

MOLECULAR STRUCTURE

For each of the following molecules, make the models and then draw the models, using the hash/wedge/straight-line convention. Use tetravalent atoms. Make double bonds by using two of the soft, flexible white bonds to make “banana double bonds”.

- **For molecules involving lone-pairs, draw them with the lone pairs shown.** Use a hash, wedge, or straight-line to show where in 3-D space the lone pair is, and then put a “double-dot” on the end to illustrate that it’s a lone-pair rather than an atom.
- **Draw in all hydrogens.** Use a hash, wedge, or straight-line to show where in 3-D space the hydrogen is, and draw an H at the end. (In regular “skeleton structures” H’s may be omitted, but for this exercise you need to draw them in to practice and to help understand where they actually sit.)
- **You do not need to write “C” on carbons.** As in regular “skeleton structures”, the understanding is that any vertex (or end of stick) is a C unless indicated otherwise. But anything that isn’t a carbon (whether H, N, O, Br, or lone-pair) you need to specify.

Guidelines for Drawing Models:

A. 3-D Perspective

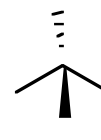
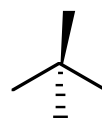
1. Keep as many atoms as possible in a single plane (plane of the paper) by zig-zagging.
Connections within the paper are drawn with straight lines.
2. Use wedges to indicate atoms that are in front of the plane.
3. Use hashes to indicate atoms behind the plane.

B. For any tetrahedral atom, only 2 attachments can be in the plane, 1 must be in front, and 1 behind.

- if the two in the plane are “down”, the hash/wedge should be up
- if the two in plane are “up”, the hash/wedge should be down.
- the hash/wedge should never point in same direction as the in-plane lines, or else the atom doesn’t look tetrahedral
- for polyatomic molecules, it is strongly preferable to NOT have either of the in-plane atoms pointing straight up. Straight-up in-plane atoms do not lend themselves to extended 3-D structures.



Good! Look tetrahedral



Bad! These don't look tetrahedral!

1. ALKANE. butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

- take the chain and wiggle around all the single bonds.
- The most stable actual shape is the one with the carbons zig-zagged and co-planar.
- Notice the symmetry possible.

2. ALKANE. Pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

3. HALOALKANE. 2-bromobutane, $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$

-notice that if the 4 carbons are co-planar zig-zagged, the attached Br can't be in the same plane.

-Compare with a partner two structure in which the Br is in front(wedged) in one versus behind (hashed) in the other. Are they the same molecule, or isomers? (Q2 on "same-or-different" page)

-ignore the lone pairs on the Br (in this case)

4. ALKENE. Draw both: a) trans-2-butene, $\text{CH}_3\text{CH}=\text{CHCH}_3$
and b) cis-2-butene

(trans means the two CH_3 groups are on the opposite sides of the double bond; cis means they are on same side)

-notice that not only the 2 double-bonded

C's but also the four atoms directly

attached are all co-planar.

5. ALKYNE. 2-butyne, CH_3CCCH_3

-draw Lewis structure first

6. WATER. H_2O

-DRAW at least 2 different orientations, and specify the lone-pairs.

-Draw pictures in which both the oxygen and both the hydrogens are in the plane of the paper.

-For building the model, visualize a lone-pair by using a stick without an atom at the end.

-draw in the lone pairs for this and all following pictures. (For this assignment; not normally required for class!)

7. ALCOHOL. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$

8. ETHER. Diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

9. FORMALDEHYDE. CH_2O .

-for 9-16, make sure you draw the Lewis structure before you build models and draw the 3-D picture. If you don't know the connectivity, you have no chance!

10. ALDEHYDE. $\text{CH}_3\text{CH}_2\text{CHO}$.

11. KETONE. $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3$.

12. ACID. $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$.

13. ESTER. $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$.

14. AMMONIA. NH_3

15. AMINE. $(\text{CH}_3\text{CH}_2)_2\text{NH}$

16. AMIDE CH_3CONH_2 .

17. CYCLIC COMPOUNDS

A. Cyclopropane (CH₂)₃

-notice how hard this is, how the bonds “bend”, etc.. Real cyclopropane experiences real “ring strain” based on the impossibility of achieving 109° bond angles.

18. Things that can't be completely drawn “3-D”. 2-methylbutane, CH₃CH₂CH(CH₃)₂

-notice that not all 5 of the carbons can be coplanar. Structures like this can't be illustrated completely or easily. What you should do is simply draw “CH₃” as being out-of-plane, but don't try to illustrate the “3-D-ness” of that carbon. Ask instructor for confirmation.

19. CYCLIC COMPOUNDS

B. Cyclohexane (CH₂)₆

-Don't bother to draw! Too tough! But do build the model.

1) notice that the 6 carbons do not easily remain coplanar. By puckering, ideal 109° bond angles can be achieved.

2) In the best model, 3 H's point straight down, 3 H's point straight up, and 6 H's essentially extend almost horizontally. The “horizontal” H's are called “equatorial” and the “vertical” H's are called “axial”.

3) Try to put colored balls into the “axial” positions. Then try to manipulate the model so that the “axial” atoms become “equatorial”, and the “equatorial” atoms become “axial”.

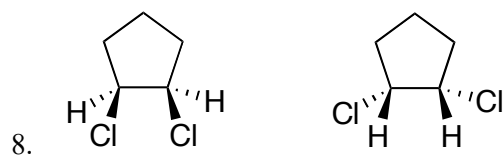
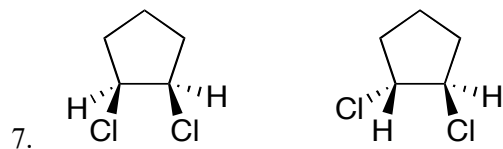
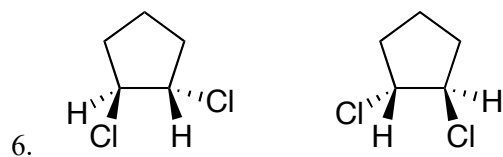
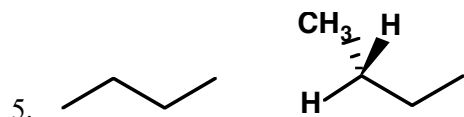
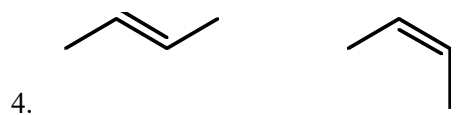
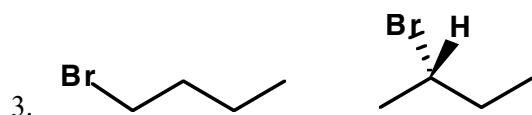
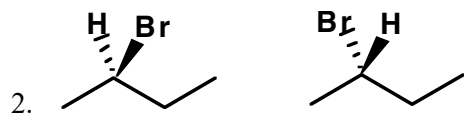
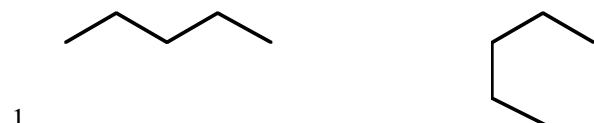
-ask instructor to come over and give you cyclohexane spiel

SAME OR DIFFERENT?

Rules:

1. Structures which can be interchanged or made equivalent by rotations around single bonds are considered to be the same.
2. “Isomers” are things with the same formula that can't be made superimposable by simple rotations around single bonds.
(not required, but for class will eventually need to be able to distinguish “structural isomers” from “stereoisomers”)

Classify the following pairs as “same” or “isomers”



Chem 355 Jasperse

RECRYSTALLIZATION-Week 2

1. Mixed Solvent Recrystallization of Acetanilide
2. Mixed Solvent Recrystallization of Dibenzylacetone
3. Recrystallization of an Unknown

Background

Review: Recrystallization is an important technique for purifying organic solids. The contaminated solid is dissolved in a minimum of hot solvent, then cooled. The amount of solvent that is used should be just enough so that the solvent is just barely saturated or almost saturated when it is boiling hot. Upon cooling the solubility decreases, and crystal formation can occur. The new crystals are purer than the original because impurities are left in the solvent. Slow, gradual cooling is best for formation of pure crystals. Filtration then provides purified material. Some mass loss always occurs, because the solvent holds not only the impurities but also some of the desired material as well. Additional unnecessary mass loss can occur if you use too much solvent, don't heat your solution to boiling in the process of dissolving your sample, if you don't cool adequately, or if you wash your product crystals excessively. An appropriate solvent needs to have mediocre dissolving power: strong enough to dissolve the sample when boiling hot, but not able to dissolve too much of the sample when cold.

General Mixed Solvent Procedure, Concept: Often it's difficult to find a single solvent with appropriate dissolving power. Further, it's often difficult to decide exactly how much of the solvent is ideal. Frequently the use of mixed solvents is a practical and convenient solution.

In the usual mixed solvent recrystallization procedure, dissolve your sample in a sufficient quantity of your "better" solvent by heating it up to the boiling point. A 4 mL/1 g ratio is the default starting guess. Add more solvent if necessary, or boil some off if you judge it's obviously way more than needed. Then add "bad" solvent (usually hot water), until either you reach a visible "saturation" point (the "lucky" situation, where you can see crystals or slight cloudiness beginning to form) or until you have a 1:1 solvent ratio. Let cool so as to grow more crystals and harvest by filtration.

An alternative and often preferred strategy is if you intentionally or unintentionally start with a solvent that does not have enough dissolving power to dissolve the solid, even when hot. You can then add as much hot "better solvent" as needed to barely dissolve the sample (while boiling hot.)

When mixed solvents are used, it is essential that they be co-soluble. Otherwise the bad solvent will simply create a second layer, but the sample can remain soluble in the original layer.

Ethanol/water combinations are commonly used because ethanol has good dissolving ability for many organics, but is also infinitely co-soluble with water. Addition of water can rapidly and dramatically reduce the solubility of many organics and thus induce crystallization. While organic mixtures are also frequently useful, the difference in character between two organics is rarely as dramatic as the difference between water and an organic solvent.

Difficult Crystallizations: Sometimes crystallization is slow or difficult. Crystallization must start on some nucleation center. (Crystals grow when molecules "fit" onto some preexisting surface.) Sometimes this will happen spontaneously, but sometimes it is difficult. The formation of "supersaturated" solutions, in which the solvent holds more sample than it could if equilibrium existed, are routine. Some common techniques for initiating crystallization include:

- Seeding the saturated solution with some of the desired sample that is already in solid form.
- Scratching the insides of your flask with a rough glass rod. (By scratching the surface of your glass, you can get a rough edge which may coincidentally serve as a crystallization surface.)
- Using old, scratched up flasks!
- Leaving a boiling stick, preferably broken off so it has rough shards sticking out at the end.
- Adding an ice chip. (The surface is often rather rough, and can serve as a nucleation site. In addition, because the surface is pure water, the solvent composition near the ice chip is not representative of the bulk solvent distribution. Being water-rich, solubility may be especially poor resulting in crystal initiation. The ice chip serves to provide a local area of extremely "bad solvent".)
- Wait a long time!
- Find a better solvent.