

Bond strengths in the gas phase, in solution, and in silico: computational chemistry and experiment diverge

*Prof. Dr. Peter Chen**

Laboratorium für Organische Chemie, ETH Zürich, Zürich, Switzerland

**peter.chen@org.chem.ethz.ch*



Prof. Dr. Peter Chen

Abstract

Van der Waals attractive forces have often been neglected because each individual interaction is small. Nevertheless, for organic and organometallic molecules of distinctly moderate size, e.g. 100-200 atoms, the large number of small, attractive interactions lost upon cleavage of a covalent bond can add up to a significant contribution to the bond dissociation energy, in the range of tens of kcal/mol. Whereas structural evidence for an “extra” stabilization has been reported, experimental measurement of bond dissociation energies for large molecules in the gas phase are surprisingly rare, given some not-so-obvious technical constraints. We report a comprehensive experimental and computational study of 36 proton-bound dimers for which a central +N–H···N bond is constant, but the number and extent of non-bonding interactions can be varied systematically. We report experimental BDE measurements in the gas phase, and in solution, accompanied by computational studies using DFT and DLPNO-CCSD(T) methods taken to the CBS limit. Moreover, we include solvation with dispersion-corrected PCM models. Lastly, we take the experiments and computations on to more complicated systems with metal-metal bonds for which the same kind of constraints are even more serious.
