DO YOU EVEN BENCH, BRO?

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In a recent publication by Kraus and Frank,[a] 89 computational methods were used to predict the gas-phase geometries of 16 dimers and trimers whose structures we determined using rotational spectroscopy of isotopically substituted species. The experimental data set, called NCDT16, sampled various non-covalent interaction of four categories: dispersion dominated interactions, hydrogen bonded dimers, $CH\cdots\pi$ & $\pi\cdots\pi$ interactions, and a general category for trimers. For each method, a least-squares structure fit of experimental rotational constants was carried out using the respective predicted geometry as input, and the mean absolute errors were used to gauge the value of the method. The top performing methods of each category, as well as an overall category, are prescribed by the authors. This represents one of the few benchmarking studies of non-covalent interactions against experimental structures in the gas-phase.

From the prescribed methods, we test the quality of the benchmarking study. With a focus specifically on $CH\cdots\pi$ interactions, we compare 7 complexes containing a halogenated methane and either acetylene or propyne (a $C\equiv C$ bond). All compared complexes have structures determined by rotational spectroscopy. Our computational and fitting methods are outlined, and we discuss the strengths and weaknesses of such a study, with an emphasis on the benefits to spectroscopic research.

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