Chapter 3: Introduction to Organic Molecules and Functional Groups

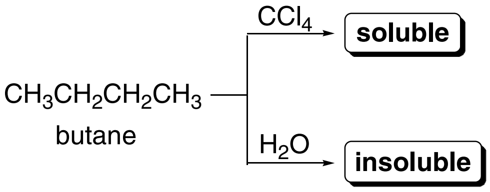
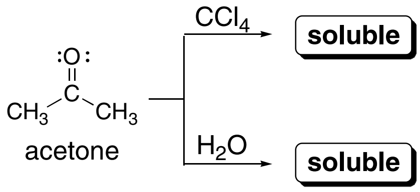
♦ Types of intermolecular forces (3.3)

Increasing strength ↓

Type of force	**Cause**	**Examples**
van der Waals (VDW)	Due to the interaction of temporary dipoles • Larger surface area, stronger forces • Larger, more polarizable atoms, stronger forces	All organic compounds
dipole–dipole (DD)	Due to the interaction of permanent dipoles	$(CH_3)_2C{=}O$, H_2O
hydrogen bonding (HB or H-bonding)	Due to the electrostatic interaction of a H atom in an O–H, N–H, or H–F bond with another N, O, or F atom.	H_2O
ion–ion	Due to the interaction of two ions	NaCl, LiF

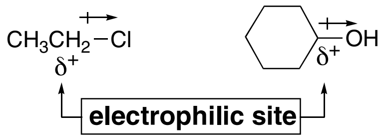
♦ Physical properties

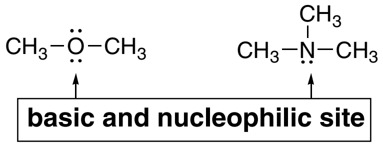
Property	**Observation**
Boiling point (3.4A)	• For compounds of comparable molecular weight, the stronger the forces the higher the bp. $CH_3CH_2CH_2CH_2CH_3$ — VDW — MW = 72 — bp = 36 °C $CH_3CH_2CH_2CHO$ — VDW, DD — MW = 72 — bp = 76 °C $CH_3CH_2CH_2CH_2OH$ — VDW, DD, HB — MW = 74 — bp = 118 °C → **Increasing strength of intermolecular forces** **Increasing boiling point** **3.1** For compounds with similar functional groups, the larger the surface area, the higher the bp. $CH_3CH_2CH_2CH_3$ — bp = 0 °C $CH_3CH_2CH_2CH_2CH_3$ — bp = 36 °C → **Increasing surface area** **Increasing boiling point** • For compounds with similar functional groups, the more polarizable the atoms, the higher the bp. CH_3F — bp = –78 °C CH_3I — bp = 42 °C → **Increasing polarizability** **Increasing boiling point**

Melting point (3.4B)	• For compounds of comparable molecular weight, the stronger the forces the higher the mp. $CH_3CH_2CH_2CH_2CH_3$ — VDW — MW = 72 — mp = −130 °C $CH_3CH_2CH_2CHO$ — VDW, DD — MW = 72 — mp = −96 °C $CH_3CH_2CH_2CH_2OH$ — VDW, DD, HB — MW = 74 — mp = −90 °C $\xrightarrow{\hspace{3cm}}$ **Increasing strength of intermolecular forces** **Increasing melting point** • For compounds with similar functional groups, the more symmetrical the compound, the higher the mp. $CH_3CH_2CH(CH_3)_2$ — mp = −160 °C $(CH_3)_4C$ — mp = −17 °C $\xrightarrow{\hspace{3cm}}$ **Increasing symmetry** **Increasing melting point**
Solubility (3.4C)	Types of water-soluble compounds: • Ionic compounds • Organic compounds having ≤ 5 C's, and an O or N atom for hydrogen bonding (for a compound with one functional group). Types of compounds soluble in organic solvents: • Organic compounds regardless of size or functional group. • Examples:  
	Key: VDW = van der Waals, DD = dipole–dipole, HB = hydrogen bonding MW = molecular weight

◆ Reactivity (3.8)

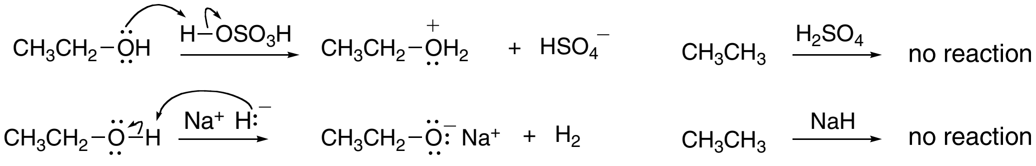
- **Nucleophiles react with electrophiles.**
- Electronegative heteroatoms create electrophilic carbon atoms, which tend to react with nucleophiles.
- Lone pairs and π bonds are nucleophilic sites that tend to react with electrophiles.



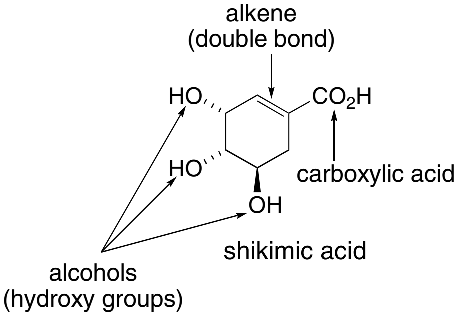


Chapter 3: Answers to Problems

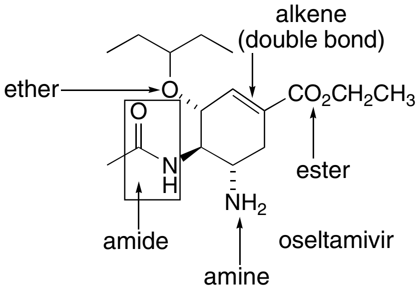
3.1



3.2 Identify the functional groups based on Tables 3.1, 3.2, and 3.3.

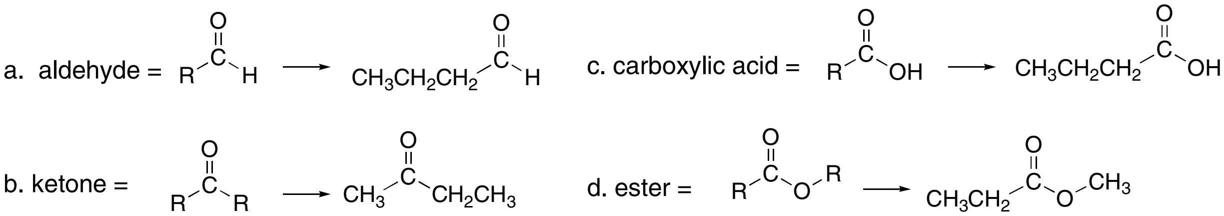


shikimic acid

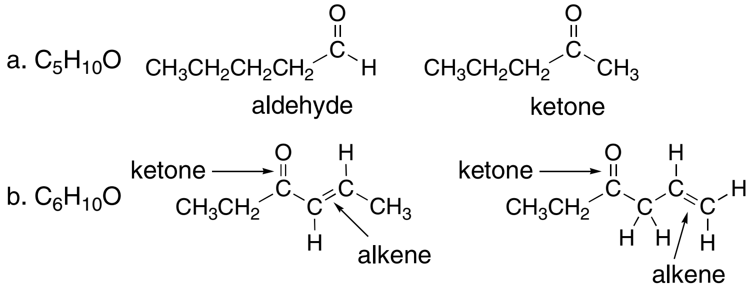


oseltamivir

3.3 One possible structure for each functional group:

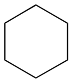


3.4 One possible structure for each description:

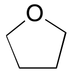


3.5 Summary of forces:

- **All compounds exhibit van der Waals forces (VDW).**
- **Polar molecules have dipole–dipole forces (DD).**
- **Hydrogen bonding (H-bonding)** can occur only when a **H is bonded to an O, N, or F.**

a. 

only nonpolar C–C and C–H bonds
VDW only

b. 

- **VDW forces**
- 2 polar C–O bonds and a net dipole - **DD**
- no H on O so no H-bonding

c. $(CH_3CH_2)_3N$

- **VDW forces**
- polar C–N bonds - **DD**
- no H on N so no H-bonding

d. $CH_2{=}CHCl$

- **VDW forces**
- polar C–Cl bond - **DD**

e. $CH_3CH_2CH_2COOH$

- **VDW forces**
- polar C–O bonds and a net dipole - **DD**
- H bonded to O - **H-bonding**

f. $CH_3{-}C{\equiv}C{-}CH_3$

only nonpolar C–H and C–C bonds
VDW only

3.6 One principle governs boiling point:

- **Stronger intermolecular forces = higher bp.**
  Increasing intermolecular forces: van der Waals < dipole–dipole < hydrogen bonding

Two factors affect the strength of van der Waals forces, and thus affect bp:

- **Increasing surface area = increasing bp.**
  Longer molecules have a larger surface area. Any branching decreases the surface area of a molecule.
- **Increasing polarizability = increasing bp.**

a. $(CH_3)_2C{=}CH_2$ or $(CH_3)_2C{=}O$

$(CH_3)_2C{=}CH_2$: only VDW

$(CH_3)_2C{=}O$: VDW and DD
polar, stronger intermolecular forces
higher boiling point

b. CH_3CH_2COOH or CH_3COOCH_3

CH_3CH_2COOH: VDW, DD, and H-bonding
stronger intermolecular forces
higher boiling point

CH_3COOCH_3: no H-bonding

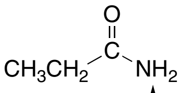
c. $CH_3(CH_2)_4CH_3$ or $CH_3(CH_2)_5CH_3$

$CH_3(CH_2)_5CH_3$: longer molecule, more surface area
higher boiling point

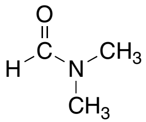
d. $CH_2{=}CHCl$ or $CH_2{=}CHI$

$CH_2{=}CHI$: I is more polarizable.
higher boiling point

3.7 Increasing intermolecular forces: van der Waals < dipole–dipole < hydrogen bonding

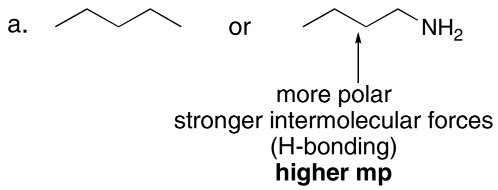


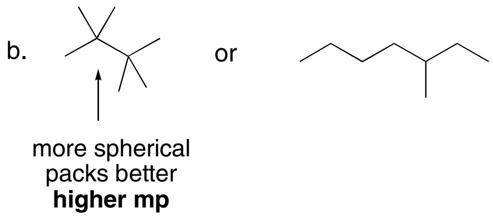
N–H bonds allow for hydrogen bonding.
stronger intermolecular forces
higher boiling point



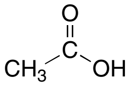
no hydrogen bonding
weaker intermolecular forces

3.8



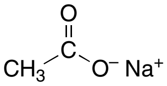


3.9 Compare the intermolecular forces to explain why sodium acetate has a higher melting point than acetic acid.



$CH_3C(=O)OH$

acetic acid



$CH_3C(=O)O^- Na^+$

sodium acetate

a. VDW, DD, and H-bonding	a. VDW, DD, ionic bonds
b. not ionic, lower melting point	b. Ionic bonds are the strongest: **higher melting point.**

3.10 In the more ordered solid phase, molecules are much closer together than in the less ordered liquid phase. The shape of a molecule determines how closely it can pack in the solid phase so symmetry is important. In the liquid phase, molecules are already farther apart, so symmetry is less important and thus it doesn't affect boiling point.

3.11 A compound is water soluble if it is ionic or if it has an O or N atom and ≤ 5 C's.

a. $CH_3CH_2OCH_2CH_3$

an O atom that
can H-bond with water
≤ 5 C's
water soluble

b. $CH_3CH_2CH_2CH_2CH_3$

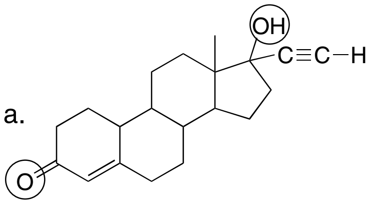
nonpolar
not water soluble

c. $(CH_3CH_2CH_2CH_2)_3N$

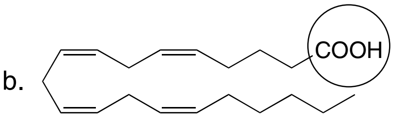
an N atom that can
H-bond to H_2O, but
> 5 C's
not water soluble

3.12 **Hydrophobic** portions will primarily be hydrocarbon chains. **Hydrophilic** portions will be polar.

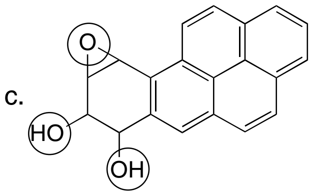
Circled regions are **hydrophilic** because they are polar.
All other regions are **hydrophobic** since they have only C and H.



norethindrone



arachidonic acid

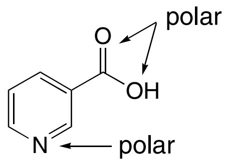


benzo[*a*]pyrene derivative

3.13 Like dissolves like.

- To be **soluble in water**, a molecule must be ionic, or have a polar functional group capable of H-bonding for every 5 C's.
- Organic compounds are generally **soluble in organic solvents** regardless of size or functional group.

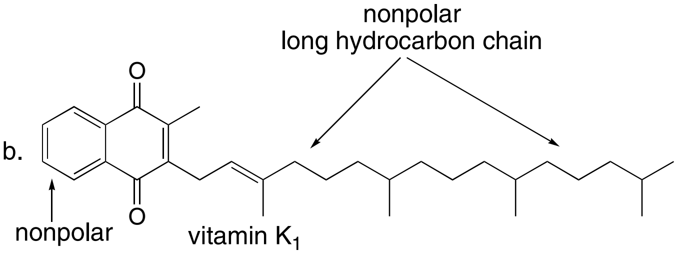
a.



vitamin B_3
(niacin)

soluble in water due to
two polar functional groups
and only 6 C's in the molecule

b.



vitamin K_1
(phylloquinone)

soluble in organic solvents
two polar C–O bonds but the
compound has > 10 C's
water insoluble

3.14 A soap contains both a long hydrocarbon chain and a carboxylic acid salt.

a. $CH_3CO_2^-Na^+$
↑
short chain
carboxylic acid salt

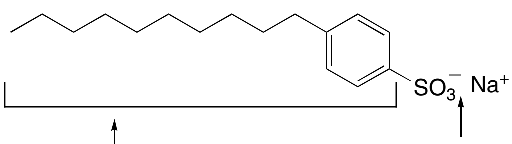
ionic salt
↓
b. $CH_3(CH_2)_{14}CO_2^-Na^+$
↑
long chain
This is a soap because it contains both a long chain and a carboxylic acid salt.

c. $CH_3(CH_2)_{12}COOH$
↑
no salt

ionic salt
↓
d. $CH_3(CH_2)_9CO_2^-Na^+$
↑
long chain
This is a soap because it contains both a long chain and a carboxylic acid salt.

3.15 Detergents have a polar head consisting of oppositely charged ions, and a nonpolar tail consisting of C–C and C–H bonds, just like soaps do. Detergents clean by having the **hydrophobic ends of molecules surround grease**, while the **hydrophilic portion of the molecule interacts with the polar solvent** (usually water).

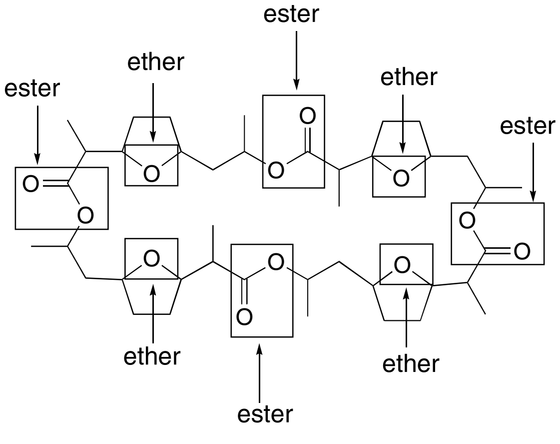
a detergent



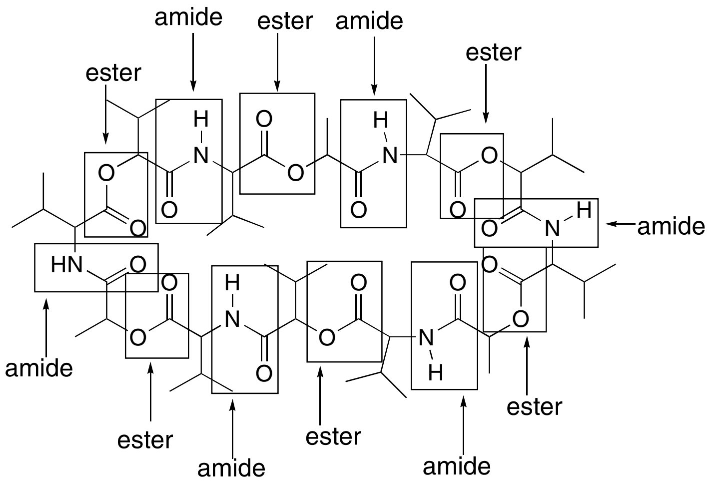
nonpolar tail
hydrophobic
This end interacts with
the grease to dissolve it.

polar head
ionic - hydrophilic
This end interacts with the water solvent
to maintain the micelle's solubility in water.

3.16

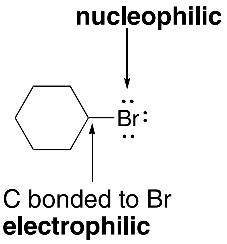


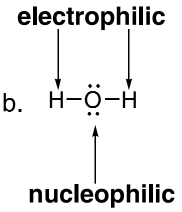
nonactin

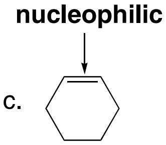


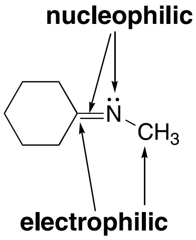
valinomycin

3.17 Electronegative heteroatoms like N, O, or X make a carbon atom an *electrophile*.
A lone pair on a heteroatom makes it basic and nucleophilic.
π Bonds create *nucleophilic* sites and are more easily broken than σ bonds.

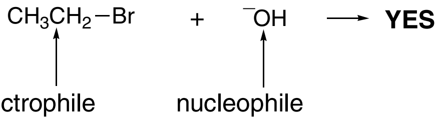
a.


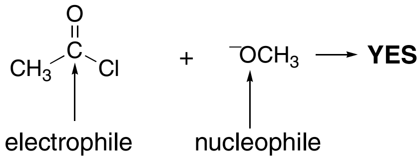
b.


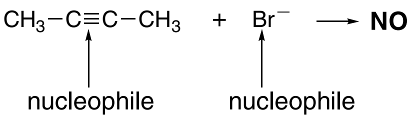
c.


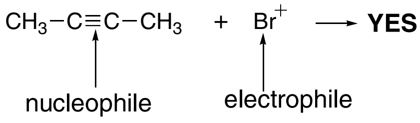
d.


3.18 Electrophiles and nucleophiles react with each other.

a.

$CH_3CH_2{-}Br \quad + \quad {}^{-}OH \longrightarrow$ **YES**

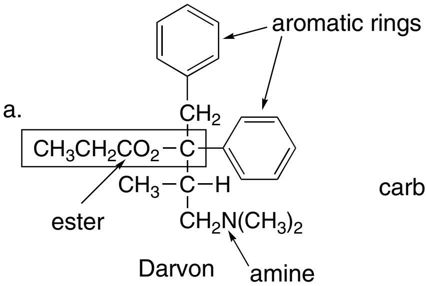
c.

$CH_3C(=O)Cl \quad + \quad {}^{-}OCH_3 \longrightarrow$ **YES**

b.

$CH_3{-}C{\equiv}C{-}CH_3 \quad + \quad Br^{-} \longrightarrow$ **NO**

d.

$CH_3{-}C{\equiv}C{-}CH_3 \quad + \quad Br^{+} \longrightarrow$ **YES**

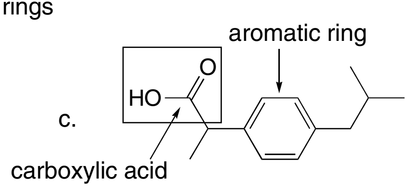
3.19 Identify the functional groups based on Tables 3.1, 3.2, and 3.3.

a.



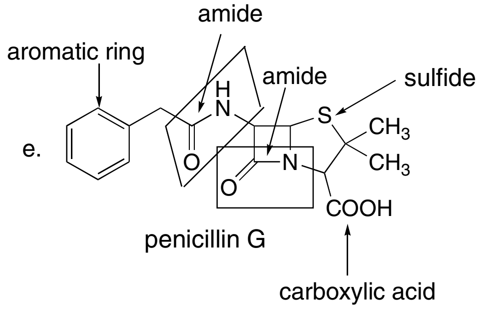
Darvon

c.



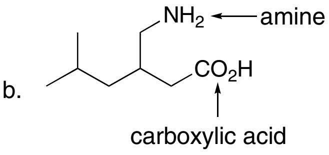
ibuprofen

e.



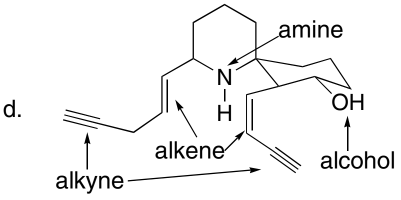
penicillin G

b.



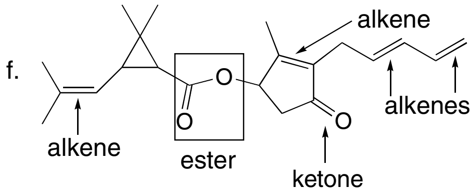
pregabalin

d.



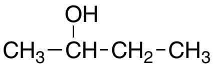
histrionicotoxin

f.



pyrethrin I

3.20

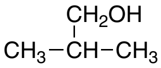


$$CH_3-\overset{OH}{CH}-CH_2-CH_3$$

alcohol

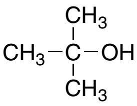
$CH_3CH_2CH_2CH_2-OH$

alcohol



$$CH_3-\overset{CH_2OH}{CH}-CH_3$$

alcohol

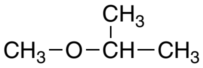


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

alcohol

$CH_3CH_2-O-CH_3CH_2$

ether



$$CH_3-O-\overset{CH_3}{CH}-CH_3$$

ether

$CH_3-O-CH_2CH_2CH_3$

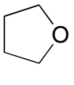
ether

3.21 A cyclic ester is called a lactone. A cyclic amide is called a lactam.

a.

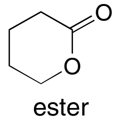
amine

b.



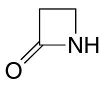
ether

c.



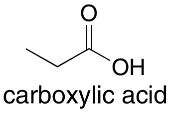
ester
lactone

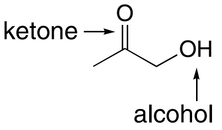
d.

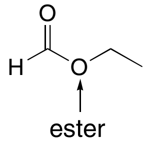


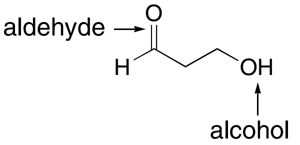
amide
lactam

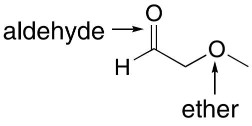
3.22 Draw the constitutional isomers and identify the functional groups.

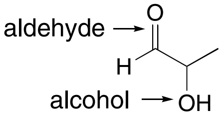


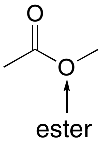




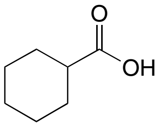




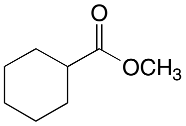




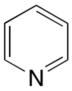
3.23 Use the rules from Answer 3.5.

a. 

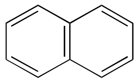
VDW
dipole–dipole
H-bonding (O–H bond)

b. 

VDW
dipole–dipole
no H-bonding (no O–H bond)

c. 

VDW
dipole–dipole
no H-bonding (no N–H bond)

d. 

VDW
no dipole–dipole
(nonpolar C–C, C–H bonds)
no H-bonding (no O, N, F)

3.24 Increasing intermolecular forces: van der Waals < dipole–dipole < H-bonding

a. **increasing intermolecular forces:**

CH_3CH_3 <	CH_3Cl <	CH_3NH_2
VDW	VDW dipole–dipole	VDW dipole–dipole H-bonding

b. **increasing intermolecular forces:**

$$CH_3Cl < CH_3Br < CH_3I \quad \xrightarrow{\hspace{3cm}}$$

Increasing polarizability
stronger intermolecular forces

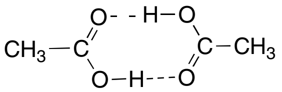
c. **increasing intermolecular forces:**

$(CH_3)_2C{=}C(CH_3)_2$ <	$(CH_3)_2CHCOCH_3$ <	$(CH_3)_2CHCOOH$
VDW	VDW dipole–dipole	VDW dipole–dipole H-bonding

d. **increasing intermolecular forces:**

CH_3Cl <	CH_3OH <	NaCl
VDW dipole–dipole	VDW dipole–dipole H-bonding	ionic

3.25



hydrogen bonding between
two acetic acid molecules

3.26 **A** = VDW forces; **B** = H-bonding; **C** = ion–ion interactions; **D** = H-bonding; **E** = H-bonding; **F** = VDW forces.

3.27 Use the principles from Answer 3.6.

a. $CH_3(CH_2)_4{-}I \qquad CH_3(CH_2)_5{-}I \qquad CH_3(CH_2)_6{-}I$

$$\xrightarrow{\hspace{6cm}}$$

Increasing size, increasing surface area, increasing boiling point

b.

$CH_3CH_2CH_2CH_3$ <	$(CH_3)_3N$ <	$CH_3CH_2CH_2NH_2$
VDW	VDW dipole–dipole	VDW dipole–dipole H-bonding

$$\xrightarrow{\hspace{5cm}}$$

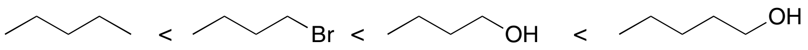
Increasing boiling point

c. $(CH_3)_3COC(CH_3)_3 < CH_3(CH_2)_3O(CH_2)_3CH_3 < CH_3(CH_2)_7OH$

VDW dipole–dipole smaller surface area	VDW dipole–dipole larger surface area	VDW dipole–dipole H-bonding highest bp

Increasing boiling point

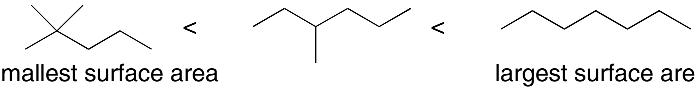
d.



VDW	VDW dipole–dipole	VDW dipole–dipole H-bonding	VDW dipole–dipole H-bonding larger surface area

Increasing boiling point

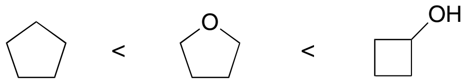
e.



smallest surface area most branching		largest surface area

Increasing boiling point

f.

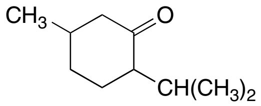


VDW	VDW dipole–dipole	VDW dipole–dipole H-bonding

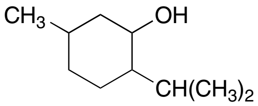
Increasing boiling point

3.28 In $CH_3CH_2NHCH_3$, there is a N–H bond so the molecules exhibit intermolecular hydrogen bonding, whereas in $(CH_3)_3N$ the N is bonded only to C, so there is no hydrogen bonding. The hydrogen bonding in $CH_3CH_2NHCH_3$ makes it have much **stronger intermolecular forces** than $(CH_3)_3N$. As intermolecular forces increase, the boiling point of a molecule of the same molecular weight increases.

3.29 Stronger forces, higher mp.



menthone
VDW
dipole–dipole
lower melting point



menthol
VDW
dipole–dipole
H-bonding
stronger forces
higher melting point

3.30 Stronger forces, higher mp. More symmetrical compounds, higher mp.

a. $(CH_3)_3CH < (CH_3)_2C{=}O < (CH_3)_2CHOH$

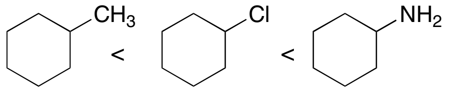
$(CH_3)_3CH$	$(CH_3)_2C{=}O$	$(CH_3)_2CHOH$
VDW	VDW DD	VDW DD H-bonding

$$\xrightarrow[\text{Increasing melting point}]{\text{Increasing intermolecular forces}}$$

b. $CH_3F < CH_3Cl < CH_3I$

$$\xrightarrow[\text{Increasing melting point}]{\text{Increasing polarizability}}$$

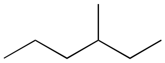
c.



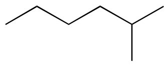
VDW	VDW DD	VDW DD H-bonding

$$\xrightarrow[\text{Increasing melting point}]{\text{Increasing intermolecular forces}}$$

3.31

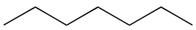


−119 °C
not symmetrical



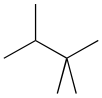
−118 °C
not symmetrical

In both compounds the CH_3 group dangling from the chain makes packing in the solid difficult, so the mp is low.



−91 °C
symmetrical
higher mp

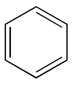
This molecule can pack somewhat better since it has no CH_3 group dangling from the chain, so the mp is somewhat higher. It also has the most surface area and this increases VDW forces compared to the first two compounds.



−25 °C
most spherical
highest mp

This compound packs the best since it is the most spherical in shape, increasing its mp.

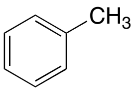
3.32 **Boiling point is determined solely by the strength of the intermolecular forces.** Since benzene has a smaller size, it has less surface area and weaker VDW interactions and therefore a lower boiling point than toluene. The increased melting point for benzene can be explained by symmetry: benzene is much more symmetrical than toluene. More symmetrical molecules can pack more tightly together, increasing their melting point. Symmetry has no effect on boiling point.



benzene
bp = 80 °C
mp = 5 °C

very symmetrical
closer packing in solid form
higher mp

and



toluene
bp = 111 °C
mp = −93 °C

less symmetrical
lower mp

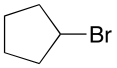
3.33 Increasing polarity = increasing water solubility.

Neither compound is very H_2O soluble.

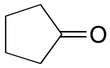
a. $CH_3CH_2CH_2CH_3$ < $(CH_3)_3CH$ < $CH_3OCH_2CH_3$ < $CH_3CH_2CH_2OH$

$CH_3CH_2CH_2CH_3$	$(CH_3)_3CH$	$CH_3OCH_2CH_3$	$CH_3CH_2CH_2OH$
VDW	VDW more spherical (This nonpolar, hydrophobic molecule is more compact, making it more water soluble than its straight-chain isomer, drawn to the left.)	VDW DD	VDW DD H-bonding

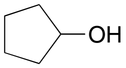
b.



polar
no H-bonding



polar
H-bonding to H_2O,
not itself



polar and
H-bonding
More opportunities
for H-bonding with its
O atom and its H on O.

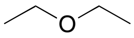
3.34 Look for two things:

- To H-bond to another molecule like itself, the molecule must contain a **H bonded to O**, **N, or F**.
- To H-bond with water, a molecule need **only contain an O**, **N**, **or F**.

Each of these molecules can H-bond to another molecule like itself. Both compounds have N–H bonds.
b. CH_3NH_2, e. $CH_3CH_2CH_2CONH_2$

These molecules can H-bond with water. All of these molecules have an O or N atom.
b. CH_3NH_2, c. CH_3OCH_3, d. $(CH_3CH_2)_3N$,
e. $CH_3CH_2CH_2CONH_2$, g. CH_3SOCH_3,
h. $CH_3CH_2COOCH_3$

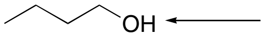
3.35 Draw the molecules in question and look at the intermolecular forces involved.



no H bonded to O

diethyl ether

VDW forces
dipole–dipole forces



H bonded to O:
hydrogen bonding

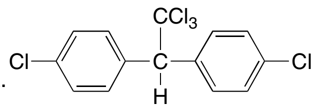
1-butanol

VDW forces
dipole–dipole forces
H-bonding

- Both have ≤ 5 C's and an electronegative O atom, so they can H-bond to water, making them soluble in water.
- Only 1-butanol can H-bond to another molecule like itself, and this increases its boiling point.

3.36 Use the solubility rule from Answer 3.13.

a.

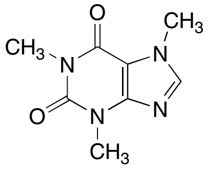


DDT

no N or O

not water soluble

b.



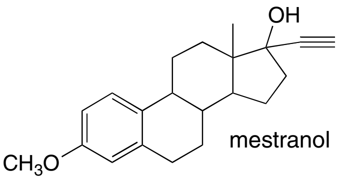
caffeine

many polar bonds with N and O atoms

many opportunities for H-bonding

water soluble

c.



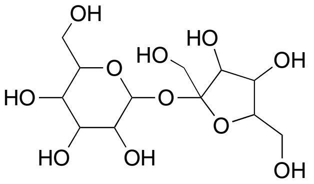
mestranol

2 polar functional groups

but > 10 C's

not water soluble

d.



sucrose

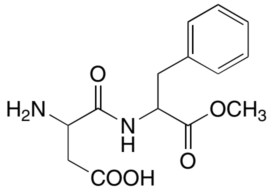
many polar bonds with O

11 O's and 12 C's

many opportunities for H-bonding with H_2O

water soluble

e.



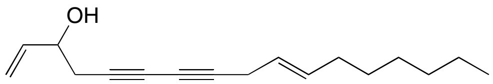
aspartame

many polar bonds with N and O atoms

many opportunities for H-bonding

water soluble

f.



carotatoxin

1 polar functional group

but > 10 C's

not water soluble

3.37

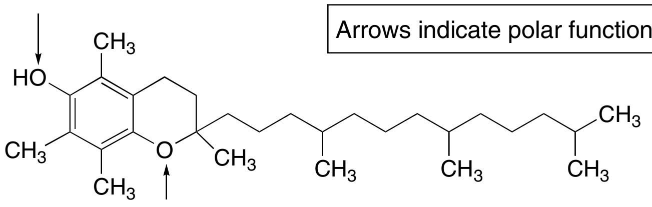
$(CH_3)_2CHCH(CH_3)_2$	$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_5CH_3$	$CH_3(CH_2)_6CH_3$
B	**C**	**D**	**A**
6 C's	6 C's	7 C's	8 C's
Branching makes less surface area, weaker VDW. **lowest bp**	no branching		**highest bp**

C, **D**, and **A** are all long chain hydrocarbons, but the size increases from **C** to **D** to **A**, increasing the VDW forces and increasing bp.

3.38 Water solubility is determined by polarity. Polar molecules are soluble in water, while nonpolar molecules are soluble in organic solvents.

Arrows indicate polar functional groups.

a.



vitamin E

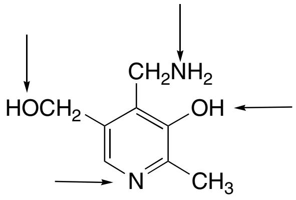
only 2 polar functional groups

many nonpolar C–C and C–H bonds (29 C's)

soluble in organic solvents

insoluble in H_2O

b.



pyridoxine

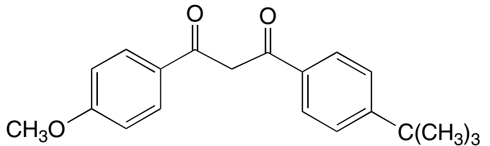
vitamin B_6

many polar bonds and few nonpolar bonds

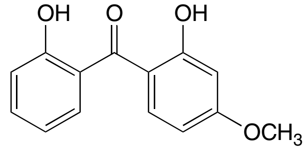
soluble in H_2O

It is also **soluble in organic solvents** since it is organic, but is probably more soluble in H_2O.

3.39 Compare the functional groups in the two components of sunscreen. Dioxybenzone will most likely be washed off in water because it contains two hydroxy groups and is more water soluble.

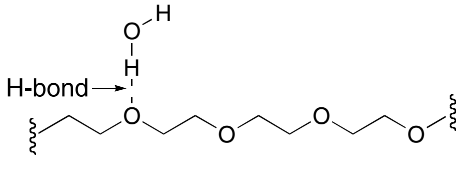


avobenzone
two ketones
one ether

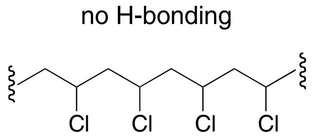


dioxybenzone
two hydroxy groups
one ketone
one ether
more water soluble

3.40 Because of the O atoms, PEG is capable of hydrogen bonding with water, which makes PEG water soluble and suitable for a product like shampoo. PVC cannot hydrogen bond to water, so PVC is water insoluble, even though it has many polar bonds. Since PVC is water insoluble, it can be used to transport and hold water.

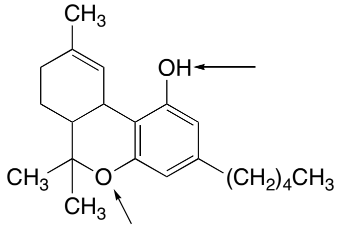


poly(ethylene glycol)
PEG
water soluble



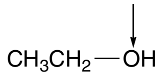
poly(vinyl chloride)
PVC
water insoluble

3.41 Molecules that dissolve in water are readily excreted from the body in urine whereas less polar molecules that dissolve in organic solvents are soluble in fatty tissue and are retained for longer periods. Compare the solubility properties of THC and ethanol to determine why drug screenings can detect THC and not ethanol weeks after introduction to the body.



tetrahydrocannabinol
THC

THC has relatively few polar
bonds compared to the number
of nonpolar bonds, making it
soluble in organic solvents
and therefore **soluble in fatty tissue.**



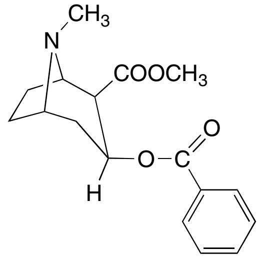
CH_3CH_2-OH

ethanol

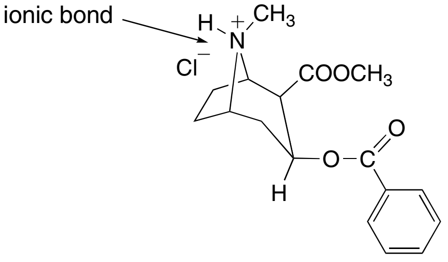
Ethanol has 1 O atom and
only 2 C's, making it
soluble in water.

Due to their solubilities, **THC is retained much longer in the fatty tissue of the body,** being slowly excreted over many weeks, while ethanol is excreted rapidly in urine after ingestion.

3.42 Compare the intermolecular forces of crack and cocaine hydrochloride. Stronger intermolecular forces increase both the boiling point and the water solubility.



cocaine (crack)
neutral organic molecule

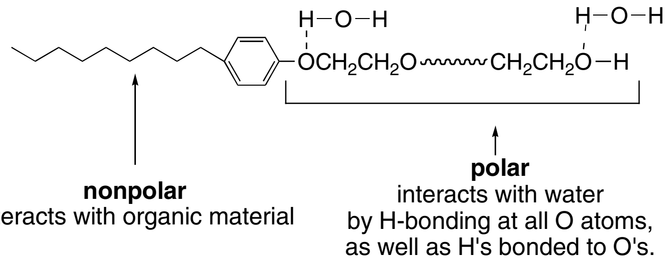


cocaine hydrochloride
a salt

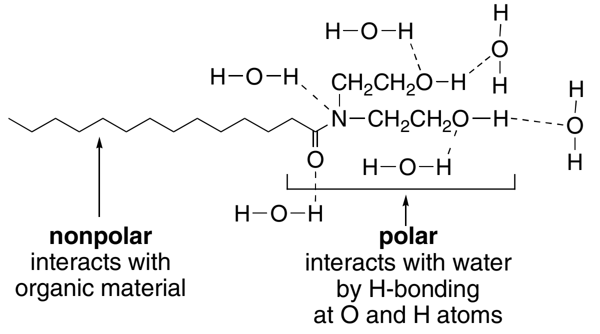
The molecules are identical except for the ionic bond in cocaine hydrochloride. Ionic forces are extremely strong forces, and therefore the cocaine hydrochloride salt has a much **higher boiling point and is more water soluble.** Since the salt is highly water soluble, it can be injected directly into the bloodstream where it dissolves. Crack is smoked because it can dissolve in the organic tissues of the nasal passage and lungs.

3.43 A laundry detergent must have both a highly polar end of the molecule and a nonpolar end of the molecule. The polar end will interact with water, while the nonpolar end surrounds the grease/organic material.

a.



b.



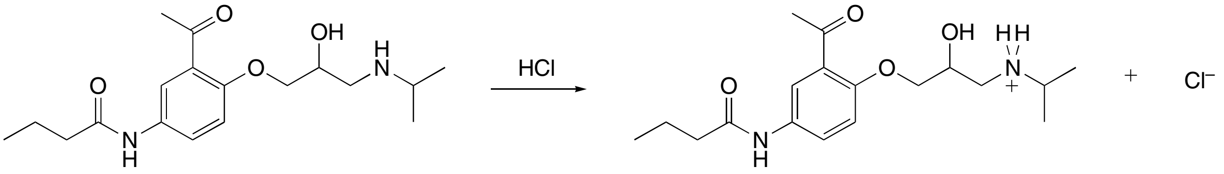
3.44 An emulsifying agent is one that dissolves a compound in a solvent in which it is not normally soluble. In this case the phospholipids can dissolve the oil in its nonpolar tails and bring it into solution in the aqueous vinegar solution. Or, the nonpolar tails dissolve in the oil, and the polar head brings the water-soluble compounds into solution. In any case, the phospholipids make a uniform medium, mayonnaise, from two insoluble layers.

vinegar	oil
aqueous	organic
hydrophilic	hydrophobic

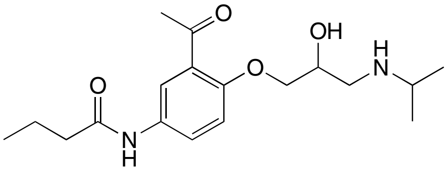
These two ingredients will not mix. The emulsifying agent (egg yolk) has phospholipids that have both hydrophobic and hydrophilic portions, making the mayonnaise uniform.

3.45

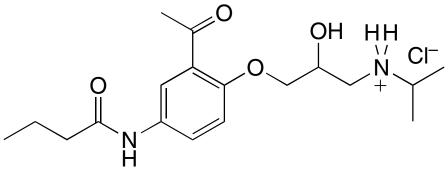
a.



b.



five functional groups that have many opportunities for H-bonding
water soluble

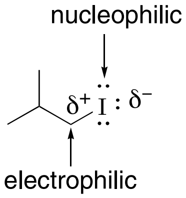


ionic salt
more water soluble

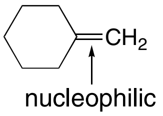
c. Since the hydrochloride salt is ionic and therefore more water soluble, it is more readily transported in the bloodstream.

3.46 Use the rules from Answer 3.17.

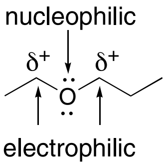
a.



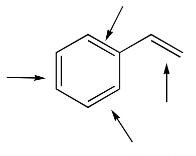
b.



c.

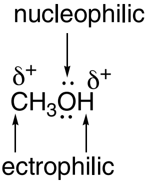


d.

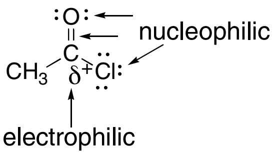


All the C=C's are nucleophilic.

e.



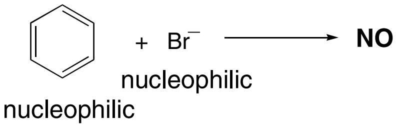
f.



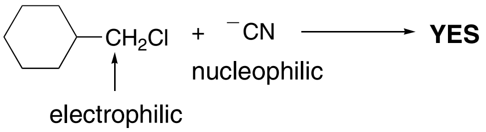
(All lone pairs on O and Cl are nucleophilic.)

3.47

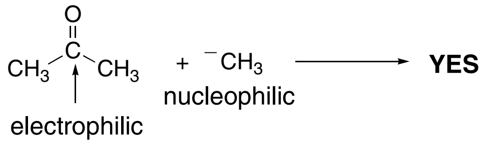
a.



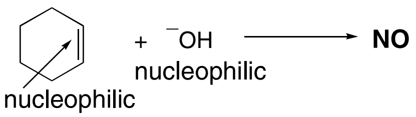
b.



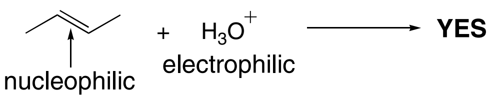
c.



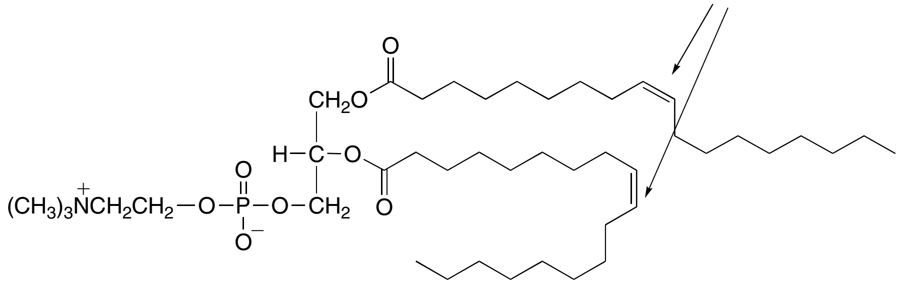
d.



e.

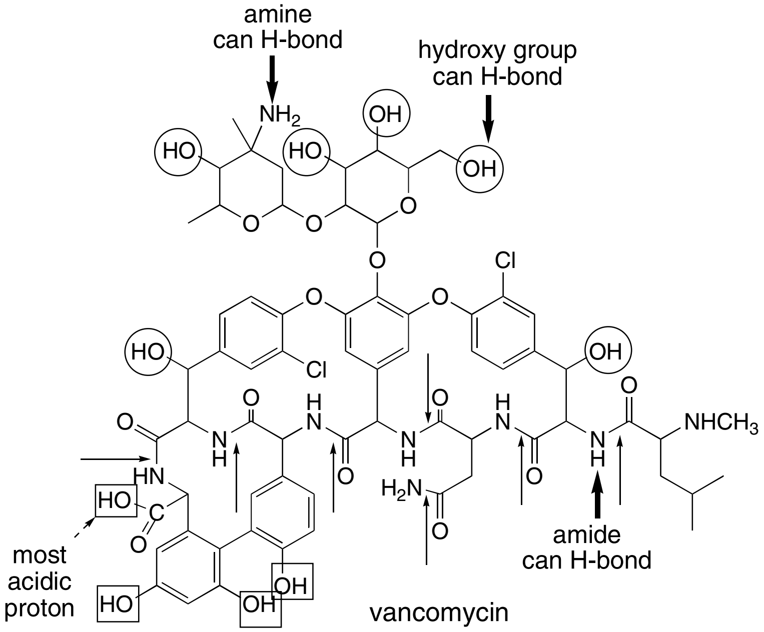


3.48 More rigid cell membranes have phospholipids with *fewer* C=C's. Each C=C introduces a bend in the molecule, making the phospholipids pack less tightly. Phospholipids without C=C's can pack very tightly, making the membrane less fluid, and more rigid.



The double bonds introduce kinks in the chain, making packing of the hydrocarbon chains less efficient. This makes the cell membrane formed from them more fluid.

3.49



vancomycin

a. 7 amide groups [regular (unbolded) arrows]

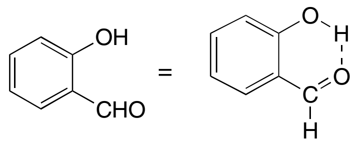
b. OH groups bonded to *sp*^{3} C's are circled. OH groups bonded to *sp*^{2} C's have a square.

c. Despite its size, vancomycin is water soluble because it contains many polar groups and many N and O atoms that can H-bond to H$_2$O.

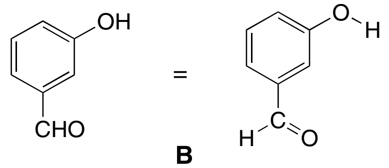
d. The most acidic proton is labeled (COOH group).

e. Four functional groups capable of H-bonding are ROH, RCOOH, amides, and amines.

3.50



A



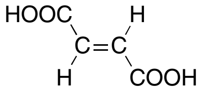
B

The OH and CHO groups are close enough that they can intramolecularly H-bond to each other. Since the two polar functional groups are involved in intramolecular H-bonding, they are less available for H-bonding to H_2O. This makes **A** less H_2O soluble than **B**, whose two functional groups are both available for H-bonding to the H_2O solvent.

The OH and the CHO are too far apart to intramolecularly H-bond to each other, leaving more opportunity to H-bond with solvent.

3.51

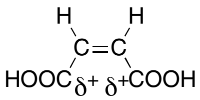
a. melting point



fumaric acid

Fumaric acid has its two larger COOH groups on opposite ends of the molecule, and in this way it can pack better in a lattice than maleic acid, giving it a **higher mp**.

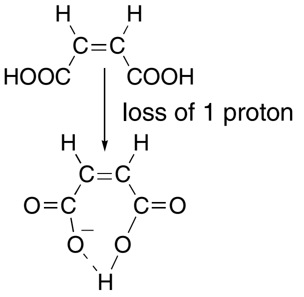
b. solubility



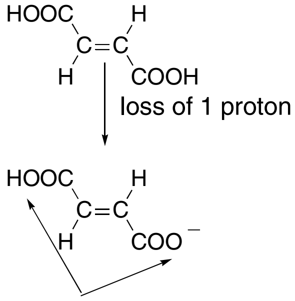
maleic acid

Maleic acid is more polar, giving it greater **H_2O solubility.** The bond dipoles in fumaric acid cancel.

c. removal of the first proton (pK_{a1})

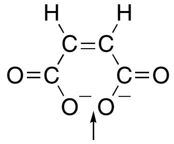


In maleic acid, intramolecular H-bonding stabilizes the conjugate base after one H is removed, making maleic acid more acidic than fumaric acid.

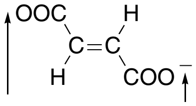


Intramolecular H-bonding is not possible here.

d. removal of the second proton (pK_{a2})



Now the dianion is held in close proximity in maleic acid, and this destabilizes the conjugate base. Thus, removing the second H in maleic acid is harder, making it a weaker acid than fumaric acid for removal of the second proton.



The two negative charges are much farther apart. This makes the dianion from fumaric acid more stable and thus pK_{a2} is lower for fumaric acid than maleic acid.