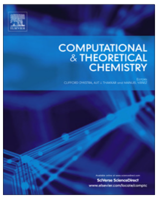
Computational and Theoretical Chemistry 1013 (2013) 7–14

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

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



Performance of ONIOM in the investigations of tri-*n*-butyltin compounds

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ARTICLE INFO

Article history:
Received 14 December 2012
Received in revised form 22 February 2013
Accepted 22 February 2013
Available online 7 March 2013

Keywords:
Organotin compounds
Tributyltin chloride
Tributylmethyltin
ONIOM
Chemical shift

ABSTRACT

The performance of ONIOM was systematically assessed in the calculations of various properties for six conformers of tri-*n*-butyltin chloride and tri-*n*-butylmethyltin. Three ONIOM combinations of levels of theory, namely ONIOM(B3PW91/IGLO:HF/3-21G*), ONIOM(B3PW91/IGLO:PM3) and ONIOM(B3PW91/IGLO:UFF), were used and for each combination three ONIOM partitioning schemes of the investigated molecules were probed. The results of such molecular properties as structural parameters, relative conformational energies, dipole moments, vibrational frequencies and chemical shifts obtained by the ONIOM combinations were compared in a statistical manner with the reference data calculated using B3PW91/IGLO. It was found that ONIOM(B3PW91/IGLO:HF/3-21G*) and ONIOM(B3PW91/IGLO:PM3) reproduce the structural parameters of the investigated conformers accurately when the core layer contains the $(-CH_2CH_2CH_2)_3SnX$ or $(-CH_2CH_2)_3SnX$ fragment (X = Cl, Me). ONIOM(B3PW91/IGLO:HF/3-21G*) with the $(-CH_2CH_2)_3SnX$ core is recommended for fast predictions of relative conformational energies, dipole moments and vibrational frequencies. A good agreement with the reference results of ^{119}Sn, ^{13}C and ^{1}H NMR chemical shifts was obtained only in one case, namely for ONIOM(B3PW91/IGLO:HF/3-21G*) and the largest possible core layer.

1. Introduction

Tri-*n*-butyltin (TBT) compounds are an interesting group of organotin(IV) compounds. They have found many commercial large-scale applications that cover fungicides, bacteriocides, protective agents in antifouling marine paints, etc. [1–6]. These applications are associated with the biological activity of TBT compounds. However, the toxicity of TBT to aquatic organisms is a serious disadvantage because the accumulation of TBT compounds in the environment has a harmful impact on some aquatic species: it inhibits their development or increases mortality [7–9]. TBT compounds are also important in laboratory organic synthesis, e.g. TBT hydride serves as a chain carrier agent in free-radical reactions and TBT chloride is used in the stannylation of alkynes [1–3].

The determination of molecular properties of TBT compounds is necessary to find new applications for these compounds or make the existing applications more efficient. Various experimental techniques are applied to obtain molecular properties of organotin compounds [2] but ^{119}Sn NMR spectroscopy seems to be one of the most useful and powerful tools for the determination of molecular structure and conformation [2,10,11]. The investigations of molecular properties of organotin compounds can also be performed using quantum-chemical computational methods [3,12,13]. There are a large number of computational studies on the properties of organotin compounds, e.g. [14–28] to mention the most recent ones, and the majority of these studies were performed within the framework of density functional theory (DFT) [29]. The reason behind the choice of DFT methods lies in the good balance between the accuracy of these methods and their computational cost. DFT methods can also be used for determining chemical shifts [12] and the calculated values of ^{119}Sn NMR chemical shifts are often very close to experimental results [17,25,30,31].

Although DFT methods have turned out to be highly successful owing to their relatively modest computational cost (compared to traditional post-HF methods), these methods may be computationally too expensive to carry out an exhaustive search of conformational space or to calculate some computationally demanding properties (such as NMR spin–spin coupling constants) even for moderately large molecules. For the studies of molecular structure and properties, hybrid methods are an interesting alternative to DFT. Hybrid methods divide a single molecule or a larger system into at least two parts and then different levels of theory are applied to the different parts [32,33]. A high-level calculation is performed on a small part of the system that is the most important from the chemical point of view, whereas lower levels of theory describe the remaining part of the system. The concept of partitioning a molecular system into parts treated with different levels of theory leads to a significant saving in computational cost. However, the division of a molecular system into parts may result in a

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http://dx.doi.org/10.1016/j.comptc.2013.02.022

loss of accuracy and this is the reason why a reasonable partitioning scheme and selecting proper computational methods are essential.

Calculations carried out by hybrid methods for organotin compounds have been presented in a very small number of studies so far [34–40]. In these studies hybrid methods were applied solely to obtain structural and energetic properties of organotin compounds. Hu and Su in a series of papers [34–36] combined the B3LYP density functional with the PM3 semiempirical method within the framework of ONIOM (our Own N-layer Integrated molecular Orbital molecular Mechanics) [41,42] scheme and the resulting computational approach was used to optimize structures of molecules in which one bulky substituent is bonded to an Sn atom. The same DFT functional but in conjunction with the AM1 semiempirical method, both working within ONIOM, were used in other studies of organotin compounds [37,38]. Theoretical investigations using hybrid methods for TBT compounds have also been reported [39,40]. Vincent et al. [39] identified stationary structures on the potential energy surfaces for the reactions of various allyltri-*n*-butyltins with aldehydes. In that study the terminal C_3H_7– part of *n*-butyl group (*n*-Bu) was represented by a molecular mechanics (MM) method, whereas the rest of molecule at the DFT level of theory.

In this work the results of benchmark calculations performed for two TBT compounds have been presented. Various molecular properties of tri-*n*-butyltin chloride (TBTCl) and tri-*n*-butylmethyltin (TBTMe) were calculated by means of three combinations of computational methods within the framework of ONIOM, and for each combination three partitioning schemes of the TBTX (X = Cl, Me) molecules were used. The calculated molecular properties covered structural parameters, relative conformational energies, electric dipole moments, vibrational frequencies and NMR chemical shifts. Not the whole set of these properties was obtained by all the three ONIOM combinations because of the limitations of some computational methods applied. Among the calculated properties, ^{119}Sn chemical shifts seem to be the most interesting because ^{119}Sn NMR spectroscopy has become indispensable to organotin chemistry. Moreover, computational studies in which ^{119}Sn chemical shifts are predicted by hybrid methods are lacking in the literature.

The goal of this work is to assess quantitatively the performance of three ONIOM combinations of computational methods upon varying partitioning schemes for the calculations of the above-mentioned molecular properties. The results of ONIOM calculations were compared with reference DFT results and on this basis a conclusion can be drawn whether it is really necessary to adopt DFT rather than less computationally expensive hybrid methods.

2. Computational details

An ONIOM scheme combining two levels of theory was used for the TBTX molecules. Each molecule was divided into two regions (so-called layers): the core region consisting of the Sn atom, the Cl or Me substituent, and three fragments of *n*-Bu groups bonded to Sn; and the surrounding region comprising the remaining fragments of the *n*-Bu groups. As there is a covalent bond between the two fragments of the *n*-Bu group, the core layer was saturated with hydrogen link atoms. Each layer was described by a different computational method. The coupling between the core layer and the surrounding layer was included using the low level of theory. The resulting ONIOM energy E^{ONIOM} of a given molecule was calculated as an extrapolation:

$$E^{\mathrm{ONIOM}} = E^{\mathrm{high}}_{\mathrm{core}} + E^{\mathrm{low}}_{\mathrm{molecule}} - E^{\mathrm{low}}_{\mathrm{core}}$$

where 'core' and 'molecule' refer to the core region of the molecule and the whole molecule, respectively. The levels of theory applied to the core region and to the whole molecule are indicated in the superscripts.

Three combinations of computational methods used within the framework of the two-layer ONIOM were selected. The core layer was always described by the B3PW91 hybrid density functional [43,44]. The IGLO-II basis set [45] was ascribed to the Sn atom, whereas the IGLO-III basis sets [45] were adopted for the H, C and Cl atoms. The choice of B3PW91/IGLO was motivated mainly by the methodology applied successfully in earlier studies [22–25,30] to calculate ^{119}Sn chemical shifts. However, the IGLO basis sets are based on Huzinaga's basis sets [46] and they should be flexible enough to describe reasonably other molecular properties (an evaluation of the IGLO basis sets for performing conformational analysis of TBT compounds is described in Supplementary Material). The surrounding region was treated with three low levels of theory: ab initio Hartree–Fock with the 3-21G* basis set [47,48]; the semiempirical PM3 method [49,50]; and the MM universal force field (UFF) [51]. The resulting ONIOM combinations of levels of theory are denoted further in the text by the following abbreviations: OC1 for ONIOM(B3PW91/IGLO:HF/3-21G*); OC2 for ONIOM(B3PW91/IGLO:PM3); and OC3 for ONIOM(B3PW91/IGLO:UFF). The OC3 calculations were done with mechanical embedding.

Apart from the computational methods and basis sets applied within ONIOM, the proper selection of the size of the core layer is essential for the reliable description of molecular properties. Three partitioning schemes, PS1–PS3, assigning different parts of the *n*-Bu groups to the core and to the surrounding layer were used. In PS1, the core layer was the largest and it was represented by the $(–CH_2CH_2CH_2)_3SnX$ fragment of the TBTX molecules, whereas the core layer of PS3 comprised $(–CH_2)_3SnX$ (see Fig. 1). The remaining fragments of TBTX, that is, from the terminal $(CH_3–)_3$ groups of PS1 to $(CH_3CH_2CH_2–)_3$ of PS3, belonged to the surrounding layer.

Conformational analysis was performed for the TBTX molecules. The initial sets of conformers were generated by changing the X–Sn–C–C and C–Sn–C–C dihedral angles in the TBTX molecules. Three values of these angles were considered, namely −60°, 60° and 180°, and various combinations of these values allowed us to form the conformers with different arrangements of three *n*-Bu groups with respect to each other. The optimized geometries of conformers were subjected to frequency calculations and then the conformers were ordered with respect to their extrapolated E^{ONIOM} energies whose values included zero-point energy (ZPE) corrections. In the case of OC1 the extrapolated ZPEs were used, whereas for OC2 and OC3 their ZPEs were approximated by the ZPEs obtained from separate B3PW91/IGLO calculations with the frozen atoms of the surrounding layer (obviously, those B3PW91/IGLO calculations were done for the OC2- and OC3-optimized geometries of conformers).

The determination of the chemical shifts of the ^{1}H, ^{13}C and ^{119}Sn nuclei in the TBTX molecules required the isotropic shielding constants of these nuclei. The isotropic shielding constant σ of each nucleus was calculated as an extrapolated value at the OC1 level.

$$\sigma = \sigma^{\mathrm{B3PW91/IGLO}}_{\mathrm{core}} + \sigma^{\mathrm{HF/3-21G*}}_{\mathrm{molecule}} - \sigma^{\mathrm{HF/3-21G*}}_{\mathrm{core}}$$

The individual σ values for the nuclei in the core region and in the whole molecule were calculated using the gauge-independent atomic orbitals (GIAO) [52,53] at the levels of theory indicated in the superscripts. The chemical shift δ of a nucleus N in a given TBTX molecule was, in turn, obtained by means of the formula:

$$\delta(N, \mathrm{TBTX}) = \sigma(N, \mathrm{ref}) - \sigma(N, \mathrm{TBTX})$$

where $\sigma(N, \mathrm{ref})$ stands for the isotropic shielding constant of the nucleus N in a reference molecule. In the case of $\delta(^{119}\mathrm{Sn})$, tetramethyltin