SOME ASPECTS OF DFT/GIAO/B3LYP COMPUTATIONS FOR NMR CHEMICAL SHIFTS AND PROPER ASSIGNMENTS FOR QUATERNARY AMMONIUM SALTS

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The ^{13}C, ^{15}N, and ^{1}H NMR chemical shifts of nitrogen heterocyclic compounds have been the subject of a number of experimental and theoretical studies [1]. Computational methods for calculating magnetic shielding are continued to improve. The GIAO (gauge including atomic orbital) method is now widely used in efficient implementations, although the IGLO (individual gauge for localized orbitals), CSGT (continuous set of gauge transformations), and LORG (local orbitals-local origins) algorithms also provide satisfactory magnetic shieldings. For unsaturated and aromatic systems it is important to include, in all four methods, the electron correlation effects. Earlier GIAO calculations are shown to be much better at predicting chemical shifts when density functional theory with the B3LYP hybrid functional is used to account for electron correlation, in comparison with Hartree-Fock calculations [2].
In this work we present extensive experimental and theoretical studies of NMR magnetic shielding spectra of selected quaternary ammonium salts.

We have applied the method DFT/GIAO/B3LYP/6-31G*// B3LYP/6-31G* to compute magnetic shieldings of several ammonium salts. In most cases we have found that it is sufficient to perform computations only for the quaternary ammonium cation using empirically scaling method. Unfortunately, in the case of 1-alkyl-3-alkoxymethylimidazolium and 1-alkyl-3-alkylthiomethylimidazolium cations some signals computed in such a way are not in agreement with the experimental data. The observed deviation is especially pronounced in the case of NMR signals related to the C2 position in the imidazole ring. To solve this problem we propose to perform computational procedure not for quaternary ammonium cations but for the neutral form of the salt. We have found that the application of such a way of computation leads to a very good agreement between computed and experimental ^{1}H and ^{13}C NMR spectra for several 1-alkyl-3-alkoxymethylimidazolium chlorides and 1-alkyl-3-alkoxymethylimidazolium tetrafluoroborates. The proposed method was also successfully used for several 1-benzyl-3-alkoxymethylbenzimidazolium chlorides and 1- benzyl-3-alkoxymethylbenzimidazolium tetra-fluoroborates.

References

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