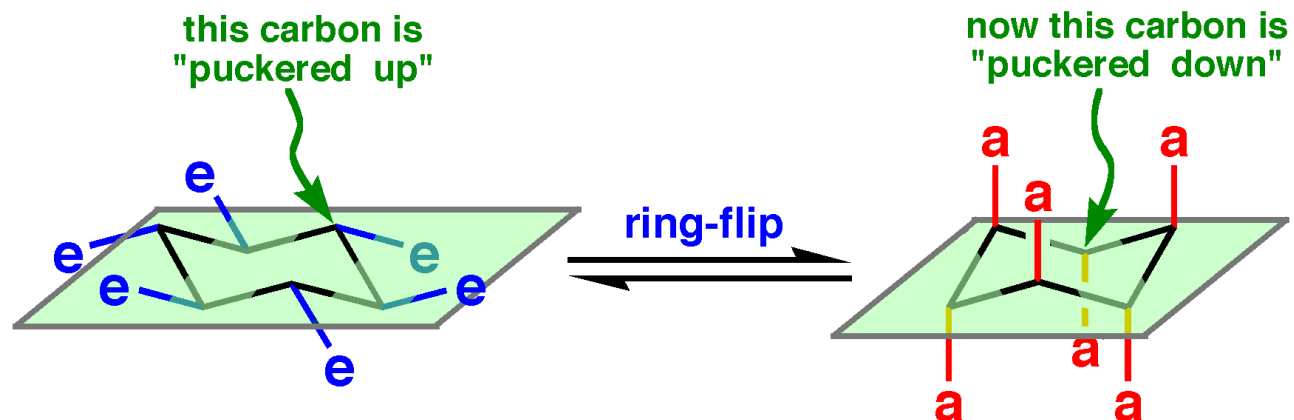
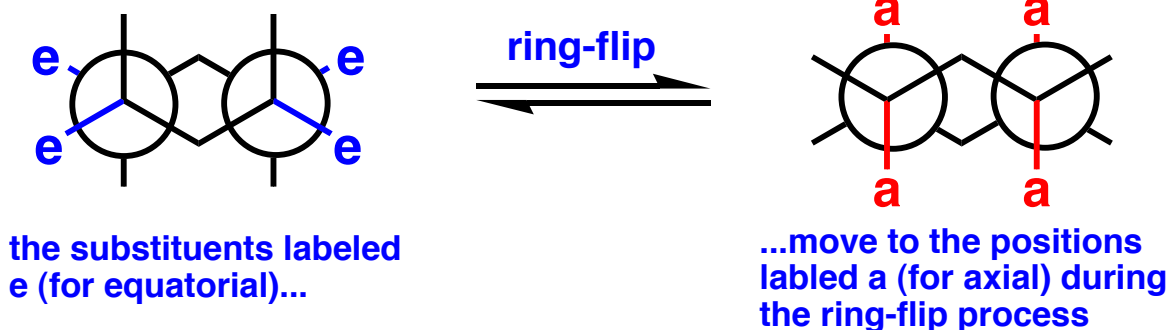


The Ring Flip Process

Cyclohexane undergoes a conformational change known as the **ring-flip process** in which each axial substituent becomes equatorial and each equatorial becomes axial. The substituents swap positions because the carbon skeleton undergoes inversion with respect to a plane slicing through the center of the ring. Those carbon atoms that were puckered up become puckered down, and vice versa.



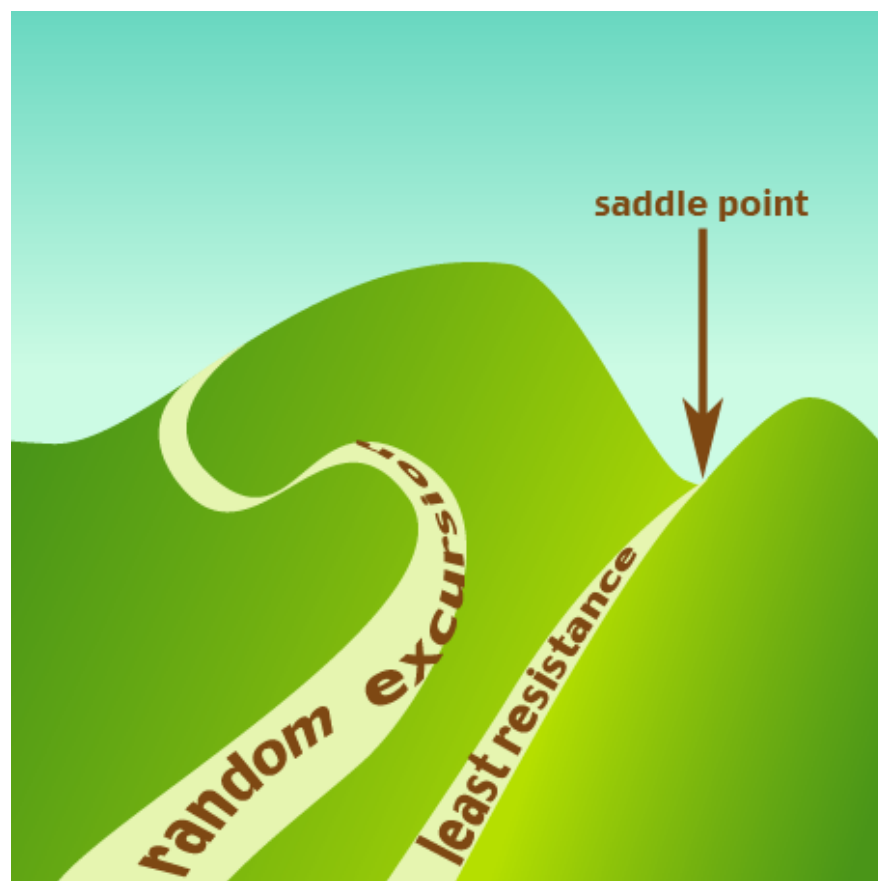
The process can be viewed along the perspective of the Newman projection as shown here. Notice the carbon bridge in front is initially "down" but then is flipped "up". The equatorial substituents twist into the axial positions and the axial substituents twist into the equatorial positions.

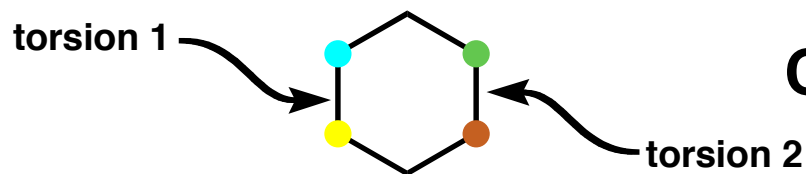


The Minimum Energy Pathway (MEP)

We are about to discuss the atomic movements that bring about the ring-flip process. The description that follows is detailed and requires concentration; it is best to build a physical model of cyclohexane and use it to understand the ring-flip process. If you don't have a model kit, study the web page listed at the bottom of this slide. Why so much detail? Generalization of this particular example will provide insight into reactivity of other complicated processes that we will encounter.

Throughout this discussion, don't lose sight of the most important point: the atomic movements follow the path of least resistance on cyclohexane's **potential energy surface** (i.e., **energy landscape**). If we think of this surface as mountain terrain in which height above sea level corresponds to energy, then the pathway that describes the ring-flip process is analogous to the route traveled by a hiker who goes from one valley to the next via a "mountain pass" (the mathematical name for the mountain pass is **saddle point** - where a minimum in one direction crosses a maximum in another). Change comes from an exact process rather than by the molecule traveling along a random excursion on its energy landscape. In other words, there is a definite, well-defined path of least resistance and this is the preferred pathway of change. This statement holds true for most of the chemical change that we'll encounter in chemistry. *We call the pathway along which change occurs the **Minimum Energy Pathway (MEP)**, also known as the **reaction coordinate**.* Let's apply these abstract ideas to the ring-flipping process of cyclohexane.

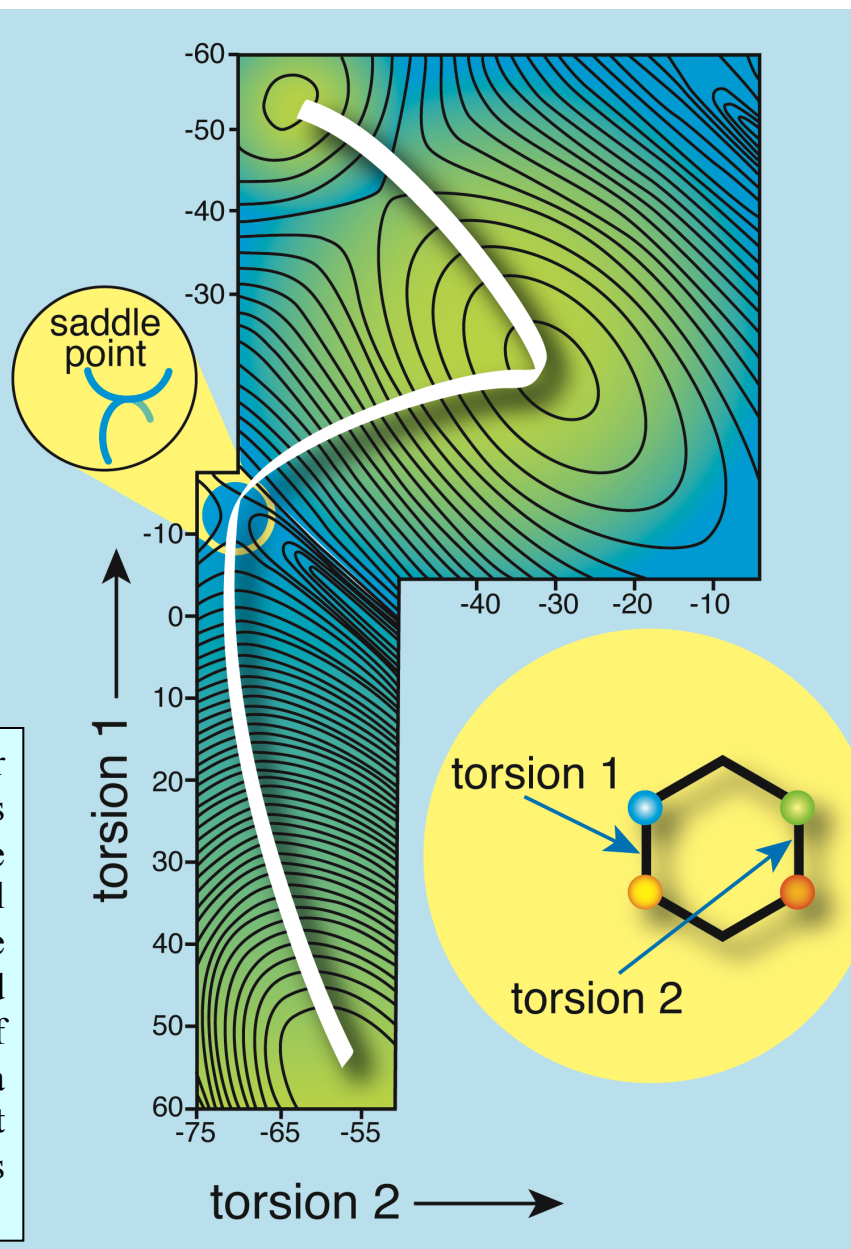




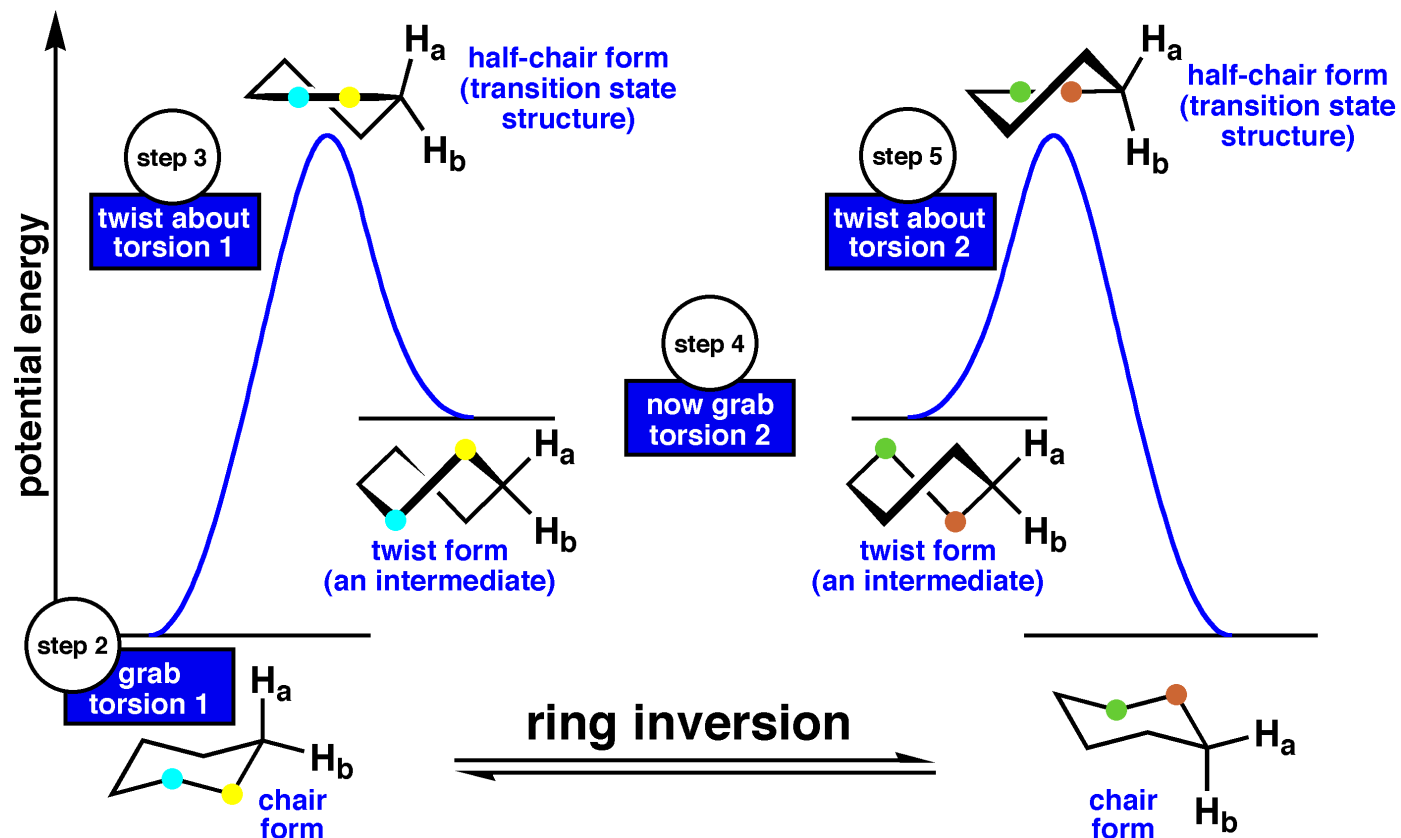
Cyclohexane's Energy Landscape

The reason we've chosen to study cyclohexane's ring-flipping process in detail is because it teaches us the connection between a MEP and its **potential energy surface** (we'll use the terms **energy landscape** and potential energy surface interchangeably). The potential energy associated with cyclohexane's conformations is fairly well described as a function of just two independent variables. These two variables are torsion angles of any two bonds in the ring positioned directly across from one another. Because of the molecule's cyclical connectivity, the other atoms are not entirely free to move independently of these torsions. The carbon atoms in the diagram are represented as colored circles so we can track the movement of individual atoms along the reaction coordinate. (Note: that only two torsions describe the process is a simplification; for a complete description see: Dunitz, J. D. *J. Chem. Educ.* **1970**, *47*, 488).

The contour plot represents a portion of the 3D energy landscape for cyclohexane (i.e., a potential energy surface). The x and y axes correspond to torsion angles 1 and 2 while energy is given by the contour lines (the z direction). The contour lines are equipotential curves; a set of points having the same energy. The contour lines are steps in energy, forming valleys (light color, low energy) and mountain passes (dark color, high energy). The preferred pathway of change (i.e., the MEP) connects one valley to another through a saddle point. The saddle point is the *transition state*; the energy at this point is the *transition energy* and the structure at this point is called the *transition structure* (commonly given the symbol \ddagger).



Working with Models



1) Build a model of cyclohexane. Make all the axial substituents red atoms and all of the equatorial substituents blue atoms. Place a piece of tape around one of the ring bonds and call this torsion 1. Then place a second piece of tape around the ring bond that is directly opposite torsion 1. Call this bond torsion 2.

2) Grab the model by holding the two carbon atoms of torsion 1, one atom in your left hand and the other in your right.

3) Simultaneously rotate your hands in opposite directions. There are two ways to twist your hands in opposite directions (i.e., you can either twist such that the axial substituents tip toward you or away from you). You'll notice that one way encounters resistance, while twisting in the other way is easy. Twisting about the easy way tips the axial substituents toward you. Go ahead and twist about torsion 1 in the easy way until you cannot twist anymore. Your model is no longer in the chair form. It is now a "twist conformation" of cyclohexane.

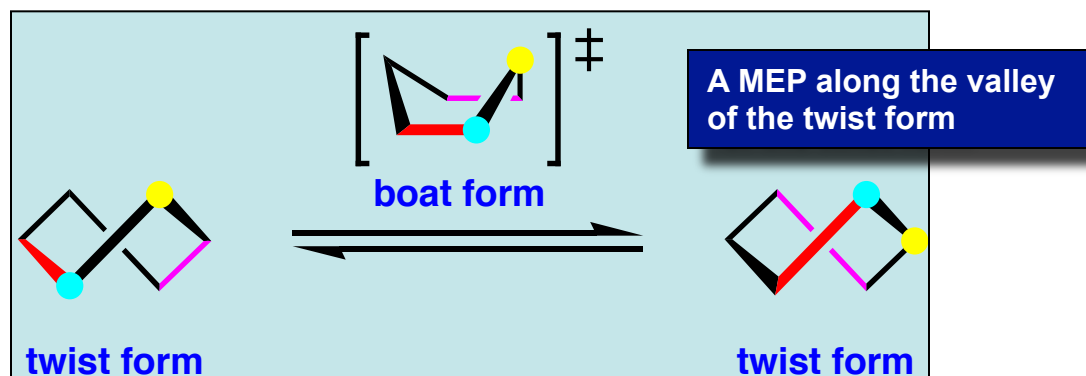
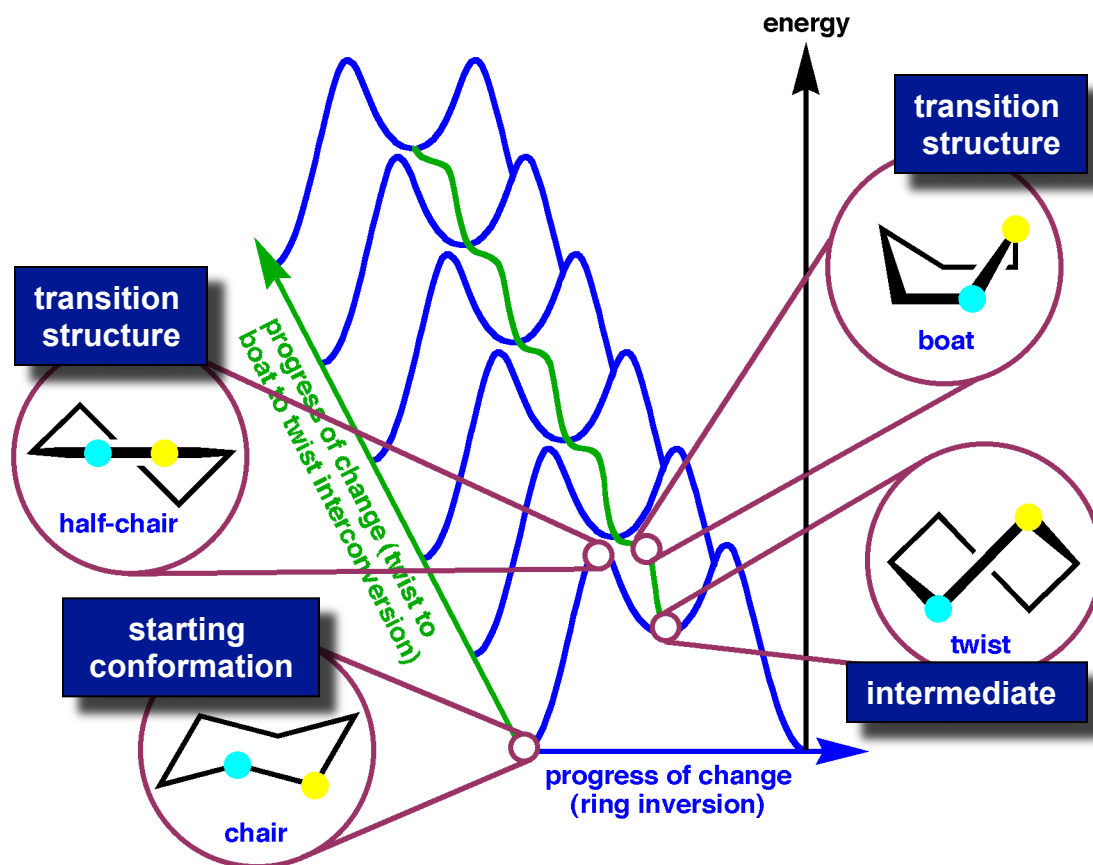
4) Now grab the model by holding the two carbon atoms of torsion 2, one atom in your left and the other in your right hand.

5) You'll again notice that twisting in one way again encounters resistance, while twisting in the other way is easy. Twist about torsion 2 in the easy way. Your model has returned to a chair form. The red atoms (formerly axial substituents) are now in the equatorial positions. The blue atoms (formerly equatorial substituents) are now in the axial positions.

The Valley of the Twist Form

There is one more feature to cyclohexane's energy landscape, and it has to do with the valley that separates ring-flipped chair forms. The region in between two chairs is called the valley of the twist form. It is a minimum valley on cyclohexane's energy landscape. If there exists a minimum point on an MEP between a starting point and product we call this minimum an **intermediate**. The twist form is thus an intermediate on the ring-flip MEP.

The energy landscape at the right shows that the valley of the twist form runs to the upper left hand corner. This is a second MEP (colored green) that converts one twist form into another. This MEP passes through a saddle point corresponding to the boat conformation of cyclohexane. The boat form is placed in brackets with a double dagger (\ddagger) to symbolize that this structure is a **transition structure**.



For details see:
Leventis, N.; Hanna, S. B.; Sotiriou-Leventis, C.
J. Chem. Educ. 1997, 74, 813