Journal of Organometallic Chemistry 724 (2013) 139–146

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

A DFT study of the vicinal $^3J(^{119}Sn,^{13}C)$ and $^3J(^{119}Sn,^1H)$ coupling constants in trimethyl- and chlorodimethylstannyl propanoates

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ARTICLE INFO

Article history:
Received 4 August 2012
Received in revised form
6 October 2012
Accepted 15 October 2012

Keywords:
OrganoTin(IV)
^{119}Sn NMR
^{119}Sn couplings
Karplus
DFT
Relativistic ZORA

ABSTRACT

We have tested the performance of DFT protocols, both at the Scalar relativistic ZORA and non-relativistic level of theory, for the calculation of the $^3J(^{119}Sn,^{13}C)$ and $^3J(^{119}Sn,^1H)$ vicinal couplings for a series of flexible organotin(IV) derivatives with formula XMe2SnCHRCHR′COOMe (X = Me, Cl; R, R′ = Me, Ph). A satisfactory agreement between experimental and calculated vicinal couplings has been obtained by taking into account the conformational behaviour of the compounds investigated. The protocols used, mainly the relativistic one, were found to give a correct picture of the populations and a sufficiently high overall performance in calculating the vicinal couplings, thereby overcoming the use of empirical Karplus-type relationships to infer geometrical parameters from $^3J(^{119}Sn,^{13}C)$ and $^3J(^{119}Sn,^1H)$.

1. Introduction

The Karplus equation [1,2] is the popular relationship used in NMR spectroscopy to correlate homo- and hetero-nuclear vicinal coupling constants ^3J with the dihedral angle formed by the four atoms involved in the coupling path. However, the usefulness of this equation is limited by the fact that it has to be empirically parameterized depending on the molecular system where it is applied and, actually, it does its best for "closely related systems" [2]. In fact, since its infancy the performance of this equation has been stressed to depend not solely on the dihedral angle but also on several contributions affecting the *s*-bonding electronic density between the coupled nuclei, such as, e.g.: the electronegativity of the atoms involved in the three-bond path that generate the coupling or the presence of substituent(s) bound to the atoms of the coupling path itself [2]. Thus, in order to accommodate the presence of atoms other than H and C (e.g. O, N, P, S) in organic systems, a host of Karplus-type equations differently parameterized have been proposed [3–19]. Moreover, Karplus-type equations, and Karplus-type behaviours, involving metal atoms have been also reported [20–22].

Organotin(IV) compounds are employed for several applications in industrial and synthetic chemistry mainly due to their biological and catalytic properties [23–28]. In all these cases, knowledge of the structural configuration of the compounds is often the key to understand the most likely mechanism of their interaction with biological substrates, their catalytic properties as well as the regioselectivity of reactions.

^{1}H, ^{13}C and ^{119}Sn NMR spectroscopies are a powerful tool to elucidate configurational and dynamical issues concerning organotin(IV) derivatives, e.g. coordination and local geometry at the tin centre, chemical exchange involving the metal, conformational flexibility of the molecular system.

As far as coupling constants involving the ^{119}Sn nucleus are concerned, $^nJ(^{119}Sn,X)$ ($n = 1, 2, 3, 4$; $X = {}^1H, {}^{13}C$) are largely used as structural indicators in organotin(IV) derivatives. For example, $^{1,2}J(^{119}Sn;^1H,^{13}C)$ couplings in methyl- and butyl-tin(IV) compounds could give useful insights concerning the local geometry at the tin centre; thus, equations which allow to estimate the C–Sn–C angle from the corresponding $^{1,2}J(^{119}Sn;^1H,^{13}C)$ values have been proposed [29–31]. However, due to their empirical nature, these relationships sometimes fail in describing peculiar structural configurations, e.g., the case of bischelate-*cis*-dimethyltin(IV) complexes [29]. In this respect, we have proposed a DFT protocol which overcomes these limitations [32].

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http://dx.doi.org/10.1016/j.jorganchem.2012.10.041

Vicinal coupling constants play an important role in the conformational study of organotin(IV) derivatives. Karplus-type equations, concerning $^3J(^{119}Sn,^{119}Sn)$, $^3J(^{119}Sn,^{29}Si)$, $^3J(^{119}SnCX^{13}C)$ (X = N, O), $^3J(^{119}SnCC^{13}C)$ (see Eq. (1)) and $^3J(^{119}SnCC^2H)$ (see Eq. (2)) (in the latter case, a simple conversion allows to apply it also to tin-proton couplings) have been proposed for organotin(IV) derivatives since the seventies and eighties of the last century. In some cases, the effect upon the ^3J values by atoms other than H and C present in the coupling path, namely N and O, was taken also into account in the parametrization of such relationships [33–39].

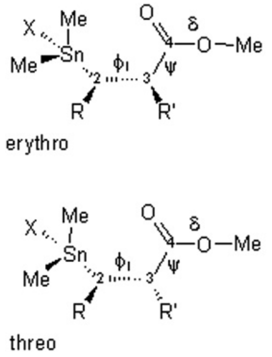
$$^3J(^{119}Sn,{}^{13}C) = 30.4 - 7.6\cos\theta + 25.2\cos2\theta \tag{1}$$

$$^3J(^{119}Sn,{}^{2}H) = 8.5 - 3.0\cos\theta + 9.0\cos2\theta \tag{2}$$

When several conformers are present in the system, the experimental ^3J value just represents a weighted average over the conformers population: therefore, the corresponding dihedral angle estimated by a Karplus-type equation does not necessarily correspond to any of the existing conformers. Computational approaches for the study of flexible compounds can be helpful to get more insights concerning conformer populations and structural features of the system investigated, thus overcoming the need of a dedicated Karplus-type equation. *Ab initio* and DFT molecular dynamics simulations can provide reliable information on molecular conformational population but usually they become computationally infeasible if long samplings and high accuracy are required. Alternatively, a suitable picture of the conformations that a molecule can adopt can be obtained by a systematic search, which is the approach used to study the title systems.

We have recently performed an extensive DFT study, both at the ZORA relativistic and non-relativistic level of theory, where we have proposed some suitable protocols for calculating $^3J(^{119}SnCXY)$ (X = C, N, O, S; Y = ^1H,^{13}C) [40,41]. The protocols showed a good performance for a wide set of alkyltin(IV) moieties bound to cyclic organic substituents after accounting for the conformational behaviour of the systems studied. Calculations also revealed a change of the sign of the ^3Js for some model systems, analogously to what observed for $^3J(^1H,^1H)$ in several compounds [42].

In this work we will test the reliability of such protocols for a set of more flexible, non-cyclic systems. We have chosen a set of trimethylstannyl- and chlorodimethylstannyl-propanoates of formula $XMe_2SnCHRCHR'COOMe$ (X = Me, Cl; R, R' = Me, Ph) (see Scheme 1) for which the corresponding experimental values were reported by Mitchell and co-workers [43]. These systems are characterized by the presence of open-chain substituents with high degrees of conformational freedom bound to tin atom. This allows to explore if the computational protocols, used to calculate the $^3J(^{119}Sn,^{13}C)$ and $^3J(^{119}Sn,^1H)$, are also able to reproduce the necessary correct conformers population to reproduce experimental data. Moreover, the set of $ClMe_2SnCHRCHR'COOMe$ molecules, where a methyl group bound to the tin atom has been substituted by a chlorine, also allows to test the performance of such protocols when intramolecular interactions with tin occur.



X	R	R'	ery	thr
Me	Me	Me	Ia	Ic
Me	Me	Ph	IIa	IIc
Me	Ph	Me	IIIa	IIIc
Me	Ph	Ph	IVa	IVc
Cl	Me	Me	Ib	Id
Cl	Me	Ph	IIb	IId
Cl	Ph	Me	IIIb	IIId
Cl	Ph	Ph	IVb	IVd

Scheme 1. The 16 compounds of the series $XMe_2SnCHRCHR'COOMe$ investigated. In the upper scheme the torsional angles that determine the conformations are labelled, ϕ, δ and ψ, while in the box the shorthand labels used throughout the text are reported (these labels are the same as those used in Ref. [43]). [$\phi_{i;\ i=1,2,3}$]; $\phi_1 = SnC_2C_3H_3$; $\phi_2 = SnC_2C_3(R')$; $\phi_3 = SnC_2C_3C_4$. The Erythro (Ery) and Threo (Thr) labels refer to the relative configurations of R and R′ according to Ref. [43].

2. Computational methods

The Gaussian 03 package [44] has been used for all the calculations in the non-relativistic protocol. Geometry optimizations (Optimization Protocol 1; OP1) have been performed by using the B3LYP functional. [45–47] Gaussian-type basis sets were chosen as follows: the correlation consistent polarized triple zeta valence, cc-pVTZ, basis set [48,49] was used for all atomic species except Sn, which was treated with a 28-core electrons relativistic effective core potential coupled with a cc-pVTZ quality valence basis set with contraction scheme (21s20p9d1f)/[5s4p3d1f] (cc-pVTZ-PP) [50,51]. Scalar relativistic effects have been taken into account to some extent, as regards the geometry optimization, by using relativistic effective core potentials on the tin centre. The character of minimum in the potential energy surface of a conformation has been checked by inspection of the harmonic vibrational frequencies; the energetics of the conformations are discussed in terms of zero-point corrected energy values. The vicinal coupling constants (J Protocol 1; JP1) were calculated on the optimized geometries with the non-relativistic protocol extensively tested by us [40,41], i.e. using the BLYP functional with the Pople-style 6-31G(d,p) basis set for light atoms and the all-electron double zeta valence plus polarization, DZVP, basis set [52–54] for tin. Finally, based on our previous experience, calculation of $^1J(^{119}Sn,^{13}C)$ and shielding constants (σ) for ^{119}Sn were performed according to Refs. [32,55–57] In particular: (i) $^1J(^{119}Sn,^{13}C)$ were calculated [32] by using the B3LYP functional with the 6-31G(d,p), for H, C, O and DZVP basis set for Sn while (ii) calculation of the shielding constants (σ) for ^{119}Sn was performed [55–57], in conjunction with the Gauge-Including Atomic Orbital (GIAO) formalism, by using the B3LYP hybrid functional combined with the 6-31G(d,p) (H,C,O) and IGLO-II(Sn) [58] basis set. Calculated isotropic ^{119}Sn chemical shifts (δ) were obtained as $\delta = \sigma_{ref} - \sigma$, where σ_{ref} is the isotropic ^{119}Sn shielding constant of Me_4Sn, used as reference, and σ is the isotropic ^{119}Sn shielding constant of the studied molecule.

The relativistic protocol is based on the Zeroth Order Regular Approximation (ZORA) formalism as implemented in the software package ADF [59]. Geometry optimizations (Optimization Protocol 2; OP2) were performed at the scalar relativistic ZORA level, starting from the non-relativistic optimized geometries by using the BLYP [48,60,61] functional and the all-electron Slater-type TZ2P basis set. Coupling constants (J Protocol 2; JP2) were calculated using the cpl module [62,63] still with BLYP and TZ2P basis set according to our previous experience [40,41,64].

All the optimized structures, both at ZORA relativistic and non-relativistic level, for the conformers reported in Tables 1 and 2 are given as Supplementary Information (See Table S12).

With both protocols, for the calculation of the NMR properties, JP1 and JP2, all contributions to the coupling constants have been evaluated, namely: the spin-dipole (SD), the diamagnetic (DSO) and paramagnetic (PSO) spin-orbit and the Fermi-contact (FC) terms, though at the relativistic level of theory cross terms occur. For all the calculated coupling constants the FC term resulted largely predominant.