Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Computational Modeling of Photoswitches and Diels-Alder Reactions



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Introduction

The computational modeling of molecular transformations in organic chemistry, e.g. photo-inducible isomerizations of azobenzenes, or Diels-Alder reactions, allows one to predict and design novel photoswitches or reaction pathways. Molecular switches are of high importance for biology and material science, whereas catalyzed Diels-Alder reactions of phthalazines allow the synthesis of complex, valuable compounds, e.g. for pharmaceuticals.

Methods

Molecular geometries and thermochemical properties were computed using Density Functional Theory (DFT) such as B3LYP or PBE0 in combination with empirical dispersion correction (D3(BJ)). Highly precise energies were obtained using ab initio DLPNO-CCSD(T) when necessary.

Results

Molecular switches: The stabilization of metastable (Z)-azobenzenes by intramolecular London Dispersion (LD) interactions and hydrogen bonds was quantified. It was found that LD become a decisive stabilization factor in polar solvent environment. After computing the stabilized geometries, the attractive forces in the molecules were visualized via noncovalent interaction plots.

Catalyzed Diels-Alder reactions: During our investigations on catalyzed inverse electron-demand Diels-Alder reactions of phthalazine, a novel amine group transfer reaction was observed. To understand the reaction mechanism, starting from a reactive and thus experimentally not accessible intermediate, computations supported the mechanism of a stepwise amine exchange within the reaction, whereas a concerted amine group migration was found to be less likely.

Publications

1. A. H. Heindl, Hermann A. Wegner (2018), Beilstein J. Org. Chem., 14, 1238-1243 https://doi.org/10.3762/bjoc.14.106

2. S. Ahles, S. Götz, L. Schweighauser, M. Brodsky, S. N. Kessler, A. H. Heindl, H. A. Wegner (2018), Org. Lett., 20, 7034-7038 https://doi.org/10.1021/acs.orglett.8b02967

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