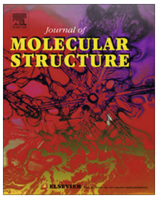
Journal of Molecular Structure 1086 (2015) 43–48

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Benchmarking quantum mechanical calculations with experimental NMR chemical shifts of 2-HADNT

Yuemin Liu [a], Thomas Junk [a], Yucheng Liu [b,*], Nianfeng Tzeng [c], Richard Perkins [a]

[a] *Department of Chemistry, University of Louisiana at Lafayette, Lafayette, LA 70504, USA*
[b] *Department of Mechanical Engineering, Mississippi State University, Mississippi State, MS 39762, USA*
[c] *The Center for Advanced Computer Studies, University of Louisiana at Lafayette, Lafayette, LA 70504, USA*

HIGHLIGHTS

- Chemical shifts of C-13 of seven carbon atoms for 2-HADNT were determined through experiments.
- Quantum mechanics GIAO calculations were implemented using MP2 and seven DFT methods.
- It was found that the O3LYP method gives the most accurate chemical shift values among the seven DFT methods.
- Three types of atomic partial charges MK, ESP and NBO were calculated using MP2/aug-cc-pVDZ method.
- Numerical calculations of NMR chemical shifts were validated by comparing with the experimental data.

ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 2 January 2015
Accepted 5 January 2015
Available online 9 January 2015

Keywords:
Quantum mechanical calculations
Chemical shifts
Partial charges
NMR
2-HADNT
C-13

ABSTRACT

In this study, both GIAO-DFT and GIAO-MP2 calculations of nuclear magnetic resonance (NMR) spectra were benchmarked with experimental chemical shifts. The experimental chemical shifts were determined experimentally for carbon-13 (C-13) of seven carbon atoms for the TNT degradation product 2-hydroxylamino-4,6-dinitrotoluene (2-HADNT). Quantum mechanics GIAO calculations were implemented using *Becke-3-Lee–Yang–Parr* (B3LYP) and other six hybrid DFT methods (*Becke-1-Lee–Yang–Parr* (B1LYP), *Becke-half-and-half-Lee–Yang–Parr* (BH and HLYP), *Cohen–Handy-3-Lee–Yang–Parr* (O3LYP), *Coulomb-attenuating-B3LYP* (CAM-B3LYP), modified-Perdew–Wang-91-*Lee–Yang–Parr* (mPW1LYP), and *Xu-3-Lee–Yang–Parr* (X3LYP)) which use the same correlation functional LYP. Calculation results showed that the GIAO-MP2 method gives the most accurate chemical shift values, and O3LYP method provides the best prediction of chemical shifts among the B3LYP and other five DFT methods. Three types of atomic partial charges, Mulliken (MK), electrostatic potential (ESP), and natural bond orbital (NBO), were also calculated using MP2/aug-cc-pVDZ method. A reasonable correlation was discovered between NBO partial charges and experimental chemical shifts of carbon-13 (C-13).

Introduction

Reliability of theoretical calculations has been recognized in predicting nuclear magnetic resonance (NMR) shielding and chemical shifts [1–8]. Accurate prediction of chemical shifts can be achieved through calculations using the coupled-cluster singles and doubles (CCSD) model augmented by perturbative correction for triple excitation (CCSD(T)) method [9–11], with a deviation of 1 ppm between the experimental chemical shifts and the calculated results for C-13. The accuracy can be further improved by the inclusion of zero-point vibrational correction in the Hartree–Fock (HF), MP2, CCSD, and CCSD(T) calculations of the chemical shifts except for the DFT calculations [11].

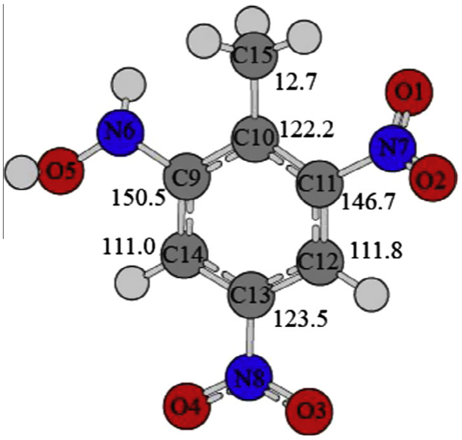
The gauge that includes atomic orbital (GIAO) was first implemented with X-α approximation of the exchange–correlation functional (DFT) [12,13]. The second-order property shielding tensor has also been described using other methods such as the individual gauge for localized orbitals (IGLO) [14,15], the individual gauge for local origin (LORG) [16], the continuous set of gauge transformations (CSGT) [17], and the individual gauges for atoms in molecules (IGAIM) [18]. Among these methods, the GIAO method is most commonly applied because of its high efficiency and low dependence on basis set quality [19].

The chemical shifts for C-13 have been calculated using wave function based methods such as MP2 [20–22], multiconfigurational self-consistent field (MCSCF) [22,23], CCSD

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.molstruc.2015.01.007



2-HADNT

Fig. 1. Schematic structure of 2-HADNT with numbering scheme displayed.

[24,25], CCSD(T) [26], and coupled cluster theory with single, double, and triple excitations (CCSDT) [27,28]. However, the computational cost of those methods is so high, which prevents full application of those methods for routine simulations. The DFT methods are more cost-effective approaches because that in those methods electron correlation is treated at a more affordable semi-empirical level. The C-13 chemical shift calculated from DFT methods such as GIAO and B3LYP can provide structural information for different charge states [29]. On the other hand, the experimental C-13 chemical shifts can be well reproduced using B3LYP for monomeric bilirubin molecule [30]. It is also known that DFT methods generate much more accurate geometries and potential energy profiles than HF method at a similar computational expense. Unfortunately, DFT methods could not demonstrate decisive superiority over HF method in the calculations of chemical shifts of all types of compounds. DFT methods are different based on different exchange–correlation functionals (XC) implemented and the different DFT methods used may lead to different accuracies in the calculated chemical shifts [31]. Additionally, DFT methods tend to provide lower chemical shifts for regular organic compounds but higher chemical shifts for transition metals than their actual values because the paramagnetic components are overestimated in non-transition metal compounds while underestimated in the compounds containing transition metals [32]. The deficiency in the chemical shifts prediction is due to the lack of terms that describe non-vanishing electric current in popular DFT methods [33], the underestimation of the highest and lowest unoccupied molecular orbital (HOMO–LUMO) gap, as well as the unrealistic larger paramagnetic values than their experimental results for the regular organic compounds that contain no transition metals [34,35]. Currently, calculations of chemical shifts can be performed at fundamental HF level with reasonable accuracy for small weakly correlated organic molecules. Electron correlation has to be fully considered in order to achieve high accuracy on chemical shifts for dispersion dominated large molecules. The DFT treatment of electron correlations varies in how to formulate the following four components: spin density based local density approximation (LDA), a generalized gradient approximation (GGA) for density derivatives, HF exchange, and kinetic energy density terms. For example, the popular DFT method B3LYP represents the combination of a standard LDA, a gradient correction GGA, and the HF exchange [36,37]. It was reported that DFT O3LYP differs from B3LYP in an optimized exchange functional, while performs better than B3LYP in describing van der Waals force in highly correlated molecules [38,39]. One of the goals of this work is to test how the different exchange functionals impact the performance of the seven DFT methods in evaluating chemical shifts of the highly correlated aromatic 2-HADNT. In concept, electronic environments of nuclei in chemical structure determine nuclear chemical shifts or nuclear resonance frequencies [40]. In fact, C-13 chemical shift was suggested to be linearly proportional to electron density. A study of C-13 chemical shift of the cyclopentadienide anion suggested that the proportionality coefficient is 128.5 ppm/electron [41]. A strong correlation was also reported between the partial charges calculated by Matsumoto et al. and the experimental chemical shifts of C-13 and N-15 for pyridinium bis (methoxycarbonyl) methylides [42]. For a highly electron correlated molecule, it is especially meaningful in both theory and practice to explore the correlation between the experimental C-13 chemical shifts and electron partial charges and calculated C-13 chemical shifts and electron partial charges respectively for 2-HADNT (Fig. 1) [43]. In this study, both quantum mechanics gauge including atomic orbital-density functional theory (GIAO-DFT) and quantum mechanics gauge including atomic orbital-second order Moller–Plesset perturbation theory (GIAO-MP2) simulations are performed to reproduce experimental C-13 chemical shifts of 2-HADNT from NMR measurement. From the simulation results, the correlations between the calculated partial charges of C-13 of 2-HADNT and the experimental C-13 chemical shifts can be found. Effects of different exchange functionals on the accuracy of the calculated chemical shifts will also be discussed. All the chemical shifts and partial charges will be calculated using MP2 and the seven DFT methods, compared with the experimental chemical shifts afterwards.

Research approaches

Experimental setup

The 2-HADNT was prepared following the procedure in the authors' previous work [43]. Chloroform ($CHCl_3$) (analytical purity, made by Merck) was used as a solvent for measurement. Tetramethylsilane (TMS) (made by Fluka) was applied as the internal reference. The C-13 magnetic resonance spectra were recorded at a radio frequency of 500.1 Mc/s on a Varian 500 spectrometer in the Department of Chemistry at the University of Louisiana at Lafayette. The sample of concentration was maintained at 25 ± 1 °C. The effect of proton coupling was removed using a noise decoupling technique.

Computational approach

The chemistry application Gaussian 09 package was used in all computations of this work [44]. Initial crystal structure of 2-HADNT was optimized using MP2/aug-cc-pVDZ. The C-13 NMR calculations were carried out using GIAO method [19]. The NMR shifts were computed using MP2 and seven DFT hybrid methods and the C-13 chemical shifts were referenced to C-13 chemical shifts for TMS using GaussView Version 5. The chemical shift of 128.5 ppm for C-13 of benzene was used to calculate chemical shift differential. The solvation effect of chloroform with a dielectric constant of 4.7 was evaluated using the universal solvation model (SMD) presented by Truhlar et al. [45], which includes electrostatic term based on integral equation formalism polarized continuum model (IEF-PCM) and non-electrostatic cavity–dispersion–solvent–structure term. The NBO charges were computed following the NBO scheme implemented within the Gaussian 09 platform. The basis set of aug-cc-pVDZ was used throughout all calculations.