
03 Jan 2023

Rotation-Inversion Isomerization of Tertiary Carbamates: Potential Energy Surface Analysis of Multi-Paths Isomerization using Boltzmann Statistics

Brian Jameson

Rainer Glaser

Missouri University of Science and Technology, glaserr@mst.edu

Follow this and additional works at: https://scholarsmine.mst.edu/chem_facwork

 Part of the [Chemistry Commons](#)

Recommended Citation

B. Jameson and R. Glaser, "Rotation-Inversion Isomerization of Tertiary Carbamates: Potential Energy Surface Analysis of Multi-Paths Isomerization using Boltzmann Statistics," *Chemphyschem : a European journal of chemical physics and physical chemistry*, vol. 24, no. 1, p. e202200893, Wiley, Jan 2023.
The definitive version is available at <https://doi.org/10.1002/cphc.202200893>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemistry Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Rotation-Inversion Isomerization of Tertiary Carbamates: Potential Energy Surface Analysis of Multi-Paths Isomerization Using Boltzmann Statistics



Brian Jameson



Prof. Rainer Glaser

MISSOURI S&T

www.mst.edu

The front cover artwork is provided by Prof. Rainer Glaser's group at the Missouri University of Science and Technology. The image shows one of four potential energy surfaces generated from our rotation-inversion study of tertiary carbamates and highlights two of the eight possible transition state pathways between two ensembles of *E*- and *Z*-minima. In the context of synthetic studies of fluorinated carbamates $R_1O-CO-N(R_2)CH_2CF_3$, we unexpectedly observed two sets of ^{13}C NMR quartets for the CF_3 group and we needed to understand their origin. Read the full text of the Research Article at 10.1002/cphc.2022005442.

What is the most significant result of this study?

We were able to show that the two sets of CF_3 NMR quartets are due to the presence of ensembles of *E*- and *Z*-rotamers. A fully consistent interpretation is proposed and supported by the results of a complete stereochemical analysis, the exploration of all isomerizations with focus on the rotation-inversion, and the computation of chemical shifts $\delta(^{13}C)$ and $^1J(^{13}C,^{19}F)$ coupling constants. More generally, the approaches described in our study will facilitate similar studies of rotation-inversion dynamics in carbamates $R_1R_2N-CO-OR_3$ and ureas $R_1R_2N-CO-NR_3R_4$.

What was the inspiration for this cover design?

The rotation-inversion pathways of carbamates inherently present a two-dimensional problem and deep understanding requires plots of the rotation-inversion surfaces as a function of parameters describing CN rotation and *N*-inversion. Four such surfaces were determined, and we chose to highlight the surface that features the most stable minima and most traversed TS structure. Negative hyperconjugation is key to understanding the electronic structure of the TS structures.

What was the biggest challenge on the way to the results presented in this paper?

The analysis of our computational model showed **eight** TS structures connecting **four** *E*- and *Z*-minima. This scenario required a clear conceptual approach to predict the barrier that would be experimentally measured. The Boltzmann analysis

shows that all eight isomerization paths are travelled, and the application of proper statistics resulted in a computed barrier which was in complete agreement with the experimentally determined barrier of a very similar fluorinated carbamate, *N*-Boc-*N*-(2,2,2-trifluoroethyl)-4-aminobutan-1-ol II (within 1%).

Acknowledgements

The high-performance compute cluster was purchased in part with MRI funding by the National Science Foundation under Grant No. OAC-1919789. This work was supported by grant #1665487 from the National Science Foundation.

