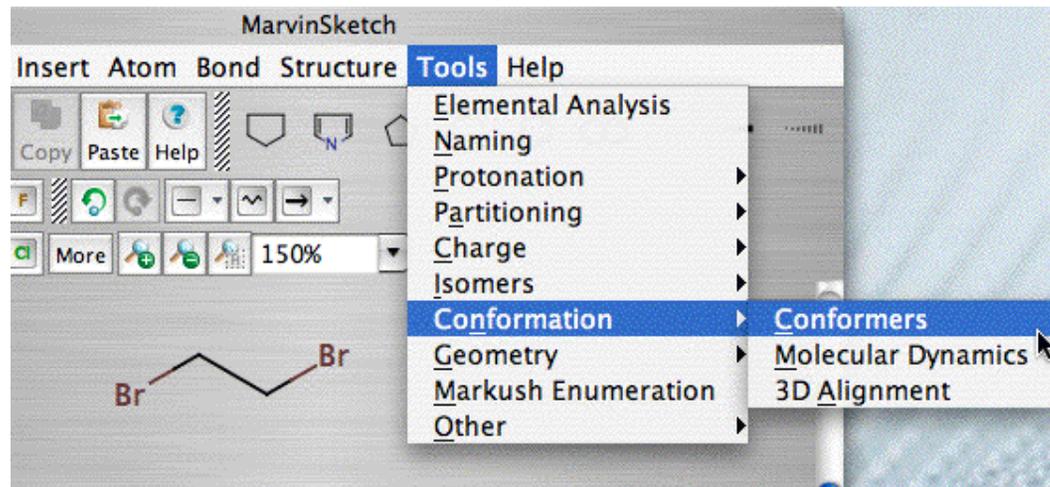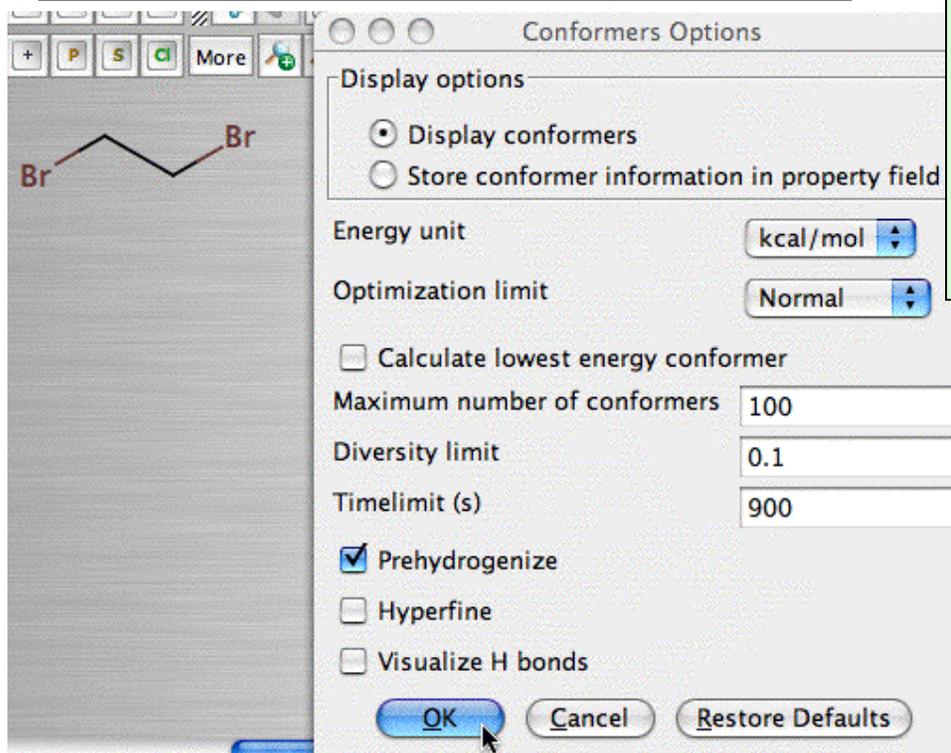# 1,2-Dibromoethane Conformations

For ethylbromide, each conformational minimum had an identical structure. That is, the structure at the 60° minimum cannot be distinguished from that at 180°. Because these conformational isomers have indistinguishable structures, they also possess identical energies (i.e., each one of the conformational states are equally populated).
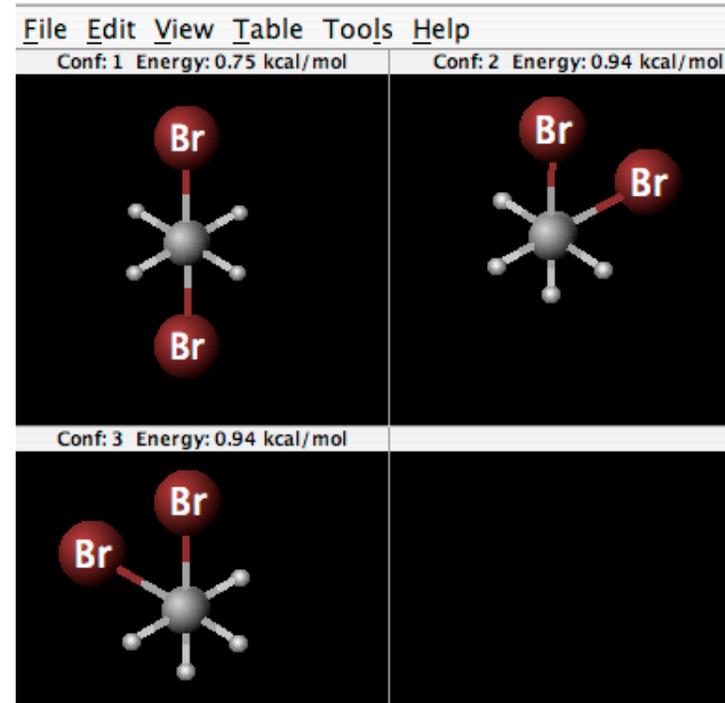
The situation is different with 1,2-dibromoethane. In MarvinSketch (http://butane.chem.uiuc.edu/jsmoore/marvin_scripts/MarvinSketch_Practice.html) draw 1,2-dibromoethane. Use the conformation tool as shown by these screenshots to find the conformational states of this molecule (the default settings may differ slightly for PC vs. Mac platforms).
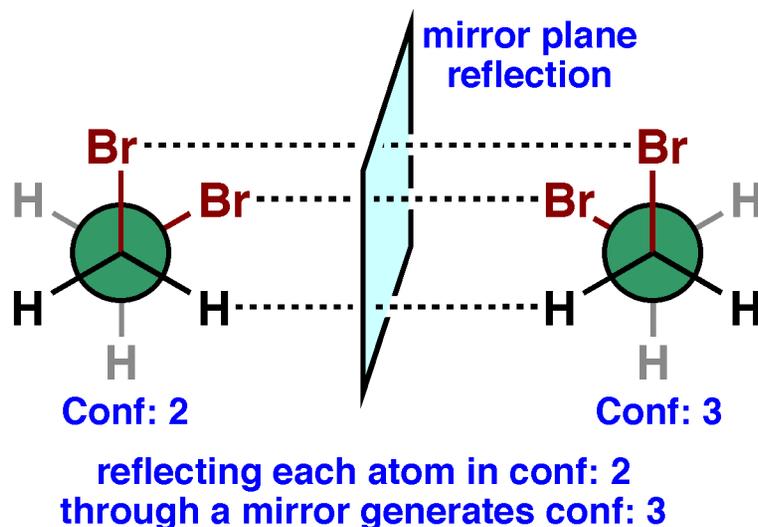
Minimum Energy Conformations of 1,2-Dibromoethane

For 1,2-dibromoethane, MarvinSketch finds three staggered conformations, as shown. Each structure has been oriented in order to present a view comparable to a Newman projection. The energy is listed above each conformation. The lowest energy conformation is assigned a value of 0.75 kcal/mole while the other two conformations have values of 0.95 kcal/mol each. Conformations labeled 2 and 3 look similar, but in fact they cannot be superimposed one on the other; instead they have a mirror image relationship as shown below.

File   Edit   View   Table   Tools   Help

Conf: 1 Energy: 0.75 kcal/mol   Conf: 2 Energy: 0.94 kcal/mol

Br

Br

Br

Br

Conf: 3 Energy: 0.94 kcal/mol

Br

Br

The staggered conformations of 1,2-dibromoethane have special names. Conf: 1 in which the two bromine atoms are oriented in opposite directions (i.e., antiperiplanar) is given the name "**anti**". Conf: 2 and Conf: 3 are called "**gauche**" conformations. The word gauche means "skewed, or not planar".

mirror plane reflection

Br · Br

H   Br · · · · · · · · · · · · · · · Br   H

H   H · · · · · · · · · · · · · · · H   H

H   H

Conf: 2   **Conf: 3**

reflecting each atom in conf: 2 through a mirror generates conf: 3

If you could take a snapshot of a large number of 1,2-dibromoethane and counted the number of molecules in the anti and gauche conformations, you'd see that the populations of these two states would be unequal.

Estimating Anti / Gauche Populations

$$\text{gauche} \underset{}{\overset{K}{\rightleftharpoons}} \text{anti} \qquad K = \frac{[\text{anti}]}{[\text{gauche}]}$$

$$\text{mol\% anti} = \frac{[\text{anti}]}{[\text{gauche}] + [\text{anti}]} = \frac{K}{1 + K}$$

Convention: use capital K for equilibrium constant (and small k for rate constants)

We know $\Delta G = -RT \ln K$

Not $\Delta G^{\neq}$

Free energy difference in cal·mol^{-1}

1.986 cal·mol^{-1}·K^{-1}

Temperature in Kelvin

at 25 °C

Assume that potential energy difference = ΔG (i.e., ignore ΔS)

ΔG (kcal·mol^{-1})	K	mol% anti
-1.0	5.4	84.4
-2.0	29.3	96.7
-4.0	862	99.9

For 1,2-dibromoethane $\Delta G = -0.2$ kcal·mol^{-1}
The calculation predicts a mol% anti of 58.4%

Conformational Energy Profile for 1,2-Dibromoethane

unequal barrier heights

unequal energy levels

Br conf: 1

H conf: 2

conf: 3

Energy →

Dihedral Angle, θ (degrees) →
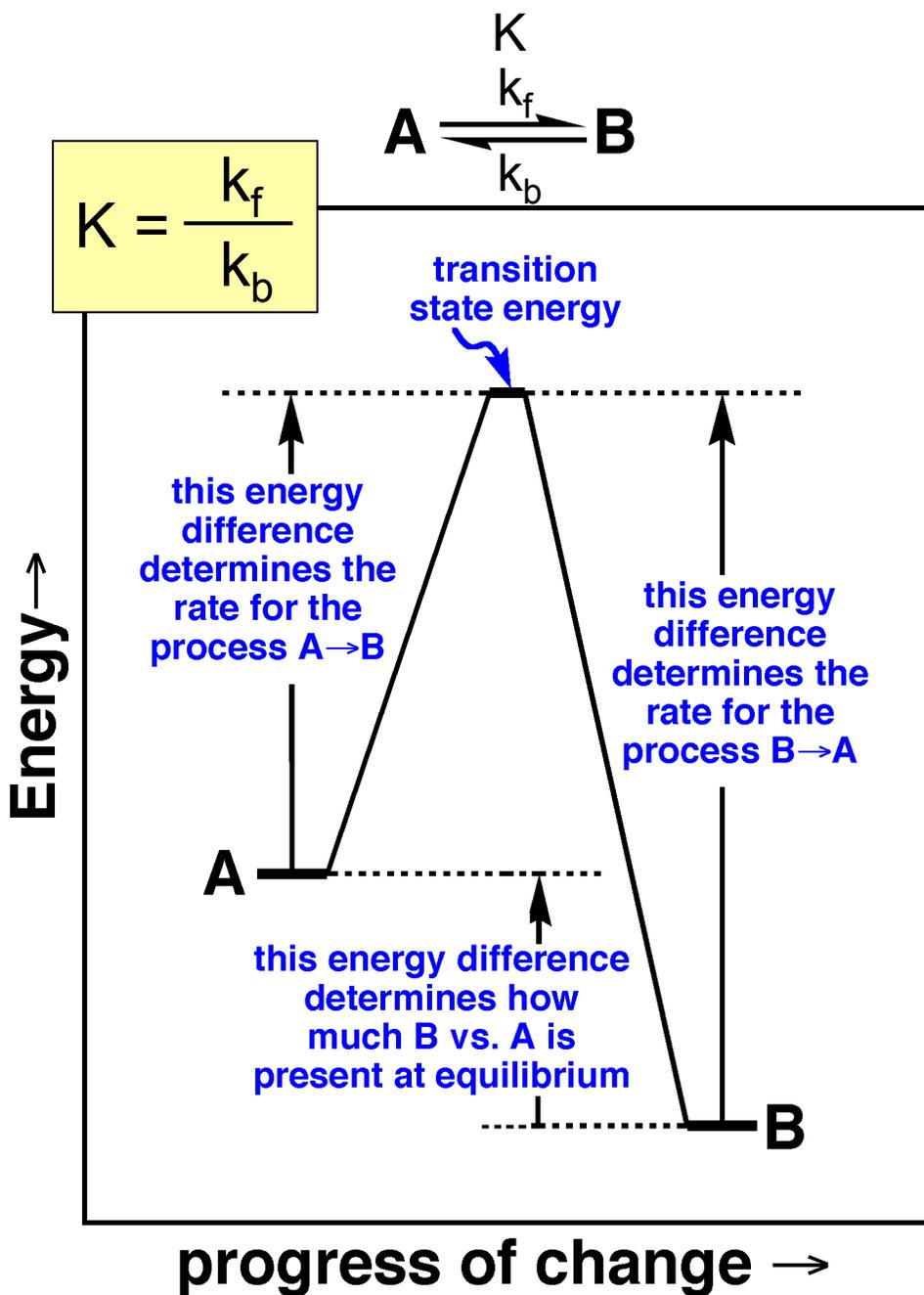
0   120   240   360
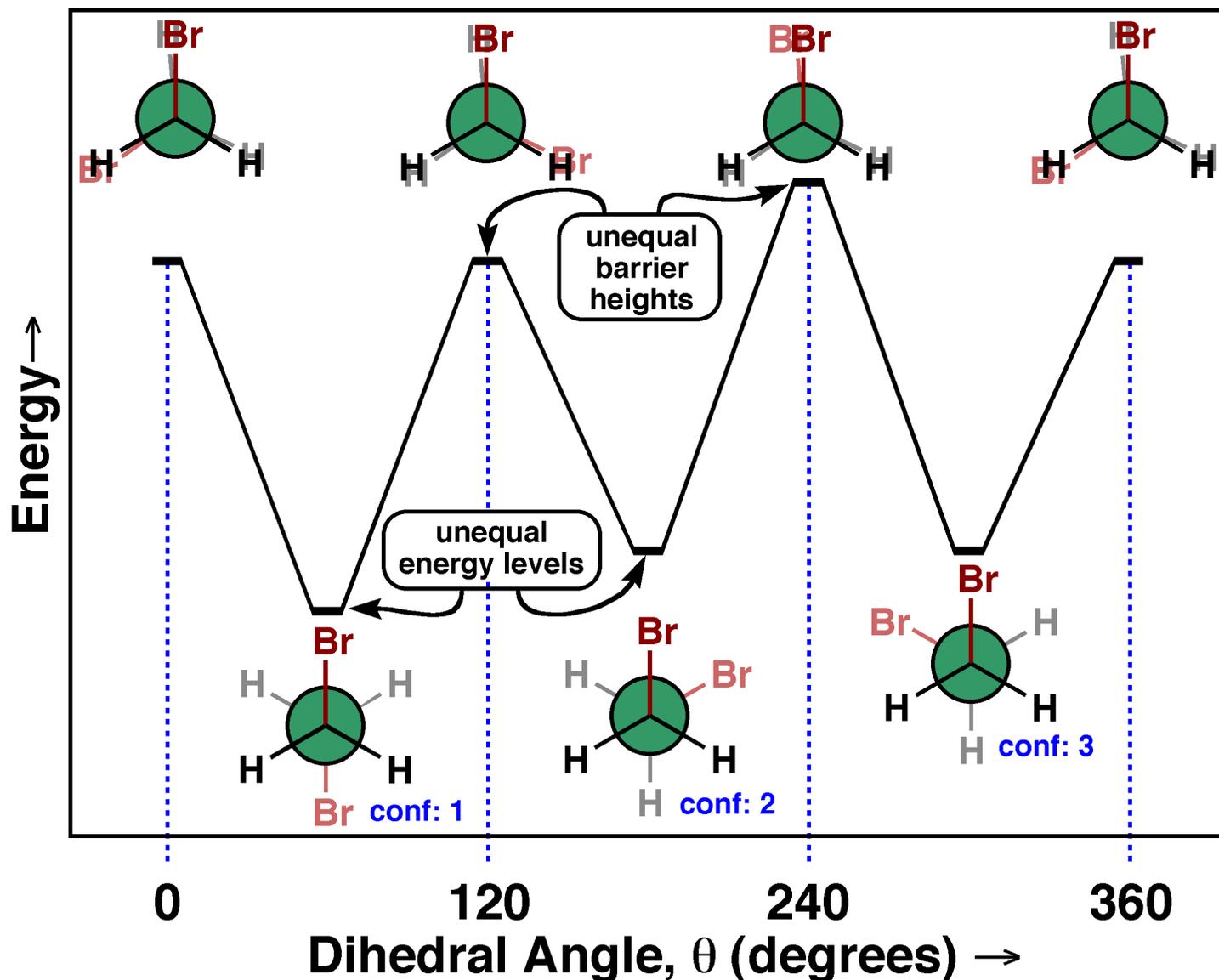
The energy levels of conf: 2 and conf: 3 are equal but higher than that of conf: 1. Likewise, the barrier that separates conf: 2 from conf: 3 is larger than the barriers separating every other conformation. This is because the size of bromine is larger than hydrogen, and the transition from conf: 2 to conf: 3 requires that these two atoms come in close proximity of one another.

Here's another example (butane)
http://chemapps.stolaf.edu/jmol/docs/examples-11/jmol-flot-energy.htm

Rates vs. Amounts on Potential Energy Plots

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

K

$$K = \frac{k_f}{k_b}$$

transition state energy

this energy difference determines the rate for the process A→B

this energy difference determines the rate for the process B→A

this energy difference determines how much B vs. A is present at equilibrium

Energy →

A

B

progress of change →

We can generalize the potential energy vs. dihedral angle plots into a useful tool that we'll call a **reaction coordinate diagram**. Such a diagram tells us *how fast* a process takes place, and it tells us *how much* of each component is present at equilibrium. In the example shown, "progress of change" has replaced "dihedral angle". The potential energy profile for the process in which **A** transforms reversibly into **B** is described by the solid line. This process could be a chemical reaction, or it may be a change in molecular geometry, such as conformation. In the example shown, **B** is lower in energy than **A**, so more **B** than **A** will be present at equilibrium. Three important parameters describe the rates of interconversion and relative amounts of **A** and **B**. The difference in energy between **A** and **B** determines *how much* **A** is present relative to **B** once equilibrium has been reached.

There are two barrier heights on this plot. One barrier height governs the rate of the *forward* process, **A→B**. The other barrier height governs the rate of the *backward* process, **B→A**. The peak position in the energy curve corresponds to a species that is in the process of changing; this species is called the **transition state structure**. Its energy is known as the **transition state energy**.