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Very fast and surprisingly accurate GIAO-mPW1PW91/3-21G//PM7 scaling factor for ^{13}C NMR chemical shifts calculation

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In this work, we present a new GIAO-HDFT universal scaling factor (mPW1PW91/3-21G//PM7(I)) and a comparative study in which its ability to predict NMR ^{13}C chemical shifts (δ) with high cost-effectiveness ratio is investigated. A set of 22 small molecules providing 27 different ^{13}C δ determined in the gas phase was used for all scaling factors protocols: B3PW91/cc-pVDZ//B3PW91/cc-pVDZ (II), B3PW91/cc-pVTZ//B3PW91/cc-pVDZ (III), B3LYP/6- 311+(2d,p)// B3LYP/6-31G(d) (IV), mPW1PW91/6-31G(d)//PM7(V), mPW1PW91/6-31G(d)//mPW1PW91/6-31G(d) (VI). Geometry optimizations were performed in gas phase. HDFT and semi-empirical calculations were carried out using Gaussian09 and MOPAC software, respectively. Geometries were verified as local minima by vibrational frequencies calculations. 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. Despite the calculation approximations the δ calculated at the GIAO- mPW1PW91/3-21G//PM7 using a simple relationship (δscal=1.14 δcalc–4.7, where δcalc and δscal are calculated and the linearly scaled values of the ^{13}C δ, respectively) were able to yield MAD and RMS errors as small as those obtained with other GIAO-HDFT with bigger basis sets (protocols (II) to (VI)). The robustness of the new protocol and its applicability to practical problems was evaluated by the calculation of the δ for two natural compounds with synthesis, biological and therapeutic interest: tryptanthrin (indolo[2,1- b]quinazoline-6,12-dione) and (-)-loliolide (7aR)-6-hydroxy-4,4,7a- trimethyl-6,7-dihydro-5H-1-benzofuran-2-one. For both compound, the six protocols presented good agreement with experimental data. Moreover, for the second compound, the new protocol performs even better than the five others. In conclusion, GIAO-mPW1PW91/3- 21G//PM7 linear regression obtained by using the experimental and the calculated data, is a very attractive tool as an alternative to more computationally demanding approaches, which are usually applied in order to achieve ^{13}C NMR δ calculations.

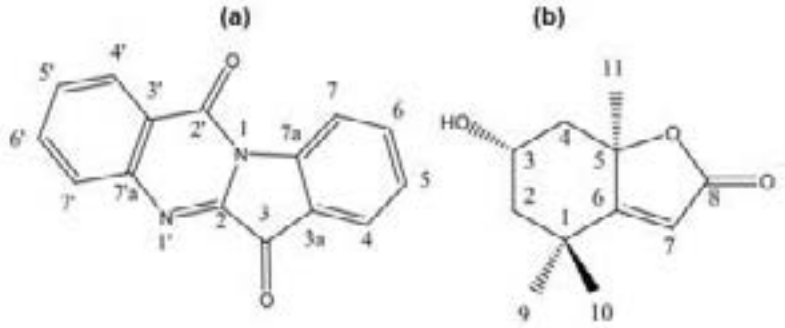

Figure 1: Tryptanthrin (a) and (-)-loliolide (b) structures.

Biography

Fabio L P Costa has completed his PhD in Chemistry of Natural Products from the Federal University of Rio de Janeiro (2011); Doctorate degree at Center of Research and Advanced Studies of the Polytechnic Institute and; Post-doctorate at the Fluminense Federal University (2012) working on organic synthesis of chaconnes. He has experience in the field of Chemistry, with emphasis in Theoretical Chemistry and synthesis of natural and analogous products, working mainly in the following subjects: *Ab initio* calculations and molecular modeling, with emphasis on the calculation of spectroscopic properties, electronic structure and properties of natural products. Actually his research is focusing on NMR-GIAO chemical shifts calculations of organic molecules and has expertise in computational chemistry. Recently his is working in scaling factor NMR protocols with low computational cost.

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