A Systematic Benchmarking of ^{31}P and ^{19}F NMR Chemical Shifts Predictions at Different DFT/GIAO Methods and Applying Linear Regression to Improve the Prediction Accuracy

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Abstract

A systematic benchmark of phosphorus and fluorine NMR chemical shifts predictions at six different density functional theory (DFT) / the gauge-including atomic orbital (GIAO) methods was conducted. Two databases were compiled: one consists of 35 phosphorus-containing molecules, which cover the most common intra-molecular bonding environments of trivalent and pentavalent phosphorus atoms; the other is composed of 46 fluorine-containing molecules. The characteristics of each DFT/GIAO method with different solvent models were demonstrated in details. The application of linear regression between the calculated isotropic shielding constants and experimental chemical shifts was applicable to improve the prediction accuracy. And, the best methods with the SMD and CPCM implicit solvent models for ^{31}P chemical shifts predictions, are able to yield a root-mean-square deviation (RMSDs) of 5.58 ppm and 5.42 ppm, respectively; for ^{19}F, the corresponding lowest prediction errors with these two applied solvent models are 4.43 ppm and 4.12 ppm. The developed scaling factors fitted from linear regression are applicable to enhance the chance of successful structural elucidations of phosphorus or fluorine-containing compounds, as an efficient complement to ^{13}C, ^{1}H, ^{11}B and ^{15}N chemical shifts predictions.

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