Molecular Dipole Moments: Critical Evaluation of Predictive Capabilities and Available Experimental Data

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Molecular dipole moment is one of the most seemingly uncontroversial and well-understood molecular properties widely used in empirical estimation methods and simplified simulation models. Extensive tabulations of critically evaluated historic experimental data exist and are the basis for most practical uses. In recent years, quantum-chemical calculations (and density functional methods in particular) are also routinely utilized to supplement the experimental data. In several benchmark studies reported recently, good performance of density functional methods was observed, although some notable outliers were recognized as well. It is also of note that most of the critical evaluations of experimental data currently in-use were conducted prior to wide-spread availability of quantum-chemical methods (i.e., without additional validation that they can provide). In this study, we perform large-scale detailed comparison of the results of quantum-chemical calculations and the evaluated experimental data for nearly 800 compounds. We find that density functional methods do provide reasonably accurate estimates for the dipole moments. Additionally, a notable number of erroneous experimental points was identified in the process. Finally, the importance of proper conformational averaging for the comparison with the bulk-averaged experimental points from dielectric measurements was demonstrated. Recommendations for estimation of dipole moments using quantum-chemical calculations and assessment of the resulting uncertainties will be discussed.