Conformations of Alkanes

Semi-empirical AM1 calculations are used to construct energy profiles for rotation in n-butane and in 2-methylhexane. The latter provides information about the relationship between rotation barrier and degree of substitution.

Acyclic alkanes prefer conformations in which CH and CC bonds are staggered. Steric interactions between alkyl groups, however, can affect both the geometry and energy of these conformers. For example, the anti conformer of n-butane is known experimentally to be 0.8 kcal/mol more stable than the gauche conformer, a fact that can be rationalized if CH₃/CH₃ gauche interactions are larger than CH₃/H and H/H gauche interactions.

The conformational behavior of larger alkanes is more difficult to predict, both because there are more degrees of conformational freedom, and because steric interactions between atoms separated by several bonds can be difficult to anticipate. 2-Methylhexane, for example, can experience internal rotation about any of its six CC bonds, and there may be as many as 3⁶ staggered conformations.

In this experiment, you will use AM1 calculations to map the energy for internal rotation about the C₂-C₃ bond in n-butane, and about the C₂-C₃ and C₃-C₄ bonds in 2-methylhexane. While the latter do not constitute a complete map of the energy surface for this molecule, they still provide interesting insight into the importance of "long range" steric interactions, and the difficulty of analyzing the conformational preferences of complex molecules.

Procedure

n-Butane: Build completely staggered conformers of n-butane in which the CCCC dihedral angle is 0°, 30°, 60°, ..., 180° (constrain this angle). Optimize the geometry of each constrained molecule using the AM1 method. Tabulate the final heat of formation for each conformer, and plot the heat of formation versus CCCC dihedral angle.

Which structures correspond to minima, and which correspond to maxima? One way a molecule might relieve unfavorable steric interactions is to expand its CCC bond angle; how do the CCC bond angles vary with CCCC dihedral angle? Make a plot. What can you infer from your data about the relative magnitude of CH₃/CH₃, CH₂/H, and H/H gauche interactions?

2-Methylhexane: Build completely staggered conformers of 2-methylhexane in which the C₁-C₂-C₃-C₄ dihedral angle is 0°, 60°, 120°, ..., 300° (constrain this angle). Optimize the geometry of each constrained molecule using the AM1 method, and plot the heat of formation versus dihedral angle. Repeat this procedure using staggered conformers in which the C₂-C₃-C₄ dihedral angle is constrained to be 0°, 60°, 120°, ..., 300°, and plot the heat of formation versus dihedral angle. Examine your plots and determine whether they have the expected symmetry (what does an unsymmetric plot indicate and how should it be corrected?). Identify the most stable conformer on each energy plot, and characterize its structure, i.e., is the carbon skeleton perfectly staggered or do some CCCC dihedral angles deviate from ±60° or 180°? Which bond, the trisubstituted C₂-C₃ bond, or the disubstituted C₃-C₄ bond, has a higher barrier to complete rotation? Try to rationalize your observations in terms of steric interactions.

Optional

Use AM1 calculations to map energy profiles for rotation about the C₂-C₃ and C₃-C₄ bonds in 2,2-dimethylpentane. How many minimum-energy conformers are there for each rotation? What is the barrier to complete 360° internal rotation about each bond? How do you account for these results?