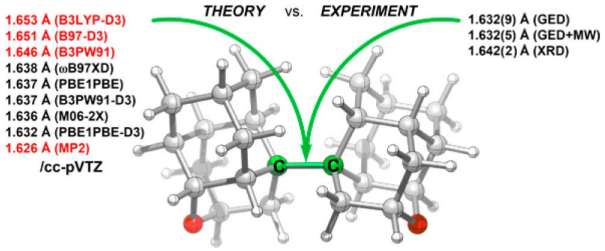
Rostislav Fedorov | 04.04.2023

Intramolecular dispersion

Intramolecular dispersion interactions, considered weak, can escalate quickly with molecular size.



Diamantyl dimers bear the inherent conflict of repulsion between the two extremely bulky moieties held together by a single C–C bond and significant attraction by London dispersion forces between these units.

Intramolecular N–H···C hydrogen bonds, C–H···Au, C–H···N, C–H···C, and C–H···H–C dispersive interactions work cooperatively to stabilize a flexible double-macrocyclic ring system

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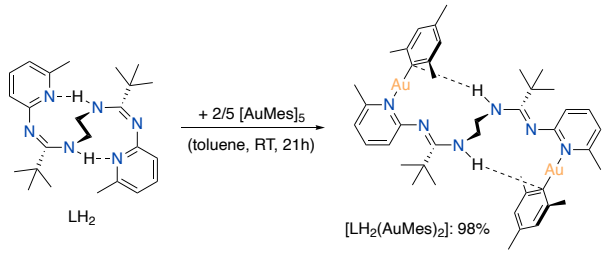
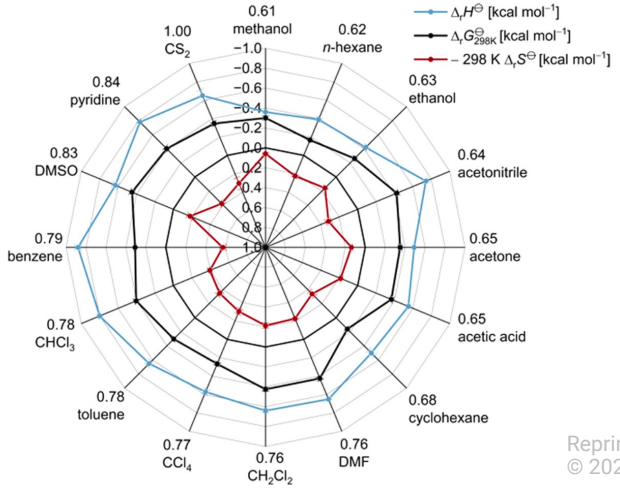
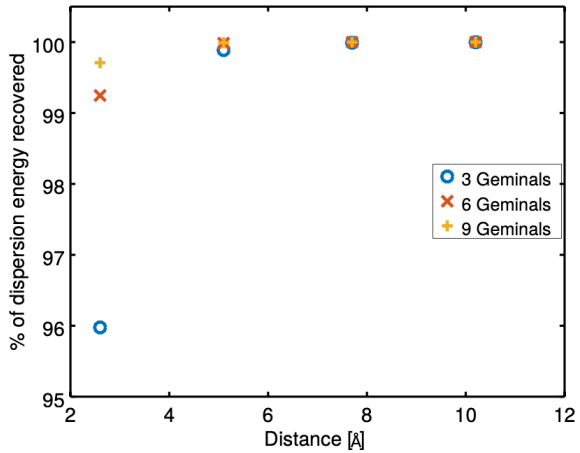
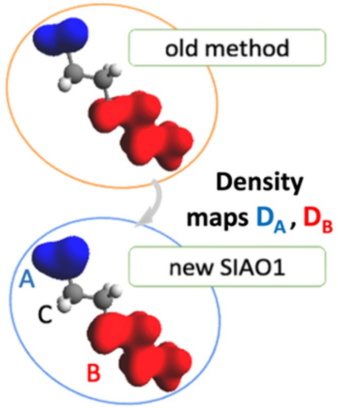




Dispersion in solution is often underestimated, but recent research shows that solvents affect dispersion interactions, mainly through changes in the solvent reorganization entropy. The correlation between thermodynamic quantities and solvent polarizabilities emphasizes that intramolecular dispersion plays a significant role in the stabilization of COT isomers in different solvents.

Compressed intramolecular long-range dispersion interactions: singular value decomposition (SVD) of coupled cluster doubles amplitudes showed that as few as three important geminals arise and account for the majority of dispersion interactions at long range.





Intramolecular symmetry-adapted perturbation theory (ISAPT) is a method to compute and decompose the noncovalent interaction energy between two molecular **A** and **B** covalently connected via a linker **C**. ISAPT(SIAO1) approach successfully addresses issues of artificially repulsive electrostatic energy and large induction and exchange-induction terms by reassigning one electron from the linker to each fragment.

Intramolecular symmetry-adapted perturbation theory with a single-determinant wavefunction (intraSAPT):

dispersion in hairpin alkanes evolves from negligible in the short chains up to being the driving force for the formation of the hairpin pattern in the long chains.