

Butadiene Conformational Preferences

Christopher J Harris
Department of Chemistry
University of Maine

Abstract

A periodic study of ligands attached to the butadiene were carried out through semiempirical calculations. Of interest, were conformational preferences and rotational barriers. Only saturated ligands attached to the number two carbon were considered. Butadiene was calculated to have a 0.7730 kcal/mol difference between cis and trans configurations, while the rotational barrier approached 1.9624 kcal/mol.

Introduction

Semiempirical mathematical modeling of chemical compounds involves approximating the electron core with a core potential and looking at the valence electrons to predict chemical properties. The valence electron basis sets are fitted to trial experimental data, which may or may not reflect properties similar to the molecule of interest. Although absolute energy values are in significant error, semiempirical methods do take into account pi interactions, to elucidate energy differences between chemical structures. In comparison, molecular modeling techniques tend to calculate geometry better than semiempirical counterparts, but the force fields usually ignore pi effects unless specifically told to consider such effects. As such, molecular modeling techniques generally lead to less accurate energy calculations relative to semiempirical methods.

With pi electron consideration, the semiempirical approach may reveal the conformational landscape within butadiene. An example of a conjugated pi system, butadiene has two stable, planar conformations, cis and trans. The energy difference between the two structures, the rotational barrier separating the two states, and ligand influences on these properties, represents a legitimate inquiry.

Procedure

Use Spartan's energy profile feature to rotate the central bond of butadiene through a dihedral angle of 0 to 360 degrees. Structurally, the cis conformation has a 0 degree dihedral angle, while the trans configuration possesses a 180 degree dihedral. Since no

transition metals are present, compute semiempirical energies with AM1 parameters, rather than PM3 coefficients. Replace a hydrogen on the backbone of the central butadiene bond with another saturated substituent within the first row of the periodic table, such as -F, -OH, -NH₂, -CH₃, to explore the behavior on the energy landscape.

Results

The following energies were tabulated from the graphs in figures 1 through 5:

	E cis	E trans	ΔE conform	ΔE barrier
Butadiene	30.6871	29.9141	0.7730	1.9624 kcal/mol
-F	-14.5744	-14.6574	0.0830	2.2010
-OH	-14.2547	-14.1051	-0.1497	2.2537
-NH ₂	32.1558	29.7762	2.3796	2.5761
-CH ₃	23.2403	23.3324	-0.0921	1.4102

E cis and E trans represent the total energies for the cis and trans conformations, ΔE conform is the energy difference between the two structures, and ΔE barrier signifies the rotational barrier.

Discussion

In order to distinguish which structure is more stable, ΔE conform carries a negative or positive sign, consistent with the mathematical difference between E cis and E trans. Therefore, only -OH and -CH₃ favor the cis conformation over the trans configuration.

The hydrogen on the backbone of the butadiene central bond was chosen for substituent replacement, because I perceived it to have the most dramatic influence on energetics due to its close proximity to the neighboring hydrogen relative to the terminating hydrogens on both ends of the molecule. Thus, my interpretation of the cis versus trans preferences should be determined by a balance between short range forces between the two central substituents and the long range forces present among the terminating hydrogens.

So with this model in mind, let's consider the results. For the cis configuration, fluorine lowers ΔE conform relative to butadiene, perhaps due to weak hydrogen bonding between the fluorine and the hydrogen attached to the interior carbons. This hydrogen bonding effect is enhanced for an -OH ligand, leading to a negative ΔE conform. With the methyl substituent, more interactions come into play, leading to a negative ΔE conform; however, the cis configuration is no longer stable. Additionally, the rotational barrier is reduced relative to butadiene. For the -NH₂ ligand, the energies come into

question, because one would expect a symmetric curve about the 0 dihedral angle. The asymmetric profile is characteristic of nonconverging solutions, leading to dissimilar results for comparable dihedral angles. The discontinuity between the cis position and neighboring energy points should also raise some concern about the reliability of the calculations. Despite the shortcomings in the ammonium curve, it would appear that neither the cis nor the trans configurations are stable, and the rotational barrier coincides with the cis position.

Conclusion

Hydrogen bonding along the backbone of the butadiene seems to stabilize the cis configuration for -OH and -F, while the methyl ligand lowers the rotational energy barrier. Although the ammonium calculations seem unreliable, they offer some intriguing results for further investigation.

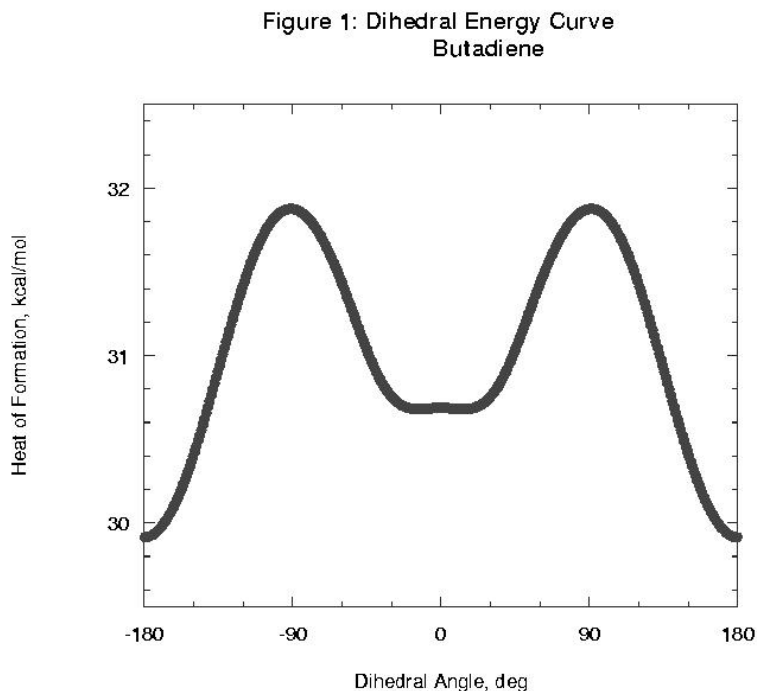


Figure 2: Dihedral Energy Curve
-F Group

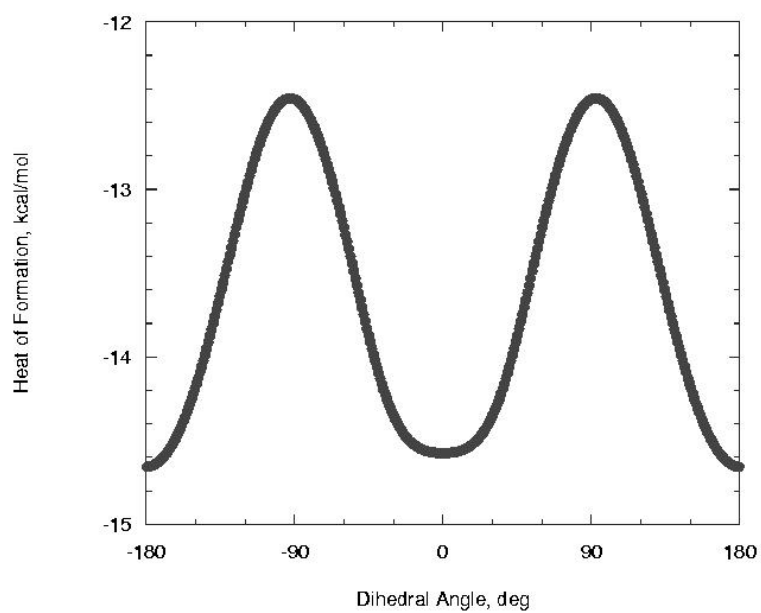


Figure 3: Dihedral Energy Curve
-OH Group

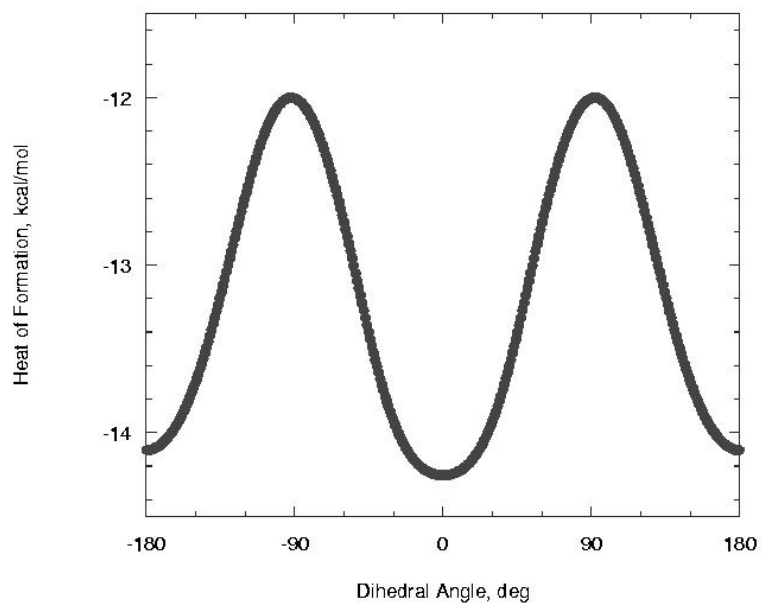


Figure 4: Dihedral Energy Curve
-NH₂ Group

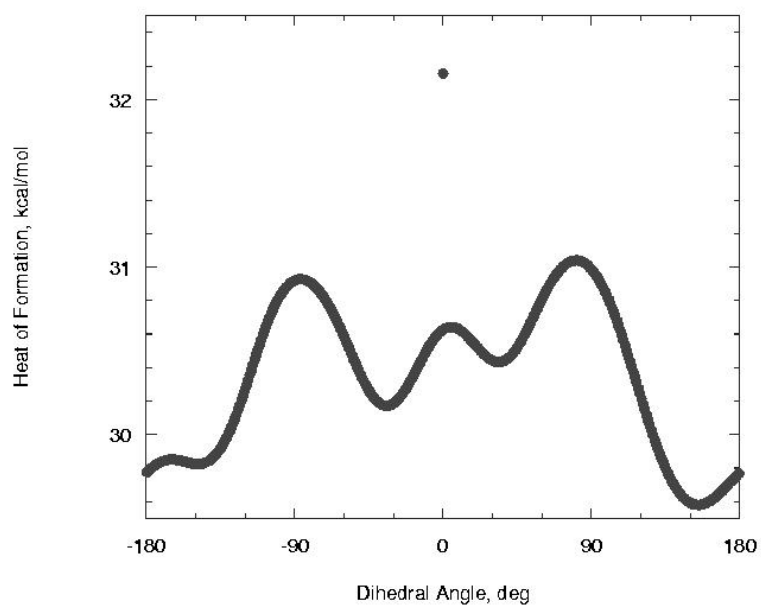


Figure 5: Dihedral Energy Curve
-CH₃ Group

