

The *p*-block challenge: assessing quantum chemistry methods for inorganic heterocycle dimerizations

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p-block elements play an important role in various chemical and technical applications such as frustrated Lewis pairs or optoelectronic devices. However, hardly any comprehensive and reliable benchmark data exist for the assessment of approximate quantum chemical methods such as the workhorse of computational modeling, density functional theory (DFT). The aim of this work is to improve this situation. To this end, we introduce a new benchmark set (*IHD302*)[1] consisting of dimerization energies of 302 “inorganic benzenes” composed of all *p*-block elements (except carbon) of main groups III to VI up to polonium. Two dimer structure motifs were considered, on the one hand those resulting from covalent bonds and on the other hand those resulting from weaker donor-acceptor interactions (WDA), but with shorter distances than typically in pure non-covalently bonded dimers.

Since a large number of *p*-block element bonds are formed simultaneously and because significant core-valence correlation effects are present for the heavier elements, the generation of accurate reference dimerization energies is a major challenge, especially due to the slow basis set convergence. After extensive test calculations, we derived a protocol for the reference values based on explicitly correlated local coupled cluster theory with an additional basis set correction (PNO-LCCSD(T)-F12/cc-VTZ-pp-F12(corr.)). We used these reference values to analyze the performance of different DFT methods and semiempirical approaches for the *IHD302*. It turned out that many functionals are too attractive and also the tested dispersion corrections overestimate these large correlation contributions in the short- to medium-range regime, so that the COV subset in particular poses a considerable challenge even for the best available DFT methods. The inclusion of reference data from the *IHD302* set in, e.g., fits of functional parameters or dispersion corrections may help to develop more accurate and more generally applicable approximate quantum chemical methods for modeling the important *p*-block chemistry in the future.

[1] M. Bursch, T. Gasevic, Q. Ma, S. Grimme, H.-J. Werner, AH, *Phys. Chem. Chem. Phys.* under review.