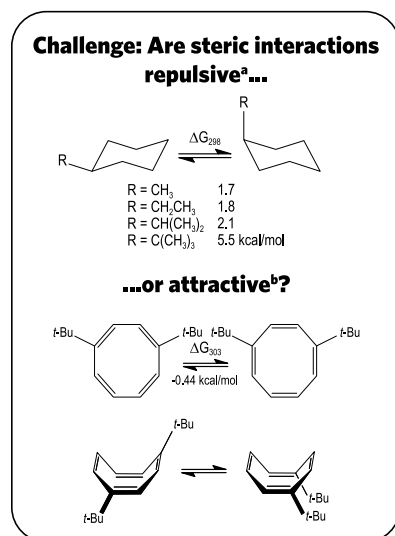


# DETERMINATION OF SPECTROSCOPICALLY-STRUCTURAL CONNECTION IN THE PYRIDINIUM SERIES TO PROBE LONDON DISPERSION FORCES

VLADIMIR GORBACHEV, ALEXANDRA TSYBIZOVA, LARISA MILOGLYADOVA, PETER CHEN,  
*Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland.*



London dispersion, the attractive part of the van der Waals potential, is an omnipresent force in molecules. However, even a cursory glance at presumably driven by the London dispersion two systems from references<sup>a,b</sup> gives curiously conflicting answers, raising a legitimate question: are steric interactions repulsive or attractive?

To address this issue a new molecular torsion balance was proposed.<sup>c</sup> Obtained systematic CIVP-spectroscopic pattern – structural connection in the series of large molecules, *o,o*-disubstituted pyridiniums, could be used as an effective tool to explore London dispersion experimentally. Analysis of the conformer spaces: energies, frequencies, geometries as well as an extensive data set: X-ray and solid-state FT-IR data unambiguously link the gas-phase fingerprint with well-determined structures for all test-compounds in the series. Even among homologues, London dispersion significantly affects the resulting geometry starting from a change in the pendant substituents' relative position with respect to each other and ending with a total change of conformation. Remarkably, for the pyridinium featuring the highest DED-properties in the series, dispersion corrected methods appear to overestimate the magnitude of London dispersion forces, which leads to the principal improper assignment of the conformer in contradiction to the experimental data.

<sup>a</sup>Muller, P. *Pure and Applied Chemistry*. **1994**, *66*, 1077.

<sup>b</sup>Lyttle, M. H.; Streitwieser, A. Jr.; Kluttz, R. Q. *J. Am. Chem. Soc.* **1981**, *103*, 3232.

<sup>c</sup>Tsybizova†, A.; Fritsche†, L.; Gorbachev†, V.; Miloglyadova. L.; Chen, P. *J. Chem. Phys.* **2019**, *151*, 234304.