Appropriate Problems from McMurry Chap 2

Section 2.1: Problems 2-1 – 2-4

Section 2.2: Problems 2-5, 2-6, 2-28 – 2-30, 2-32, 2-53, 2-59, 2-63

Section 2.3: Problems 2-7, 2-8, 2-35, 2-36

Sections 2.4 – 2.6: Problem 2-9, 2-10, 2-20, 2-21, 2-23, 2-26, 2-37, 2-38, 2-56, 2-57, 2-61, Challenging Problems 2-33, 2-34, 2-39

Section 2.7: Problem 2-11

Section 2.8: Problems: 2-12, 2-13

Section 2.9: Problems 2-14 – 2-16

Section 2.11 Problems: 2-17, 2-18, 2-24, 2-25, 2-40 (2-42 is a good question but the Lewis acid-base concept is not strongly emphasized in our organic class), 2-43, 2-44, 2-46, 2-47, 2-48, 2-54, 2-55, 2-61, 2-64

2.12 Problems: 2-19, 2-65

Identify ionic interactions, polar covalent bonds, and nonpolar covalent bonds

Interpret electrostatic potential maps

Identify polar bonds and molecules

Determine the formal charge of atoms in a molecule

Interpret formal charge

Draw resonance contributors

Draw resonance hybrids

Weight the amount a contributor contributes to the resonance hybrid

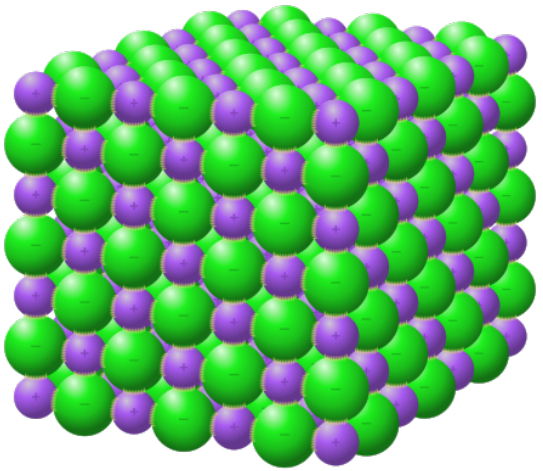
Interpret the effects of electron delocalization

Identify Brønsted-Lowry acid and bases in acid-base reactions

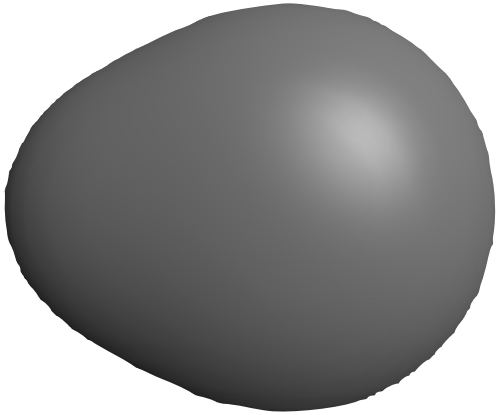
Determine acid or base strength based on pK_a

Determine or explain acid or base strength based on molecular structure

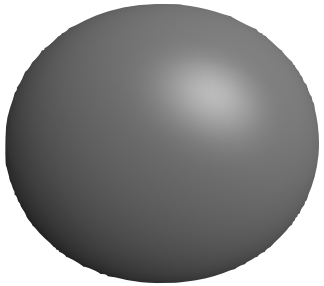
NaCl Na^+ and Cl^-



HF H—F

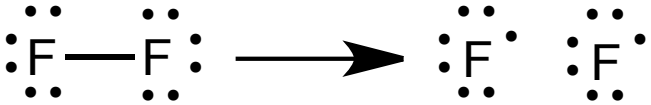


H_2 H—H

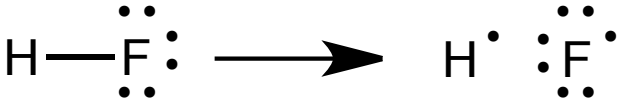


[1]https://en.wikipedia.org/wiki/Sodium_chloride#/media/File:NaCl_bonds.svg

ΔH_{BDE} = 436 kJ/mol[1]



ΔH_{BDE} = 155 kJ/mol[1]

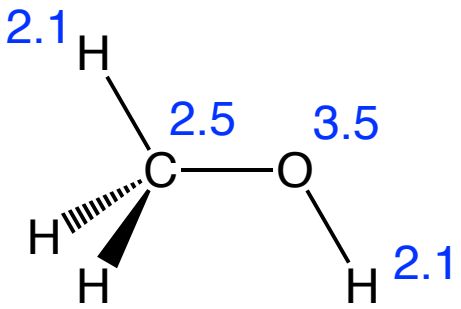


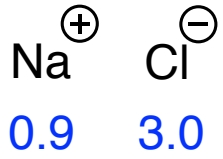
assuming BDE is average of H_2 and F_2 BDE

predicted ΔH_{BDE} = 296 kJ/mol

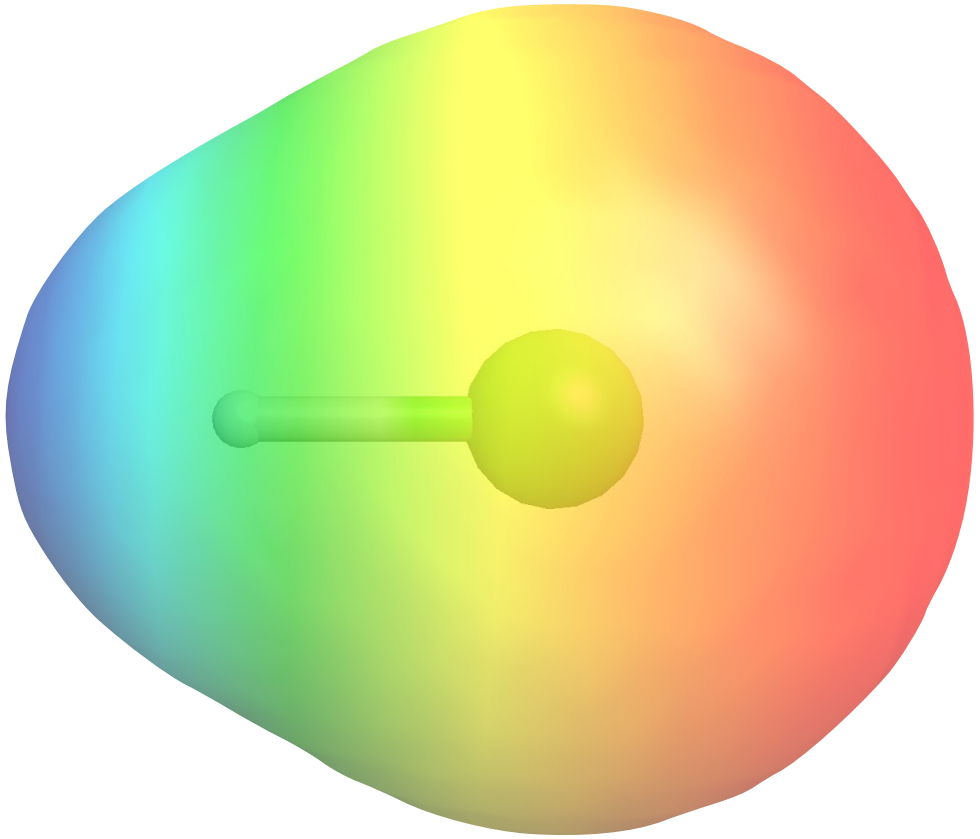
1. Atkins, Physical Chemistry, 3rd ed. p 882 565

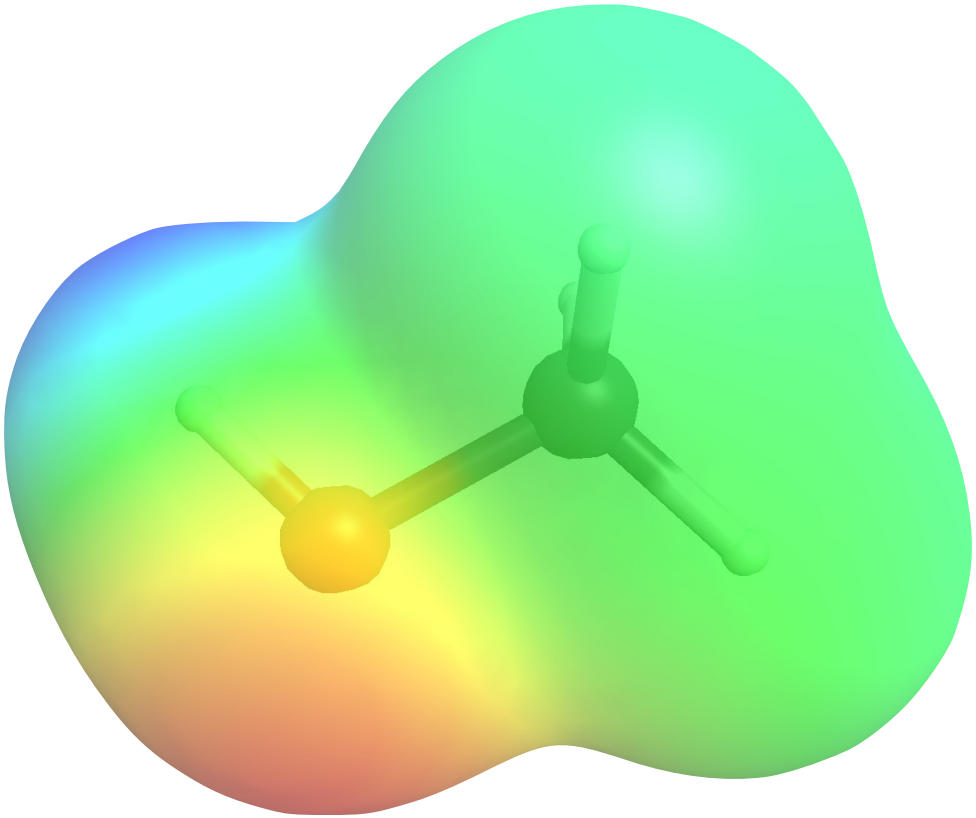
"As a rough guide, bonds between atoms whose electronegativities differ by less than 0.5 are [considered] nonpolar covalent, bonds between atoms whose electronegativities differ by 0.5 to 2 are polar covalent, and bonds between atoms whose electronegativities differ by more than 2 are largely ionic."[1]

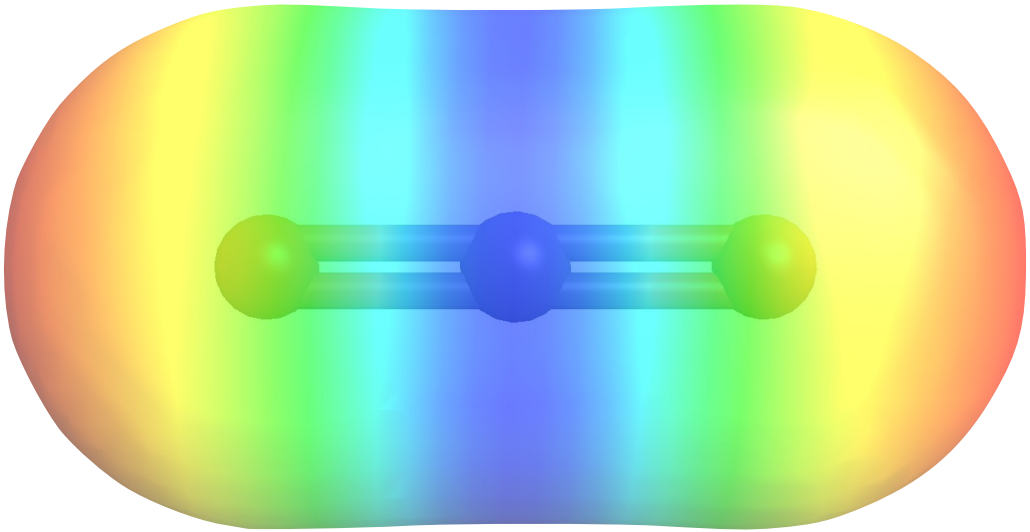




[1] Organic Chemistry, 10th ed., McMurray, OpenStax (2023) https://openstax.org/details/books/organic-chemistry







Draw Lewis Structure

Draw VSEPR Structure

Draw Dipole arrows on polar bonds

If (+) and (-) are on opposite sides (front and back, left and right, top and bottom, upper left and lower right) then the molecule is polar otherwise it isn't.

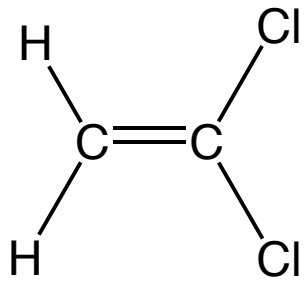
CH_2Br_2

Draw Lewis Structure

Draw VSEPR Structure

Draw Dipole arrows on polar bonds

If (+) and (-) are on opposite sides (front and back, left and right, top and bottom, upper left and lower right) then the molecule is polar otherwise it isn't.

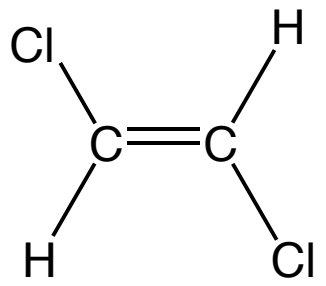


Draw Lewis Structure

Draw VSEPR Structure

Draw Dipole arrows on polar bonds

If (+) and (-) are on opposite sides (front and back, left and right, top and bottom, upper left and lower right) then the molecule is polar otherwise it isn't.



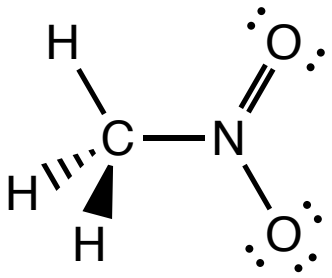
Formal Charge of an atom	=	# valence e⁻'s in the neutral atom	-	(	# of lone pair electrons	+	1/2 of the e⁻'s in the bonds	)

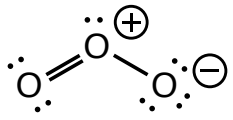
O_3

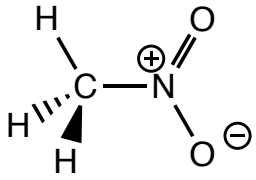
Formal Charge of an atom	=	# valence e⁻'s in the neutral atom	-	(	# of lone pair electrons	+	1/2 of the e⁻'s in the bonds	)

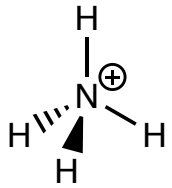
CH_3OH

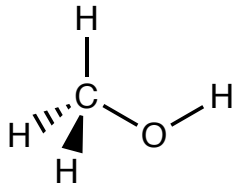
Formal Charge of an atom	=	# valence e⁻'s in the neutral atom	-	(	# of lone pair electrons	+	1/2 of the e⁻'s in the bonds	)




O
O
O

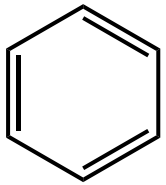

H
O
C
N
H
H
O

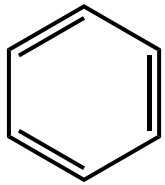

H
N
H
H
H


H
C
H
O
H
H

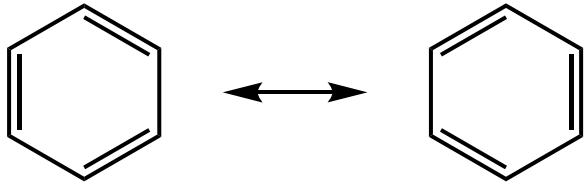
Also a way to move charge around a molecule...

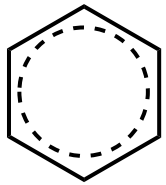
Which one is correct?



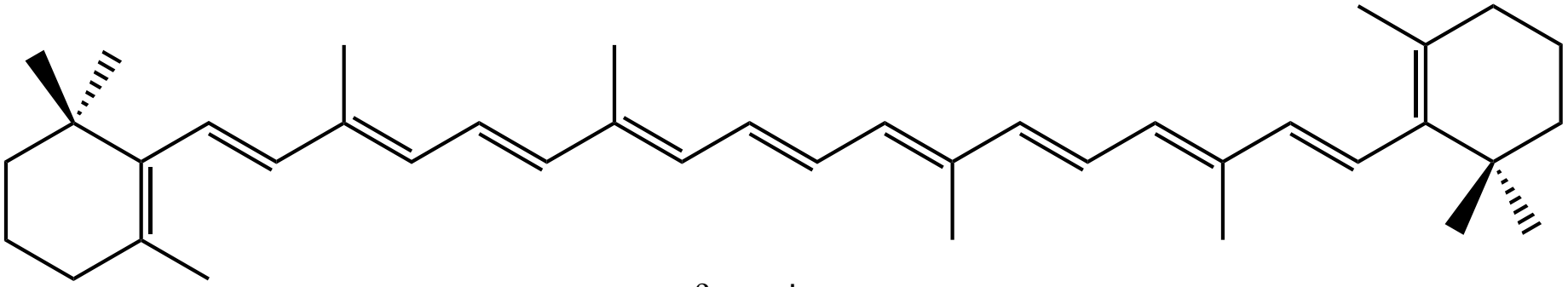


Whenever 3 or more p orbitals are in a row experiments and MO theory say that the electrons are delocalized over all of the p orbitals.

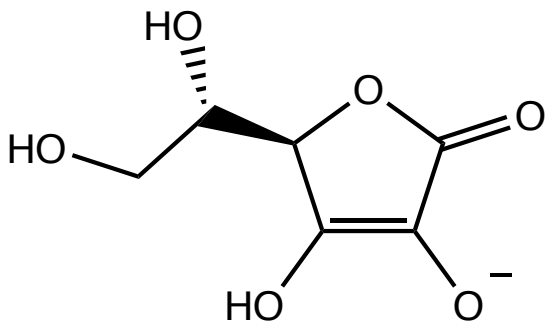




Resonance: Where else do we see extended π systems/electron delocalization?



β-carotene



Vitamin C

Identify ionic interactions, polar covalent bonds, and nonpolar covalent bonds

Interpret electrostatic potential maps

Identify polar bonds and molecules

Determine the formal charge of atoms in a molecule

Interpret formal charge

Draw resonance contributors

Draw resonance hybrids

Weight the amount a contributor contributes to the resonance hybrid

Interpret the effects of electron delocalization

Identify Brønsted-Lowry acid and bases in acid-base reactions

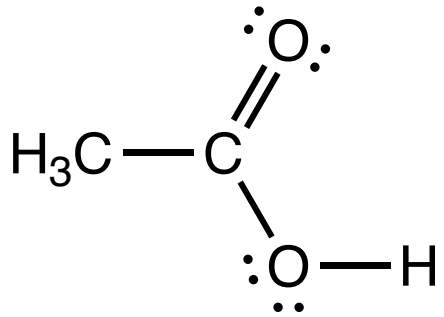
Determine acid or base strength based on pK_a

Determine or explain acid or base strength based on molecular structure

Identify noncovalent interactions molecules use to interact with other molecules

Explain differences in MP, BP, or solubility using noncovalent interactions

Whenever 3 or more p orbitals are in a row experiments and MO theory say that the electrons are delocalized over all of the p orbitals.



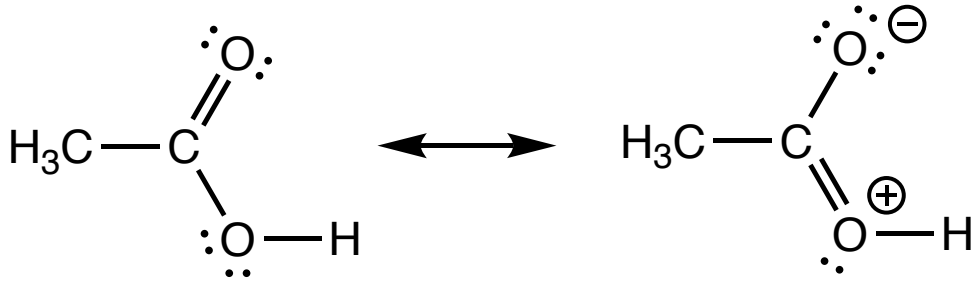
The more stable the resonance contributor is, the more it contributes to the resonance hybrid

What factors make the contributor less stable

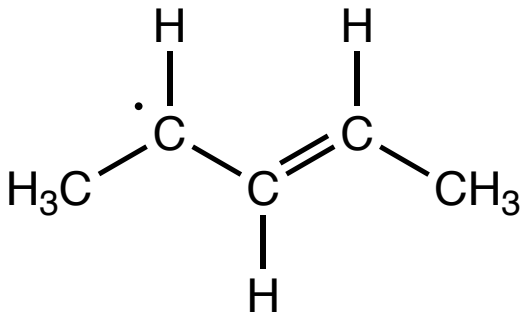
1. Charge separation

2. “Wrong” charges
   - negative charge is not on the most electronegative element and
   - a positive charge is on the most electronegative element

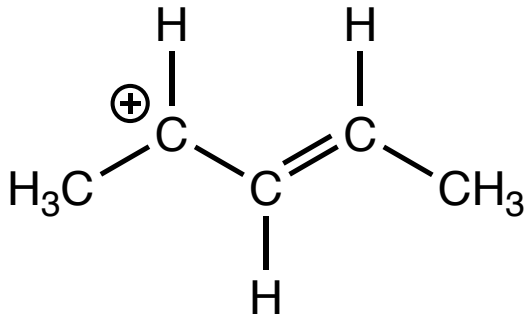
3. Incomplete octets



Whenever 3 or more p orbitals are in a row experiments and MO theory say that the electrons are delocalized over all of the p orbitals.

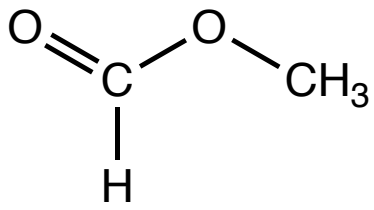


Whenever 3 or more p orbitals are in a row, experiments and MO theory say that the electrons are delocalized over all of the p orbitals.



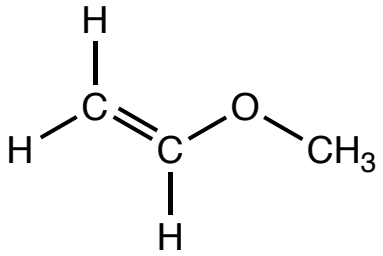
Rules for drawing Resonance Contributors

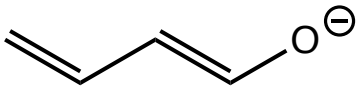
1. **atoms don't move**, only electrons
2. **don't move σ bonds**, only π bonds, lone pair e–'s, or unpaired e–'s (radicals)
3. the total number of electrons must stay the same, **don't change the net charge**
4. p orbitals must be able to line up parallel to each other

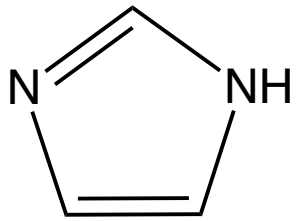


Rules for drawing Resonance Contributors

1. **atoms don't move**, only electrons
2. **don't move σ bonds**, only π bonds, lone pair e–'s, or unpaired e–'s (radicals)
3. the total number of electrons must stay the same, **don't change the net charge**
4. p orbitals must be able to line up parallel to each other

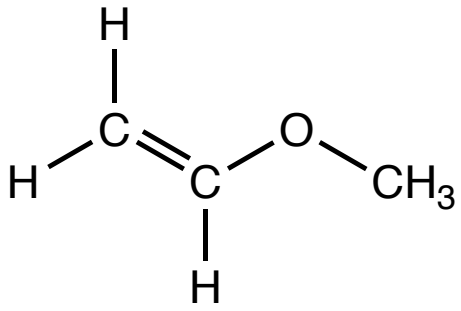






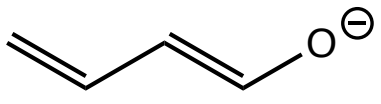
Rules for drawing Resonance Contributors

1. **atoms don't move**, only electrons
2. **don't move σ bonds**, only π bonds, lone pair e–'s, or unpaired e–'s (radicals)
3. the total number of electrons must stay the same, **don't change the net charge**
4. p orbitals must be able to line up parallel to each other



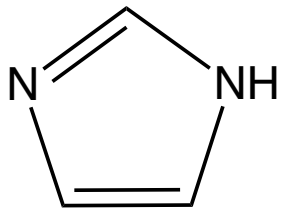
Rules for drawing Resonance Contributors

1. **atoms don't move**, only electrons
2. **don't move σ bonds**, only π bonds, lone pair e–'s, or unpaired e–'s (radicals)
3. the total number of electrons must stay the same, **don't change the net charge**
4. p orbitals must be able to line up parallel to each other



Rules for drawing Resonance Contributors

1. **atoms don't move**, only electrons
2. **don't move σ bonds**, only π bonds, lone pair e–'s, or unpaired e–'s (radicals)
3. the total number of electrons must stay the same, **don't change the net charge**
4. p orbitals must be able to line up parallel to each other



Acids and Bases and Language

In aqueous solutions, the solution is considered **acidic** if the concentration of **H^+** is **greater than** the concentration of **OH^-**. At 25 °C, this occurs when the pH is less than 7.

In every day language, we might say that the solution is an acid. More precisely, there is a molecule **in the solution that acing as an acid and is causing the solution to be acidic**.

We will call molecules or ions **acids or bases based on how they react** (or could react).

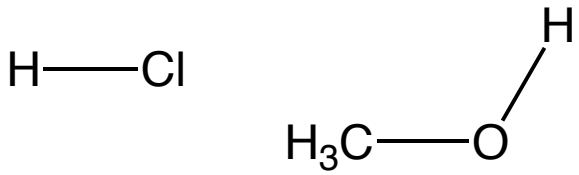
There are **many molecules** that can **act as a base** in some circumstances **or an acid** in other circumstances.

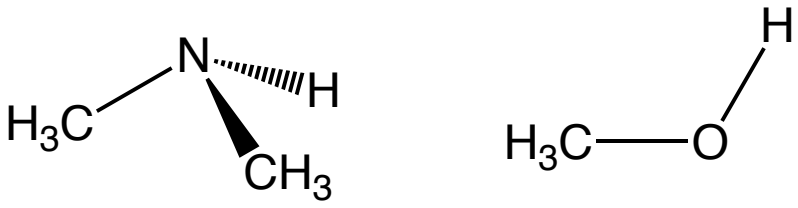
Molecules or compounds that are very likely to react as an acid are often called acids, but technically, the molecules are referred to as acids and bases based on how they react.

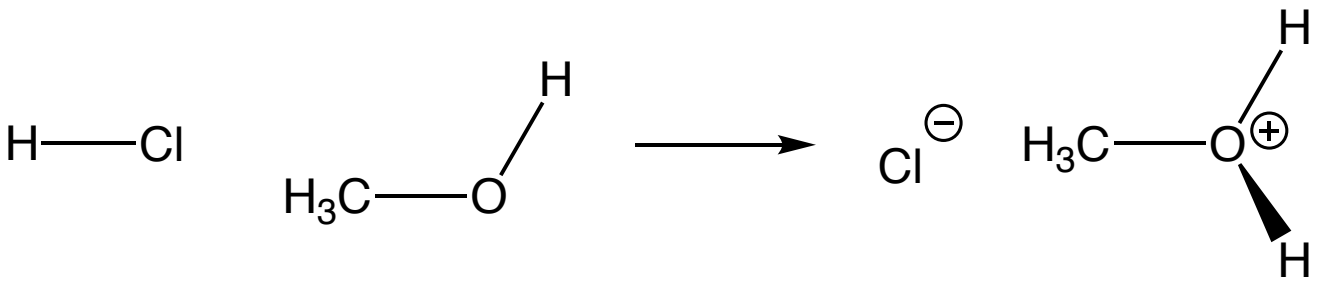
HNO_3, for example...

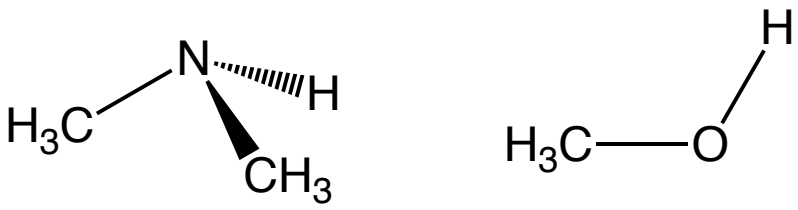
A Brønsted-Lowry acid is a proton (H^+) _____.

A Brønsted-Lowry base is a proton (H^+) _____.

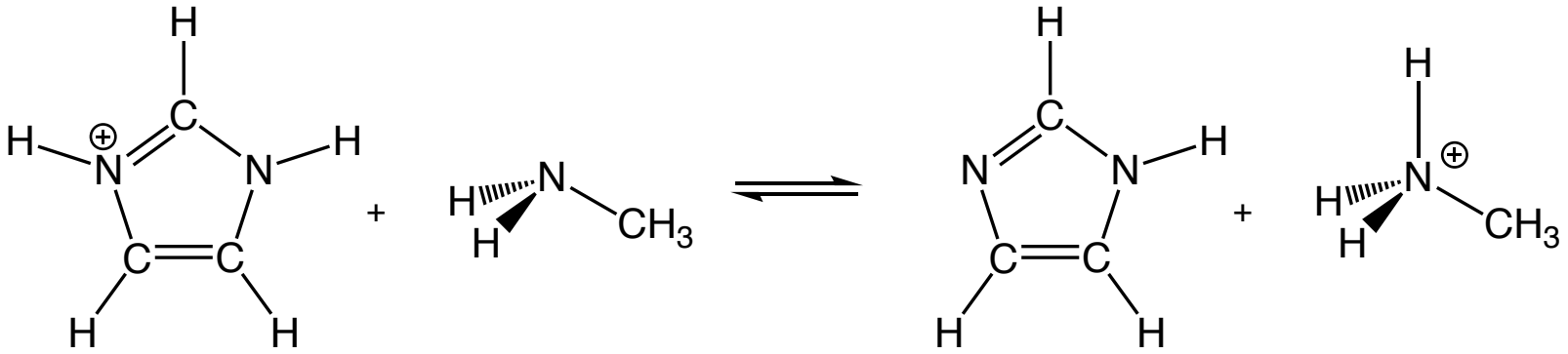

H
Cl
H
H_3C
O


N
H
H_3C
CH_3
H
H_3C
O


H
Cl
H
H3C
O
Cl
H3C
O
H
H


N
H3C
H
CH3

H
H3C
O



$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$pK_a = -\log K_a$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

pK_a - Which is the strongest acid?

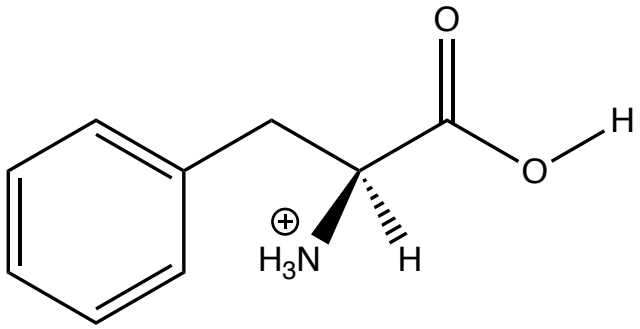
$pK_a \sim 50$ CH_4

$pK_a \sim 36$ NH_3

$pK_a = 14.0$ H_2O

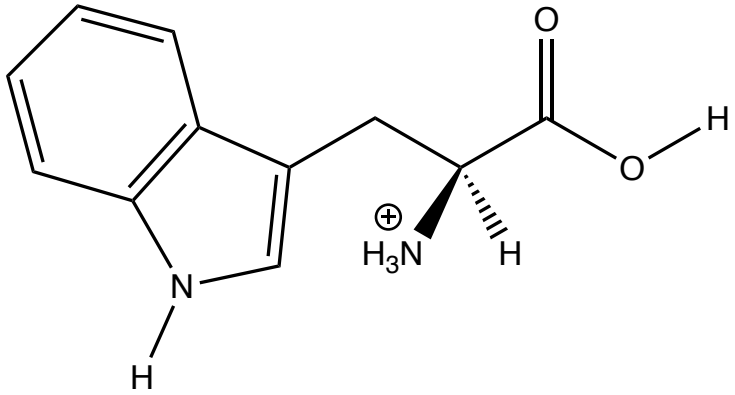
$pK_a = 3.18$ HF

pK_a - Which is the stronger acid?



phenylalanine

pK_a = 1.83



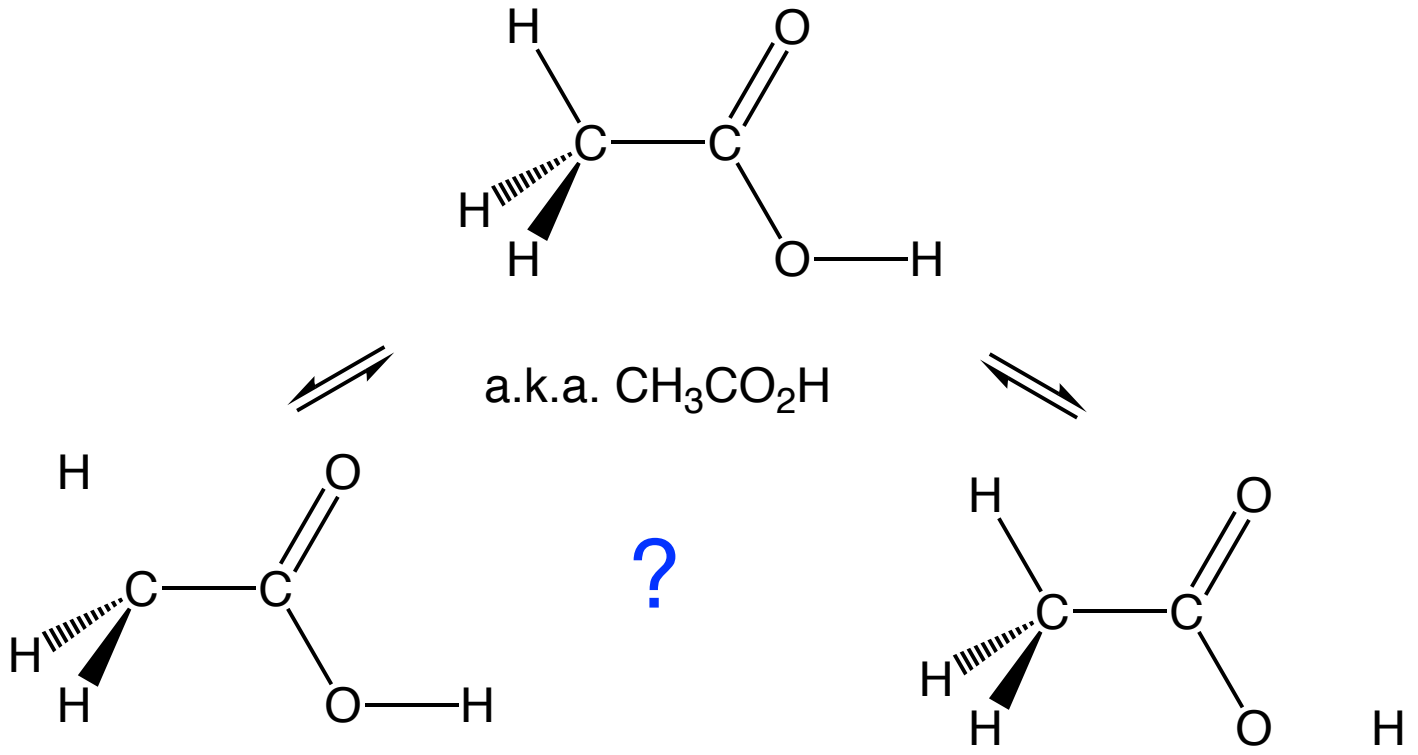
tryptophan

pK_a = 2.83

pK_a values from Organic Chemistry, 10th ed. McMurry, (2023) openstax.

Which is the acidic H^+ in acetic acid ($HC_2H_3O_2$)?

Section 2.7, 2.8



The one that leaves the more/most stable base behind

Same Period More Positive Nucleus

pK_a ~ 50 CH_4

pK_a ~ 36 NH_3

pK_a = 14.0 H_2O

pK_a = 3.18 HF

Same Column Larger Valence Shell

HI

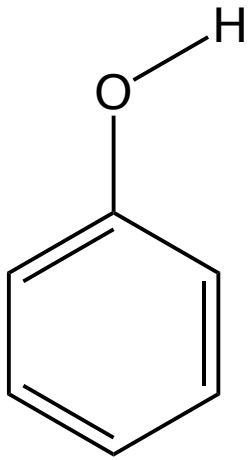
HBr

HCl

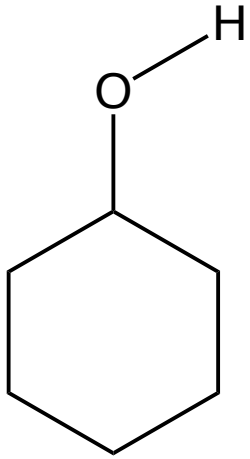
HF

pK_a's HF, 3.18 HCl, -7 HBr, -9 HI, -10

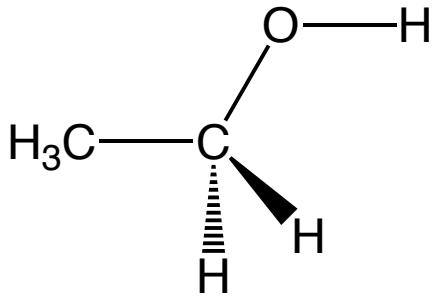
Resonance



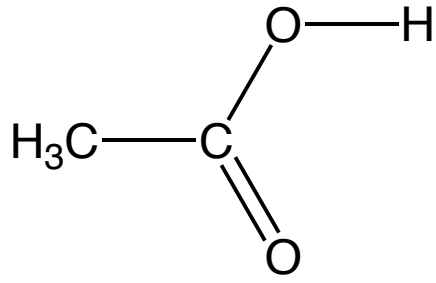
phenol



cyclohexanol



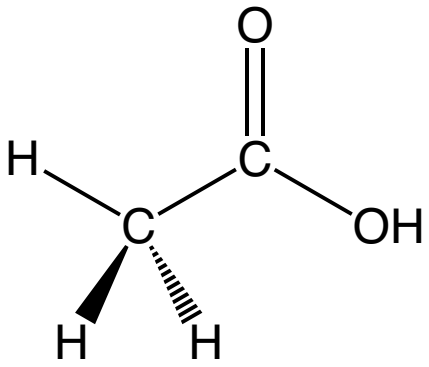
ethanol

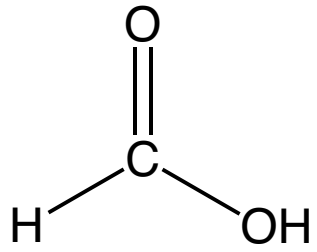


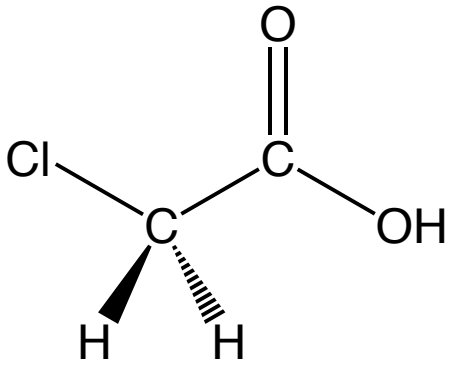
acetic acid

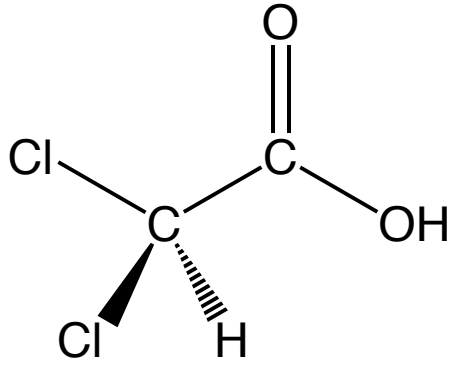
pK_a's cyclohexanol, 16.0 phenol, 10.0 ethanol 16.0 acetic acid 4.74

Inductive Effect



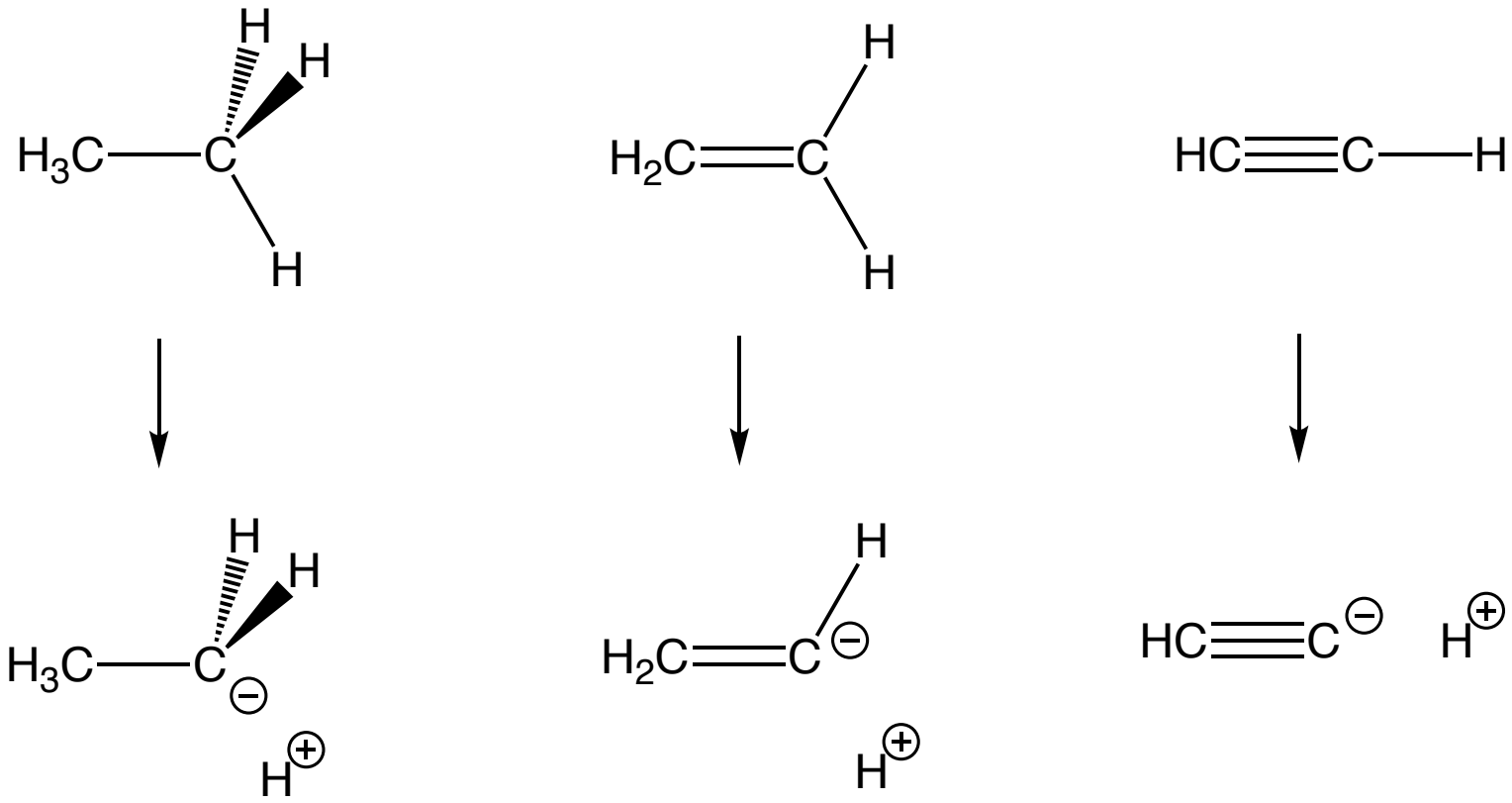






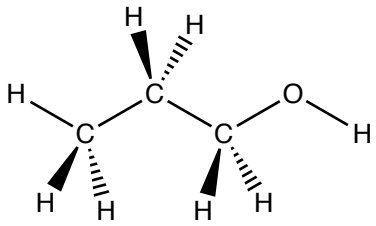
acetic, 4.76; formic, 3.75; chloroacetic, 2.87; dichloroacetic, 1.25

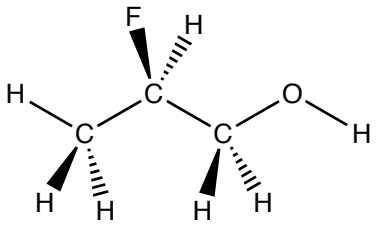
Greater s character

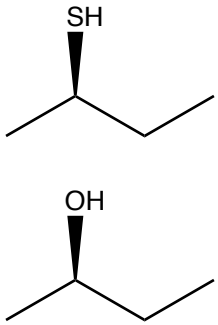


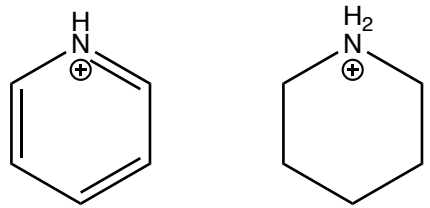
pK_a's ethane 50, ethene 44, ethyne 25

Practice: For each molecule, which proton is the most likely to be lost and for each pair, which is the stronger acid









Collectively referred to as...

intermolecular forces, van der Waals forces, or noncovalent interactions

London Dispersion Forces (LDF)

- All molecules interact with other molecules using LDFs
- Interaction between spontaneous, random dipoles and induced dipoles
- Weak for molecules with few valence electrons and low surface area
- Strength increases with increasing valence electrons, surface area, and volume

Dipole-dipole interactions

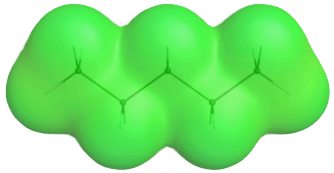
- Occurs between opposite ends of dipoles on polar molecules
- Presence of dipole dipole interactions can have a substantial affect on attraction between molecules

H Bond interactions

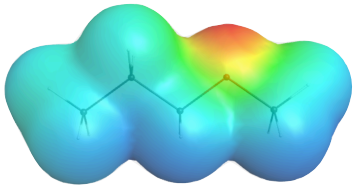
- Occurs between H-bond donors and H-bond acceptors
- The strongest of these intermolecular forces (on an interaction by interaction basis)
- Important for water solubility and in biochemistry

Collectively referred to as...

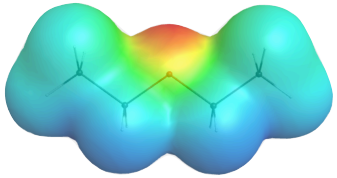
intermolecular forces, van der Waals forces, or noncovalent interactions



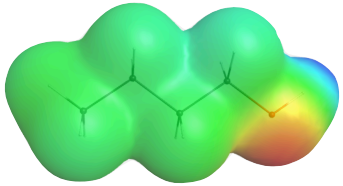
35.9 °C



40.2 °C



36.4 °C

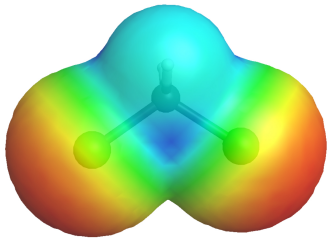


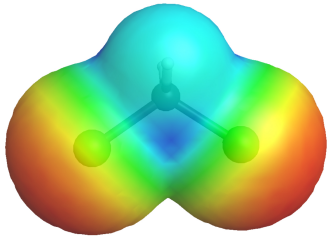
117 °C

Collectively referred to as...

intermolecular forces, van der Waals forces, or noncovalent interactions

dipole-dipole interactions

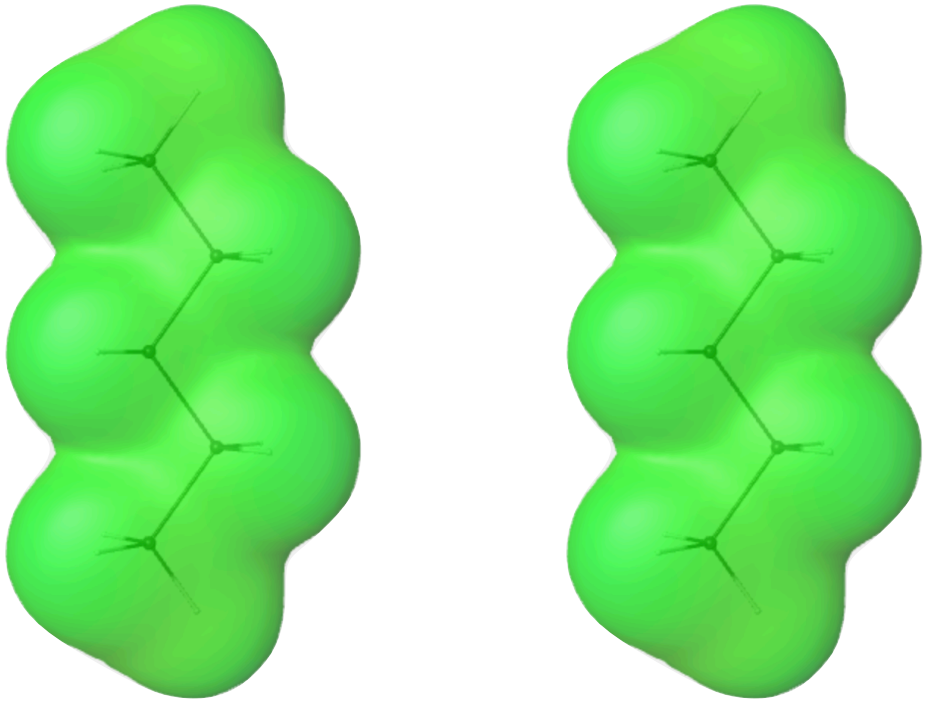




Collectively referred to as...

intermolecular forces, van der Waals forces, or noncovalent interactions

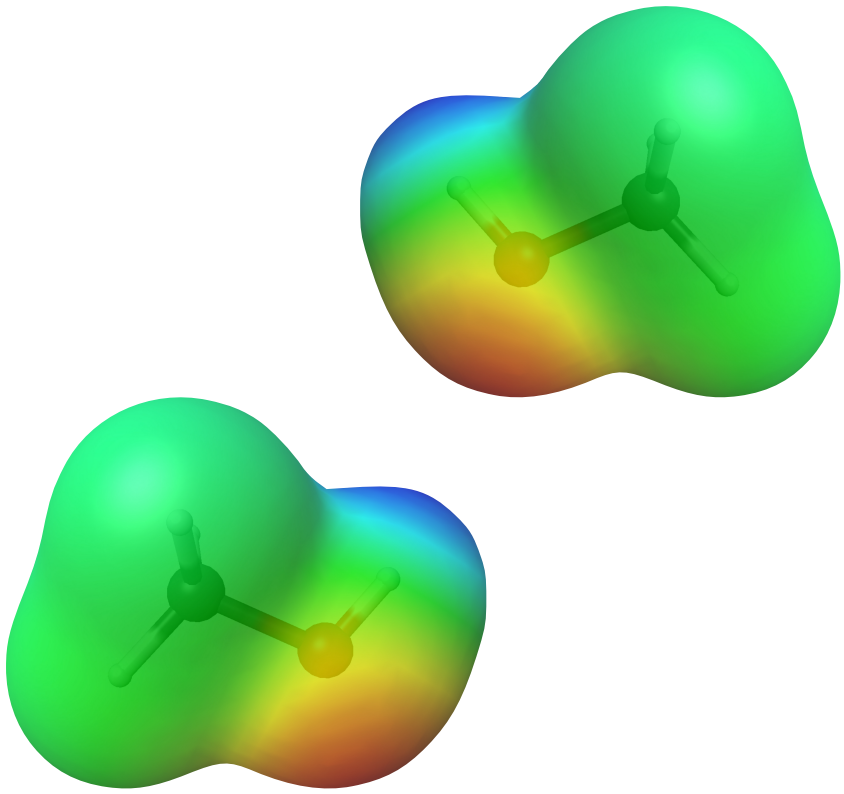
London dispersion forces (sometimes called dispersion forces)



Collectively referred to as...

intermolecular forces, van der Waals forces, or noncovalent interactions

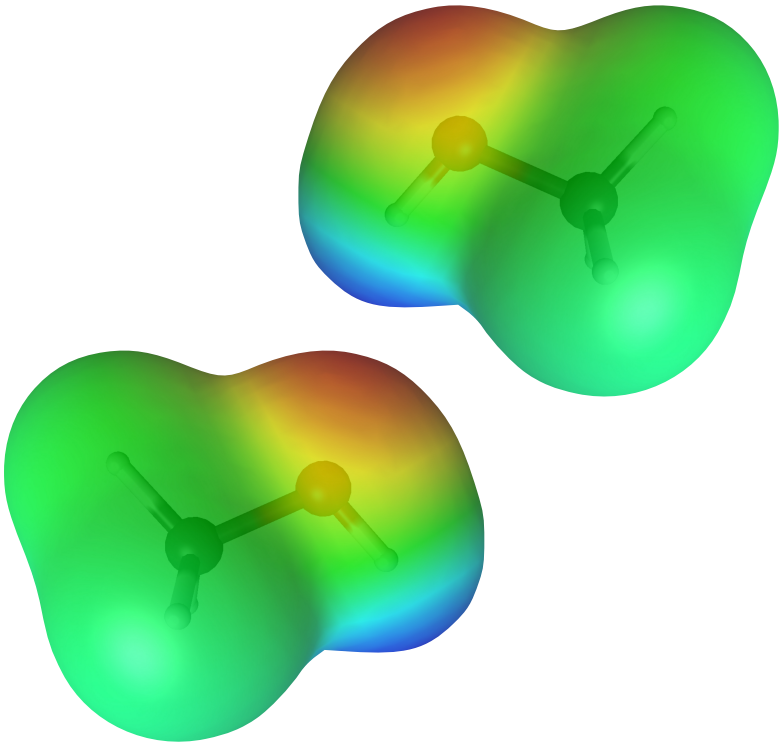
Hydrogen bonds or H-bonds



Collectively referred to as...

intermolecular forces, van der Waals forces, or noncovalent interactions

A hydrogen bond requires an H-Bond donor and an H-bond acceptor

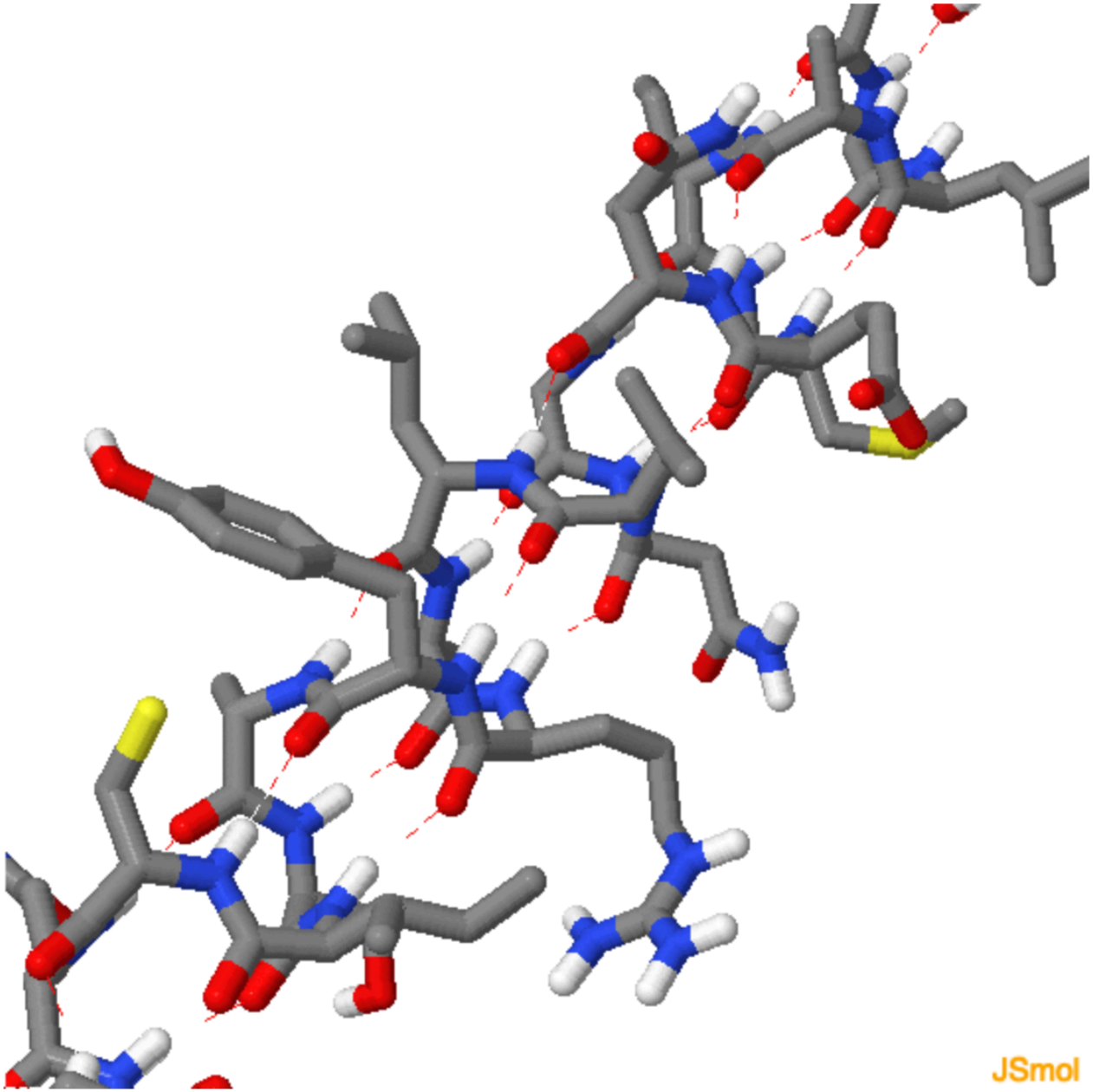


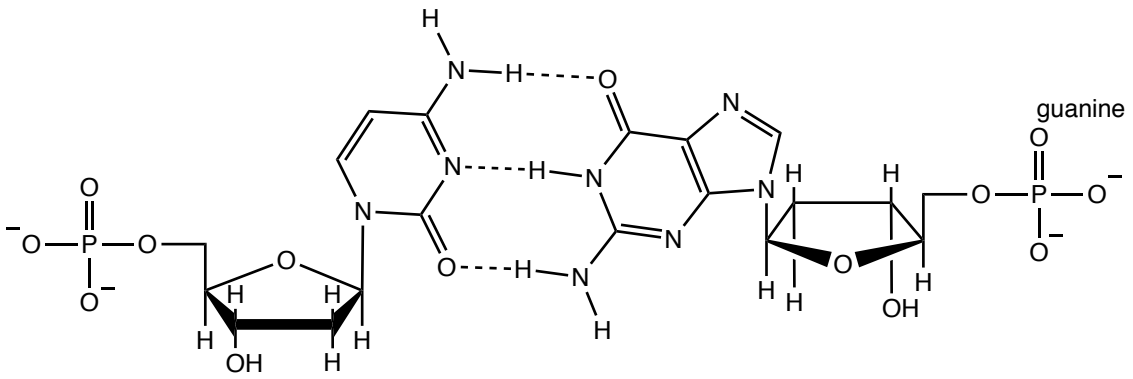
H-bond donor

any H atom that is covalently bonded to an N, O, or F atom

H-bond acceptor

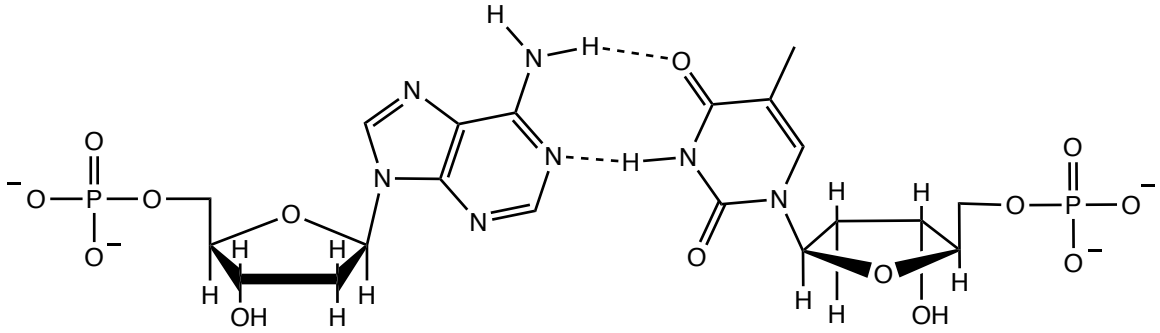
any N, O, or F atom


JSmol



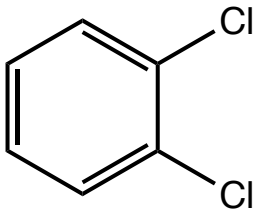
deoxycytidine monophosphate

deoxygaunosine monophosphate



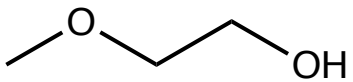
deoxyadenosine monophosphate

deoxythymidine monophophate



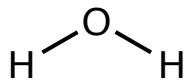
1,2-dichlorobenzene

dipole moment = 2.14 D*



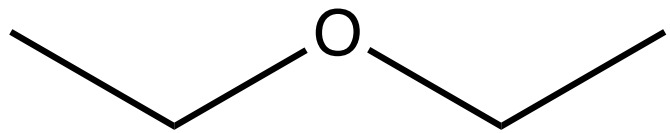
2-methoxyethanol

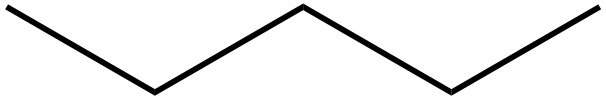
dipole moment = 2.04 D*



dipole moment = 1.87 D*

*https://macro.lsu.edu/Howto/solvents/dipole%20moment.htm accessed Oct. 16, 2023





60 g/L and 0.038 g/L