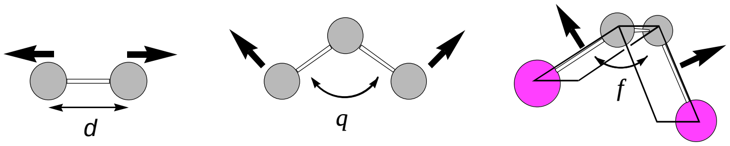
3. An Introduction to Molecular Mechanics

Introduction

When you use Chem3D to draw molecules, the program assigns bond lengths and bond angles based on experimental data. The program does not contain real data for all compounds. The molecular model you draw uses *typical* values for lengths and angles. Any deviation from the *optimal* structure of a molecule, as defined by optimum bond lengths (*d*), bond angles (*?*) and torsion angles (*f*), will increase its potential energy.



The increase in energy arising from distortions of bond lengths, bond angles and torsion angles is called strain energy, E_s. Molecular mechanics is a method for calculating the strain energy of a molecule, and for the program to try to optimize the structure (*i.e.*, minimize E_s) by stretching or contracting bond lengths, opening and closing of angles, and twisting around single bonds. The optimized structure has the lowest strain energy where:

$$E_s = E_{\text{bond stretching}} + E_{\text{angle bending}} + E_{\text{torsion strain}} + E_{\text{non-bonding interactions}}$$

The effects of stretching, bending and twisting on the total energy of a molecule is known from experimental observations. Molecular mechanics treats bonds as springs which can be stretched, bent or twisted. The program adjusts each parameter (*d*, *?* and *f*) independently, many time over (in an iterative process), until the strain energy is minimized.

Bond Stretching

The energy required to stretch a spring is determined by a spring constant and can be calculated from Hooke's law. Similarly, the approximate strain energy associated with stretching or contracting a bond to a length *d* from its equilibrium length, d_o, can be determined from the equation:

$$E_{\text{bond stretching}} = K_s\,(d - d_o)^2$$

where K_s is a measure of bond stiffness. As expected, the energy increases as you stretch or contract the bond further from its equilibrium length.

Angle Bending

The strain associated with bending an angle away from its equilibrium value, $?_o$, is a function of the angular displacement ($? - ?_o$):

$$E_{\text{bending}} = K_b\,(? - ?_o)^2$$

where K_b is a measure of resistance to bending.

Torsion Angle Strain

The contribution of twisting around a bond to the strain energy is given by:

$$E_{\text{torsion}} = \sum_{n=1}^{n=3} \frac{V_n}{2}\left[1 + \cos(nf - f)\right]$$

where V_n is a torsional force constant. The only issue of importance to us here is that the energy depends on the torsion angle (f). We will explore torsion angles in more detail in Exercise 4.

Non-bonding Interactions

There is a small attractive force between atoms which are not bonded to one another (van der Waals interaction). When the atoms get too close, there is a strong repulsion. The attractive force falls off very quickly (by a factor of d^6, where d is the distance), so it is very small even at short distances (a few Å). The repulsive force increases rapidly only when the atoms make contact.

Another force between non-bonded atoms arises from the interaction of charges and bond dipoles. The electrostatic interaction of two charged particles is given by:

$$E_{\text{electrostatic}} = q_1 \cdot q_2 / d \cdot \mathrm{D}$$

where q_1 and q_2 are the charges, d is the distance between the charged particles, and D is a dielectric constant. Since the charges may be positive or negative, this equation accounts for the attraction of opposite charges (if q_1 and q_2 have opposite signs $E_{\text{electrostatic}}$ is negative, corresponding to a decrease in energy). It also accounts for repulsion of similar charges (an increase in energy). In uncharged molecules, there will be electrostatic interactions between bond dipoles. Since bond dipoles (μ) are vector quantities, the interaction depends on both the magnitude and relative orientation of two dipoles. Thus, alignment of dipoles raises the potential energy of a molecule.

In the following problems, you will draw simple molecules in Chem3D. Since the first structure you will draw is only a best guess at the most stable geometry, you will let the computer optimize the bond lengths (d), angles ($?$) and dihedral angles (f) by minimizing the strain energy. Then you will change a single parameter (d, $?$ or f) to examine its effect on the energy of the molecule.

Limitations

It is especially important to realize and understand the limitations of molecular mechanics. ChemOffice Ltd does not specifically calculate electronic effects and cannot do any calculations related to transition states. If you receive an error message saying “Sorry the Minimize Energy... command cannot be completed because some of the atoms in this model cannot be assigned atom types” or “Warning: Errors in the model may prevent minimization. [See Messages window]”, the program may not be able to do the calculation because the molecule contains an unknown, or rarely found arrangement of atoms or functional groups. Many functional groups and reactive intermediates cannot be modeled. Energy values that are calculated are strain energies. Energy *differences* between isomers or conformers may or may not be a close approximation of differences in free energy (*?G*) or enthalpy (*?H*).

Problem 3.1

Analyze the effect of changing the C-C bond length of ethane on the strain energy of the molecule..

i. *Build a cylindrical bond model of ethane (see Exercises 1 and 2).*
ii. *Perform an energy minimization: Select Minimize Energy from the MM2 menu and click Run. Let the calculation run until the total energy is displayed in the Messages window. Measure the length of the C-C bond (see Exercise 2).*
iii. *Compress the C-C bond length to 1.2 Å: Choose the Selection tool, click on the C-C bond; select Set Bond Length from the Object menu; type* 1.2 (in the Measurements Window that appears) *and hit return.*
iv. *Select Minimize Energy from the MM2 menu and Compute Properties from the Job Type Box to measure the strain energy without reminimizing. The strain energy will appear in the Messages window.*

Problem 3.2

Analyze the effect of bending the C-C-C angle of propane on the strain energy of the molecule.

i. *Build a cylindrical bond model of propane (see Exercises 1 and 2).*
ii. *Perform an energy minimization: Select Minimize Energy from the MM2 menu and click Run. Let the calculation run until the total energy is displayed in the Messages window. Measure the C-C-C angle.*
iii. *Compress the C-C-C angle to 95E: Shift-click on the three carbon atoms; select Set Bond Angle from the Object menu; type* 95 *and hit return.*
iv. *Select Minimize Energy from the MM2 menu and Compute Properties from the Job Type Box to measure the strain energy without reminimizing. The strain energy will appear in the Messages window.*

Problem 3.3

Analyze the effect of rotating around the C(2)-C(3) bond of butane on the strain energy of the molecule.

i. *Build a cylindrical bond model of butane (see Exercises 1 and 2).*

ii. *Set the dihedral angle between the two methyl groups to 180 E: Shift-click on the four carbon atoms in sequence; select Set Dihedral Angle from the Object menu; type* 180 *and hit return.*

iii. *Perform an energy minimization: Select Minimize Energy from the MM2 menu and click Run. Let the calculation run until the total energy is displayed in the Messages window. Measure the C-C-C-C torsion angle.*

iv. *Set the dihedral angle between the two methyl groups to 150E: Shift-click on the four carbon atoms in sequence; select Set Dihedral Angle from the Build menu; type* 150 *and hit return.*

v. *Select Minimize Energy from the MM2 menu and Compute Properties from the Job Type Box to measure the strain energy without reminimizing. The strain energy will appear in the Messages window.*

Problem 3.4

Analyze the effect of separating the ions of ammonium iodide (NH_4^+ I^-) on the strain energy.

i. *Build a cylindrical bond model of ammonium iodide. One way to do this is to select the bond drawing tool in Chem3D and then click-and-drag to draw a molecule of ethane which we will modify. Choose the Selection tool, and select one of the carbons. Type* N ammonium (or N+) *in the text replacement box at the top of the window and hit return. Select the other carbon, type I- in the text replacement box and hit return. Now delete the N-I bond; select the bond and then select Break Bond from the Object Menu. Move the iodide atom to a new position for clarity. To do this select the iodide atom, hold down the left mouse button and drag it to a new location in the window. Check that you have a tetrahedral* NH_4^+ *and a separate* I^- *ion.*

ii. *Perform an energy minimization: Select Minimize Energy from the MM2 menu and hit return. Let the calculation run until the total energy is displayed in the Messages window. If one of the ions disappears from the screen you can retrieve it by either clicking on the zoom out button in the bottom left-hand corner of the window, or choose Fit Model to Window from the View menu. Measure the distance between the nitrogen and the iodine (see Exercise 2).*

iii. *Set the N-I distance to 6 Å: Shift-click on the nitrogen and iodine atoms; select Set Distance from the Object menu, type* 6 *and hit return.*

iv. *Select Minimize Energy from the MM2 menu and Compute Properties from the Job Type Box to measure the strain energy without reminimizing. The strain* *energy will appear in the Messages window.*