

Name _____ Section _____

Partner(s) _____ Date _____

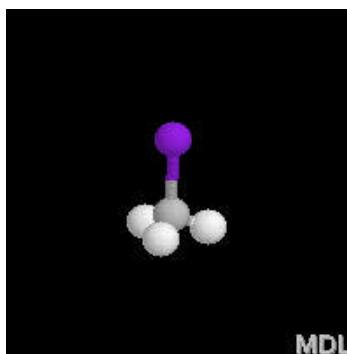
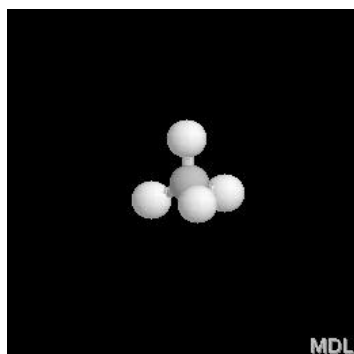
DISCOVERING INTRAMOLECULAR INTERACTIONS

To complete this activity go to the following Internet site:

http://academic.pgcc.edu/~ssinex/DII_103/intramol.htm

Images will be interactive at this site. Use these sheets to record requested information.

Methane and iodomethane have four atoms surrounding the central carbon. Based on your experience with VSEPR, what would the bond angles be? With the cursor on the image click and hold while moving the mouse to rotate the molecule.



To check if you are correct, compare the H-C-H bond angles in methane (left) and iodomethane (right) shown above. Right click, go to select and then mouse click action, and then choose angle. You can also determine bond distance and torsion angle from the same Chime menu. The table below summarizes the actions you can take on the images.

Property Measured	Action Taken on Chime Image
bond angle	select and click on three consecutive connected atoms.
distance	place the cursor on the first atom, click and then select a second atom and click.
torsion angle	click on four adjacent connected atoms in succession. The torsion angle is the angle between the first and fourth atom while sighting down the axis between the second and third.

Watch the lower left of your browser screen to get the measured property results. The distance x 100 will give you picometers (pm). See the [Chime Guide](#) for help.

Methane _____ Iodomethane _____

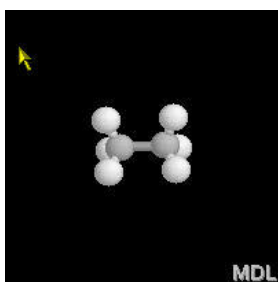
Why are they different?

A large constituent atom, such as iodine, in a molecule can push other atoms away and hence, change the bond angles. This is a type of INTRAmolecular interaction or an interaction WITHIN the molecule. This activity will explore intramolecular interactions in a variety of molecules. The bond between atoms in a molecule is a type of intramolecular interaction; however, we are not going to examine this; we are going to look at the interaction between non-bonded constituents, such as the iodine affecting the location of the hydrogens in iodomethane. The importance of intramolecular interactions in biological materials will be demonstrated.

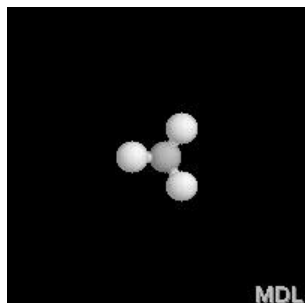
The interactions BETWEEN two different molecules (or molecules and ions) are INTERmolecular forces. Intramolecular interactions are different from the intermolecular forces (IMFs) that you studied previously to help explain differences in properties of liquids (such as boiling points). IMFs are short-range attractive forces that may be dipole-dipole, hydrogen bonds, ion-dipole, or dispersion forces.

Using the wooden ball and stick model kit, build a molecule of ethane, C_2H_6 . What motions within the molecule are possible? Feel free to manipulate the model you built.

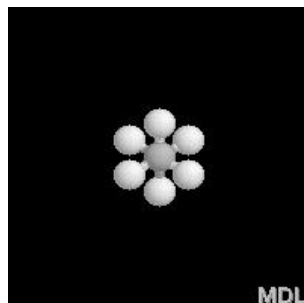
Look at the animation of the ethane molecule, C_2H_6 , and describe the motion.



Which of the two possible arrangements of ethane shown below would be the most stable (that is, have the lowest energy)? Think about interactions between the hydrogen atoms in the ethane. View the molecule in the space-filled mode and decide if your answer is reasonable. (Right click, select display, and select spacefill and then Van der Waals radii) The van der Waals radius is the estimated radius to the edge of the electron cloud in a non-bonding situation.



eclipsed

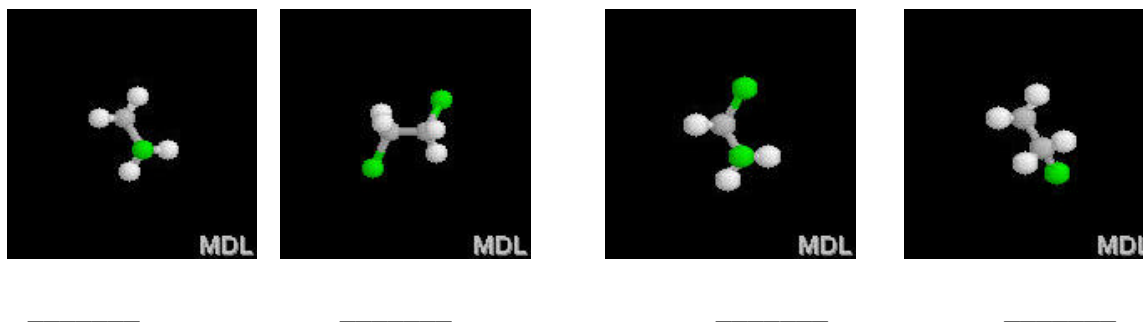


staggered

The two different arrangements of ethane above are the result of rotation around the carbon-carbon bond. This is called internal rotation. The repulsive interactions of the hydrogens can be minimized by staggering the configuration of the hydrogens in the molecule.

Now suppose we substituted one chlorine atom in place of one hydrogen atom on each carbon. Using the wooden ball and stick model kit, build a molecule of 1,2-dichloroethane ($C_2H_4Cl_2$) by replacing a hydrogen on each carbon with a chlorine.

Consider the four structures of 1,2-dichloroethane given below. What motion in the molecule yields the four structures? You may want to align the molecules and with your eyes to look down the C-C bond.



Measure the Cl-C-C-Cl [torsion angle](#) in each of the dichloroethanes and record on the lines above.

View the molecules in the space-filled display mode, which more closely illustrates the true size of the electron clouds around the atoms. How would you describe the chlorine atoms on the molecules?

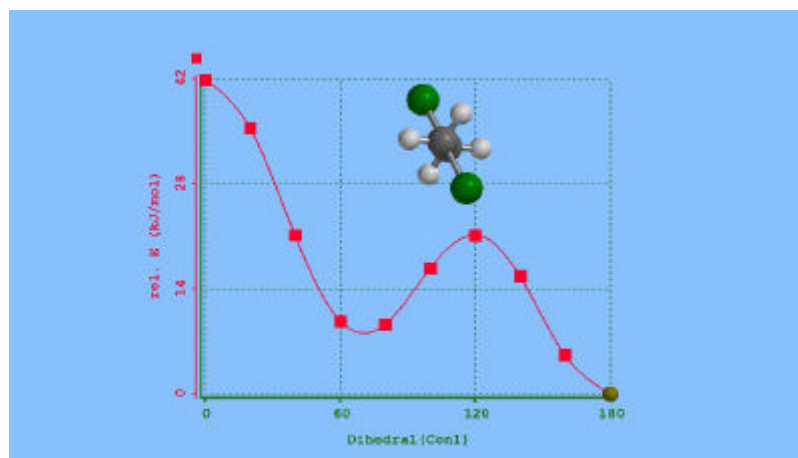
Change the display back to ball and stick and then generate the [electrostatic potential surfaces](#) for all four molecules. Use the red-white-blue color scheme, where red is negative and blue is positive. How does the charge on the chlorine atoms compare to the remaining part of the molecule?

How would the chlorine atoms interact with each other? Why?

Which of the four structures would be the most stable (lowest energy)? Why?

Would 1,2-dichloroethane have a permanent dipole moment? Explain why or why not.

These four structures differ only because of the internal rotation around the C-C single bond. No bonds were broken and/or changed. These rotationally different structures of a compound are isomers called **conformers**. Usually the interconversion of one conformer to another is so fast the isomers cannot be isolated. The conformer with the Cl-C-C-Cl torsion angle of 180° would have the lowest energy. The highest energy conformer would have a torsion angle of 0° due to the interaction of the chlorines. The molecule would not have a permanent dipole moment since these structures interconvert. The energy of the conformer can be calculated using computational software. The relative energy (y-axis) of each conformer can be graphed as a function of torsion (or dihedral) angle (x-axis) and is presented in the image below. This image is linked to a movie that shows the structure of the conformer at each point on the graph. Click on the image to bring up the Windows media player and view the animation (it's a big file, so it will take a while to load).



Produced by Spartan '02

Explain the variation of the relative energy as the torsion angle changes.

Does the molecule respond in any other way? Using Excel, plot the data in the table below where the Cl-C-C bond angle is given as the torsion angle varies, as well as, two bond lengths as a function of torsion angle. Produce two graphs- one with bond angle and the other with the bond lengths. Explain any trends in the data. You can copy the data and paste it into an Excel spreadsheet.

Torsion or Dihedral Angle Cl-C-C-Cl	Bond Angle Cl-C-C	Bond Length Cl-C (pm)	Bond Length C-C (pm)
180.00	109.40	179.16	151.60
160.00	109.91	179.22	152.03
140.00	111.07	179.24	152.93
120.00	112.08	179.18	153.28
100.00	112.50	179.04	152.53
80.00	112.62	178.74	151.64
60.00	113.54	178.41	151.61
40.00	115.41	178.16	152.63
20.00	116.92	178.08	154.04
0.00	117.45	178.06	154.73

Let's consider the total amount of variation in the bond angle and the bond lengths as the torsion angle changed for the data above. Calculate the percentage change and compare*.

$$\% \text{ Change} = 100 (\text{range})/(\text{average value})$$

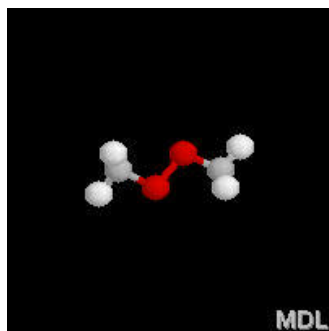
where range = high value - low value

*A better way to do this would be to calculate the standard deviation and the coefficient of variation as a percent (%CV).

quantity	Bond Angle Cl-C-C	Bond Length Cl-C	Bond Length C-C
average			
range			
% change			

How does the variation in bond angle compare to the variation in the bond length?

Now construct a molecule of dimethyl peroxide, $\text{H}_3\text{C-O-O-CH}_3$, and predict the most and least stable conformers by considering rotation around the O-O bond. Sketch the conformers. One of the conformers is shown below.



Are the possible interactions within dimethyl peroxide as it rotates around the O-O bond the same or different than those in 1,2-dichloroethane? Compare your ball and stick models.

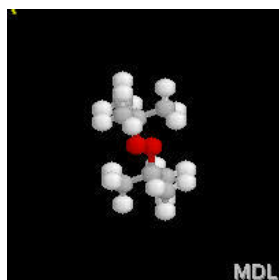
Using your model of dimethyl peroxide, move the groups through the various conformers from a torsion angle of 0° to 180° . At each stage, think of the relative energy based on interactions. Sketch a graph of relative energy as a function of torsion angle.

Once you have finished the sketch [click here](#) to see an animation of the graph of relative energy as a function of torsion angle. How close was your predicted graph to the actual?

How is the graph for the peroxide different from the 1,2-dichloroethane? Explain how and why this might be.

What will happen if the methyl groups $[-\text{CH}_3]$ are changed to the bulkier t-butyl groups $[-\text{C}(\text{CH}_3)_3]$?

Build a molecule of di-t-butyl peroxide, $(\text{CH}_3)_3\text{C}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$. One of the conformers is shown below. Using your model, move the groups through the various torsion angles.



Did you have any problems with the wooden ball and stick model?

How is the real molecule going to overcome the problems of the wooden model?

How is the C-O-O bond angle going to compare for eclipsed and staggered configuration of the two peroxides?

Let's examine some data for the two peroxides. Using Excel, plot a graph of bond angle as a function of torsion angle for both peroxides. Print and attach a copy of this graph.

Torsion or Dihedral Angle C-O-O-C	dimethyl peroxide Bond Angle C-O-O	di-t-butyl peroxide Bond Angle C-O-O
180.00	104.26	109.80
160.00	104.39	110.09
140.00	104.69	111.08
120.00	105.10	113.46
100.00	105.98	116.94
80.00	108.32	120.82
60.00	110.57	125.39
40.00	113.25	127.54
20.00	115.28	129.47
0.00	116.05	129.97

Explain the reason for the difference between the two peroxides.

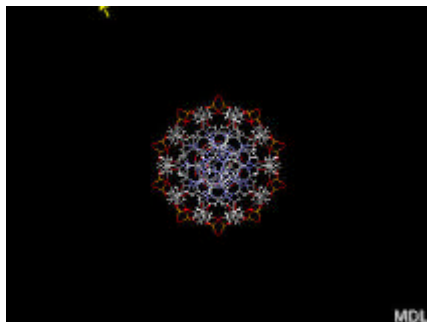
We have been looking at interactions that are repulsive. Are all intramolecular interactions repulsive? Explain.

One of the strongest IMFs is the hydrogen bond. Look at the structure of salicylic acid given below.



Can you find a position in the molecule where an intramolecular hydrogen bond can form? Indicate where this might be.

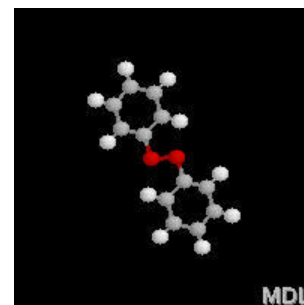
The DNA molecule is shown below. What is holding the two strands together? Right click, select options, and then display hydrogen bonds. Look for the dashed lines in the molecule. You may want to zoom in by holding the shift key down and moving the mouse.



Intramolecular hydrogen bonds play an important role in maintaining the structure of biological materials, such as secondary (coiled) and tertiary (folded) structures of proteins and the double helix of DNA. Other types of intramolecular attractions, such as electrostatic interactions between -NH_3^+ and -COO^- , also occur in proteins.

Post-laboratory Questions

1. How do you think the graph of the C-O-O bond angle as a function of torsion angle for diphenyl peroxide, $\text{C}_6\text{H}_5\text{-O-O-C}_6\text{H}_5$, will compare to the other two peroxide examined earlier? Is the phenyl [$\text{-C}_6\text{H}_5$] group (MM = 77 g/mole) as bulky as the t-butyl [$\text{-C}(\text{CH}_3)_3$] group (MM = 57 g/mole)? Ball and stick model is available! The phenyl group is derived from benzene, a planar six member carbon ring with alternating single and double bonds.



Sketch your prediction as a dashed line on your earlier graph. Attach your graph.

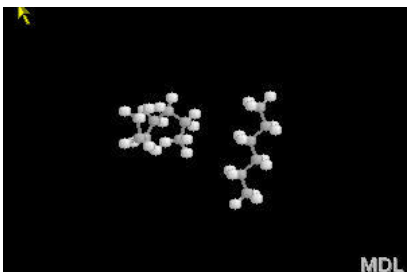
2. Hydrogen peroxide, H_2O_2 or H-O-O-H, has a permanent dipole of 2.0D, which is comparable to water at 1.9D. What does this infer about internal rotation around the O-O bond?

[Click here](#) to see how the relative energy varies with the torsion angle for H_2O_2 . How is this graph different from previous relative energy as a function of the torsion angle plots?

What is the torsion angle for the lowest energy structure? Sketch and label the graph for H_2O_2 .

3. In general, the overall shape of a molecule can change. How does this occur?

Which conformer of hexane, C_6H_{14} , has the lower energy? Why?



4. Is the flexibility of a molecule shown by larger changes in bond lengths or bond angles?
5. In a molecule, are bond angles and bond lengths constant? Explain.