Theoretical calculation of ^{13}C NMR chemical shifts using scale factors

Mariana Martins^{1*} (IC), Sara Souza¹ (PG), Fabio Luiz Paranhos Costa¹ (PQ).

¹Departament of Chemistry, Federal University of Jataí 75801-615, Brasil.

*mariana-aparecida2009@hotmail.com

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Introduction

Although, in many studies, environmental effects are neglected, the GIAO-HDFT (Gauge Including Atomic Orbital with Hybrid Density Functional Theory) approach have been successfully applied in order to determine chemical shift (δ), the most important magnetic property.¹ In this work, we present a comparative study using GIAO-HDFT (10 hibrids functionals with 3 different basis set) with linear regressions to predict NMR ^{13}C chemical shifts (δ). A set of 22 small molecules providing 27 different ^{13}C δ determined in the gas phase was used for all scaling factors protocols.^{2,3}

Methodology

Geometry optimizations were performed in gas phase. HDFT calculations were carried out using Gaussian09 software.⁴ Geometries (PBE0/3-21G) were verified as local minima by vibrational frequencies calculations (PBE0/3-21G). Two-electron integrals and their derivatives were calculated using an ultrafine grid option (Int =Ultrafine). NMR δ were computed using the GIAO method and are given relative to that of TMS calculated at the same level of theory. In this work we used combinations of 10 functionals (PBE0 (FI), HSEH1PBE (FII); mPW1PW91 (FIII), B3PW91 (FIV), B3LYP (FV), X3LYP (FVI), BHANDHLYP (FVII), CAM-B3LYP (FVIII), ω B97X-D (FIX) and MPW1K (FX)) with 3 different basis set (3-21G (B1), 6-31G* (B2) and 6-31+G**, totaling 30 levels of theory to obtain the calculated δ . The scaled δ (δ_{scal}) were obtained linear regressions between experimental and δ_{cal} .

Results

In order to achieve widespread application of a scaling factor to GIAO-HDFT ^{13}C δ , it is desirable to have excellent accuracy of RMS (root mean square deviation). For ^{13}C NMR, the RMS errors should be less than 4.4 ppm (2%).⁵ As expected, the values of the RMS errors became smaller starting from isotropic shielding constants (σ_{iso}) to the calculated δ (δ_{cal}) and finally to the scaled δ (δ_{scal}), regardless of the basis set used. Thus, the averages of the RMS error values, in ppm, were: σ_{iso} = 23.75 (B1), 8.30 (B2) and 8.45 (B3); δ_{cal} = 8.80 (B1), 6.39 (B2) and 5.33 (B3) and δ_{scal} = 6.84 (B1), 5.68 (B2) and 5.09 (B3). It is interesting to note that, from σ_{iso} to the δ_{scal} , the mean value of the RMS error decreased by almost 300% for B1. On the other hand, the RMS error value for σ_{iso} , from B2 to B3, shows a slight increase in the mean RMS value.

Taking into account the values of RMS errors for δ_{scal} , the largest and smallest error values (in ppm) are, respectively: **B1**: mPW1PW91=8.56 and HSE1PBE=6.13; **B2**: BHANDHLYP=7.21 and HSE1PBE =4.06 and **B3**: BHANDHLYP=6.36 and HSE1PBE = 4.41. Thus HSE1PBE ($R^2 = 0.997$, $\delta_{\text{scal}}=0.99\delta_{\text{calc}}+0.9$) functional had the best performance.⁶

Conclusions

The correlations between experimental and calculated δ were subjected to statistical analysis to identify the best-performing functionals. The basis set used for the optimization of the geometry i.e., 3-21G proved to be, however small, adequate. The functional which showed the best performance was HSEH1PBE. Using B2 and B3, after scaled the δ by means of linear regressions, the ability of all levels of theory to

reproduce the experimental data was very similar. However, using B3 the results were slightly better. So, in order to obtain the best relation between computational cost and reproduction of the experimental data, we recommend using the B3 base. We thought it would be interesting that this study been extended to others molecules in order to test the 30 combinations used here to generate universal scaling factors. The information contained in this work can be used for the assignment of experimental NMR spectra and will motivate further studies involving the theoretical calculation of ^{13}C NMR δ .

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