Computational Study of Inversion-topomerization Pathways in 1,3-Dimethylcyclohexane and 1,4-Dimethylcyclohexane: Ab Initio Conformational Analysis

Huiting Bian[1], Yifan Zhang[1], Yongjin Wang[1], Jun Zhao[1], Xiaohui Ruan[1], and Jing Li[1]

[1]Zhengzhou University

December 18, 2020

Abstract

This work concerns the typical conformational behaviors for di-substituted cyclohexanes that inherently depend on spatial orientations of side chains in flexible cyclic ring. The 1,3-dimethylcyclohexane and 1,4-dimethylcyclohexane in both cis- and trans-configurations were focused here to unravel their conformational inversion-topomerization mechanisms. Full geometry optimizations were performed at B3LYP/6-311++G(d,p) level of theory to explicitly identify all distinguishable molecular structures, and thus explore potential energy surfaces (PES) of the complete interconversion routes for two stereoisomers of 1,3-dimethylcyclohexane and 1,4-dimethylcyclohexane. Additional quantum calculations were carried out by separately applying MP2/6-311++G(d,p), G4, and CCSD(T)/6-311++G(d,p) methods to further refine all PES' stationary points. With respect to quantum results, the conformational analysis was conducted to gain insight into the determination, thermodynamic stabilities, and relative energies of distinct molecular geometric structures. On base of highly biased conformational equilibria, the temperature-dependent populations of stable local minima for four studied dimethylcyclohexanes were obtained by utilizing Boltzmann distribution within 300-2500 K. Moreover, two unique interconversion processes for them, including inversion and topomerization, were fully investigated, and their potential energy surfaces were illustrated with the rigorous descriptions in two or three-dimensional schemes for clarify.

Hosted file

`Manuscript.pdf` available at https://authorea.com/users/383638/articles/499509-computational-study-of-inversion-topomerization-pathways-in-1-3-dimethylcyclohexane-and-1-4-dimethylcyclohexane-ab-initio-conformational-analysis