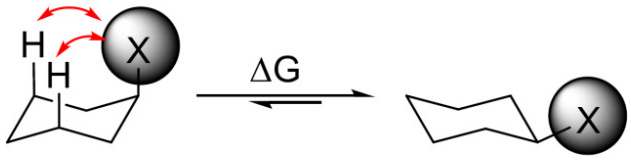
Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Toward a Better Understanding of Dispersion Interactions in Organic Reactions



Project Manager
Prof. Dr. Peter R. Schreiner

Researchers
Ephrath Solel

Principal Investigator
Prof. Dr. Peter R. Schreiner

Project Term
2019 - 2021

Clusters
Goethe-HLR Frankfurt

Software
GAUSSIAN, ORCA

Additional Software
psi4, GFN2-xtb, NCIPlot

Institute
Institute of Organic Chemistry

University
Justus Liebig University Giessen

Introduction

London Dispersion (LD)[1-3] interactions are noncovalent interactions that hold together nonpolar or weakly polar molecules. Dispersion interactions are considered weak, but the accumulation of many such interactions can result in a significant attractive force.[4,5] However, organic chemists tend to overlook the influence of dispersion on reactions, and focus on alkyl groups mainly as a source of steric repulsion and not as potential attractors. Examples of reactions that were shown to be affected by dispersion interactions are still rare,[6,7] so finding more such reactions and quantifying the dispersion effects would greatly improve our understanding of chemical reactivities. This could allow for the design of more efficient catalysts and reactions. This project explores the influence of dispersion interactions between alkyl groups on the reactivities and selectivities of organic reactions.

Methods

Optimized geometry computations are computed using DFT methods or MP2. Single point energies at the coupled-cluster level of theory are used for benchmarking and comparisons. The influence of dispersion is evaluated by use of DFT (employing DFT methods with and without dispersion corrections, such as B3LYP and the D3BJ dispersion correction[8]), by using symmetry-adapted perturbation theory (SAPT)[9] or energy decomposition analysis (EDA) schemes.[10] Noncovalent interaction (NCI)[11] plots are used to identify the groups that form LD interactions.

Results

Our initial results point to the importance of LD interactions even in relatively small systems. The effect of different groups of varying sizes on interaction energetics was judged based on computations, and the part of LD was studied.

Outlook

Further computations and quantitative evaluation of LD effects in more elaborate systems will be performed, and the results would be compared to experimentally and calculated factors in order to analyze trends.

Reference

[1] London, F. The General Theory of Molecular Forces. Trans. Faraday Soc. 1937, 33, 8–26. https://doi.org/10.1039/TF937330008B

[2] Eisenschitz, R.; London, F. Über das Verhältnis der van der Waalsschen Kräfte zu den homöopolaren Bindungskräften. Z Phys. 1930, 60, 491–527. https://doi.org/10.1007/BF01341258

[3] Wagner, J. P.; Schreiner, P. R. London Dispersion in Molecular Chemistry—Reconsidering Steric Effects.Angew. Chem. Int. Ed. 2015, 54 (42), 12274–12296. https://doi.org/10.1002/anie.201503476

[4] Rösel, S.; Quanz, H.; Logemann, C.; Becker, J.; Mossou, E.; Cañadillas-Delgado, L.; Caldeweyher, E.;Grimme, S.; Schreiner, P. R. London Dispersion Enables the Shortest Intermolecular Hydrocarbon H···HContact. J. Am. Chem. Soc. 2017, 139 (22), 7428–7431. https://doi.org/10.1021/jacs.7b01879

[5] Rösel, S.; Balestrieri, C.; Schreiner, P. R. Sizing the Role of London Dispersion in the Dissociation of All-Meta Tert-Butyl Hexaphenylethane. Chem. Sci. 2017, 8 (1), 405–410. https://doi.org/10.1039/c6sc02727j

[6] Wende, R. C.; Seitz, A.; Niedek, D.; Schuler, S. M. M.; Hofmann, C.; Becker, J.; Schreiner, P. R. The Enantioselective Dakin–West Reaction. Angew. Chem. Int. Ed. 2016, 55, 2719–2723. https://doi-org/10.1002/anie.201509863

[7] Jung, J.; Loeffler, S.; Langmann, J.; Heinemann, F. W.; Bill, E.; Bistoni, G.; Scherer, W.; Atanasov, M.; Meyer, K.; Neese, F. Dispersion Forces Drive the Formation of Uranium-Alkane Adducts. J. Am. Chem. Soc. 2019, jacs.9b10620. https://doi-org/10.1021/jacs.9b10620

[8] Grimme, S.; Hansen, A.; Brandenburg, J. G.; Bannwarth, C. Dispersion-Corrected Mean-Field Electronic Structure Methods. Chem. Rev. 2016, 116 (9), 5105–5154. https://doi-org/10.1021/acs.chemrev.5b00533

[9] Jansen, G. Symmetry-Adapted Perturbation Theory Based on Density Functional Theory for Noncovalent Interactions: Symmetry-Adapted Perturbation Theory. WIREs Comput. Mol. Sci. 2014, 4 (2), 127–144. https://doi-org/10.1002/wcms.1164

[10] Altun, A.; Neese, F.; Bistoni, G. Local Energy Decomposition Analysis of Hydrogen-Bonded Dimers within a Domain-Based Pair Natural Orbital Coupled Cluster Study. Beilstein J. Org. Chem. 2018, 14, 919–929. https://doi-org/10.3762/bjoc.14.79

[11] Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. NCIPLOT: A Program for Plotting Noncovalent Interaction Regions. J. Chem. Theory Comput. 2011, 7 (3), 625–632. https://doi-org/10.1021/ct100641a

Last Update: 2022-06-14 21:13