

## CHE 2060: Principles of Organic Chem



### 2. Introduction to organic structure & bonding, II

#### 2.1: Covalent bonding in organic molecules

- A. The  $\sigma$  bond in the H<sub>2</sub> molecule
- B. sp<sup>3</sup> hybrid orbitals and tetrahedral bonding
- C. sp<sup>2</sup> and sp hybrid orbitals and  $\pi$  bonds

VSEPR

#### 2.2: Molecular orbital theory

- A. Another look at the H<sub>2</sub> molecule using MO theory
- B. MO theory and conjugated  $\pi$  bonds
- C. Aromaticity

#### 2.3: Resonance

- A. What is resonance?
- B. Resonance contributors for the carboxylate group
- C. Rules for drawing resonance structures
- D. Major vs minor resonance contributors

#### 2.4: Non-covalent interactions

- A. Dipoles
- B. Ion-ion, dipole-dipole, ion-dipole interactions
- C. Van der Waals forces
- D. Hydrogen bonds
- E. Noncovalent interactions and protein structure

#### 2.5: Physical properties of organic compounds

- A. Solubility
- B. Boiling and melting points
- C. Physical properties of lipids and proteins

1

## 2. Intro to organic structure & bonding II



### Big ideas?

1. **Orbitals hybridize** to allow atoms to form varied structures and geometries.
2. **Resonance** extends the idea of the probable location of electrons from atoms to molecules, and provides unexpected stability.

2

## 2. Intro to organic structure & bonding II



### 2.1: Covalent bonding in organic molecules

- A. The  $\sigma$  bond in the  $H_2$  molecule
- B.  $sp^3$  hybrid orbitals and tetrahedral bonding
- C.  $sp^2$  and  $sp$  hybrid orbitals and  $\pi$  bonds

3

## 2. Intro to organic structure & bonding II



### 2.1A: The $\sigma$ bond in the $H_2$ molecule

- Process
- Energetics
- Length & strength
- Orbitals, not sticks

4

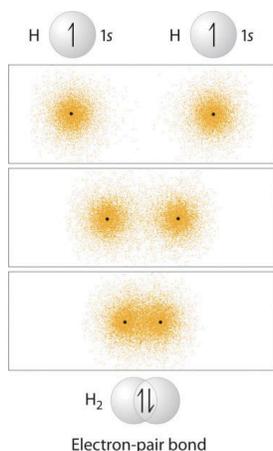
## Valence bond theory



In **valence bond theory**, bonds form when two atomic orbitals overlap.

- This brings two atoms together.
- And the **covalent bond** forms when each shares one electron.

This concept is most easily understood using **unhybridized s and p orbitals**.



Here we can see that the hydrogen gas molecule ( $H_2$ ) forms when two hydrogen atoms approach, make contact and overlap.

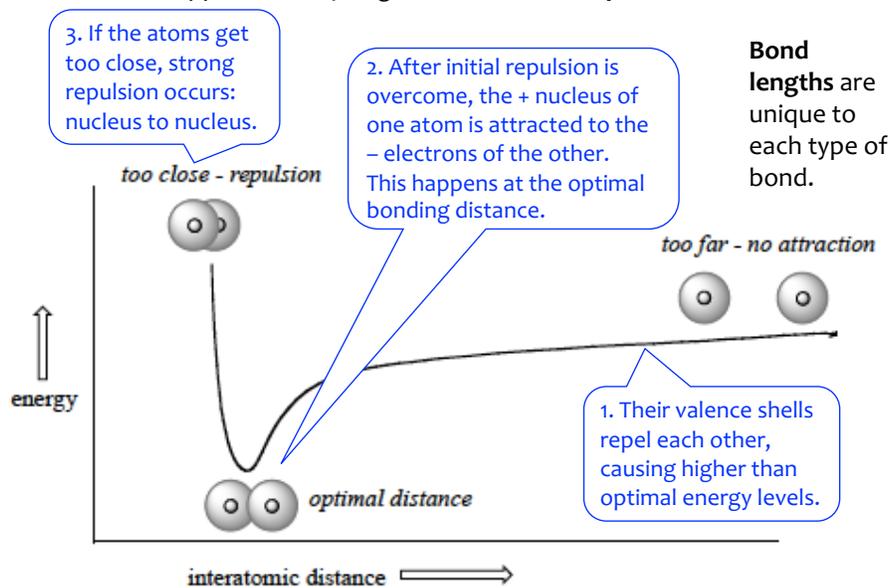
Once they overlap, the two atoms share their single electrons ( $\uparrow\downarrow$ ) form a shared electron pair, or **covalent bond**.

5

## Energetics for bond formation



As two atoms approach, they begin to **exert forces upon each other**.



6

## Examples of bond length & strength



Here are a few examples of **covalent bond lengths and energies (strengths)**.

Notice these trends:

- the number of bonds **decreases** bond length; but
- **Increases** bond energies

But, bond lengths and strengths depend on the **nature of the bonded atoms**.

| Bond         | Length (pm) | energy (kJ/mol) |
|--------------|-------------|-----------------|
| H - H        | 74          | 432             |
| C - H        | 109         | 411             |
| C - C        | 154         | 346             |
| C = C        | 134         | 602             |
| C $\equiv$ C | 120         | 835             |
| C - O        | 143         | 358             |
| C = O        | 120         | 799             |
| C $\equiv$ O | 113         | 1072            |

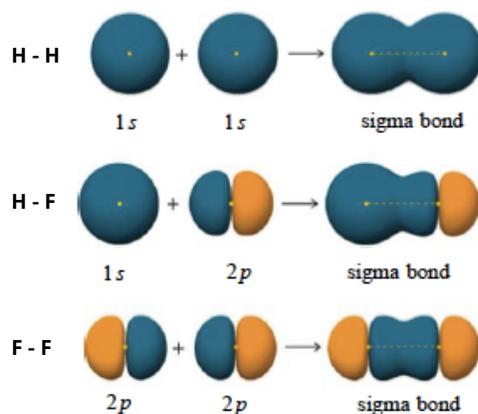
7

## Bonds: orbitals rather than sticks



Rather than thinking of covalent bonds as sticks between atoms, we should think of bonds as the shapes (probabilities) formed by **overlapping atomic orbitals**.

- These are **molecular orbitals**: *mathematical functions describing the wave-like behavior of an electron in a molecule.*



**Sigma ( $\sigma$ ) bonds** are single covalent bonds formed by the overlap of orbitals.

- Shared pair of electrons
- Cylindrical shape
- Free rotation

8

## Can you?



- (1) Define the term 'covalent bond'?
- (2) Describe the process, and forces, occurring as two atoms approach and bond?
- (3) Describe the energetics of covalent bond formation?
- (4) Describe the range of covalent bond lengths and strengths?
- (5) Draw overlapping s or p orbitals to create a more realistic image of covalent bonding?

9

## 2. Intro to organic structure & bonding II



### **2.1B $sp^3$ hybrid orbitals & tetrahedral bonding**

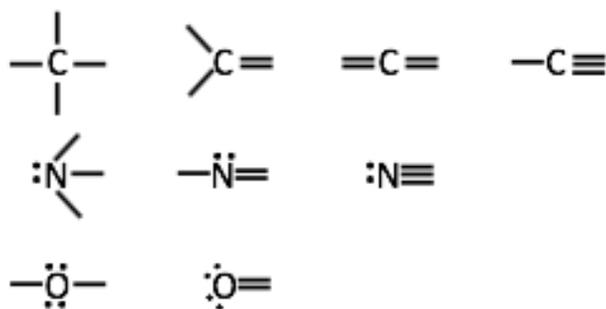
- *Hybridization allows methane*
- *Slot-arrow diagrams*
- *VSEPR*
- *Dash-wedge '3D' drawings*
- *Free rotation around  $\sigma$  bonds*

10

## How: one configuration many patterns?



How can carbon (and oxygen, nitrogen, sulfur, etc.,) have just a single **ground state electron configuration** but **many bonding patterns** that allow no formal charge?



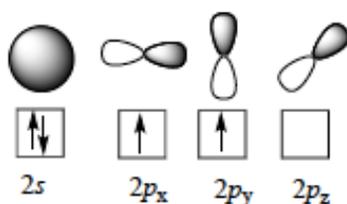
11

## Methane: a contradiction?



Remember the **valence electron configuration** of carbon?

- $1s^2 2s^2 2p^2$



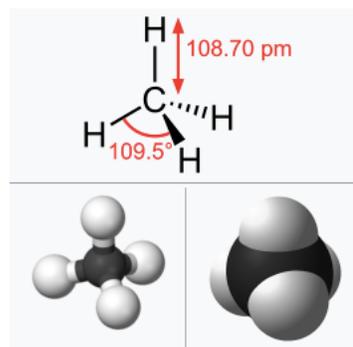
Now think about methane,  $\text{CH}_4$ .

- Draw its Lewis dot structure.
- Build a molecular model.

**Experimental work shows that:**

- Methane has a **tetrahedral geometry**.
- Its four C-H bonds have **equal lengths and strengths**.

So, how can electrons in different orbitals form equivalent bonds?



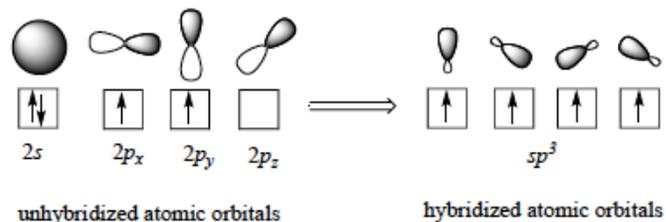
<https://en.wikipedia.org/wiki/Methane>

12

## Hybrid orbitals explain methane

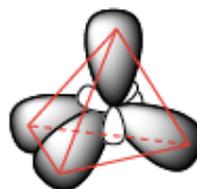


If the orbitals of carbon are **hybridized** we can explain the structure of methane and all other carbon-based molecules.



Once hybridized, all four of carbon's electrons occupy identical ( $sp^3$ ) orbitals with identical energy levels.

- Thus, they can form equal bonds with hydrogen.



**Tetrahedral:**  
All angles are  $109.5^\circ$ .

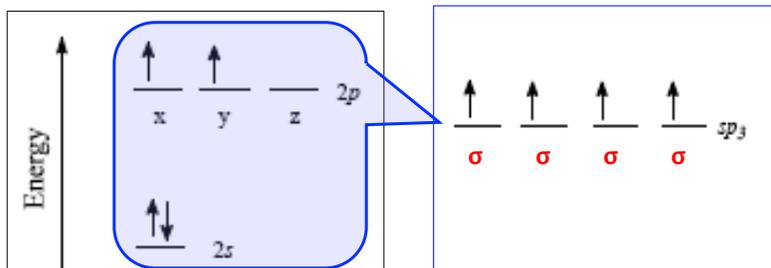
<http://www.chemtube3d.com/orbitalshybrid.htm>

13

## A closer look at $sp^3$ hybridization



Using **slot-arrow diagrams** can help explain how hybridization works.



### unhybridized carbon

Unhybridized carbon cannot form – or explain – methane's four equal bonds.

Instead, all four of carbon's electrons must be in identical orbitals.

### $sp^3$ hybridized carbon

All four orbitals (1s and 3p) are 'blended' to create four equal orbitals with identical energy levels.

- $sp^3 = 1s + 3p$
- $sp^3$  energy level is much closer to p than to s.

14

## Try this:



What types of orbitals overlap to form chloroform, trichloromethane ( $\text{CHCl}_3$ )?

C:  $2s^2 2p^2 \rightarrow$  hybridizes to four  $2sp^3$  orbitals

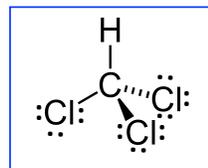
H:  $1s^1$

Cl:  $3s^2 2p^5$

Bonds:

C – H =  $sp^3 - s$

C – Cl =  $sp^3 - p$



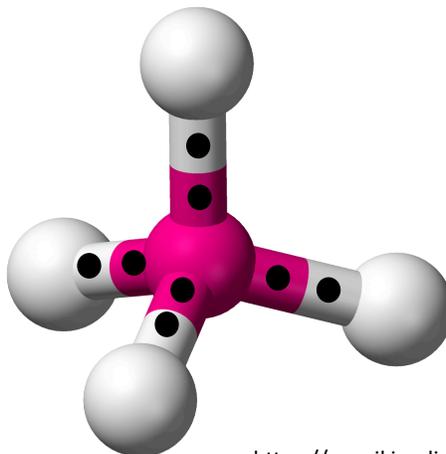
15

## VSEPR explains geometry



Hybrid orbital geometry is dictated by **VSEPR** (*valence shell e- pair repulsion*)

***“Since e- pairs occupying orbitals are all negatively charged they repel each other & therefore occupy spaces as far from other pairs as possible.”***



[https://en.wikipedia.org/wiki/VSEPR\\_theory](https://en.wikipedia.org/wiki/VSEPR_theory)

16

## Using VSEPR



| # lone e- pr | # atoms bonded | e- pair geometry     |  | Molecular geometry   | Bond Angle (°) |
|--------------|----------------|----------------------|--|----------------------|----------------|
| 0            | 2              | linear $sp$          |  | linear               | 180            |
| 0            | 3              | trigonal planar      |  | trigonal planar      | 120            |
| 1            | 2              | trigonal planar      |  | bent                 | < 120          |
| 0            | 4              | tetrahedral          |  | tetrahedral          | 109.5          |
| 1            | 3              | tetrahedral          |  | trigonal pyramidal   | < 109.5        |
| 2            | 2              | tetrahedral          |  | bent                 | < 109.5        |
| 0            | 5              | trigonal bipyramidal |  | trigonal bipyramidal | 90, 120, 180   |
| 1            | 4              | trigonal bipyramidal |  | seesaw               | 90, 120, 180   |
| 2            | 3              | trigonal bipyramidal |  | T-shaped             | 90, 180        |
| 3            | 2              | trigonal bipyramidal |  | linear               | 180            |
| 0            | 6              | octahedral           |  | octahedral           | 90, 180        |
| 1            | 5              | octahedral           |  | square pyramidal     | 90, 180        |
| 2            | 4              | octahedral           |  | square planar        | 90, 180        |

<http://intro.chem.okstate.edu>

17

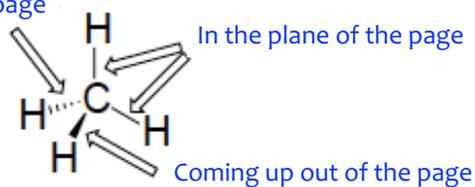
## Dash-wedge drawings are '3D'



So, how do we show 3D structure using 2D paper and pens, chalkboards or whiteboards?

**Dash-wedge** structures provide some 3D information.

Going back into the page



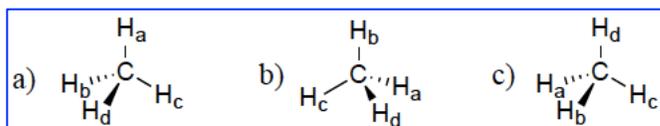
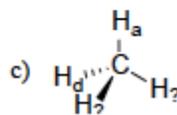
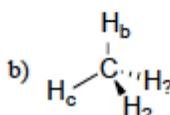
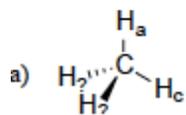
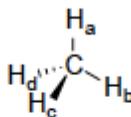
18

## Try this:



In a-c, the methane molecule shown at the right is rotated and flipped.

- Draw the missing hydrogen atom labels. (Make a model!)



19

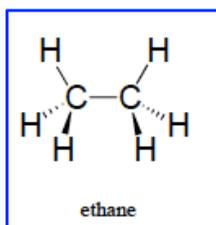
## Try this:



Ethane is C<sub>2</sub>H<sub>6</sub>.

- Draw the line-bond structure.
- Use VSEPR to determine the orbital hybridization of the carbon atoms.
- What is the molecular geometry?
- Use dash-wedge to represent the molecule's 3D structure.

VSEPR: Each carbon is bonded to four atoms and as no lone pairs. So, both carbons are sp<sup>3</sup> hybridized.



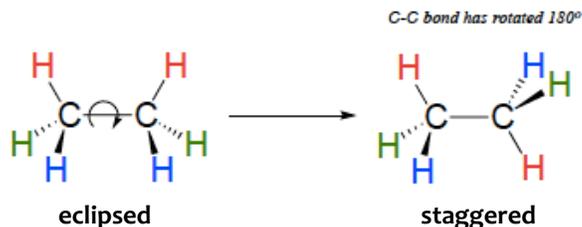
Both sides (or halves) of the molecule are tetrahedral.

20

## Free rotation around sigma bonds



There is **free rotation** around all single (aka sigma,  $\sigma$ ) bonds.



So the hydrogens bonded to the two carbon atoms of ethane can either be lined up with one another (**eclipsed**) or **staggered**.

- The speed and frequency of rotation increase as energy is added to a solution of molecules: heat, mixing, vibration, light, etc.,.

Build a model and rotate methyl groups to convert eclipsed to staggered.

Watch rotation of a space-filling model of ethane.

<https://www.youtube.com/watch?v=V2pr7e9g3E4>

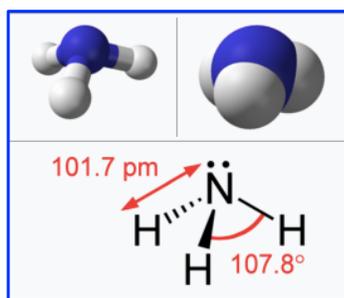
21

## Other $sp^3$ hybridizations



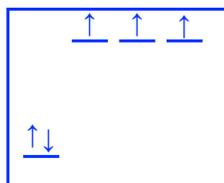
Amines, like ammonia, have  **$sp^3$ -hybridized nitrogen atoms**.

- Create a line-bond drawing of ammonia,  $NH_3$ .
- Use the VSEPR to determine the orbital hybridization of its nitrogen, its electron pair geometry and molecular geometry.
- Use a dash-wedge drawing to show ammonia's 3D structure.
- Create a slot-arrow diagram to show how nitrogen's valence electrons are  $sp^3$ -hybridized.

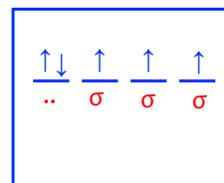


VSEPR: 3 bonds, 1 lone pair

- N is  $sp^3$  hybridized.
- E pair geometry is tetrahedral.
- Molecular geometry is trigonal pyramidal.
- The lone pair closes the H's angle.



unhybridized



$sp^3$  hybridized

<https://en.wikipedia.org/wiki/Ammonia>  
<http://www.chemtube3d.com/gallery/structurepages/nh3.html>

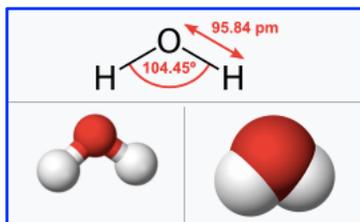
22

## Other $sp^3$ hybridizations



Water has an  $sp^3$ -hybridized oxygen atom.

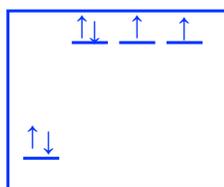
- Create a line-bond drawing of water,  $H_2O$ .
- Use the VSEPR to determine the orbital hybridization of its oxygen, its electron pair geometry and molecular geometry.
- Use a dash-wedge drawing to show water's 3D structure.
- Create a slot-arrow diagram to show how oxygen's valence electrons are  $sp^3$ -hybridized.



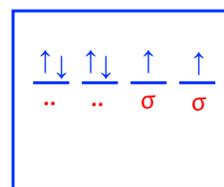
Since all three atoms are in the same plane, there is no need for dashes or wedges.

VSEPR: 2 bonds, 2 lone pairs

- O is  $sp^3$  hybridized.
- E pair geometry is tetrahedral.
- Molecular geometry is bent.
- The lone pairs closes the H's angle.



unhybridized



$sp^3$  hybridized

[https://en.wikipedia.org/wiki/Properties\\_of\\_water](https://en.wikipedia.org/wiki/Properties_of_water)

23

## Can you?



- (1) Explain why unhybridized carbon could not form four equivalent bonds?
- (2) Describe how carbon's orbitals are hybridized to form four equivalent  $sp^3$  orbitals?
- (3) Define the term 'VSEPR' and explain how this concept determines geometry?
- (4) Differentiate between electron pair geometry and molecular geometry?
- (5) Describe the effect of free electron pairs on molecular geometry?

24

## 2. Intro to organic structure & bonding II



### 2.1C: $sp^2$ and $sp$ hybrid orbitals & $\pi$ bonds

- $sp^2$  hybridization for double bonds
  - The  $\pi$  bond
  - Trigonal planar
  - Carbonyls and carbocations
- $sp$  hybridization for triple bonds
  - Two perpendicular  $\pi$  bonds
  - Linear
  - More acidic!

25

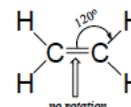
## Ethene: we need a different model



Experimental data shows that the 2-carbon alkene, ethene:

- Is flat, or planar;
- Has bond angles of  $120^\circ$  rather than  $109.5^\circ$ ;
- Has C-C bond lengths of 134 pm rather than the 154 pm seen in ethane; and
- Doesn't have free rotation around the C=C double bond.

So  $sp^3$  hybridized carbons don't explain this.



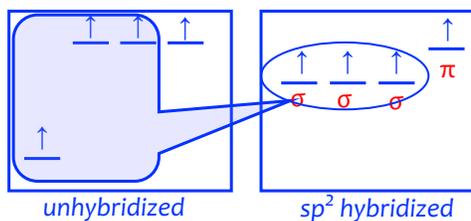
What does?  $sp^2$  hybridized carbons!

**VSEPR?**

- 3 atoms bonded, no free pairs =  $sp^2$  with trigonal planar geometry

The hybridized carbon needs to form three identical  $\sigma$  bonds (to C, H, H) and one double (aka  $\pi$ ) bond.

- So hybridize 3 orbitals
- Leave an unhybridized p

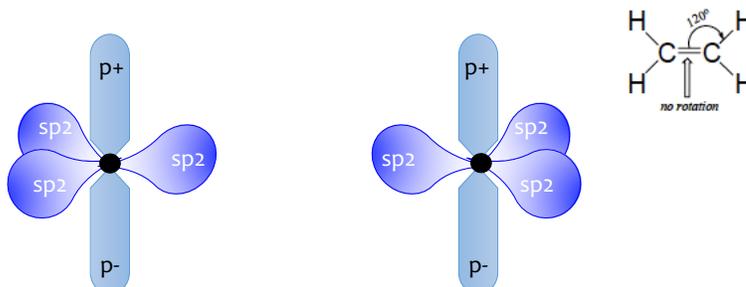


26

## Formation of ethene from $sp^2$ carbons



$sp^2$  hybridized carbons form double bonds to make molecules like  $CH_2CH_2$ , ethene.



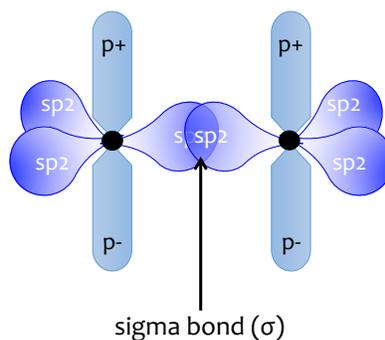
- Each carbon has 3 trigonal planar hybridized  $sp^2$  orbitals and an unhybridized p orbital that is perpendicular to the plane of the  $sp^2$  orbitals.
- Two of the  $sp^2$  orbitals approach to overlap and bond.

27

## Formation of ethene from $sp^2$ carbons



$sp^2$  hybridized carbons form double bonds to make molecules like  $CH_2CH_2$ , ethene.



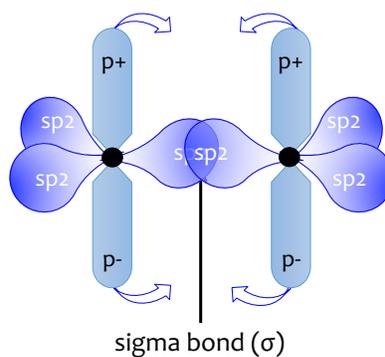
- The overlapping  $sp^2$  orbitals form a sigma (single) bond between the carbons.

28

## Formation of ethene from $sp^2$ carbons



$sp^2$  hybridized carbons form double bonds to make molecules like  $CH_2CH_2$ , ethene.



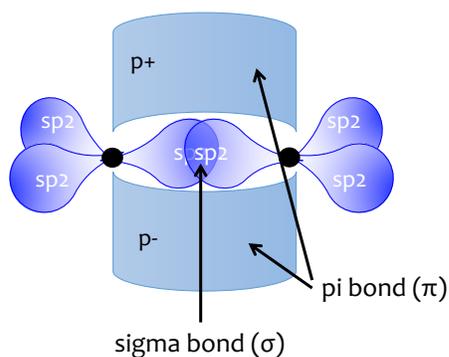
- The overlapping  $sp^2$  orbitals form a sigma (single) bond between the carbons.
- The 2 unhybridized p orbitals bend in towards one another to share  $e^-$ .

29

## Formation of ethene from $sp^2$ carbons



$sp^2$  hybridized carbons form double bonds to make molecules like  $CH_2CH_2$ , ethene.



<http://www.chemtube3d.com/orbitalsethene.htm>

- The parallel p orbitals “fuse” to form a  $\pi$  bond.
- The  $\pi$  bond has both + and – lobe that sit further from the nucleus, above & below the sigma bond.
- The  $\pi$  bond is the “second” bond of the double bond.
- There is no **rotational freedom** around a  $\pi$  bond.

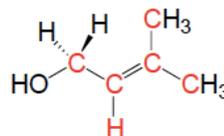
30

## Extent of trigonal planar geometry

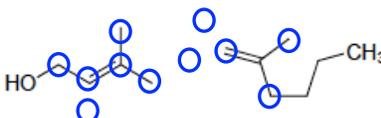


The **trigonal planar geometry** of alkenes extends only as far as the atoms directly bonded to the double-bonded carbons.

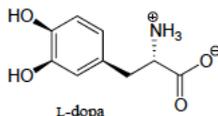
All red atoms are in the same plane.



Redraw the structures below, indicating the six atoms that lie in the same plane due to the carbon-carbon double bond.



What is wrong with the way the structure of L-dopa is drawn?



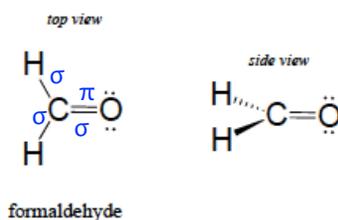
The carbons of the aromatic ring, and all atoms directly connected to them, are planar and can't come forward.

31

## Carbonyl groups are also $sp^2$ hybridized



Formaldehyde is dominated by its **carbonyl group**.



VSEPR shows that both the carbon and oxygen atoms are  $sp^2$  hybridized:

- C:** 3 bonded to, 0 lone pairs
- O:** 1 bonded to, 2 lone pairs

Geometry is **trigonal planar**.

- The lone pairs are also co-planar.

<http://www.chemtube3d.com/orbitalsformaldehyde.htm>

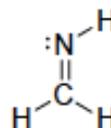
32

## Try this:



Draw the bonding structure for the **imine** shown here. Include:

- Dash-wedge;
- Hybridization of carbon and nitrogen;
- Electron pair geometry; and
- Molecular geometry.



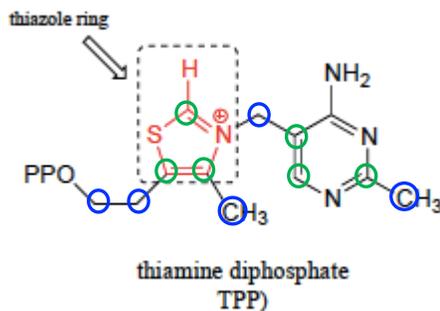
- Dash-wedge isn't necessary as all atoms are trigonal planar (coplanar).
- VSEPR shows that both C and N are  $sp^2$  hybridized.
- C's electron pair geometry and molecular geometry are trigonal planar.
- N's electron pair geometry is trigonal planar, but its molecular geometry is bent.

33

## Try this:



Determine the hybridization of all carbons and label them so.



- $sp^3$  hybridized carbon
- $sp^2$  hybridized carbon

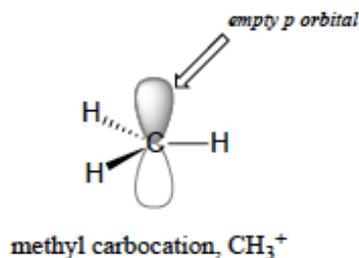
34

## Carbocations are $sp^2$ hybridized



This methyl carbocation's carbon atom is  **$sp^2$  hybridized**.

- Bonded to three atoms; no lone pairs.
- All atoms are trigonal planar.
- There is an empty, unhybridized p orbital perpendicular to the atomic plane or the plane of the  $\sigma$  bonds.

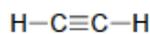


35

## Alkyne carbons are $sp$ hybridized



**Alkyne carbons**, and **nitrile carbons and nitrogens**, are **triple bonded**.



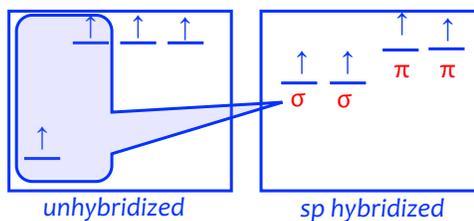
ethyne  
(common name acetylene)

**VSEPR:** 2 atoms bonded to; no lone pairs

- Carbon is  $sp$  hybridized.
- Electron pair and molecular geometries are linear.

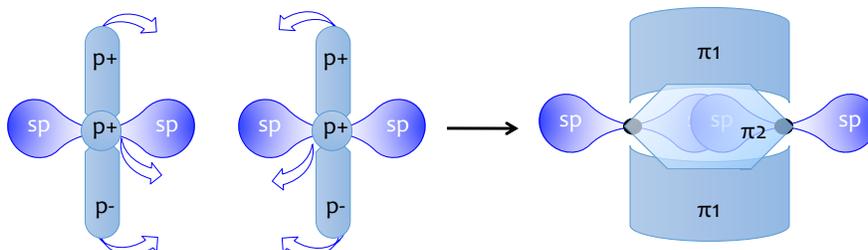
The hybridized carbon needs to form two identical  $\sigma$  bonds (to C, H) and two  $\pi$  bonds.

- So hybridize 2 orbitals
- Leave 2 unhybridized ps



36

## Alkyne formation



- Two sp orbitals overlap to form a single or  $\sigma$  bond.
- Two sets of parallel p orbitals bend toward one another & then “fuse” to form 2 perpendicular  $\pi$  bonds.
- Each  $\pi$  bond has both + and – lobe that sit further from the nucleus, above & below the sigma bond.
- The  $\pi$  bonds are the “second” & “third” bonds of the triple bond.
- There is no **rotational freedom** around the bonded carbons.

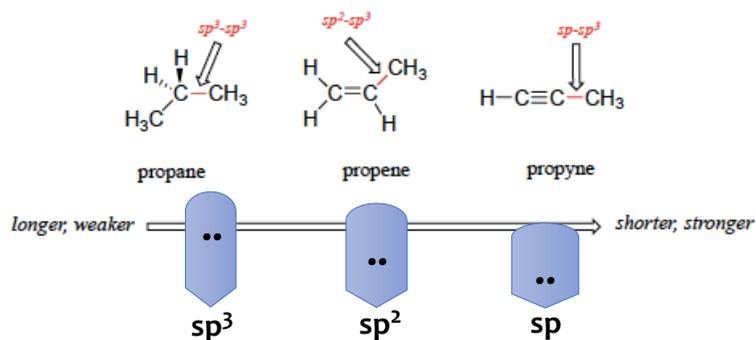
<http://www.chemtube3d.com/orbitalsacetylene.htm>

37

## Hybrid orbitals and bond length



Experimental observation shows that single bonds adjacent to multiple bonds are **shorter** and **stronger** than single bonds that sit next to other single bonds.



**Why?**

S orbitals' **spherical shape** places electrons **closer to their nucleus**, while the elongated shape of p orbitals keeps electrons further from the nucleus.

So, the more '**s**' character hybridized orbitals have, the more tightly their electrons are held and the shorter and stronger the bonds they form.

38

## Try this:



What kinds of orbitals are overlapping in bonds b-i indicated below?

- Be sure to distinguish between  $\sigma$  and  $\pi$  bonds.
- An example is provided for bond 'a'.

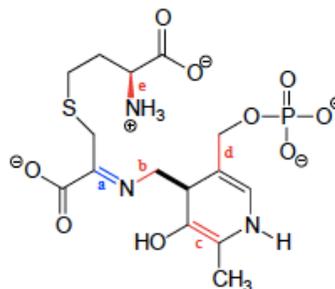
b:  $\sigma$  = overlap of N's  $sp^2$ , C's  $sp^3$

c:  $\sigma$  = overlap of  $sp^2$  orbitals of both Cs

$\pi$  = overlap of unhybridized p orbitals of both Cs

d:  $\sigma$  = overlap of  $sp^2$  orbital of the lower C with an  $sp^3$  orbital of the upper C

e:  $\sigma$  = overlap of  $sp^3$  orbitals of both the C and the N



intermediate compound in amino acid metabolism

Bond a:

- $\sigma$  bond: overlap of  $sp^2$  orbital on N and  $sp^2$  orbital on C
- $\pi$  bond: overlap of  $2p$  orbital on N and  $2p$  orbital on C

39

## Can you?



- (1) Understand that some, but not all, orbitals can be hybridized?
- (2) Describe the relative geometry of various forms of hybridized s-p orbitals with unhybridized p orbital?
- (3) Describe how and why two neighboring unhybridized p orbitals form a  $\pi$  orbital?
- (4) Draw and describe the shape of a  $\pi$  orbital and the location of its electrons?
- (5) Describe and draw the relative geometries of the  $\sigma$  and  $\pi$  bonds of double and triple bonds?
- (6) Explain why hybrid orbitals with more 's character' hold their electrons more tightly than those with more 'p character'?

40

## 2. Intro to organic structure & bonding II



### 2.2: Molecular orbital theory

- A. MOT: molecular orbital theory
- B. Conjugated  $\pi$  bonds
- C. Aromaticity

41

## 2. Intro to organic structure & bonding II



### 2.2A: Another look at H<sub>2</sub> using molecular orbital theory

- *# atomic orbitals = # molecular orbitals*
- *Bonding orbital fill, anti-bonding orbitals don't*
- *MO: constructive & destructive wave functions*

42

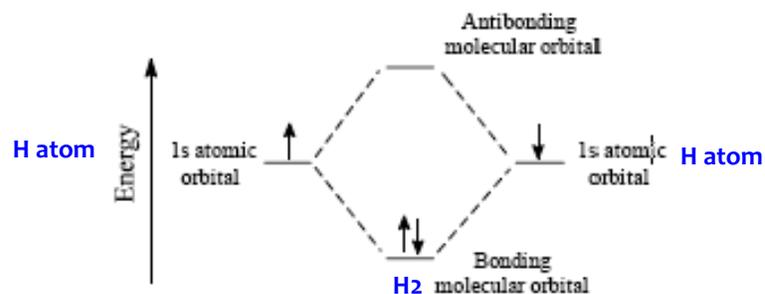
## Bonding and antibonding... huh?



When two atomic orbitals overlap, two **molecular orbitals** are formed.

The bonding MO has a lower energy level than the antibonding MO.

The **lower energy orbital (bonding) is occupied**.



Notice that when the two H atoms bond, the overall energy state drops.

The molecule, H<sub>2</sub>, forms because it allows the atoms to be in a lower energy state.

**Lower energy states rule!**

Dailey & Dailey

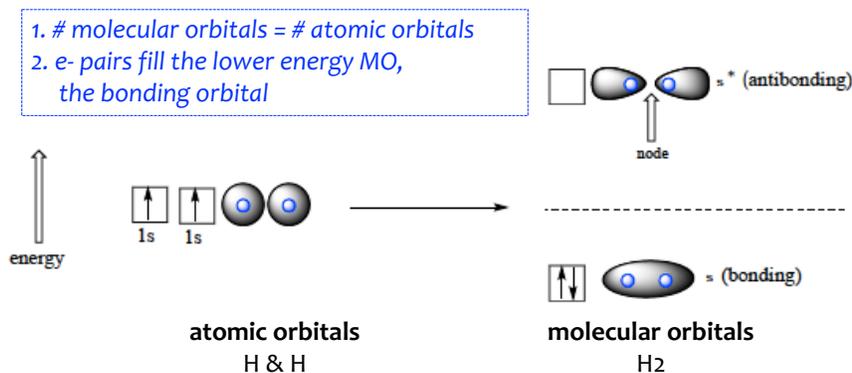
43

## Molecular orbital theory



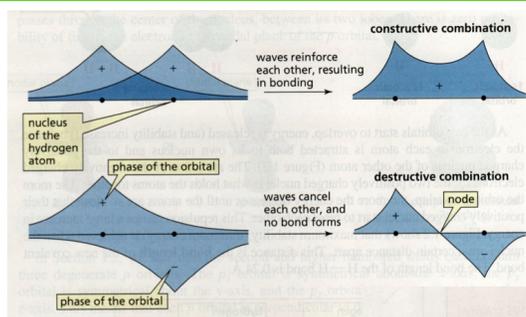
**Molecular orbital theory (MOT):** *molecular orbitals* describes the space around two or more **bonded atoms** in which their valence electrons are likely to be found.

- This view of bonding explains the special properties of resonance, critical in many organic compounds and reactions.



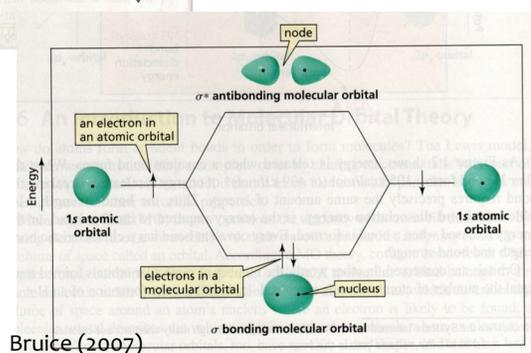
44

## Think about wawicles



When electron waveicles combine **constructively** they produce a bonding orbital: areas of **high electron probability**.  
But destructive interaction cancels out, probability: antibonding orbital or **node**.

Notice that a **node** separates the nuclei of the two atoms in the anti-bonding orbital, while the bonding orbital allows the two nuclei to share electrons.



45

## Can you?



- (1) Define the term 'molecular orbital'?
- (2) Predict the number of a compound's molecular orbitals from the number of its atomic orbitals?
- (3) Draw diagrams of the shapes of bonding molecular orbitals vs. anti-boding molecular orbitals?
- (4) Draw energy diagrams of the bonding molecular orbitals vs. anti-bonding molecular orbitals that explain why bonding orbitals fill while anti-bonding orbitals don't?
- (5) Describe how constructive and destructive wave interference contribute to the formation of bonding vs. anti-bonding molecular orbitals?

46

## 2. Intro to organic structure & bonding II



### 2.2B: Conjugated $\pi$ bonds

- Conjugation affects singles in between
- Conjugation increases stability
  - 'resonance-ish'
- $\pi$  are parallel p MOs [sidebar]

47

## Conjugated double bonds?

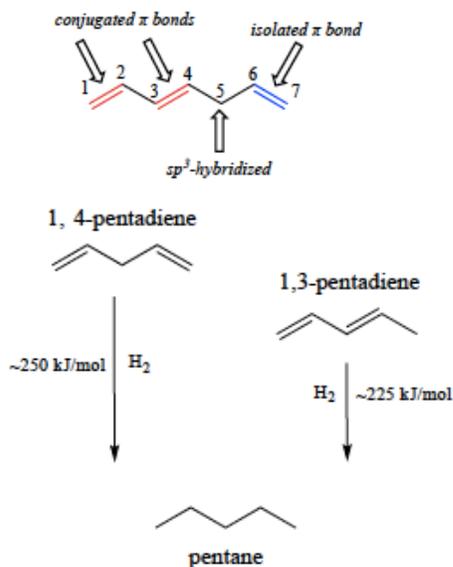


**Conjugated double bonds:** double bonds alternate with single bonds

**Conjugation increases the stability of double bonds.**

- Remember that **energy decreases** as stability increases.
- Isolated double bonds are less stable.

energy ↑

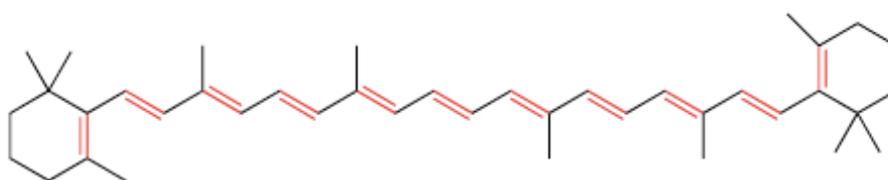
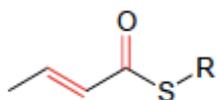


48

## Conjugated examples



Note that the systems of conjugated bonds can involve atoms other than carbon.



$\beta$ -carotene

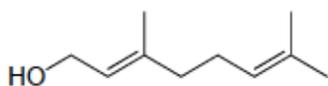
49

## Try this:

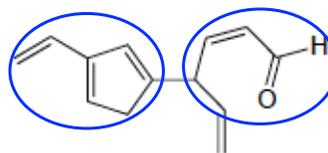


For each of these molecules:

- Identify all the conjugated bonds.
- Count the number of overlapping p orbitals.
- Count the number of electrons involved in  $\pi$  bonds.



No conjugated bonds



**Conjugated bonds:**

- 3 conjugated bonds on the left
  - 6 overlapping p orbitals
  - 6 electrons, one per p
- 2 conjugated bonds on the right
  - 4 overlapping p orbitals
  - 4 electrons, one per p

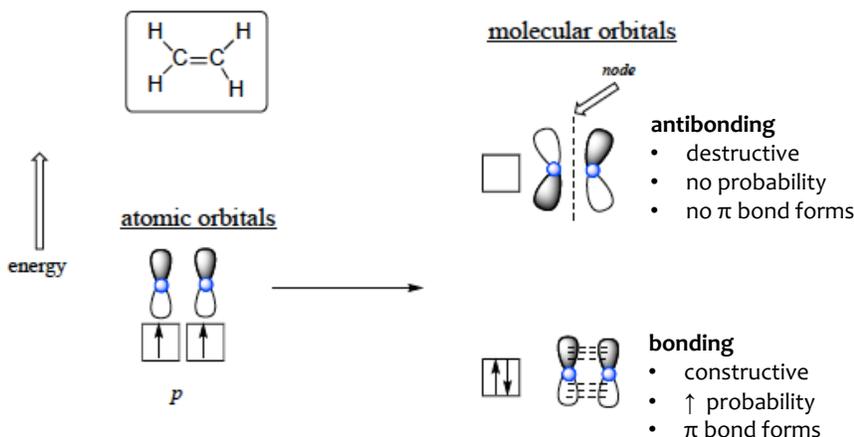
50



## π MO: p orbitals must align for bonding

So, let's start with a simple case of **one, isolated double bond**, ethene.

- And let's focus on p orbitals and π bonds only, ignoring σ bonds.



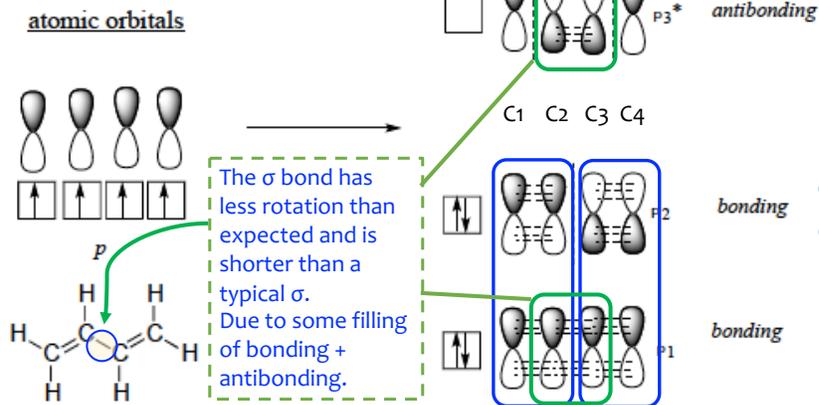
Here 'black' lobes represent the positive part of the wavefunction, while 'empty' lobes represent the negative portion.

53

.....sidebar.....

## MOT for conjugated bonds

- Each of the 4 Cs has one unhybridized p
- There are four possible MOs
- Both antibonding MOs have higher energy than both bonding MOs.
- So, the two antibonding MOs fill.
- Strong π form C1-C2 and C3-C4, and some π character is seen C2-C3 as well.



54

.....sidebar.....

## Can you?



- (1) Identify isolated, conjugated and adjacent (cumulated) double bonds?
- (2) Understand how conjugated double ( $\pi$ ) bonds influence the single ( $\sigma$ ) bonds between the  $\pi$  bonds because of extended  $\pi$  electron delocalization?
- (3) Describe how and why two neighboring unhybridized p orbitals form a  $\pi$  orbital? *[sidebar]*

55

## 2. Intro to organic structure & bonding II

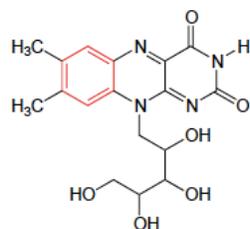


### 2.2C: Aromaticity

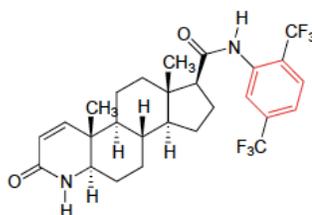
- *Common and important*
- *Definition and Hückel's rule*
- *N in aromatic rings: p not  $sp^2$*

56

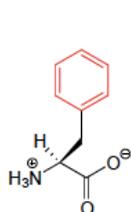
## Aromatics: common and important



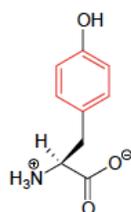
riboflavin  
(a vitamin)



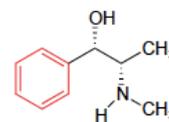
dutasteride  
(GlaxoSmithKline drug for urinary condition in men)



phenylalanine  
(an amino acid)



tyrosine  
(an amino acid)



pseudoephedrine  
(decongestant)

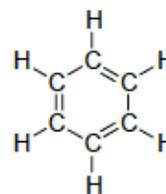
57

## What is aromaticity?



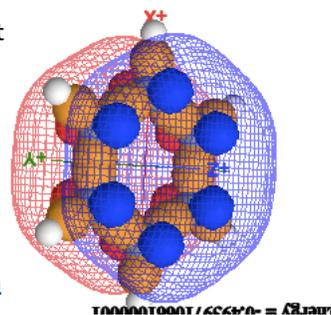
Benzene is the quintessential **aromatic** molecule.

- It is a **cyclic molecule** with **conjugated bonds**.
- Because its bonds are conjugated, their **lengths (138 pm) are intermediate**, between single bonds (154 pm) and double bonds (134 pm).
- And benzene's bonds are **less reactive** than typical single or double bonds.
- Benzene's geometry is **planar**, allowing perfect sharing of adjacent  $\pi$  bonds.



So, put this all together and create a definition for aromaticity!

<http://www.chemtube3d.com/orbitalsbenzene.htm>



58

## Hückel's rule

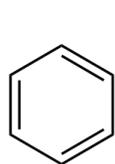


### Criteria for aromaticity:

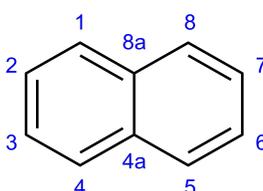
1. Cyclic
2. Planar
3. Ring atoms must be  $sp^2$ -hybridized.
4. Number of resonant ring ( $\pi$ ) electrons must be  $4n+2$ , where  $n$  is any positive integer, including zero.

Hückel's rule: 2, 6, 10, 14, 18

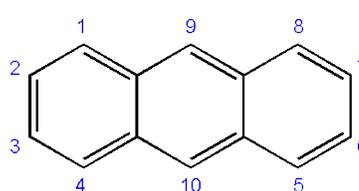
Six is the most common Hückel number, often called the 'aromatic sextet'.



benzene  
Hückel's 6



naphthalene  
Hückel's 10



anthracene  
Hückel's 14

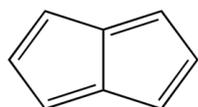
59

## Anti-aromatic

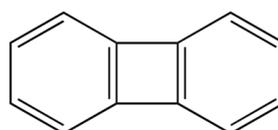


**Anti-aromatic:** cyclic molecules that are  $4n$  rather than  $4n+2$

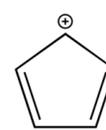
- Conjugated ring systems.
- These molecules look aromatic but **don't obey Hückel's rule.**
  - They're clever **aromatic mimics!**
- Highly unstable and very reactive



$8\pi$   
 $4n$



$12\pi$   
 $4n$



$4\pi$   
 $4n$

60

## Heterocyclic rings: N w/ $sp^2$ lone pairs

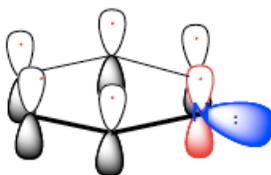


**Heterocyclic rings:** have non-carbon atoms in their rings

- Not necessarily aromatic, but may be.

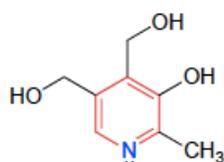


pyridine  
(aromatic)



In all of these cases, the N's :  
don't participate in the  
resonance (aromaticity) of  
their rings.  
And all N : are  $sp^2$ .

**Pyridine** and **pyridoxine**  
are aromatic heterocyclics.



pyridoxine  
(vitamin B<sub>6</sub>)

**Nicotine** has both  
aromatic and  
nonaromatic  
heterocyclic rings.

61

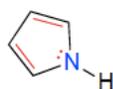
## Heterocyclic rings: N w/ p lone pairs



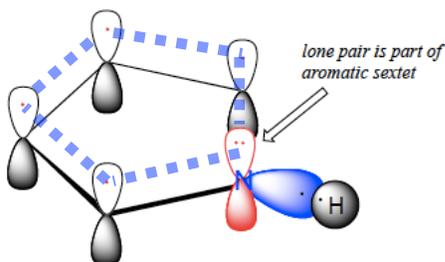
We just saw that when a six-membered ring has three  $\pi$  bonds, the N's :  
is held in an  $sp^2$  and doesn't participate in aromaticity.

**Here, the N's : is needed to create aromaticity!**

- N's  $sp^2$  orbitals form  $\sigma$  bonds.
- N's : is held in an unhybridized p and participate in resonance with the ring's  $\pi$  bonds.
  - **So N's p: are part of the aromatic sextet.**



pyrrole



*lone pair is part of  
aromatic sextet*

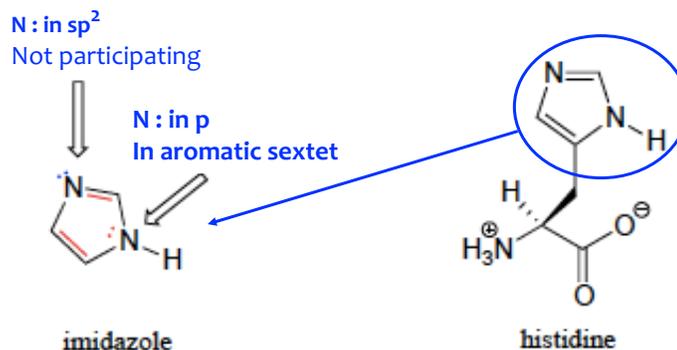
62

## Imidazole has both types of N



Imidazole's ring is **aromatic** and needs one N's lone pair.

- If N : are needed, they are taken!

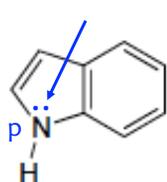


63

## N : in fused rings; in or out of sextet?

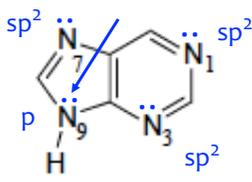


Both indole and purine are **aromatic, planar** and have **fused ring systems**. Both have the same number of  $\pi$  electrons delocalized around both rings.



**indole**

The ring R of tryptophan



**purine**

Similar to A, G bases of DNA, RNA

10 shared ring electrons for each of these fused ring systems

- All  $\pi + :$  indicated by arrows
- If a : is needed it's used.
- If a : isn't needed, it's not used.

### Try this:

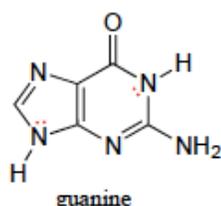
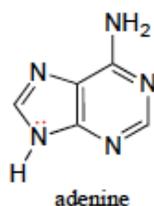
- Add the missing lone pairs.
- How many 'aromatic' or shared ring electrons does each molecule have? Which N lone pairs contribute to aromaticity?
- What orbitals are the lone pairs in?

64

## DNA / RNA bases are aromatic

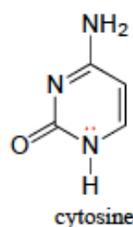
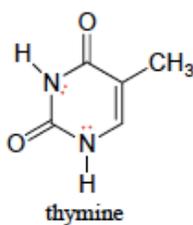
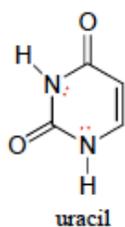


The **five bases of nucleic acids** are aromatic and therefore flat. They must be flat to form the ladders of the double helix.



- 10 shared ring e-
- all  $\pi$  in the ring
  - N : shown in red

How many  $\pi$  electrons does each of these bases have? Circle them.



- 6 shared ring e-
- all  $\pi$  in the ring
  - N : shown in red

<http://www.chem.purdue.edu/jmol/molecules/aden.html>

65

## Can you?



- (1) Describe four characteristics of aromatic compounds?
- (2) Explain Hückel's rule and give examples of carbon rings that have the aromatic sextet?
- (3) Describe how  $sp^2$  hybridized N atoms are incorporated into aromatic rings?
- (4) Describe how unhybridized p orbitals of N atoms become part of the 'aromatic sextet'?
- (5) Distinguish from those ring N atoms that contribute to (and are needed for) aromaticity and those N atoms that do not?

66

## 2. Intro to organic structure & bonding II



### 2.3: Resonance

- A. What is resonance?
- B. Resonance contributors for the carboxylate group
- C. Rules for drawing resonance structures
- D. Major vs minor resonance contributors

67

## 2. Intro to organic structure & bonding II



### 2.3A: Resonance

- *Big challenge of o-chem*
- *Resonance structures (contributors)*
- *Resonance hybrid*

68

## Listen to Soderberg!



Becoming adept at drawing resonance contributors, using the curved arrow notation to show how one contributor can be converted to another, and understanding the concepts of conjugation and resonance delocalization are **some of the most challenging** but also most important jobs that you will have as a beginning student of organic chemistry. If you work hard now to gain a firm grasp of these ideas, you will have come a long way toward understanding much of what follows in your organic chemistry course.

**Conversely, if you fail to come to grips with these concepts now, a lot of what you see later in the course will seem like a bunch of mysterious and incomprehensible lines, dots, and arrows, and you will be in for a rough ride, to say the least.** More so than many other topics in organic chemistry, understanding bonding, conjugation, and resonance is something that most students really need to work on 'in person' with an instructor or tutor, preferably using a molecular modeling kit. Keep working problems, keep asking questions, and keep at it until it all makes sense!

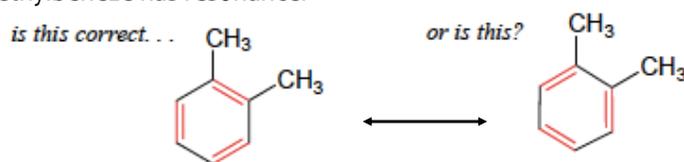
69

## Resonance

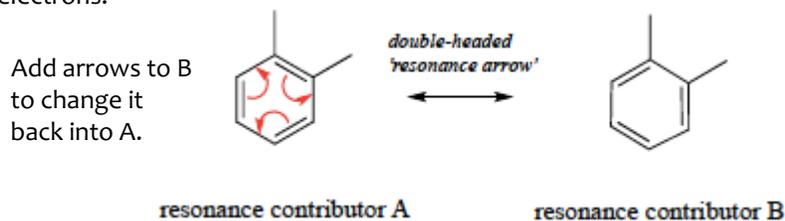


**Resonance:** a property that exists when more than one structures can be drawn for a molecule; the structures must be identical, except for the bonding pattern or arrangement of electrons.

1,2-dimethylbenzene has resonance:



These two **resonance structures** or **contributors** are equivalent. Note that we can use double headed arrows to change 'one' into the 'other' by moving  $\pi$  electrons.



70

## Resonance hybrids

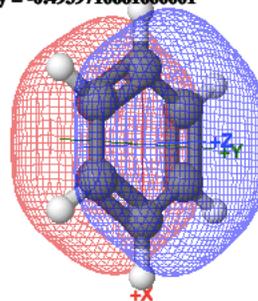


**Resonance hybrids:** a more realistic representation of the concept of resonance that uses dashed lines to show the spread of  $\pi$  electrons over the atoms involved in the conjugated bonds



Remember that there is only one benzene molecule, and it's  $\pi$  electrons spread around the ring.

$y = -0.4939710661000001$



71

## Can you?



- (1) See that resonance is something you must conquer?
- (2) Define the term 'resonance'?
- (3) Define the term 'resonance structures' or 'resonance contributors'?
- (4) Determine the number of resonance structures from the compound's Lewis structure?
- (5) Define the term 'resonance hybrid' and why it is the more realistic representation of resonance?
- (6) Understand that there is only one true structure of a molecule with resonance?

72

## 2. Intro to organic structure & bonding II



### 2.3B: Resonance contributors for the carboxylate group

- Both oxygens are  $sp^2$ !
- Major vs. minor contributors
- Carbocations

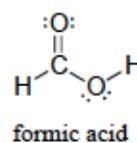
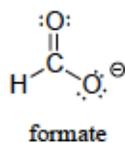
73

## Carboxylates have resonance

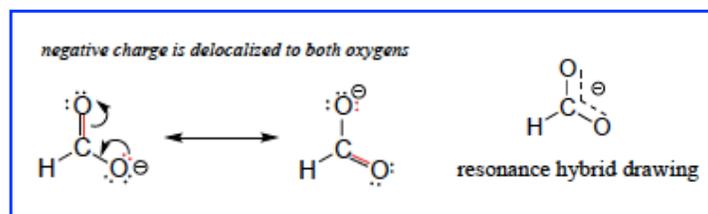


**Carboxylates:** organic anions formed by deprotonation of carboxylic acids

Can you see how  
formate has resonance?



1. Draw all resonance contributors.
2. Use double headed arrows to interconvert them.
3. Draw the resonance hybrid.

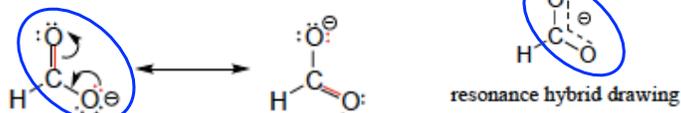


74

## Resonance orbital hybridization: tricky



negative charge is delocalized to both oxygens



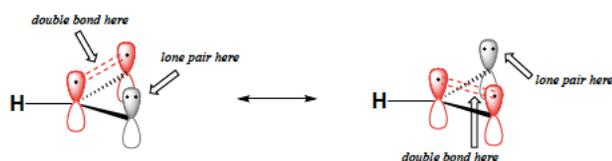
### Observations?

- Trigonal planar geometry
- VSEPR: carbon is  $sp^2$
- Double bonded O is  $sp^2$
- **Isn't the negative O  $sp^3$ ?**

### Nope!

Since formate is really much more like the hybrid, the hybridization of both oxygen atoms must be the same. And they must be capable of  $\pi$  bond formation.

**This suggests all three atoms are  $sp^2$ .**



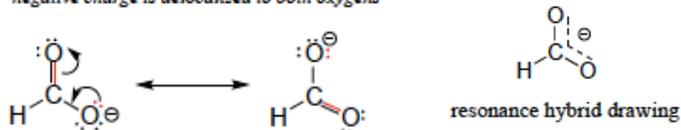
In the hybrid, all three unhybridized p orbitals are parallel and partially overlap to **form a delocalized  $\pi$  bond**. The negative charge is also delocalized.

75

## Try this:

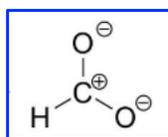


negative charge is delocalized to both oxygens



There is a third, though **very minor resonance contributor** for formate.

- Can you draw it?
- Why is it so very minor?



This is a very minor resonance structure because it's a **carbocation** and because of **immediately proximal opposite charges**.

- It's so **unstable** it won't exist for more than an instant.

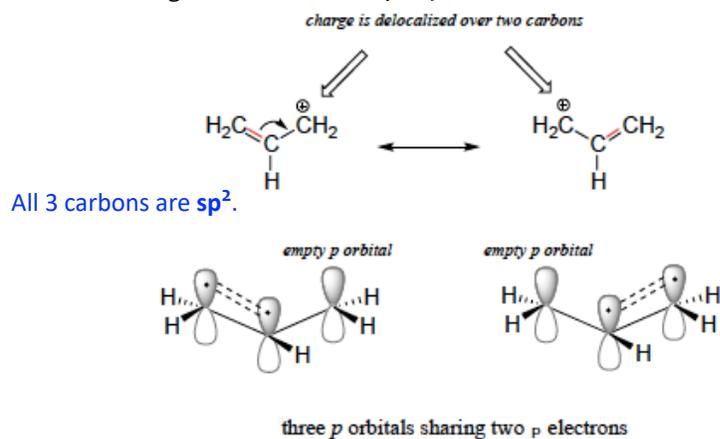
76

## Carbocation resonance



This carbocation has a pair of double-bonded carbons that are clearly  $sp^2$  hybridized.

- Notice that the positively charged carbon is also bonded to three atoms.
- Remember that the positive charge of carbocations is 'carried' by an empty p orbital.
- So the charged carbon is also  $sp^2$  hybridized.

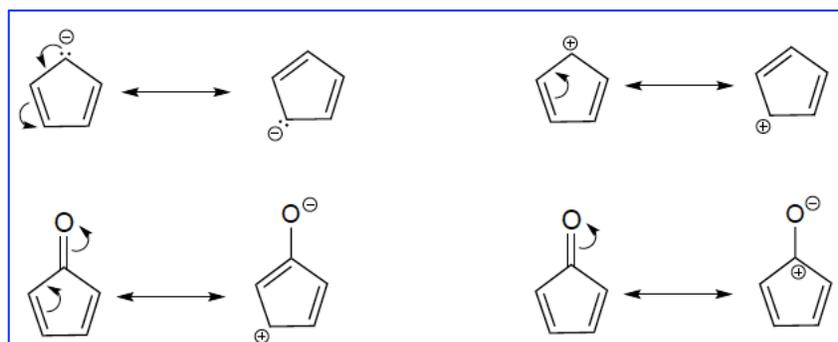


77

## Try this:



Follow the curved, double-headed arrows to move electron pairs and thus draw the missing resonance contributors.

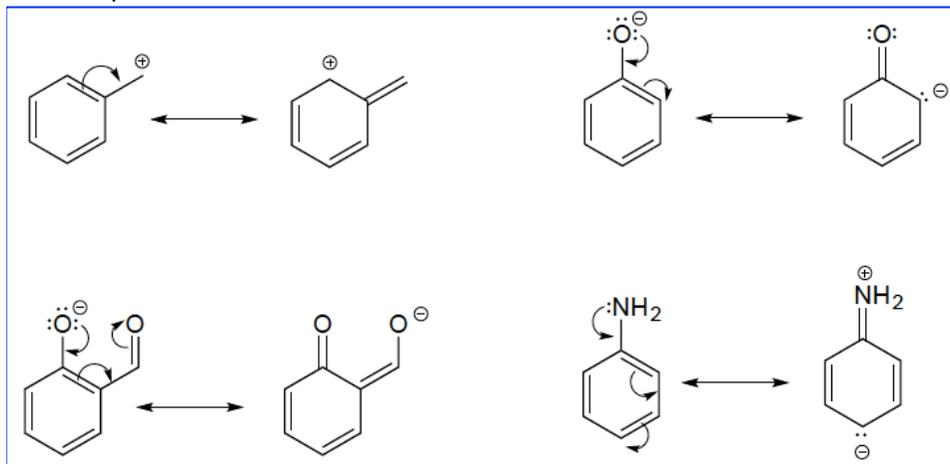


78

## Try this:



Add the curved, double-headed arrows needed to move electron pairs and convert the left-hand resonance contributor to that seen on the right side of each pair.



79

## Can you?



- (1) Understand that both equivalent atoms of a molecule with resonance have the same  $sp^2$  hybridization?
- (2) Describe why both of these atoms have the same hybridization?

80

## 2. Intro to organic structure & bonding II



### 2.3C: Rules for drawing resonance structures

- $\pi$  and :
- *Legal and illegal moves of lone pairs,  $\pi$*

81

## Rules for drawing resonance structures



1. Remember that resonance contributors are different ways of depicting one molecule or ion.
2. When comparing different resonance contributors:
  - The positions and connectivity of atoms cannot change.
  - Sigma bonds cannot be changed or broken.
  - $\pi$  bonds and lone pairs adjacent to  $\pi$  bonds can be moved.
3. All resonance contributors must have the same net charge.
4. All resonance contributors must be drawn as proper Lewis (or line-bond) structures. The octet rule must be followed for atoms like carbon, oxygen and nitrogen.

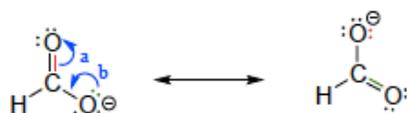
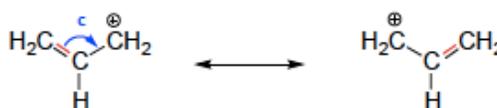
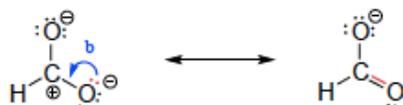
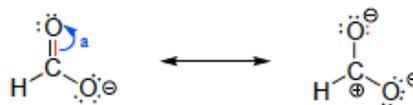
82

## Legal arrow moves



Curved arrows can move:

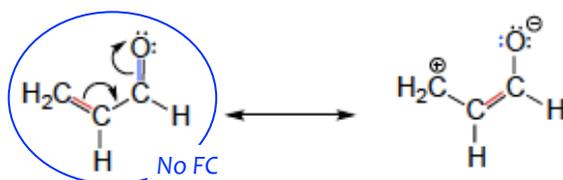
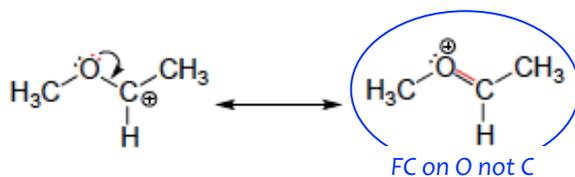
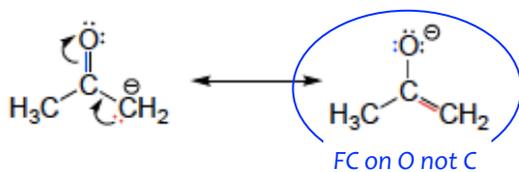
- $\pi$  to ..
- .. to  $\pi$
- move  $\pi$  over one atom



And these moves can be combined.

83

## Legal examples



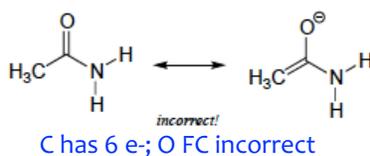
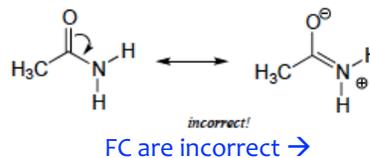
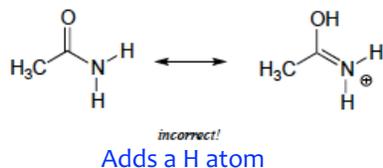
For each, which 'side' do you think is more stable or lower energy, and why?

84

## Try this:

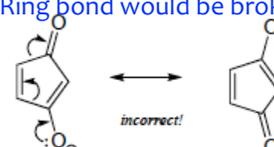
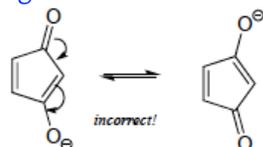


Explain **why** each of these moves is **illegal**.



Bottom C has too many bonds;  
branch C should be +  
Ring bond would be broken.

O charges & # e- incorrect



85

## Can you?



- (1) List the rules for drawing resonance structures?
- (2) Apply those rules?
- (3) Use curved arrows to move  $\pi$  or lone pair electrons to convert one resonance structure (or contributor) to another?
- (4) Describe the three types of 'legal' moves?
- (5) Understand that some resonance structures are more stable than others?

86

## 2. Intro to organic structure & bonding II



### 2.3D: Minor vs major resonance contributors

- Definitions
- Rules

87

## Not all resonance contributors are equal

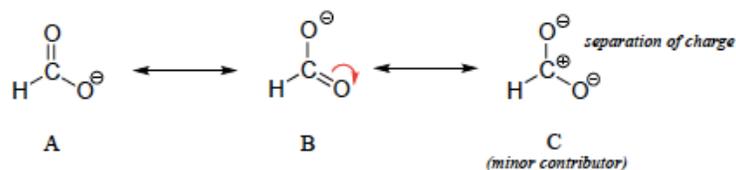


Often, some resonance contributors are closer to the hybrid reality than others.

**Major resonance contributors:** make a larger contribution to the hybrid

**Minor resonance contributors:** make smaller contributions to the hybrid

For formate, **A and B are major contributors**, while **C is a minor contributor**.

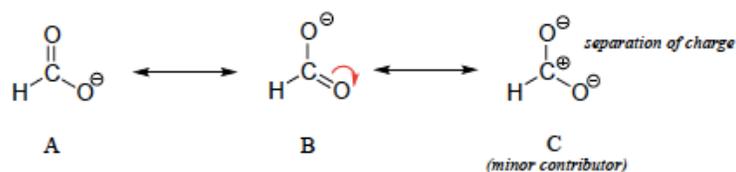


88

## Rules for determining major vs minor



1. When carbon is charged (not an octet) the contribution is likely minor.
2. Greater separation of charge? More likely to be minor.
3. Fewer bonds? More likely to be minor.
4. In major contributors, negative charges should be on more electronegative atoms.

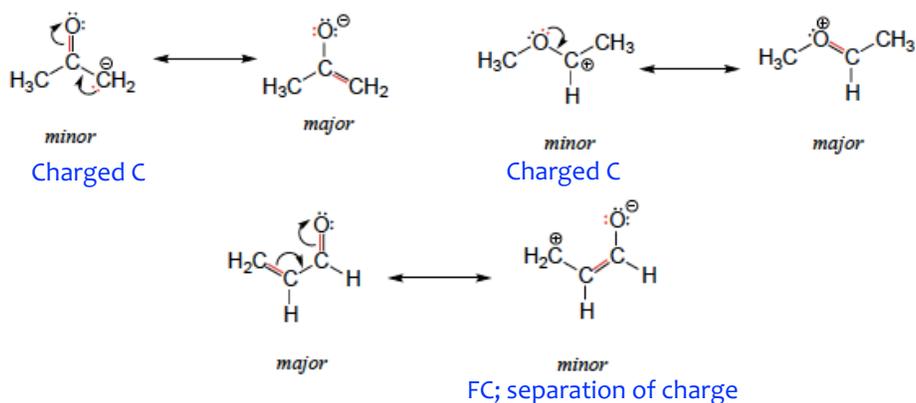


89

## Which rule here?



Which rule is at play in each of these examples of minor and major contributors?

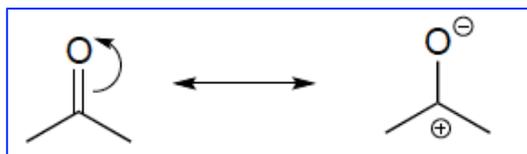


90

## Try this:

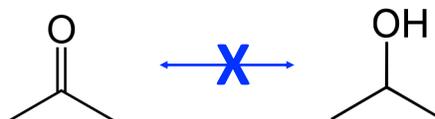


Draw a minor resonance contributor for 2-propanone.  
Why is it a minor contributor?



Charged C &  
separation of charges

Are 2-propanone and 2-propanol resonance contributors of each other?  
Explain?



No, 2-propanol has an atom (H) that 2-propanone doesn't have.

91

## Can you?



- (1) Define the terms 'minor resonance contributor' and 'major resonance contributor'?
- (2) List the rules used to determine major and minor resonance contributors?
- (3) Apply those rules?
- (4) Draw both minor and major resonance contributors?

92

## 2. Intro to organic structure & bonding II



### 2.3E: Resonance and peptide bonds

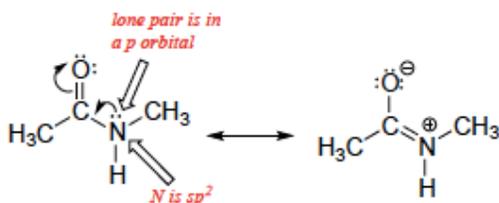
- Less rotation than expected
- More resonance examples

93

## Hybridization of the amide bond?

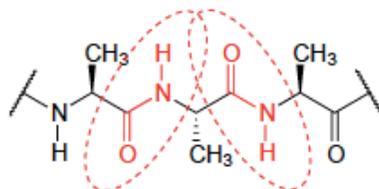


At first glance, the N of an **amide bond** would appear to be  $sp^3$  hybridized. But the other resonance contributor makes it clear that  $sp^3$  won't work, and the C, N and O of the amide bond **must be  $sp^2$  hybridized**.



And the amide bond is **trigonal planar**....  
... and **resonance stabilized**.

And, resonance **prevents free rotation** around amide (aka peptide) bonds in long protein chains or polymers. This 'rigidity' helps proteins fold into specific shapes.



<http://www.biotopics.co.uk/jsmol/leuala.html>

Notice that the amide N is planar while the side chain N is trigonal pyramidal.

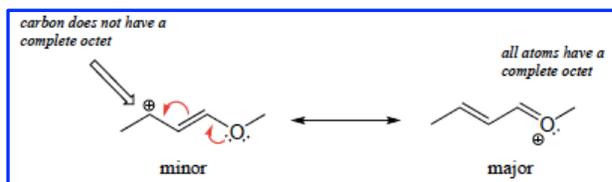
94

## Let's try an exercise:



Draw the major resonance contributor of the structure below.

- Include in your figure the appropriate curved arrows showing how you got from the given structure to your structure.
- Explain why your contributor is the major one.
- In what kind of orbitals are the two lone pairs on the oxygen?



The more en atom carries the charge

The O's lone pairs are in:

- (left) an  $sp^2$  and an unhybridized p orbital
- (right) an  $sp^2$  orbital

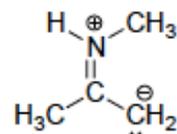
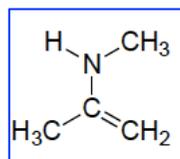
95

## Try this:



Below is a minor resonance contributor of a species known as an 'enamine', which we will study more in chapter 12.

- Draw the major resonance contributor for the enamine and explain why your contributor is the major one (refer to resonance rules for major and minor contributors from this section).



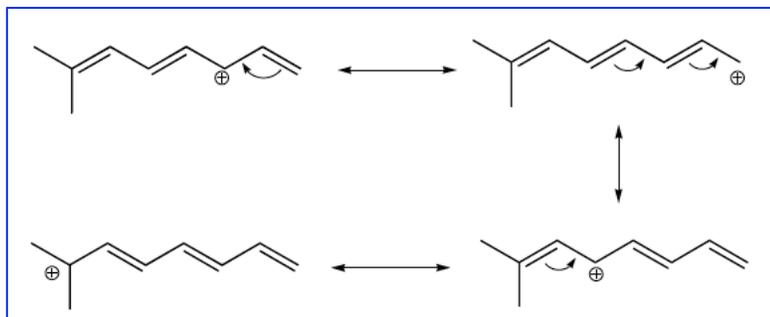
Major because no FC

96

## Another:



- (a) Draw three additional resonance contributors for the carbocation below. Include in your figure the appropriate curved arrows showing how one contributor is converted to the next.
- (b) Fill in the blanks: the conjugated  $\pi$  system in this carbocation is composed of 7 p orbitals sharing 6 delocalized  $\pi$  electrons.

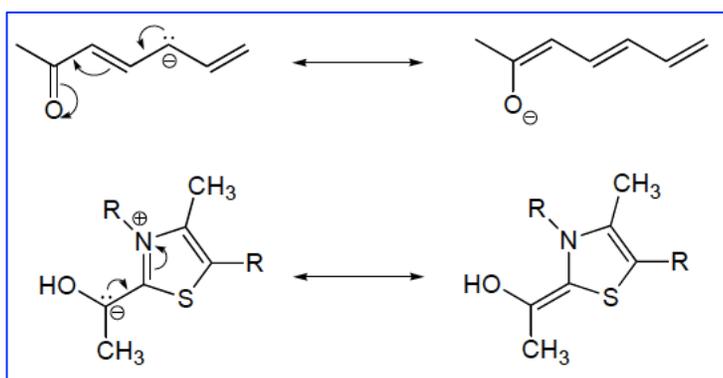


97

## Another:



Draw the major resonance contributor for each of the anions below.



98

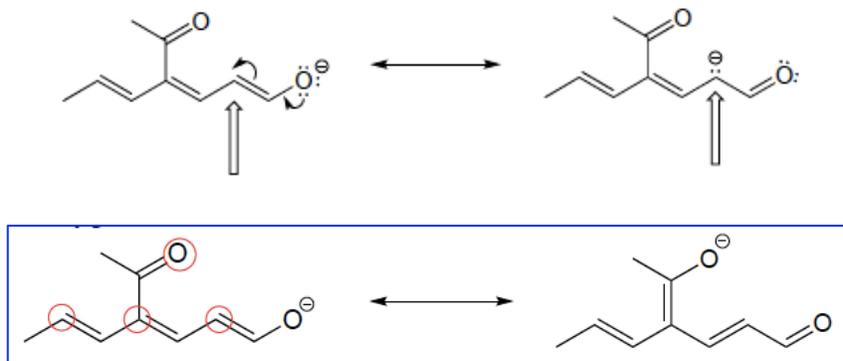
## Another:



The figure below shows how the negative formal charge on the oxygen can be delocalized to the carbon indicated by an arrow. More resonance contributors can be drawn in which negative charge is delocalized to three other atoms on the molecule.

(a) Circle these atoms.

(b) Draw the two most important resonance contributors for the molecule.



99

## Can you?



- (1) Describe the orbital hybridization of the atoms involved in the amide bond?
- (2) Describe the effects of resonance on stabilization and rotation of peptide bonds?
- (3) Cope with resonance problems!?

100

## 2. Intro to organic structure & bonding II



### 2.4: Non-covalent interactions

- A. Dipoles
- B. Ion-ion, dipole-dipole, ion-dipole interactions
- C. Van der Waals forces
- D. Hydrogen bonds
- E. Noncovalent interactions and protein structure

101

## 2. Intro to organic structure & bonding II



### 2.4A: Dipoles

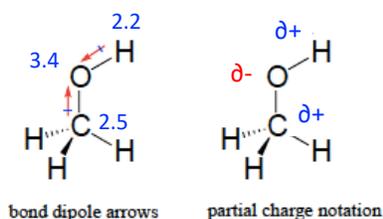
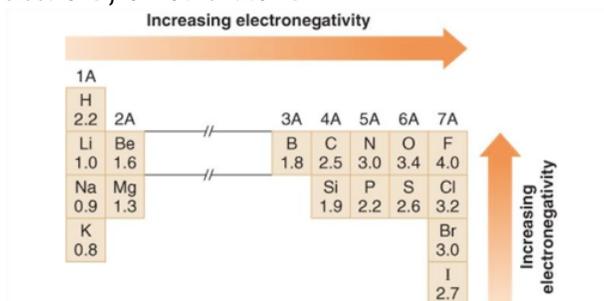
- *Electronegativity*
- *Polarity*
- *Dipole moment*

102

## Let's start with en and polarity



**Electronegativity (en):** the ability of an atom to hang on to its own electrons and attract electrons from other atoms



The electrons of covalent bonds are pulled toward the more en atom as shown by bond dipole arrows.  $\rightarrow$   
This creates a negative dipolar (partial) charge ( $\delta^-$ ) on the more en atom and a positive dipolar charge ( $\delta^+$ ) on the less en atom.

103

## Do you remember?



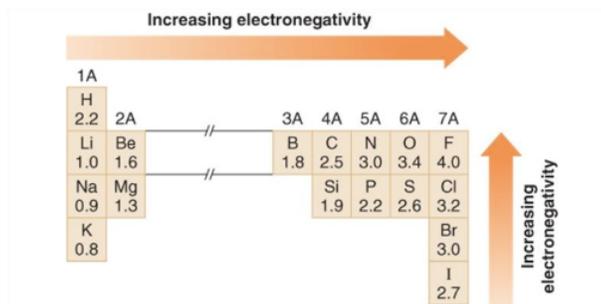
Why does electronegativity increase across and up the periodic table?

**Increasing left to right across rows:**

Within each row, the number of protons in atoms increases across the row. This increased positive charge holds electrons more tightly to the nucleus.

**Increasing bottom to top up columns:**

Within a column, the number of shells (principle energy levels,  $n$ ) increase from top to bottom. Atoms with more shells have  $e^-$  further from the nucleus, so  $e^-$  are less tightly held.



104

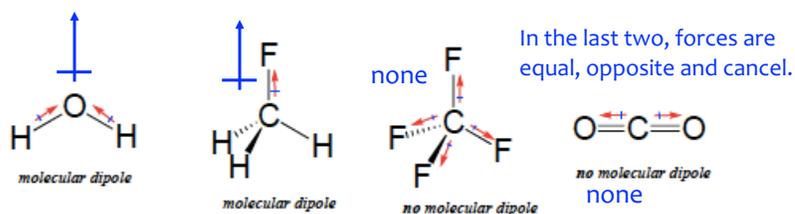
## Molecular dipole moments



**Molecular dipole moment:** a molecule's overall, or net, polarity

- Not all molecules have a dipole moment.
- Dipole arrow sum like vectors.

Which of these molecules have a dipole moment? In what direction?

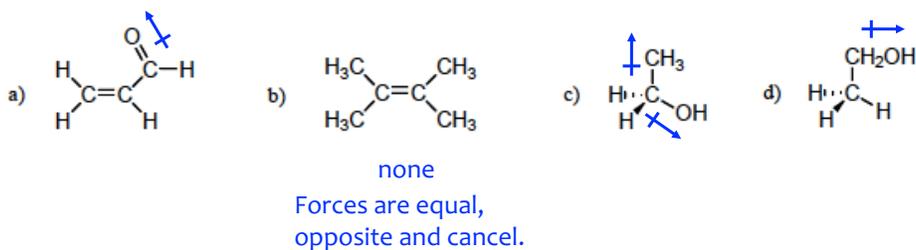


105

## Try this:



Which of these molecules have a dipole moment? In what direction?



106

## 2. Intro to organic structure & bonding II



### 2.4B: Ion-ion, dipole-dipole and ion-dipole interactions

- Ionic
- Dipole-dipole
- Ion-dipole

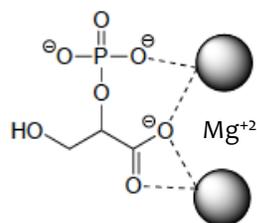
107

## Ion-ion (aka charge-charge) interactions



**Ion-ion (charge-charge) interactions:** non-covalent bonding caused by equal and opposite attractive forces

- The **strongest** of the non-covalent interactions.
- Similar to the forces that hold ions together in salts.



The Krebs's cycle metabolic molecule 2-phosphoglycerate is held in the active site of the glycolytic enzyme enolase by interacting with the two magnesium ions in the active site.

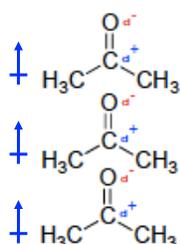
108

## Dipole-dipole interactions



**Dipole-dipole interactions:** non-covalent bonding caused by attractive forces between dipolar, or partial, charges

- Effects polar molecules since they have dipolar charges.



Here acetone molecules line up so that positive and negative dipolar charges hold them together like magnets.

This reminds me of the nose-to-tail way that dogs greet each other.

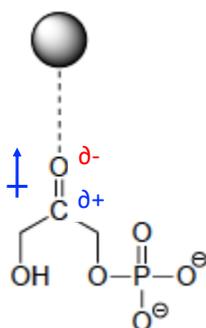
109

## Ion-dipole interactions



**Ion-dipole interactions:** non-covalent bonding caused by attractive forces between a (fully charged) ion and a molecule with the opposite dipolar charge.

- The presence of the ion causes a more extreme polarization of an already polar bond in the molecule.



Because the metal cation is very electropositive, its interaction increases the polarization of the carbonyl group, making the carbonyl group **more reactive**.

110

## 2. Intro to organic structure & bonding II



### 2.4C: Van der Waals forces

- Universal
- Induced and temporary

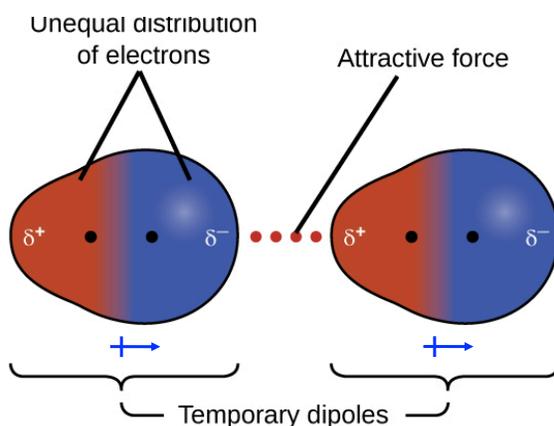
111

## Van der Waals forces



**Van der Waals forces** (aka London dispersion forces): weak non-polar interactions between nonpolar molecules like hydrocarbons

- The environment causes a **temporary induction** of polarity in nonpolar molecules by causing a shift in their internal electron density.



A in induced polarity (or dipole) can **propagate** from a few molecules throughout a solution.

As if a few 'lead fish' can turn a whole school of fish to follow them.

While weak, VdW forces act **additively** in a solution and have significant effects.

<https://www.youtube.com/watch?v=HGc9RFD7ISE>  
[https://s3-us-west-2.amazonaws.com/courses-images-archive-read-only/wp-content/uploads/sites/88/2015/06/23214344/CNX\\_Chem\\_10\\_01\\_DispForces.jpg](https://s3-us-west-2.amazonaws.com/courses-images-archive-read-only/wp-content/uploads/sites/88/2015/06/23214344/CNX_Chem_10_01_DispForces.jpg)

112

## 2. Intro to organic structure & bonding II



### 2.4D: Hydrogen bonds

- Acceptors and donors
- Relative strengths
- Role in DNA and enzymes

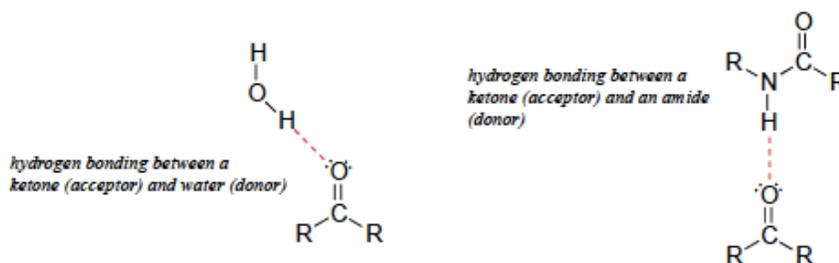
113

## Hydrogen bond



**Hydrogen bond:** a very specific type of dipolar bond between hydrogen bond donors and hydrogen bond acceptors

- **H-bond donors:** a H bonded to an N, O or F and therefore very polar
- **H-bond acceptor:** a lone pair on an N, O or F



H-bonds are usually shown as **dashed lines**, indicating that they are weak, transient noncovalent bonds.

**Water and alcohols** form hydrogen bonds readily and often.

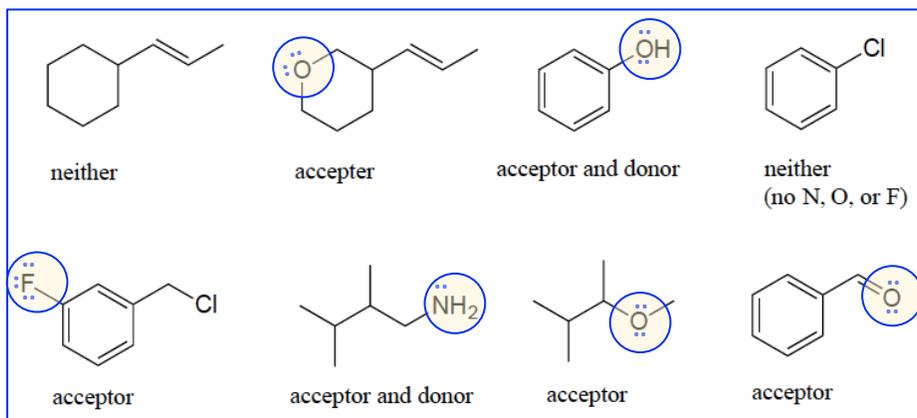
114

## Try this:



Label each of these molecules as:

- An H-bond donor
- An H-bond acceptor
- Neither



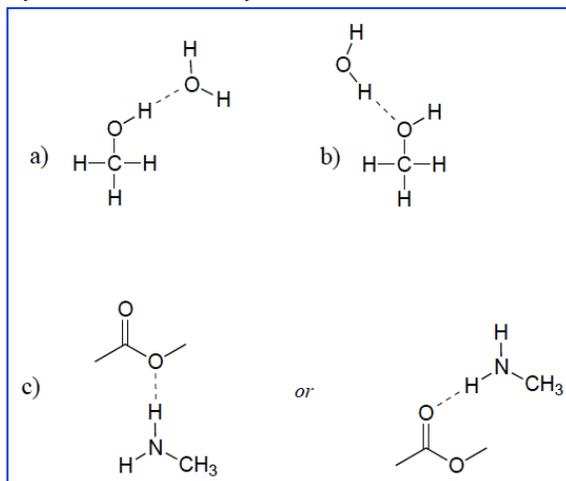
115

## Try this:



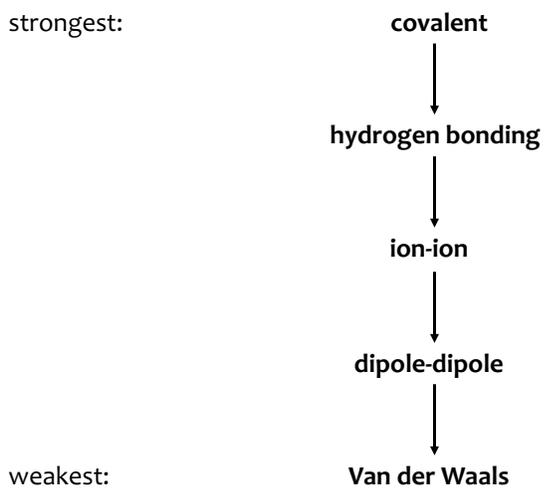
Draw the hydrogen bonding that happens between:

- Methanol (H-bond donor) and water (H-bond acceptor)
- Methanol (H-bond acceptor) and water (H-bond donor)
- Methyl acetate and methyl amine



116

## Relative strengths of noncovalent bonds

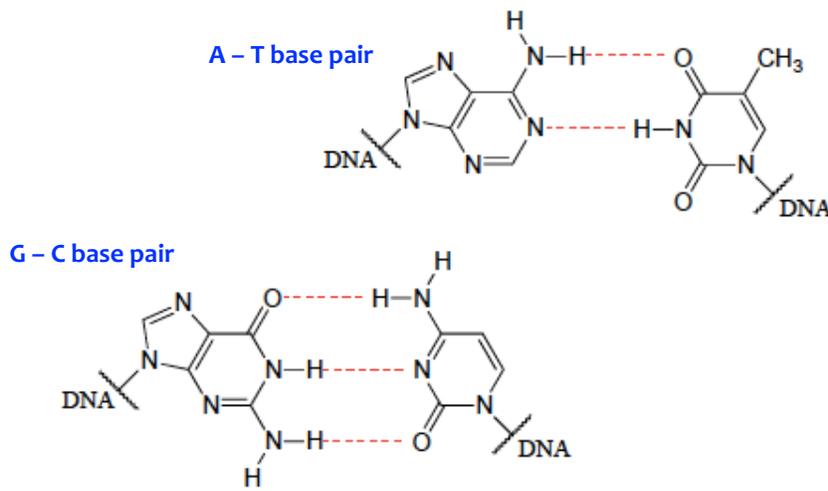


117

## H-bonds: critical roles in biomolecules



H-bonds are responsible for the 'pairing' power of the **DNA base pairs** that hold the DNA double helix together and store the genetic information needed to create entire organisms.



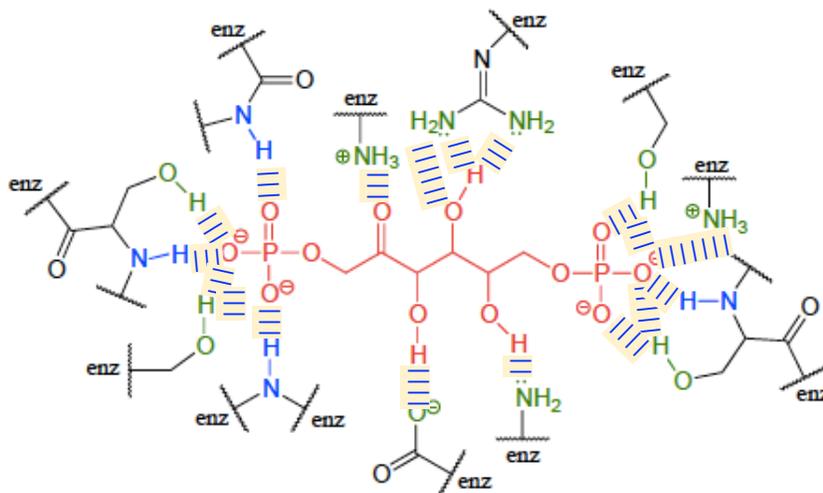
<http://www.chemtube3d.com/solidstate/DNAbases.htm>

118

## Can you see them?



Can you see where hydrogen bonds will form between the amino acid **side chains** and the **peptide backbone** of an enzyme and its **substrate**?



119

## Can you?



- (1) Define the term electronegativity and explain how and why electronegativity values vary though the periodic table?
- (2) Define the term 'molecular dipole' or 'dipole moment' and identify molecules that possess molecular dipoles?
- (3) Describe ion-ion and dipole-dipole interactions and identify them?
- (4) Describe 'van der Waals' force and understand that it is universal?
- (5) Describe the term 'hydrogen bond' and understand that hydrogen bonds are limited to three specific donors and three specific acceptors?
- (6) Rank intermolecular bonds in order of strength?

120

## 2. Intro to organic structure & bonding II



### 2.5: Physical properties of organic compounds

- A. Solubility
- B. Boiling and melting points
- C. Physical properties of lipids and proteins

121

## 2. Intro to organic structure & bonding II



### 2.5A: Solubility

- *Definition*
- *Like dissolves like*
- *Water and shells of hydration*
- *Effects of pH*
- *Biomolecules and membranes [sidebar]*

122

## Solubility: nonpolar interactions

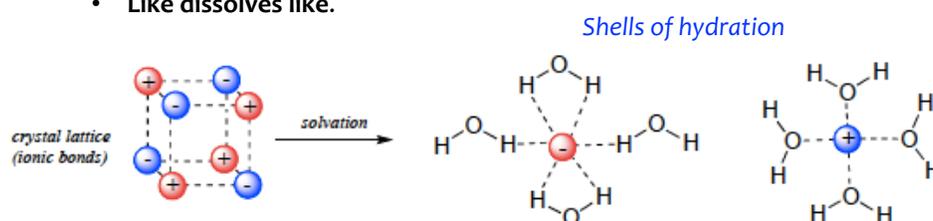


Most reactions between organic molecules happen in **solutions**.

- In biochemistry, the **universal solvent** the very polar molecule, **water**.
- However, many cellular and molecular microenvironments things are much less polar. These microenvironments are dominated by the molecules that create them.

**Solubility:** the extent to which a solute forms noncovalent bonds with a solvent ensuring that both molecules remain in the same phase

- Solubility **increases with the number of bonds** between solutes and solvents.
- **Like dissolves like.**



Here both water and salt are very **polar** and 'bond' via **ion-dipole** interactions.

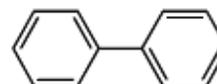
123

## Degrees of polarity



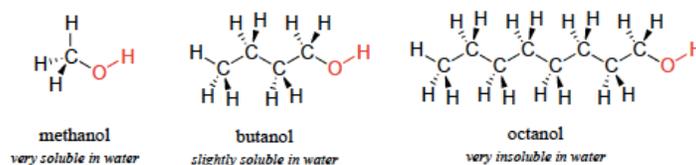
What about **nonpolar** molecules like biphenyl?

- Hydrophobic
- Doesn't interact with water or polar solvents.
- Van der Waals with itself.



Alcohols have differing levels of **amphipathicity**, or mixed nature.

- The balance determines their solubilities.



- The hydroxyl group H-bonds with water and can 'carry' a carbon or two with it.
- As the **number of carbons increases, the alcohol becomes too nonpolar** for a single hydroxyl group to solubilize the whole molecule in water; not enough bonds!

124

## So what about these?



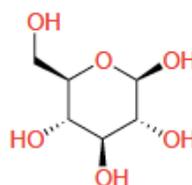
Do you think **glucose** is soluble in water?

- How many H-bonds could it form?

All possible donors and acceptors (unlikely):

**17 H-bonds**

- Most



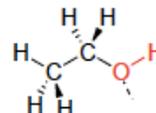
How soluble is **ethanol** in water?

- How many H-bonds could it form?

All possible donors and acceptors (unlikely):

**3 H-bonds**

- Middling



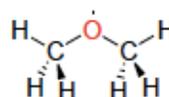
How soluble is **dimethyl ether** in water?

- How many H-bonds could it form?

All possible acceptors (unlikely):

**2 H-bonds**

- Least



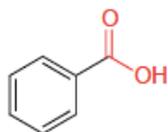
125

## Try this:

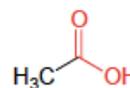


Compare these two organic acids.

- Which is more soluble in water and why?



benzoic acid



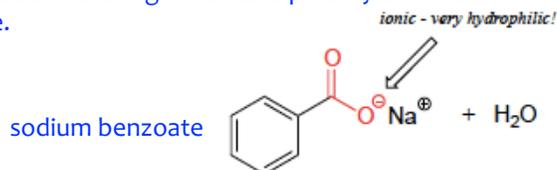
acetic acid

**Acetic acid is more water-soluble.**

Both carboxylic acids can form the same number of H-bonds with water. Those H-bonds can overcome the small nonpolar methane group of acetic acid, but not the large aromatic ring of benzoic acid.

How do things change if NaOH is added to the water and organic acids?

As NaOH is added the solution becomes more basic and the carboxylic acids are deprotonated. Both carboxylates are charged and therefore more water soluble than the carboxylic acids. The charge increases polarity and makes both molecules water soluble.



126

## Water solubility?



- **How many carbons?**  
Water solubility decreases as the number of carbons increases.
- **How many, and what type, of hydrophilic groups?**  
Water solubility increases as the number of hydrophilic groups increases.

**Hydrophilic groups** (starting with the most powerful)

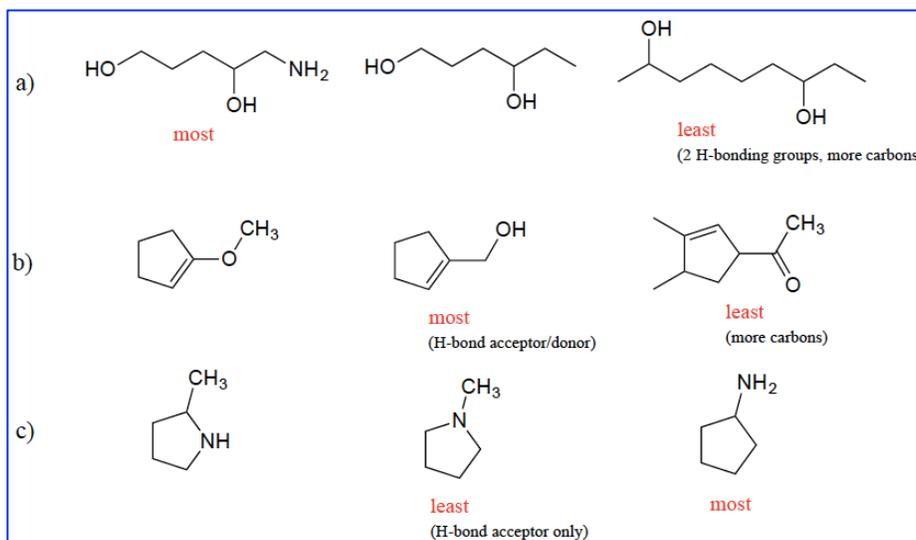
1. **Charged groups**  
Best without large nonpolar groups attached.
2. **H-bond donor: polar H**
3. **H-bond acceptor: O, N, F**
4. **Other polar groups: use electronegativities**

127

## Try these:



Rank the compounds in each set in order of most to least **soluble in water**.

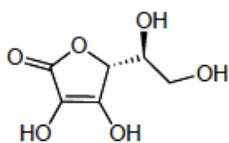


128

## Try this:

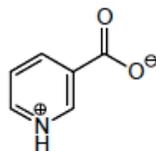


Label each of these vitamins as water-soluble or fat-soluble.



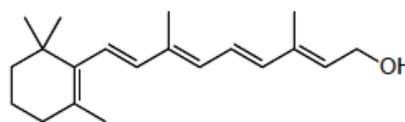
Vitamin C  
(ascorbic acid)

water soluble  
(many OH)



Vitamin B<sub>3</sub>  
(niacin)

water soluble  
(polar & charged)



Vitamin A  
(retinol)

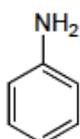
fat soluble  
(nearly all nonpolar)

129

## Try this:

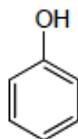


Both of these compounds are nearly insoluble in pure water.  
Which is more soluble in a 10% aqueous hydrochloric acid solution? Why?



aniline

Aniline is basic and would be protonated (and thus cationic) in aqueous HCl. Charged species are generally water soluble.



phenol

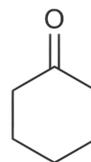
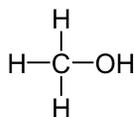
On the other hand, phenol is not basic and thus would remain as a neutral, water-insoluble molecule.

130

## Try this:



Would you predict that methanol or 2-propanol would be a better solvent for cyclohexanone? Why?



Both alcohol solvents could form H-bonds with cyclohexanone, but isopropanol is less polar (it has three carbons), and thus would be the better solvent for the relatively nonpolar cyclohexanone.

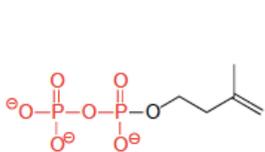
131

## What about biomolecules?

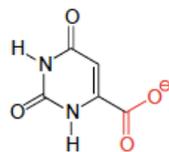


Because biomolecules exist in aqueous environments, most have **charged functional groups** like these.

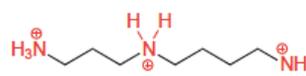
- phosphate
- ammonium
- carboxylate



isopentenyl diphosphate  
*an early precursor to cholesterol*



orotate  
*a precursor to the RNA base uridine*



spermidine  
*binds tightly to DNA in rapidly dividing cells*

Note that the charge is dependent on the molecule's **state of protonation**.

- The states you see here occur at a physiological pH, about 7.3

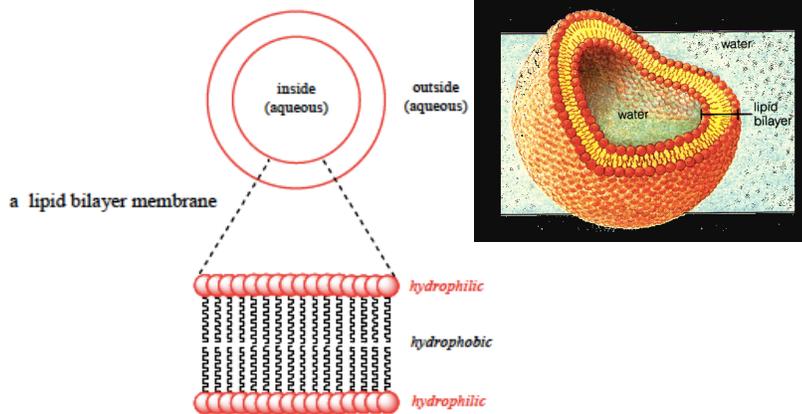
.....sidebar.....

132

## Amphipathic biomolecules?



**Amphipathic membrane lipids** self-assemble into **bilayers** in order to shield their hydrophobic tails from the aqueous environment. The lipid's hydrophilic head groups form noncovalent interactions with water.



<http://academic.brooklyn.cuny.edu/biology/bio4fv/page/lipos.gif>

133

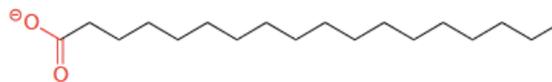
.....*sidebar*.....

## Detergents are amphipathic



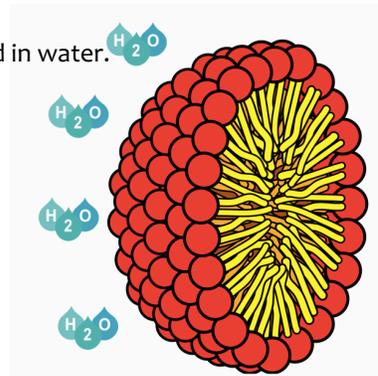
**Soaps or detergents** are amphipathic fatty acids, usually released from triacylglycerol molecules by hydrolysis with a base like lye (potassium hydroxide)

- Stearate (18:0)



**Micelles** form when detergents are placed in water.

- The charged carboxylate groups interact with water.
- The hydrophobic tail groups cluster inside the sphere to avoid contact with water.



<http://www.beautybythegeeks.com/wp-content/uploads/micelle-1024x644.png>

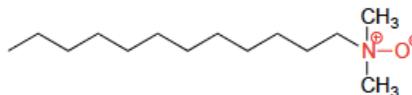
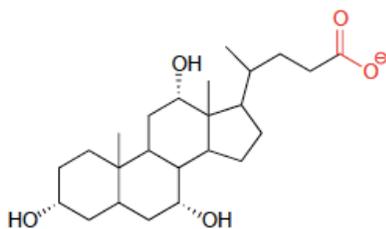
134

.....*sidebar*.....

## Other detergents



What do these synthetic detergents have in common with stearate?



All three molecules are **amphipathic**, and their hydrophilic groups are charged.

.....sidebar.....

135

## Can you?



- (1) Define the term 'solubility'?
- (2) Describe, and apply, the concept of 'like dissolves like'?
- (3) Explain how solubility is related to intermolecular bonding?
- (4) Define the term 'amphipathic'?
- (5) Assess degree of polarity and bonding to determine relative solubilities?
- (6) Describe how amphipathicity determines the behavior of membrane lipids (phospholipids) and detergents? [sidebar]

136

## 2. Intro to organic structure & bonding II



### 2.5B: Boiling and melting points

- Similarities and differences
- Factors

137

## Melting and boiling points



Traditionally, the melting and boiling points of compounds have been used to **determine purity** and sometimes identity.

**Melting point:** *the temperature at which a solid becomes a liquid*

**Boiling point:** *the temperature at which a liquid becomes a gas*

### What determines a molecule's melting and boiling points?

- The ability of the molecule to bind to itself
- The strength of its noncovalent intermolecular interactions

The **stronger** the noncovalent intermolecular interactions, the **higher** the melting and boiling points.

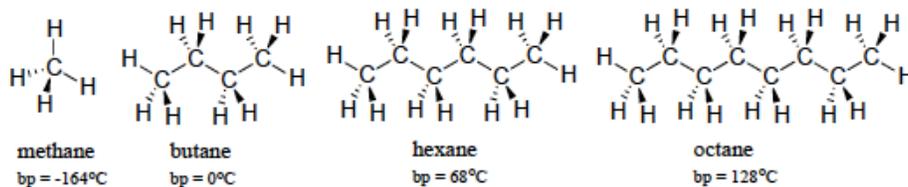
<https://www.youtube.com/watch?v=pILGRZ0nT4o>

138

## Larger molecules have higher bp



**Larger size** increases the surface area available for Van der Waals contact and extent of intermolecular interactions, increasing bp.



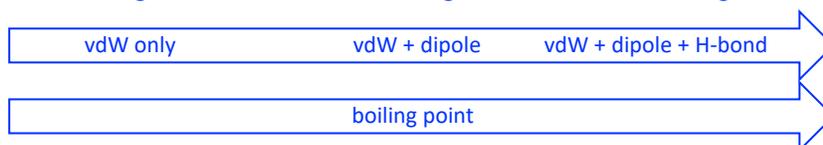
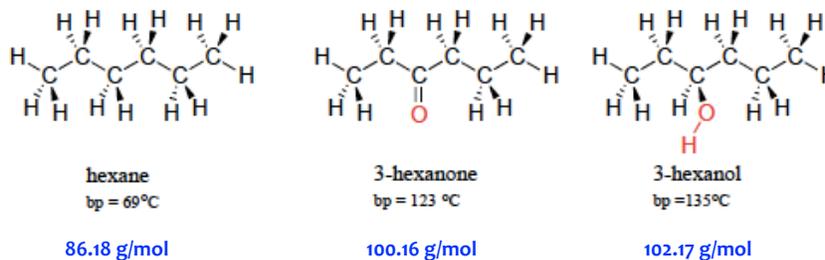
139

## H- and dipole bonds increase mp, bp



The **more H-bonding and dipole bonding** exists between molecules, the higher their mp and bp.

- All molecules experience VdW bonding.
- But not all molecules are polar or have H-bond donors and acceptors.



140

## Water punches above its weight



Why is the bp of water higher than other molecules with similar MW?

| Molecule         | MW (g/mol) | Boiling point (°C) | Possible H-bonds | <u>donor</u> acceptor |
|------------------|------------|--------------------|------------------|-----------------------|
| CH <sub>4</sub>  | 16         | -161               | 0                | NA                    |
| NH <sub>3</sub>  | 17         | -33                | 4                | 3/1                   |
| H <sub>2</sub> O | 18         | 100                | 4                | 2/2                   |
| HF               | 20         | 19                 | 4                | 1/3                   |

Water makes a huge number of H-bonds per MW and has a perfect ratio of H-bond donors to acceptors, so it networks perfectly.

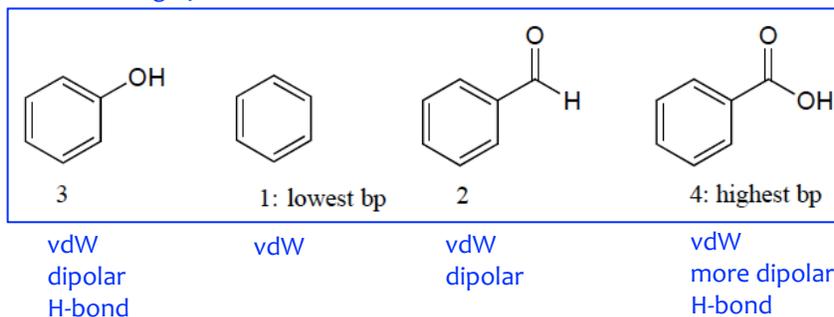
141

## Try this:



Based on their structures, rank phenol, benzene, benzaldehyde, and benzoic acid in terms of lowest to highest boiling point. Explain your reasoning.

Sizes are roughly similar



142

## Melting points are a bit more complex

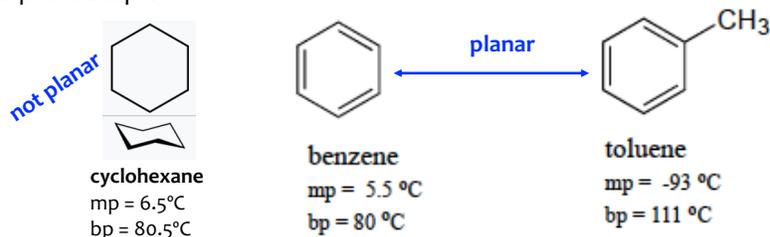


We've seen that solubility and boiling points both increase as solutes make more bonds to their solvents. This is true of melting points (mps) too.

- But with mp, **molecular shape** also matters.

The energy required to melt solids depends on **how well units stack together**.

- Better stacking increases VdW bonding and mps.
- Aromatic rings are flat and stack very well, giving aromatics higher-than-expected mps.



Explain these different trends in mps and bps.

Bp all similar because similar MW.

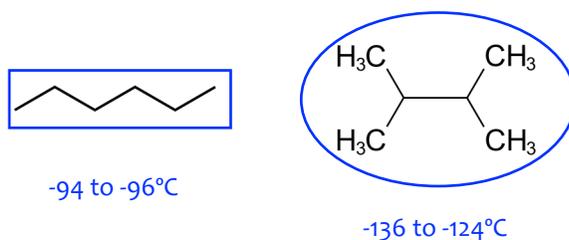
Toluene's mp is lower because the methyl group interrupts packing and stacking.

143

## Try this:



Which would you expect to have the higher melting point, 2,3-dimethylbutane or hexane? Explain.



Hexane has the higher melting point. Both compounds have an equal number of carbons and hydrogens and are nonpolar, so it comes down to shape. 2,3-dimethylbutane is more sphere-like and is capable of less efficient molecule-to-molecule packing, so it has weaker intermolecular interactions and thus a lower melting point.

144

## Can you?



- (1) Define the terms 'boiling point' and 'melting point'?
- (2) Understand what factors increase boiling points and melting points?
- (3) Understand that shape has a significant effects on melting points but not boiling points?
- (4) Rank the relative boiling points and melting points of organic molecules?

145

## 2. Intro to organic structure & bonding II



### **2.5C: Physical properties of lipids and proteins**

- *Packing and kinks*
- *Folding*
- *Adaptation and evolution*

.....*sidebar*.....

146

# Lipids

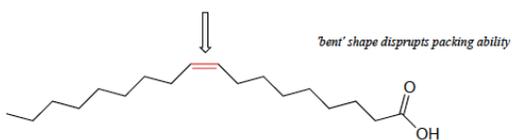
We've all seen fats (lipids) in both liquid and solid physical states. You may have noticed that – at room temperature - plant fats tend to be liquid, while animal fats tend to be solid.

- The more tightly molecules pack, the more VdW interaction they have.



Unsaturated plant lipids are **'kinked'** and **don't pack well**, so melt easily.

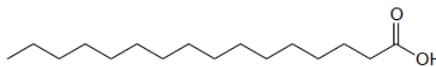
*no rotation, increased rigidity*



oleic acid  
(an unsaturated fatty acid)



Saturated animal lipids are **'straight'** and **pack tightly**, so require more energy to melt.



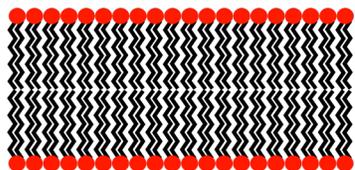
palmitic acid  
(a saturated fatty acid)

.....sidebar.....

147

# Packing determines mp

Have a look at these visuals to see how saturated lipids pack more tightly than unsaturated lipids.



Saturated lipids only



Saturated

.....sidebar.....

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

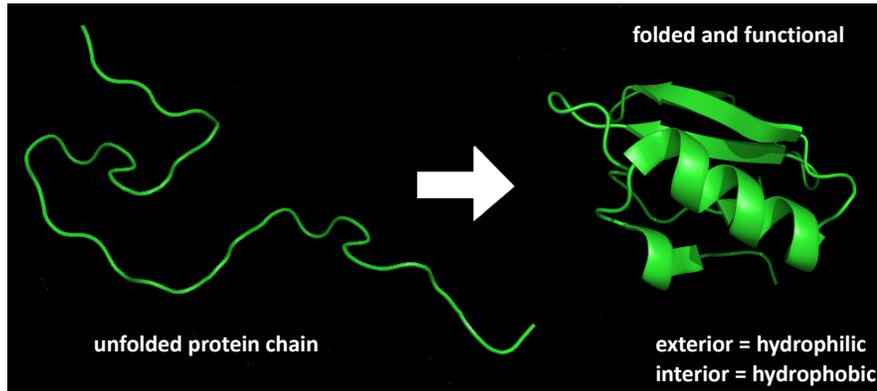
148

## Protein



Proteins must **fold** in order to **function properly**.

- Non-covalent bonds facilitate folding and then hold it in place (hairspray).



.....sidebar.....

149

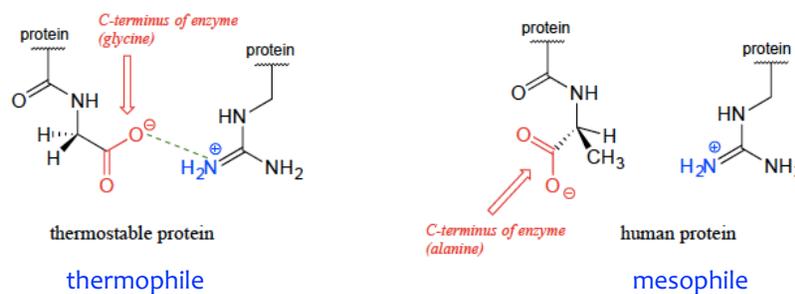
## Adaptation via non-covalent interactions



While we are most aware of organisms that live at the temperatures we like (**mesophiles**), some organisms live at much higher temperatures (**thermophiles**), in hot springs or thermal vents, or at much colder temperatures (psychrophiles), in polar ice.

Enzymes from these organisms are remarkably similar, but have **adaptations that allow them to maintain their folding and function at different temperatures**.

- Thermophiles have added more non-covalent bonds.
- Psychrophiles don't need as many.



.....sidebar.....

150

## Can you?



- (1) Understand how the physical structure of lipids affects their physical state?
- (2) That proteins must fold in order to have function?
- (3) Understand that increasing intermolecular interactions allow proteins to remain folded and functional at higher temperatures?

.....*sidebar*.....