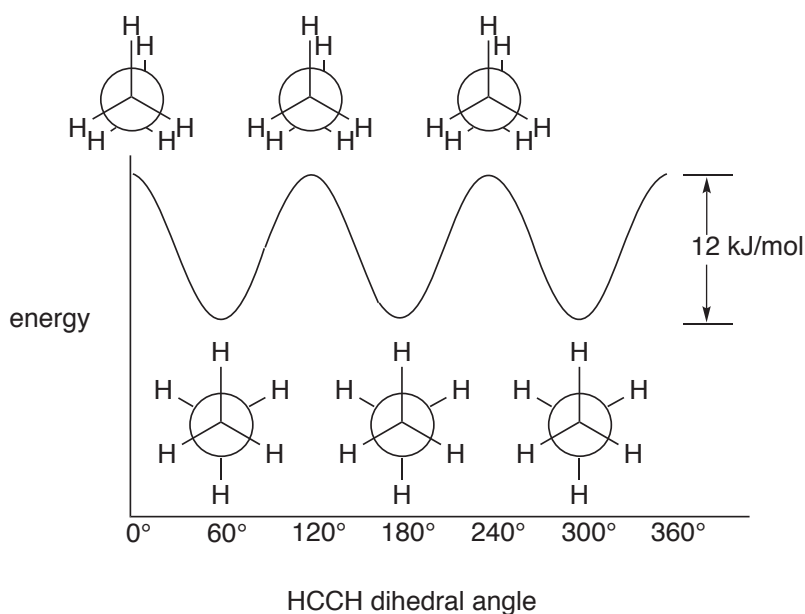





## POTENTIAL ENERGY SURFACES

### One Dimensional Energy Surfaces

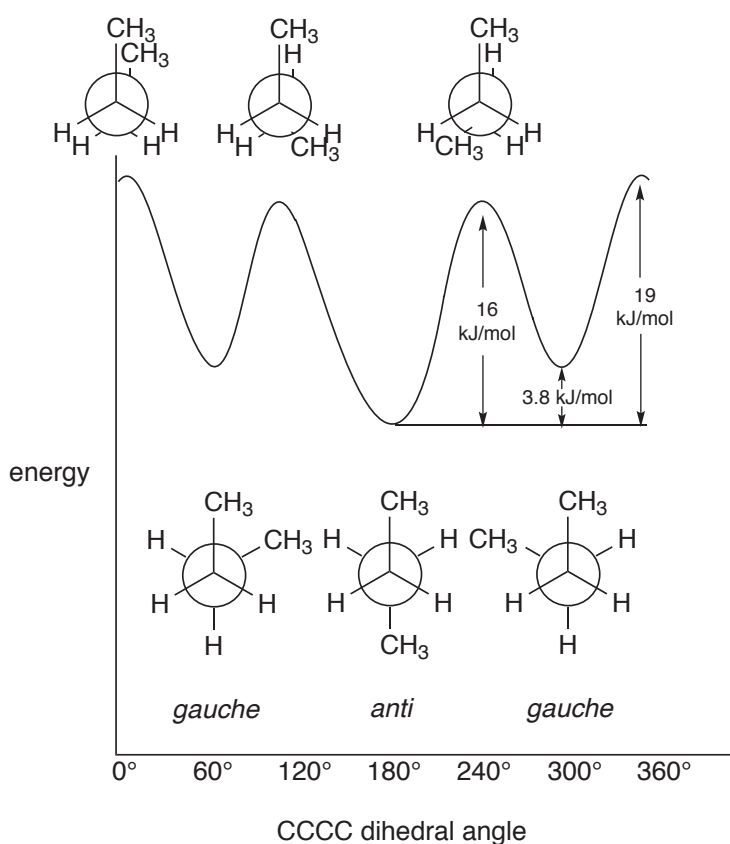
Every chemist has encountered a plot depicting the change in energy of ethane as a function of the angle of torsion (dihedral angle) around the carbon-carbon bond.



Full 360° rotation leads to three identical energy minima in which the hydrogens are staggered, and three identical energy maxima in which the hydrogens are eclipsed. The difference in energy between eclipsed and staggered structures of ethane, termed the barrier to rotation, is known experimentally to be approximately 12 kJ/mol. Note that any physical measurements on ethane pertain only to its staggered structure, or more precisely the set of three identical staggered structures. Eclipsed ethane *does not exist* in the sense that it cannot be isolated and characterized. Rather, it can only be imagined as a structure in between equivalent staggered forms.

Open **ethane rotation** in the **topics** directory\*. The image which appears is one frame in a sequence depicting rotation about the carbon-carbon bond in ethane. Click on the  and  keys at the bottom left of the screen to look at other frames. Verify that the staggered structures correspond to minima on the energy plot and that the eclipsed structures correspond to maxima. Click on the  key to animate the sequence. Close **ethane rotation** when you are finished.




Somewhat more complicated but also familiar is a plot of energy vs. the dihedral angle involving the central carbon-carbon bond in *n*-butane.



This plot also reveals three energy minima, corresponding to staggered structures, and three energy maxima, corresponding to eclipsed

\* For Windows, the **Topics** directory is found in **Program Files/Wavefunction/Spartan20**. It needs to be copied to another location available to the user prior to opening it in **Spartan**. For Macintosh, this is located at the top of the **Spartan20** disc image. For Linux, the **Topics** directory is found in the install directory. Copy the **Topics** directory to a location that allows write permission, typically the user's home directory.

structures. In the case of *n*-butane, however, the three structures in each set are not identical. Rather, one of the minima, corresponding to a dihedral angle of  $180^\circ$  (the *anti* structure), is lower in energy and distinct from the other two *gauche* minima (dihedral angles around  $60^\circ$  and  $300^\circ$ ), which are identical. Similarly, one of the energy maxima corresponding to a dihedral angle of  $0^\circ$ , is distinct from the other two maxima (with dihedral angles around  $120^\circ$  and  $240^\circ$ ), which are identical. As with eclipsed ethane, eclipsed forms of *n*-butane do not exist, and correspond only to hypothetical structures in between *anti* and *gauche* minima. Unlike ethane, which is a single compound, any sample of *n*-butane is made up of two distinct compounds, *anti n*-butane and *gauche n*-butane. The relative abundance of the two compounds as a function of temperature is given by the Boltzmann equation (see the topic ***Total Energies and Thermodynamic and Kinetic Data***).

Open ***n-butane rotation*** in the ***topics*** directory. The image which appears is one frame of a sequence depicting rotation about the central carbon-carbon bond in *n*-butane. Click on the  and  keys at the bottom left of the screen to look at other frames. Verify that the staggered structures correspond to minima on the energy plot and that the eclipsed structures correspond to maxima. Also, verify that the *anti* structure is lower in energy than the *gauche* structure. Click on  to animate the sequence. Close ***n-butane rotation*** when you are finished.

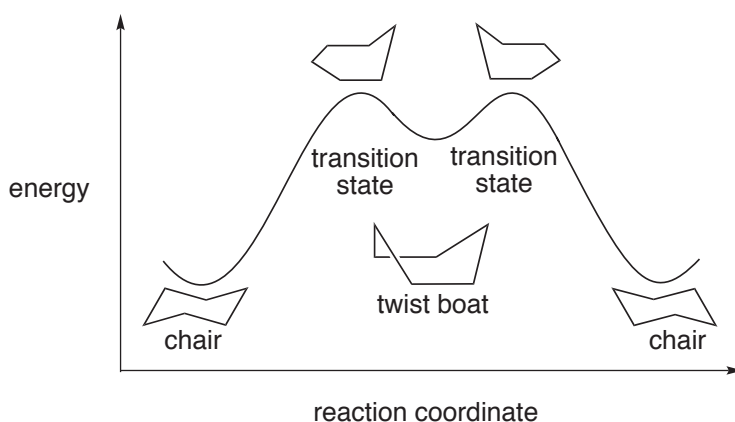
The important geometrical coordinate in *n*-butane may clearly be identified as a torsion about the central carbon-carbon bond. This is an oversimplification, as bond lengths and angles no doubt change during rotation around the carbon-carbon bond.

Quantum chemical models available in ***Spartan*** are able to account for the subtle changes in bond lengths and angles which result from changes in conformation. Open ***n-butane geometry changes*** in the ***topics*** directory. The two plots depict the variation in central CC bond distance and in CCC bond angle as a function of the CCCC torsional angle. The variation in energy is superimposed on each plot. Note how closely the bond distance and energy changes parallel each other. Note also that the

bond angle is insensitive to conformation except in the region of the *syn* ( $0^\circ$  torsional angle) structure where it has opened up by several degrees. Close *n-butane geometry changes* when you are finished.

## Many Dimensional Energy Surfaces

It will usually not be possible to identify a simple geometrical coordinate to designate a chemical transformation. A good example of this is provided by the potential energy surface for ring inversion in cyclohexane.

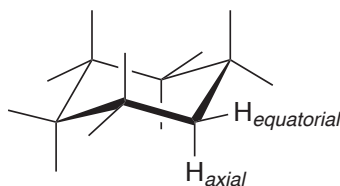


In this case, the geometrical coordinate connecting stable forms is not specified in detail (as it was in the previous two examples), but is referred to simply as the *reaction coordinate*. The two energy maxima on the *reaction coordinate diagram* have been designated as *transition states* to indicate that their structures may not be simply described (as are the energy maxima for rotation in ethane and *n*-butane).

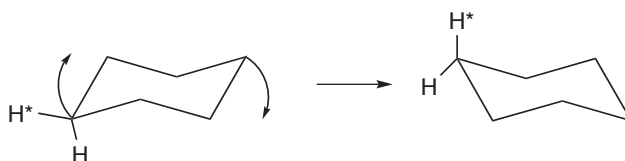
The energy surface for ring inversion in cyclohexane, like that for *n*-butane, contains three distinct energy minima, two of lower energy referred to as chair forms, and one of higher energy referred to as a twist boat form. In fact, the energy difference between the chair and twist boat structures is around 23 kJ/mol and, only the former can be observed at normal temperatures. For a discussion, see the topic *Total Energies and Thermodynamic and Kinetic Data*.

All six carbons are equivalent in the chair form of cyclohexane, but the hydrogens divide into two sets of six equivalent *equatorial*

hydrogens and six equivalent *axial* hydrogens.



However, only one kind of hydrogen can normally be observed, meaning that *equatorial* and *axial* positions interconvert via some low-energy process. This is the ring inversion process just described, in which one side of the ring is bent upward while the other side is bent downward.






As shown in the potential energy diagram on the previous page, the overall ring inversion process appears to occur in two steps, with a twist boat structure as a midway point (an intermediate). The two (equivalent) transition states leading to this intermediate adopt structures in which five of the ring carbons lie (approximately) in one plane.

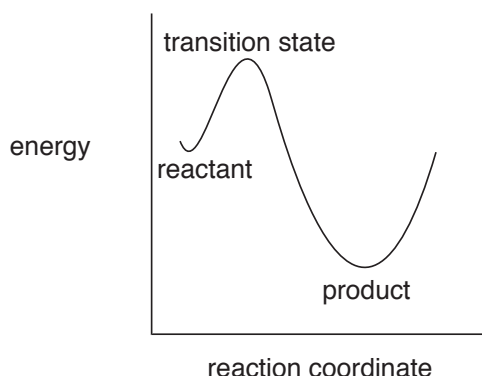
The energy profile for ring inversion in cyclohexane may be rationalized given what we have already said about single-bond rotation in *n*-butane. Basically, the interconversion of the reactant into the twist-boat intermediate via the transition state can be viewed as a restricted rotation about one of the ring bonds.



Correspondingly, the interconversion of the twist boat intermediate into the product can be viewed as rotation about the opposite ring bond. Overall, two independent bond rotations, pausing at the high-energy (but stable) twist-boat intermediate effect conversion of one chair structure into another equivalent chair, and at the same time switch *axial* and *equatorial* hydrogens.

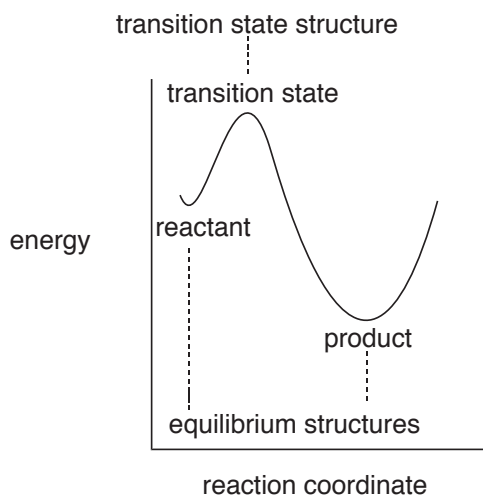
Open **cyclohexane ring inversion** in the **topics** directory. The image which appears is one frame in a sequence depicting ring inversion in cyclohexane. Click on the  and  keys at the bottom left of the screen to look at other frames. Verify that the three minima on the energy plot correspond to staggered structures and that the two maxima correspond to eclipsed structures. Also, verify that the twist boat structure is higher in energy than the chair structures. Click on  to animate the sequence. Note that the overall ring inversion appears to occur in two steps, one step leading up to the twist boat and the other step leading away from it. Close **cyclohexane ring inversion** when you are finished.

Ethane, *n*-butane and cyclohexane are all examples of the types of motions which molecules may undergo. Their potential energy surfaces are special cases of a general type of plot in which the variation in energy is given as a function of reaction coordinate.

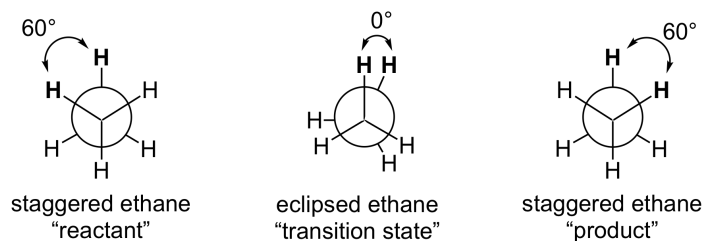


Diagrams like this provide essential connections between important chemical observables - structure, stability, reactivity and selectivity - and energy.

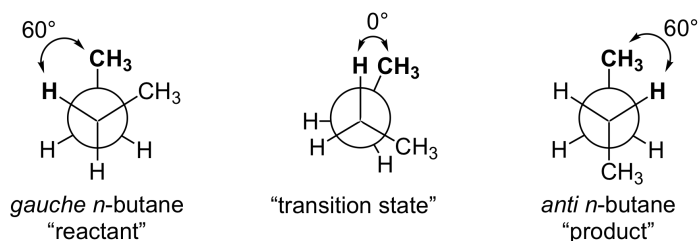
The positions of the energy minima along the reaction coordinate give the equilibrium structures of the reactant and product. Similarly, the position of the energy maximum gives the structure of the transition state. Both energy minima (which correspond to stable molecules) and the energy maximum (which may correspond to a transition state) are well defined. However, the path connecting them (reaction coordinate) is not well defined, in the sense that there are many possible paths. Liken this to climbing a mountain. The starting and ending points are well defined as is the summit, but there can be many possible routes.



The reaction coordinate for some processes may be quite simple. For example, where the “reaction” is rotation about the carbon-carbon bond in ethane, the reaction coordinate may be thought of as the HCCH torsion angle, and the structure may be thought of in terms of this angle alone. Thus, staggered ethane (both the reactant and the product) is a molecule for which this angle is  $60^\circ$  and eclipsed ethane is a molecule for which this angle is  $0^\circ$ .



A similar description applies to “reaction” of *gauche* *n*-butane leading to the more stable *anti* conformer. Again, the reaction coordinate may be thought of as a torsion about the central carbon-carbon bond, and the individual reactant, transition state and product structures in terms of this coordinate.



Equilibrium structure (geometry) may be determined from experiment, given that the molecule can be prepared and is sufficiently long-lived to be subject to measurement. On the other hand, the geometry of a transition state may not be experimentally established. This is simply because a transition state is not an energy well which can trap molecules. Therefore, it is impossible to establish a population of molecules on which measurements may be performed.

Both equilibrium and transition-state structures may be determined from quantum chemical calculations. The fact that a molecule may not be stable enough to be detected and characterized (or even exist) is not important. It would seem from our discussion that equilibrium and transition-state structures can be distinguished from one another simply by inspecting the shape of the potential energy surface in the vicinity of the structure. Of course, such a surface cannot actually be visualized for a system with more than one or at most two degrees of freedom. However, the set of frequencies associated with the vibrational motions around the structure, the same quantities measured by infrared spectroscopy, will all be real numbers for stable molecules (energy minima), whereas there will be one (and only one) vibrational frequency which is an imaginary number for a transition state. This does not guarantee that this is the transition state “of interest”, but if it is, the coordinate (vibrational motion) associated with it is the reaction coordinate. Further discussion is provided in the topic *Calculating Infrared Spectra*.