Hessisches Kompetenzzentrum
für Hochleistungsrechnen

# *Stabilization by Dispersion Donors in the Z Isomer of Non-Symmetric Azobenzene*

Project Manager
Prof. Dr. Hermann A. Wegner

Researchers
Marcel A. Strauss

Principal Investigator
Prof. Dr. Hermann A. Wegner

Project Term
2019 - 2020

Clusters
Skylla Cluster Gießen, Goethe-HLR Frankfurt

Software
GAUSSIAN, ORCA

Institute
Institute of Organic Chemistry

University
Justus Liebig University Giessen

Funded by

Deutsche Forschungsgemeinschaft

## Introduction

The determination of the strength of London dispersion interactions between polarizable groups is connected with some challenges. Geometrically well-designed model systems offer the possibility to systematically examine and quantify the dispersion contribution to interaction energies. In our previous work we demonstrated that increasing the bulkiness of electronically equal substituents in the meta-position of azobenzenes decreases the thermal reaction rates from the *Z* to the *E* isomers. DFT computations showed that attractive dispersion forces essentially lower the energy of the *Z* isomers. The knowledge we obtain from our research might provide a basis to include London dispersion for the design of chemical processes, catalysts and functional materials.

## Methods

We conduct our computations with the Gaussian16 Software. Optimization of structures were performed applying the PBE0-D3BJ method with the def2-TZVP basis set. Single point energy (SPE) computations on a DLPNO-CCSD(T)/def2-TZVP level were conducted using the previously optimized PBE0 structures. Molecular structures were visualized using the CYLview software.

## Results

The rates for the *Z* to *E* isomerization of several asymmetric azobenzes in different solvents and at different temperatures

are experimentally determined in order to estimate stabilizing or destabilizing effects of the substituents on the *Z* isomer. By DFT computations we hope to reproduce the observed tendencies. Focus is laid on computing the activation parameters for the thermal *Z* to *E* isomerization. Additionally, we gain an insight into several intramolecular distances, which change for different substituents. It is further possible to visualize and localize the non-covalent interactions in the computed structures. Taking into account all these parameters and compare the experimental with the computed values shall help to evaluate the specific contribution of each substituent to our azobenzene system. Therefore, the results provide essential background information on the influence of several combinations of polarizable groups, which will be of special interest for a variety of applications in catalysis or material chemistry. In conclusion, these supporting computations are of high value to us offering new ways for communicating our experimental observations in a conclusive manner.

## Outlook

Using the computational resources provides a reliable description of activation parameters for azobenzene isomerization and can furthermore give us structural information upon modifying the azobenzene scaffold. These benefits from computations help to find promising candidates by giving guidelines for targeted changes of the azobenzenes properties. More UV-VIS investigations are currently ongoing and will be conducted with support from accompanying computational studies on the Skylla Cluster Gießen and on the FUCHS-CSC Frankfurt.

## Reference

[1] Luca Schweighauser, Marcel A. Strauss, Silvia Bellotto, and Hermann A. Wegner. 2015. Anziehung oder Abstoßung? London-Dispersionswechselwirkungen kontrollieren Azobenzol-basierte molekulare Schalter. Angew. Chem. 127, 45, 13636–13639. https://doi.org/10.1002/ange.201506126

[2] Luca Schweighauser, Marcel A. Strauss, Silvia Bellotto, and Hermann A. Wegner. 2015. Attraction or Repulsion? London Dispersion Forces Control Azobenzene Switches. Angew. Chem. Int. Ed. 54, 45, 13436–13439. https://doi.org/10.1002/anie.201506126

[3] Marcel A. Strauss and Hermann A. Wegner. 2019. Evaluierung von London-Dispersions- und Lösungsmittel-Interaktionen an Alkyl-Alkyl-Grenzflächen mittels Azobenzolschaltern. Angew. Chem. 131, 51, 18724–18729. https://doi.org/10.1002/ange.201910734

[4] Marcel A. Strauss and Hermann A. Wegner. 2019. Exploring London Dispersion and Solvent Interactions at Alkyl-Alkyl Interfaces Using Azobenzene Switches. Angew. Chem. Int. Ed. 58, 51, 18552–18556. https://doi.org/10.1002/anie.201910734

[5] Marcel A. Strauss and Hermann A. Wegner. 2019. Molecular Systems for the Quantification of London Dispersion Interactions. Eur. J. Org. Chem. 2019, 2-3, 295–302. https://doi.org/10.1002/ejoc.201800970

*Last Update:* 2020-07-17 18:05