



Department of Chemistry Seminar

Monday, December 6th, 2021

Time 15:00

Bldg. 43 Room 015

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Dispersion vs. Steric Hindrance: Reinvestigating Classic Steric Factors

London dispersion (LD) interactions, the attractive part of the van-der-Waals interaction^{1,2} hold somewhat of a unique position in the chemical world. Although their role in influencing macroscopic phenomena (such as the higher boiling points of larger alkanes) is well recognized, they are usually overlooked when discussing molecular phenomena. Substituents in reactions are generally considered as a source of “steric hindrance” and not as “steric attractors”, better termed dispersion energy donors (DEDs). As such, their influence on reaction outcomes was quantified and presented by classic steric factors such as the A-value. We have shown, using computational quantum mechanical tools, that these well recognized steric factors have also an attractive LD component that balance part of the steric repulsion. By focusing on the LD component we can explain various non-intuitive trends between substituents, such as the inconsistency between the size of the halogens and their A-values.³ In addition, a systematic analysis of both the steric and dispersion interactions of the same molecules allows us to quantify the relative weights of the two effects and form a new DED scale.⁴ Such corrected steric and LD factors could later be applied to explore the role of LD interactions also in other reactions. Our computations show that LD interactions have a significant influence on the overall relative stabilities and energetics in cyclohexane chair conformers, and also in related concerted reactions, and must not be ignored in reaction design.

Bibliography

- (1) Eisenschitz, R.; London, F. Z. *Phys.* **1930**, *60*, 491–527.
- (2) London, F. *Trans. Faraday Soc.* **1937**, *33*, 8–26.
- (3) Solel, E.; Ruth, M.; Schreiner, P. R. London Dispersion Helps Refine Steric A-Values: The Halogens. *J. Org. Chem.* **2021**, *86* (11), 7701–7713.
- (4) Solel, E.; Ruth, M.; Schreiner, P. R. London Dispersion Helps Refine Steric A-Values: Dispersion Energy Donor Scales. *J. Am. Chem. Soc.* **2021**, *Accepted*.