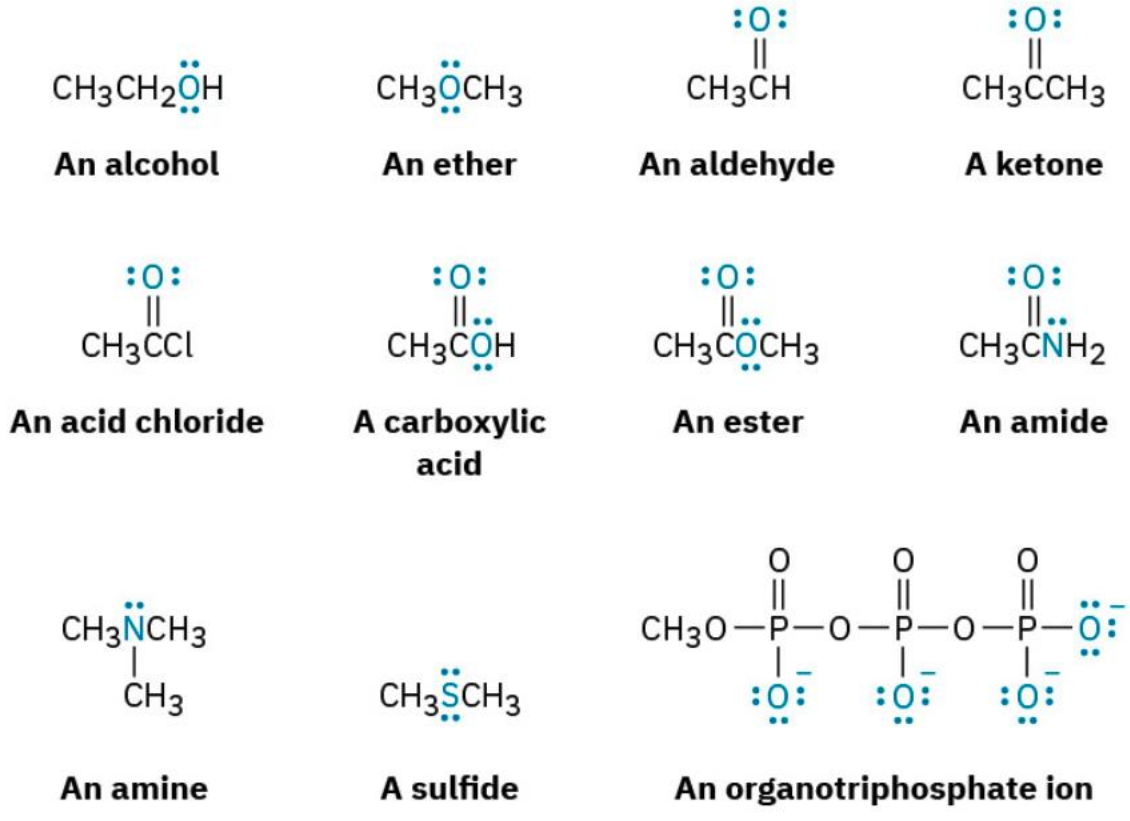
$AlCl_3$ $TiCl_4$ $FeCl_3$ $ZnCl_2$

Lewis Bases

The Lewis definition of a base—a compound with a pair of nonbonding electrons that it can use to bond to a Lewis acid—is similar to the Brønsted–Lowry definition. Thus, H_2O, with its two pairs of nonbonding electrons

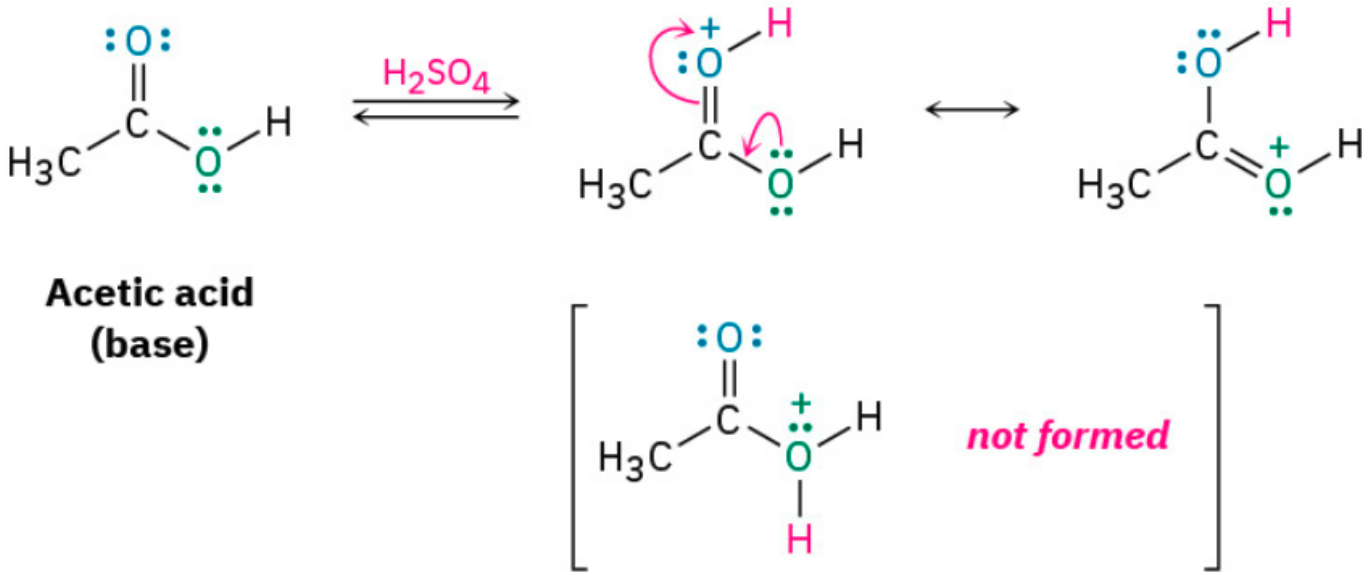


Some Lewis bases



Note also that some Lewis bases, such as carboxylic acids, esters, and amides, have more than one atom with a lone pair of electrons and can therefore react at more than one site. Acetic acid, for example, can be protonated either on the doubly bonded oxygen atom or on the singly bonded oxygen atom.

Reaction normally occurs only once in such instances, and the more stable of the two possible protonation products is formed. For acetic acid, protonation by reaction with sulfuric acid occurs on the doubly bonded oxygen because that product is stabilized by two resonance forms.



WORKED EXAMPLE 2.6

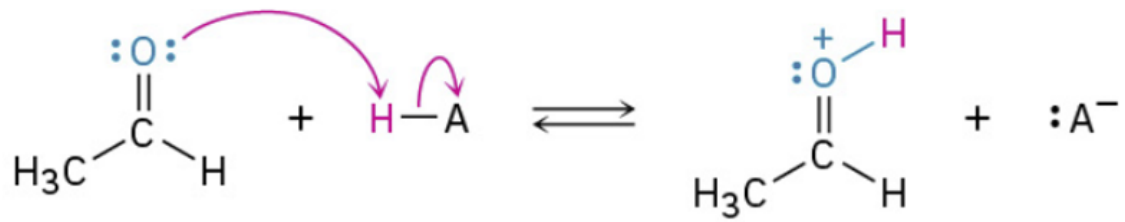
Using Curved Arrows to Show Electron Flow

Using curved arrows, show how acetaldehyde, CH_3CHO, can act as a Lewis base.

Strategy

A Lewis base donates an electron pair to a Lewis acid. We therefore need to locate the electron lone pairs on acetaldehyde and use a curved arrow to show the movement of a pair toward the H atom of the acid.

Solution

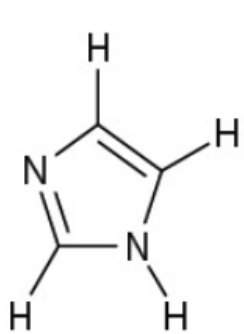


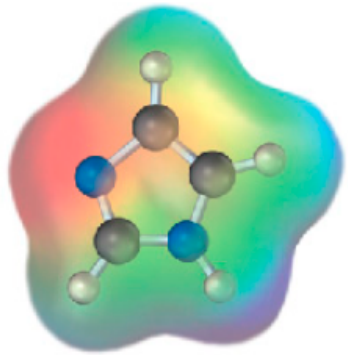
Acetaldehyde

PROBLEM 2-17 Using curved arrows, show how the species in part **(a)** can act as Lewis bases in their reactions with HCl, and show how the species in part **(b)** can act as Lewis acids in their reaction with OH^-.

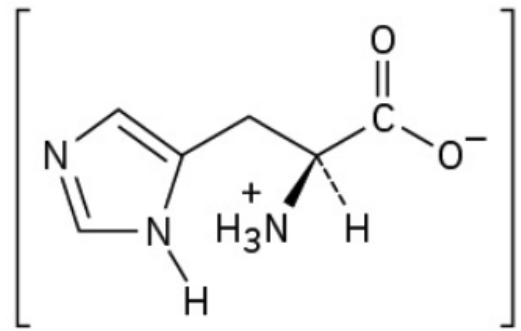
(a) CH_3CH_2OH, $HN(CH_3)_2$, $P(CH_3)_3$ **(b)** H_3C^+, $B(CH_3)_3$, $MgBr_2$

PROBLEM 2-18 Imidazole, which forms part of amino acid histidine, can act as both an acid and a base.





Imidazole



Histidine

(a) Look at the electrostatic potential map of imidazole, and identify the most acidic hydrogen atom and the most basic nitrogen atom.

(b) Draw structures for the resonance forms of the products that result when imidazole is protonated by an acid and deprotonated by a base.

2.12 Noncovalent Interactions between Molecules

When thinking about chemical reactivity, chemists usually focus their attention on bonds, the covalent interactions between atoms within molecules. Also important, however, particularly in large biomolecules like proteins and nucleic acids, are a variety of interactions between molecules that strongly affect molecular properties. Collectively called either **intermolecular forces**, **van der Waals forces**, or **noncovalent interactions**, they are of several different types: dipole–dipole forces, dispersion forces, and hydrogen bonds.

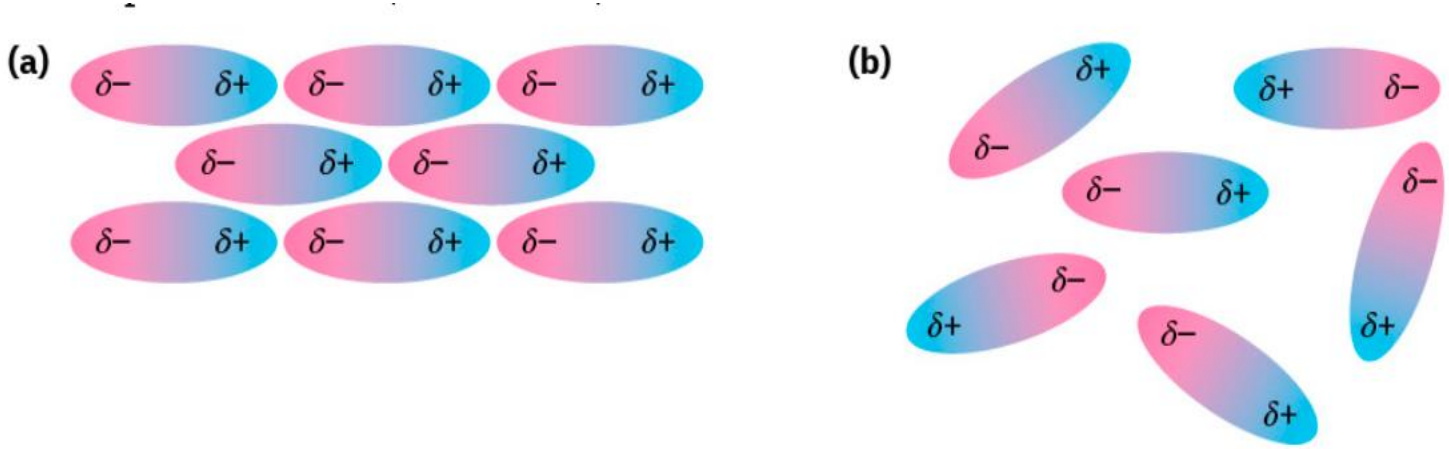
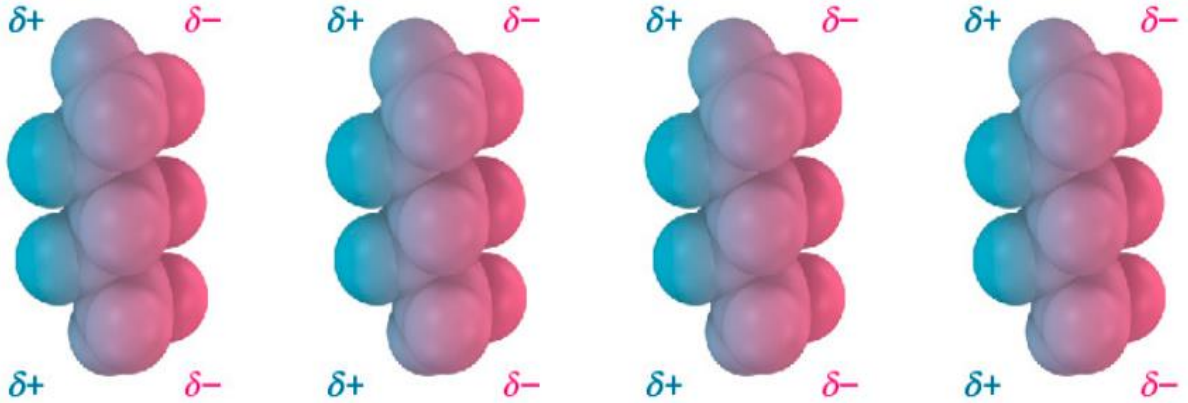
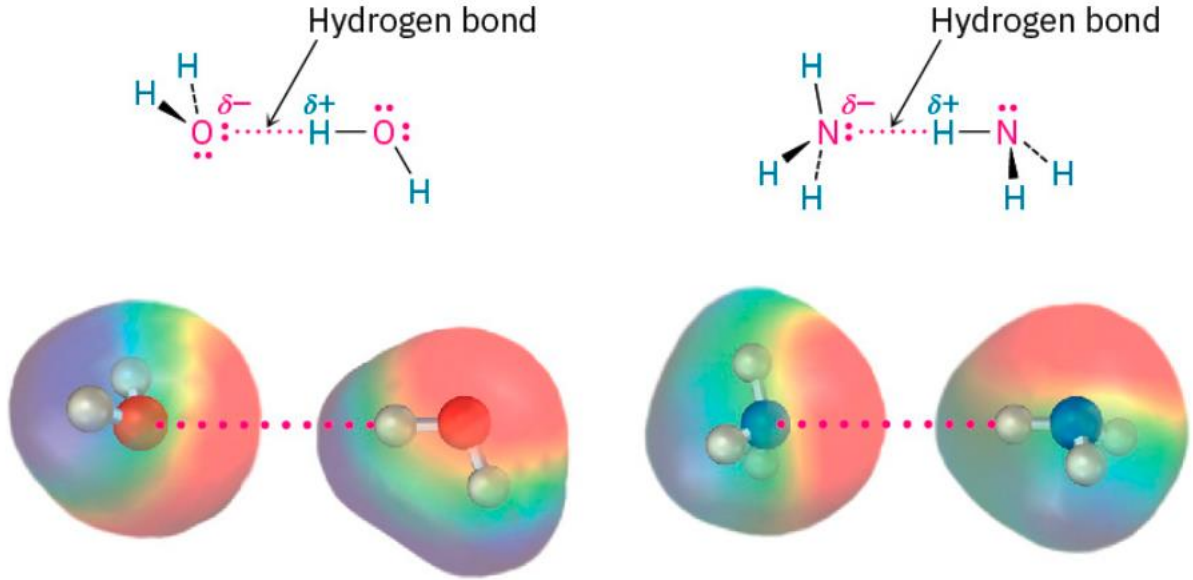


FIGURE 2.7 Dipole–dipole forces cause polar molecules (a) to attract one another when they orient with unlike charges together, but (b) to repel one another when they orient with like charges together.

FIGURE 2.8 Attractive **dispersion forces** in nonpolar molecules are caused by temporary dipoles, as shown in these models of pentane, C_5H_{12}.

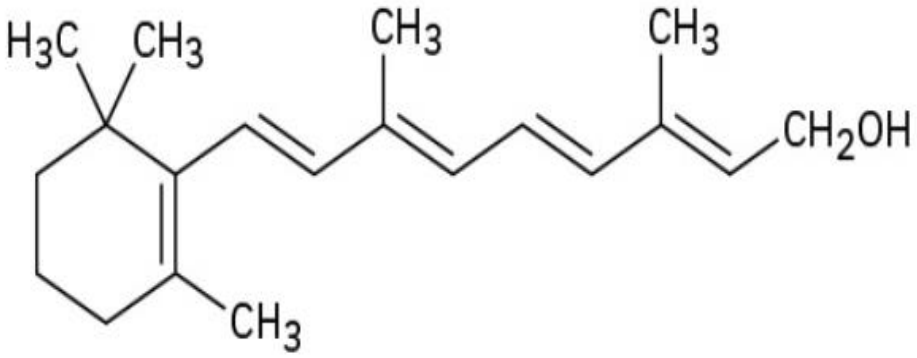


In essence, **a hydrogen bond** is a very strong dipole–dipole interaction involving polarized O–H or N–H bonds. Electrostatic potential maps of water and ammonia clearly show the positively polarized hydrogens (blue) and the negatively polarized oxygens and nitrogens (red).

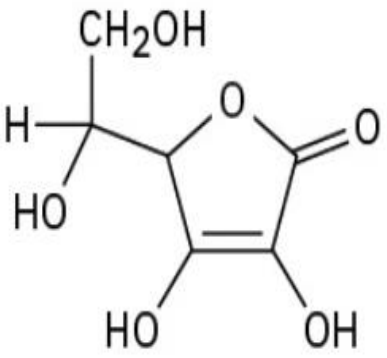


PROBLEM 2-19

Of the two vitamins A and C, one is hydrophilic and water-soluble while the other is hydrophobic and fat-soluble. Which is which?



Vitamin A
(retinol)

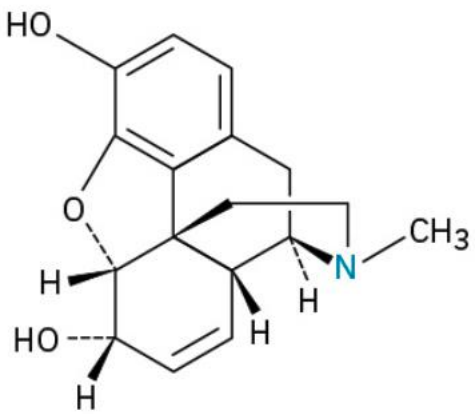


Vitamin C
(ascorbic acid)

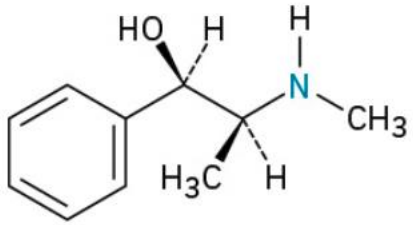
CHEMISTRY MATTERS

Alkaloids: From Cocaine to Dental Anesthetics

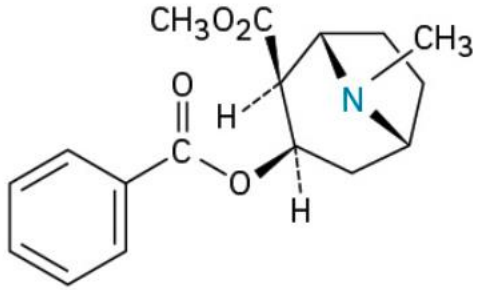
FIGURE 2.9 The coca bush Erythroxylon coca, native to upland rain forest areas of Colombia, Ecuador, Peru, Bolivia, and western Brazil, is the source of the alkaloid cocaine. (credit: "Erythroxylum coca" by Danna Guevara/Wikimedia Commons, CC BY 4.0)



Morphine



Ephedrine



Cocaine