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Influence of intramolecular Sn–chalcogen interactions on the conformational preferences for three diorganotin(IV) xanthates

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Abstract

The influence of intramolecular Sn–chalcogen interactions on the stability of different coordination possibilities available for three diorganotin(IV) xanthates [$Me_2Sn(MeOCS_2)_2$ (**1**), $Ph(Me)Sn(MeOCS_2)_2$ (**2**) and $Ph_2Sn(MeOCS_2)_2$ (**3**)] by means of theoretical methods is presented herein. A comparison of results obtained at the RHF level of theory employing STO3G, 3-21G** and augmented triple zeta quality basis sets developed for relativistic pseudopotentials is shown. RHF-STO3G all-electron calculations followed by fourth order Møeller–Plesset calculations were carried out in order to study the effect of electron correlation. It was observed that the use of correlation consistent basis sets yielded stability trends which reflect previous observations for similar xanthate molecular systems. The stabilization of the above conformers is assessed through an NBO analysis and the calculation of energy barriers by potential energy surface scans for the conformational changes. The approach described herein improves the theoretical results obtained in [M.I. Mohamed-Ibrahim, S.S. Chee, M.A. Buntine, M.J. Cox, E.R. Tiekink, Organometallics 19 (2000) 5410], where these three compounds were originally reported. It was concluded that secondary bonding in these compounds is best described by means of the computational paradigm herein described.

Keywords: Hartree–Fock; Diorganotin(IV) xanthates; Secondary bonding; NBO; Conformational analysis; Relativistic effects

1. Introduction

In recent years, the chemistry of organotin compounds has received a lot of attention due to their wide range of applications such as in catalysis [2], agrochemistry [3] and their potential antitumor activity [4]. From a theoretical point of view, tin containing compounds have also been studied in different areas ranging from their chemical properties as catalysts [5], their vibrational and electronic spectroscopy [6] to their solid state properties in different materials [7]. Their structural chemistry has also gained attention due to the wide range of possible geometries this sort of compounds can adopt, this area has also been complemented by a theoretical perspective [8].

It has been established that tin tends to increase its coordination number whenever possible. Thus intra- and intermolecular secondary interactions have frequently been found for organotin compounds in solid state [9]. The precise nature of these secondary interactions has not yet been fully understood within the current framework of chemical bonding models [10]. One possible way to approach the problem is through the study of the distribution of electron density in molecules which exhibit this kind of non-covalent weak bonding, referred to as secondary bonding [11].

It is known that theoretical calculations on molecules containing heavy atoms must take relativistic effects, which may no longer be neglected for this kind of elements, into consideration [12]. The effective core potential (ECP) approach has proven to be a successful method to address this problem [13]. The ECP replaces the inner electrons of the heavy atoms by a set of functions and operators that simulate their effect on valence electrons. These ECPs

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may include the appropriate corrections due to relativistic effects, since core electrons are the most affected by relativity [12]. This theoretical approach saves a computational effort that in turn may be employed to use large basis sets to achieve an improved description of the valence electrons and the bonds they form.

A theoretical description of secondary bonds and their effect in the total molecular properties in this kind of compounds is highly sensitive towards the methods and the employed basis sets, since they constitute a borderline between covalent bonding and van der Waals interactions. In this article, we report our results on the comparison among calculations on a small set of diorganotin(IV) compounds performed at different levels of theory, ranging from small basis sets like STO3G to large augmented correlation consistent ones.

Ab initio, all-electron calculations at restricted Hartree–Fock (RHF) with a $3\text{-}21G^{**}$ basis set for three bis(alkylxanthates)diorganotin(IV) compounds have been reported [1]. Compound bis(dimethylxanthate)dimethyltin(IV), $Me_2Sn(S_2COMe)_2$ (**1**) which according to the X-ray diffraction analysis exhibits different coordination patterns by each of the two ligands. One of them is bound through the dithiocarboxylate moiety, hereafter referred to as *S*;*S* coordination, whereas the second one uses the deprotonated thiol sulfur atom along with the oxygen atom, *S*;*O* coordination, as indicated in Scheme 1. The remaining two compounds in [1] are: bis(dimethylxanthate)methylphenyltin(IV), $Ph(Me)Sn(S_2COMe)_2$ (**2**) and bis(dimethylxanthate)diphenyltin(IV), $Ph_2Sn(S_2COMe)_2$ (**3**). The X-ray diffraction analysis of these last two compounds showed each ligand coordinated through the dithiocarboxylate moiety, *S*;*S*–*S*;*S* coordination pattern.

In [1] at the RHF/$3\text{-}21G^{**}$ level of theory, for compound (**1**) the *S*;*O*–*S*;*O* coordination was reported to be more stable than the experimentally observed *S*;*O*–*S*;*S* by 20.3 kJ/mol, and the latter was more stable than the *S*;*S*–*S*;*S* by 43.4 kJ/mol. For compounds (**2**) and (**3**) the computed energy difference between the *S*;*S*–*S*;*S* (experimentally observed coordination pattern) and the *S*;*O*–*S*;*O* conformations was 50.4 kJ/mol and 55.2 kJ/mol respectively. The computed order of relative energy for the conformers in all three compounds was

$$S;O\text{–}S;O < S;O\text{–}S;S < S;S\text{–}S;S$$

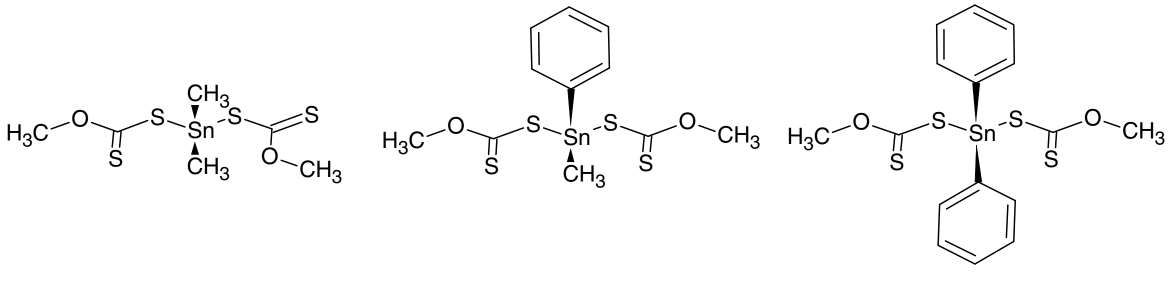
In this article we describe a series of calculations at the RHF level of theory employing STO3G basis sets; the quasi relativistic ECP approach using both their provided basis set and an augmented one. Also to account for electron correlation in the relative order of stability, Møeller–Plesset calculations at fourth order were included in our all-electron calculations.

2. Computational details

Geometry optimizations were performed using the Berny optimization algorithm [14] as implemented in GAUSSIAN98 suite of programs [15]. In all the geometry optimizations we carried out, we did not impose any constraint on any degree of freedom of the molecule under consideration. Potential energy surfaces were computed with full geometry optimization at every step, these are hereafter referred to as relaxed potential energy surface (RPES). For compound (**1**) the following basis sets and ECPs were employed: (a) STO3G [16] basis sets for every atom in the molecule; (b) with the relativistic large core R-ECP (46MWB) [17], where all of the 46 core electrons are replaced (hereafter referred to as SDD) for tin along with the ECP46MWB_AVTZ [18] basis set (hereafter referred to as TZ), for the rest of the molecule the corresponding Dunning correlation consistent double zeta basis set [19] (hereafter referred to as cc-pVDZ) was employed with no ECP. The correlation consistent basis sets we used include polarization functions by definition. Particularly for tin functions up to *D* and *F* are used. The combination of these basis sets with the SDD ECP has proven to yield good results in the theoretical description of diorganotin compounds [20].

3. Results

Table 1 shows a selection of data for the different geometry optimizations computed on compound (**1**) at the three possible coordination patterns. It is observed that the inclusion of a correlation consistent triple zeta quality basis set results in an excellent agreement between the experimental and the computed bond lengths.



(**1**) (**2**) (**3**)

Scheme 1. Experimentally observed coordination patterns for compounds (**1**), (**2**) and (**3**) as reported in [1].

Table 1
Selected bond lengths for $Me_2Sn(S_2COMe)_2$ calculated with various basis sets (Å)

	S;*O*–*S*;*O* coordination A = O(15); B = O(14)[a]			*S*;*S*–*S*;*S* coordination A = S(25); B = S(24)			*S*;*S*–*S*;*O* coordination A = S(25); B = O(14)			
	STO3G (RHF-MP2)	SDD[b] (RHF)	AE [13] ($3\text{-}21G^{**}$)	STO3G (RHF-MP2)	SDD (RHF)	AE [13] ($3\text{-}21G^{**}$)	STO3G (RHF-MP2)	SDD (RHF)	AE [13] ($3\text{-}21G^{**}$)	Experimental (*S*,*S*–*S*,*O*)
Sn–C	2.153	2.135	2.170	2.157	2.128	2.170	2.156	2.131	2.170	2.14
Sn–C	2.153	2.135	2.170	2.158	2.128	2.170	2.156	2.131	2.170	2.14
Sn–S	2.411	2.471	2.519	2.405	2.510	2.527	2.409	2.488	2.527	2.48
Sn–S	2.411	2.471	2.519	2.405	2.510	2.527	2.408	2.491	2.517	2.54
Sn–A	2.642	2.882	2.511	3.343	3.265	3.187	3.308	3.252	3.239	2.89
Sn–B	2.642	2.882	2.512	3.339	3.264	3.188	2.624	2.903	2.473	2.90

[a] See Scheme 1 for numbering relationship.

[b] Triple zeta for tin atom and double zeta quality basis set for all the other atoms.

Geometry optimizations were also carried out for compounds (**2**) and (**3**) at their three different possible conformations (*S*;*O*–*S*;*O*; *S*;*O*–*S*;*S*; *S*;*S*–*S*;*S*). In these cases we used the SDD ECP and the TZ basis set for tin and the cc-pVDZ basis sets else. Selected bond lengths from these calculations are shown in Table 2. Relative energies calculated with these ECP and basis sets for all possible conformers of the three compounds are summarized in Table 3. These relative energies are defined as $E_{\mathrm{rel}}n_i = En_i - En_{S;O\text{–}S;O}$, where i stands for the conformation of the compound of interest and n for the compound number ($n = \{1,2,3\}$). The following relative order of energy is found using a high quality basis set together with the selected R-ECP:

$$S;S\text{–}S;S < S;O\text{–}S;S < S;O\text{–}S;O$$

which is opposite to the one reported at RHF/$3\text{-}21G^{**}$ level in [1]. An argument on these discrepancies is elaborated below.

Table 2
Selected bond lengths for $Ph(Me)Sn(MeOCS_2)_2$ and $Ph_2Sn(MeOCS_2)_2$ calculated with TZ and cc-pVDZ basis sets and SDD ECP (Å)

	S;*O*–*S*,*O* A = O; B = O	*S*;*O*–*S*;*S* A = O; B = S	*S*;*S*–*S*;*S* A = S; B = S	Experimental
Compound (**2**)				
Sn–S	2.463	2.482	2.497	2.50
Sn–S	2.463	2.482	2.497	2.50
Sn–A	2.940	2.929	3.310	3.02
Sn–B	2.941	3.291	3.310	3.09
Sn–C (Ph)	2.128	2.130	2.125	2.11
Sn–C (Me)	2.130	2.129	2.126	2.12
Compound (**3**)				
Sn–S	2.461	2.477	2.487	2.50
Sn–S	2.461	2.474	2.487	2.50
Sn–A	2.970	2.963	3.388	3.13
Sn–B	2.970	3.356	3.388	3.04
Sn–C	2.129	2.130	2.125	2.13
Sn–C	2.129	2.126	2.125	2.14

Table 3
Relative energies for compounds (**1**), (**2**) and (**3**) [kJ/mol] calculated with the TZ basis set for tin with SDD ECP and cc-pVDZ basis set for the rest of the molecule at the RHF level of theory

	(**1**)	(**2**)	(**3**)
S;*O*–*S*;*O*	0	0	0
S;*O*–*S*;*S*	−11.66	−7.14	−2.82
S;*S*–*S*;*S*	−21.52	−10.16	−1.99

It was observed that at this level of theory the energy difference between conformers depends on the nature of the organic substituents on tin in the following order:

$$Ph_2 < Me, Ph < Me_2$$

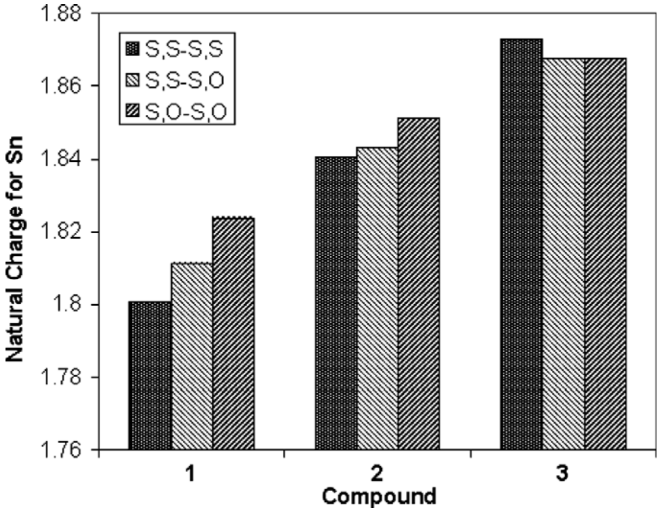
This is probably due to the larger resonance stabilization in the molecule obtained from each aromatic moiety, diminishing the contribution of the secondary bonding to the total stabilization of the molecule. Thus the adopted coordination pattern makes almost no difference in the energy of the compound. This order for the energy separation between different conformations of a given molecule is also opposite to the one obtained with the $3\text{-}21G^{**}$ basis set.

Mulliken charges on tin (calculated with TZ/SDD for tin, cc-pVDZ else) exhibit the following trends:

$$(\mathbf{1}) > (\mathbf{2}) > (\mathbf{3}) \text{ for a given conformation and;}$$
$$S;S\text{–}S;S < S;O\text{–}S;S < S;O\text{–}S;O \text{ for a given compound}$$

Thus, tin is not able to withdraw as much electron density from oxygen as from sulfur atoms, since the formers are more electronegative. Likewise the phenyl substituents are more electronegative than the methyl residues, increasing the Lewis acidity of tin within a given coordination pattern as it is reflected by the natural charges in Graph 1. However, it is observed that the $\Delta_{\mathrm{Sn\text{–}S}}$ has the following values at the *S*;*S*–*S*;*S* coordination pattern: 0.75 for (**1**); 0.81 for (**2**) and 0.90 Å for (**3**), where $\Delta_{\mathrm{Sn\text{–}S}}$ is defined as the difference between the secondary bond length minus the covalent Sn–S bond length. It would be expected that for the more acidic tin atom in (**3**) the $\Delta_{\mathrm{Sn\text{–}S}}$ were smaller. The secondary bonding becomes energetically less important for compound (**3**) than it is for compound (**1**).

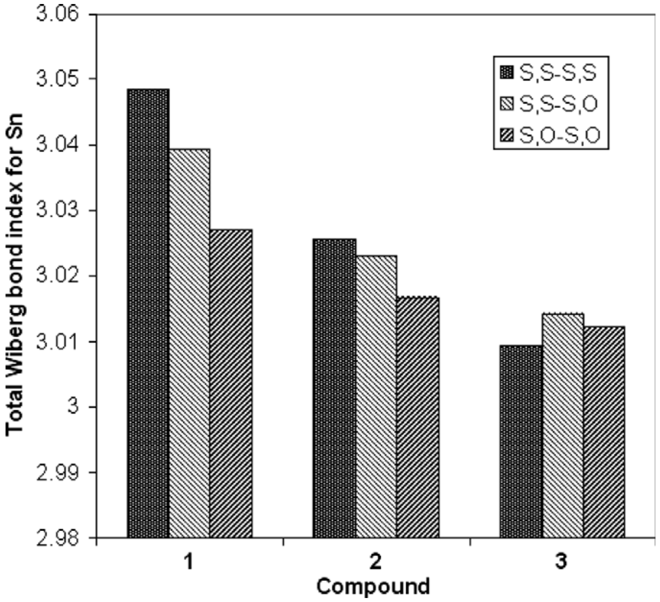
In order to study the effect of electron correlation, geometry optimizations were carried out at the Møller–Plesset fourth perturbative order for the STO3G basis set Results for these last calculations are reported in Table 4. It may be observed that at this level the same trends in rel-



Graph 1. Natural charges for tin calculated at the RHF/SDD TZ cc-pVDZ level of theory.

Table 4
Relative energies for compounds (**1**), (**2**) and (**3**) [kJ/mol] calculated at the MP4/STO3G level of theory

	(**1**)	(**2**)	(**3**)
S;*O*–*S*;*O*	0	0	0
S;*O*–*S*;*S*	13.10	12.33	9.48
S;*S*–*S*;*S*	23.94	23.11	19.35



Graph 2. Total Wiberg index for tin calculated at the RHF/SDD TZ cc-pVDZ level of theory.

Table 5
Wiberg bond indices for the coordination polyhedron at the TZ/RHF and 3-21G** level of theory

S,*A*–*S*,*B*	Sn–S	Sn–A	Sn–S	Sn–B	Sn–C	Sn–C
*Panel A: Wiberg bond index for compound (**1**)*						
S;*S*–*S*;*S*	0.6406	0.1114	0.6406	0.1114	0.7292	0.7292
S,*S*–*S*,*O*	0.67	0.113	0.6782	0.0396	0.7237	0.7237
S;*O*–*S*;*O*	0.7086	0.0403	0.7086	0.0403	0.7159	0.7159
					Sn–C (Ph)	
*Panel B: Wiberg bond index for compound (**2**)*						
S;*S*–*S*;*S*	0.6583	0.1002	0.6583	0.1003	0.6456	0.7377
S,*S*–*S*,*O*	0.6803	0.1045	0.6922	0.0368	0.646	0.7301
S;*O*–*S*;*O*	0.721	0.0355	0.721	0.0355	0.6398	0.7234
S,*A*–*S*,*B*	Sn–S	Sn–A	Sn–S	Sn–B	Sn–C	Sn–C
*Panel C: Wiberg bond index for compound (**3**)*						
S;*S*–*S*;*S*	0.6773	0.0838	0.6773	0.0838	0.6603	0.6603
S,*S*–*S*,*O*	0.6968	0.0914	0.7038	0.0341	0.6528	0.6595
S;*O*–*S*;*O*	0.7286	0.0337	0.7286	0.0337	0.6521	0.6521
*Panel D: Wiberg bond index for compound (**1**) calculated at the RHF/3-21G** level of theory*						
S;*S*–*S*;*S*	0.6076	0.1353	0.6077	0.1352	0.7179	0.7179
S,*S*–*S*,*O*	0.6081	0.1173	0.616	0.1214	0.7051	0.7051
S;*O*–*S*;*O*	0.6138	0.1128	0.6138	0.1128	0.6917	0.6917

ative molecular stability as the ones obtained at the RHF/3-21G** level, are obtained.

In order to obtain a localized description of the bonding around tin, a natural bond orbital (NBO) [21] analysis was performed on the optimized geometries at the RHF/SDD-TZ cc-pVDZ level of theory for all three compounds. In order to assess the contribution of the secondary interactions to the total bonding of tin the Wiberg bond index was computed [22]. This would allow us to know if the higher negative charge on O atoms is more likely to attract the Sn atom than the more polarizable and less negatively charged S atoms. Graph 2 shows that in each compound the total Wiberg index for tin decreases when a higher number of O atoms are present in the coordination sphere (i.e. *S*;*S*–*S*;*S* > *S*;*O*–*S*;*S* > *S*;*O*–*S*;*O*). It may also be observed from Graph 2 that in general the total Wiberg bond index for Sn shows the order (**1**) > (**2**) > (**3**).

Table 5(Panels A–D) exhibit the variation of Wiberg bond indices for all bonds in the coordination polyhedron with the change in conformation. Values in Table 5(Panels A–C) were calculated at the RHF/TZ-SDD for tin where as the all-electron cc-pVDZ was used for the rest of the atoms in the molecule. It may be observed that the Sn–S bond index increases its value around ten percent when changing from the *S*;*S*–*S*;*S* to the *S*;*O*–*S*;*O* coordination for all three compounds. The bond index for the interaction between the second donor atom and tin decreases around sixty percent when changing from sulfur to Oxygen. This implies that tin is not as able to withdraw electron density from the less polarizable oxygen atoms, establishing with them a coulombic interaction rather than a chemical interaction. To illustrate this point, in Fig. 1 the 4th and 19th MO bellow the HOMO for (**1**) in its *S*;*O*–*S*;*S* conformation are displayed. These plots were obtained with the program MOLEKEL [23]. In Fig. 1a it is possible to observe a mild overlap between the *pz* AO from the Sn and the O atom. Whereas in Fig. 1b it may be noticed an overlap between the *s* AOs of the Sn and S atoms. It is important to mention that these are the highest MOs with the Sn–O or Sn–S interactions.

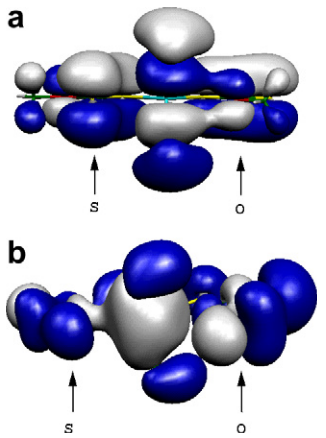
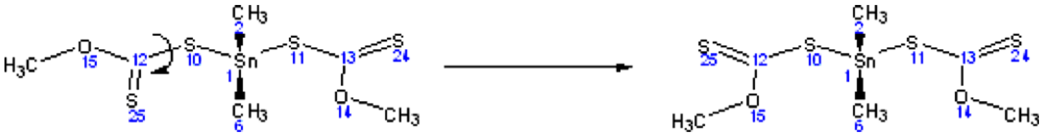


Fig. 1. Selected MOs plots for compound (**1**) in the *S*;*O*–*S*;*S* conformation. In (a) the 4th MO bellow the HOMO and in (b) the 19th MO bellow the HOMO. Computation at RHF/SDD TZ cc-pVDZ level.

The variations in the Sn–C bond index, in Table 5(Panels A–D), are almost negligible but still exhibit a decreasing tendency when oxygen atoms participate in the coordination sphere. For the sake of comparison a second NBO analysis was performed on compound (**1**) using the 3-21G** basis set at the RHF/3-21G** optimized geometry (Table 5(Panels D)). At this level it is possible to observe that practically no change occurs in the values of Sn–S bond indices. Also the decrease in the bond index for the interaction of tin with the donor atoms is around only sixteen percent. It is observed then, that this level of theory underestimates the importance of secondary bonding in the total electronic description of the molecule.

In order to gain further insight about the importance of the secondary interactions on the stabilization of the molecule, the energy barrier for the rotation of the ligands from the *S*;*O*–*S*;*S* coordination pattern to the *S*;*O*–*S*;*O* was calculated. For compound (**1**) this was accomplished by performing a relaxed scan of the dihedral angle DA {Sn1, S10, C12, O15} (hereafter referred to as DA1, see Scheme 2 for atom numbering relationship) every 45° starting from its experimental value to 180°. The same procedure was employed with the remaining two compounds. Fig. 2 shows various RPES for the change in conformation



Scheme 2. Atom numbering relationship for (**1**).

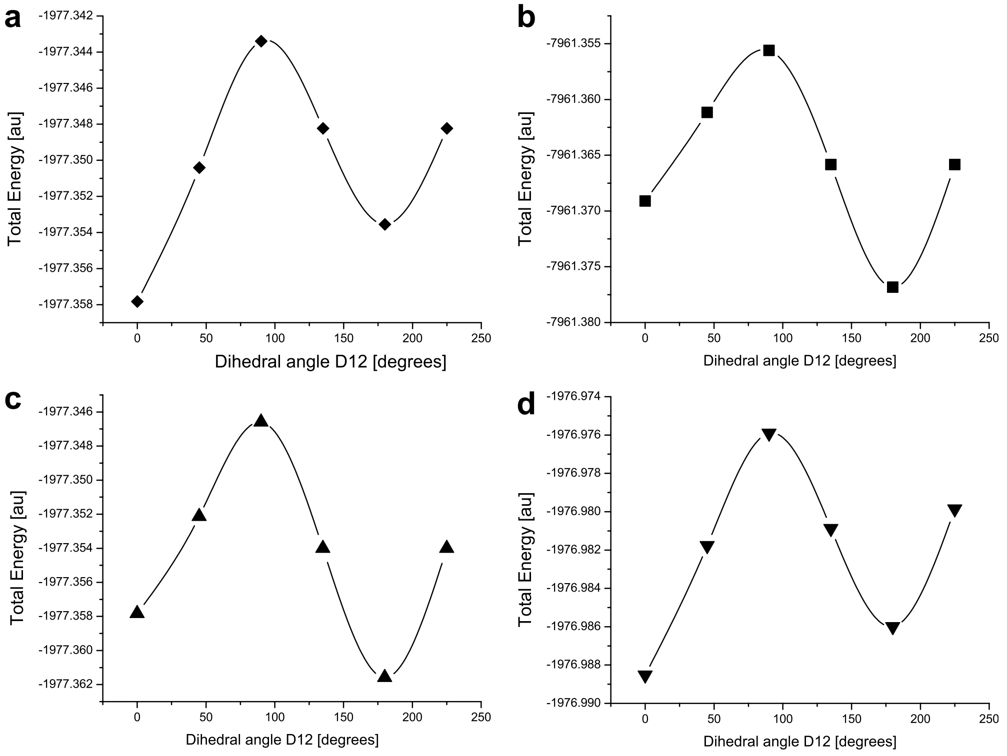


Fig. 2. RPES plots for compound (**1**) calculated at different levels of theory for the change from *S*;*O*–*S*;*S* to the *S*;*O*–*S*;*O* coordination pattern, except for (c). (a) RHF/SDD TZ cc-pVDZ, (b) RHF/3-21G**, (c) RHF/SDD-TZ cc-pVDZ (*S*;*O*–*S*;*S* to *S*;*S*–*S*;*S*), (d) RHF/SDD using SDD ECP with its minimal basis sets.

Table 6
RPES scans summary for the coordination inversion [kJ/mol] calculated with the TZ basis set for tin with SDD ECP and cc-pVDZ basis set for the rest of the molecule at the RHF level of theory

Compound	Basis set	Energy barrier (E_b)	$\Delta E = E_{\text{final conformation}} - E_{\text{Experimental}}$
(**1**) *S*;*O*–*S*;*S* to *S*;*O*–*S*;*O*	TZ/SDD & cc-pVDZ	37.91	11.24
	3-21G**	35.45	−20.23
(**2**) *S*;*S*–*S*;*S* to *S*;*O*–*S*;*S*	TZ/SDD & cc-pVDZ[a]	35.05	3.02
	TZ/SDD & cc-pVDZ[b]	30.98	3.02
(**3**) *S*;*S*–*S*;*S* to *S*;*O*–*S*;*S*	TZ/SDD & cc-pVDZ	25.40	−0.82

[a] Methoxyl group passes near the methyl substituent.
[b] Methoxyl group passes near the phenyl substituent.

from *S*;*O*–*S*;*S* to *S*;*O*–*S*;*O* performed with different basis sets for compound (**1**). Table 6 summarizes the energy values for the rotational barrier and the energy difference for all three compounds between conformers as defined by

$$E_b = E_{90^\circ} - E_{0^\circ},$$
$$\Delta E = E_{S;O\text{–}S;O} - E_{S;O\text{–}S;S},$$

respectively. All RPES scans were performed starting at the experimental coordination pattern.

The energy barrier calculated with the 3-21G** basis set is 35.4 kJ/mol which is slightly smaller than the calculated with the SDD ECP along with the TZ and cc-pVDZ basis sets, which is 37.9 kJ/mol. These values are consistent with a larger stabilization of the molecule by the secondary bonds which are best described by correlation consistent basis sets. In Table 6 it is possible to observe that the energy differences between both conformers is sensitive towards the ECP and basis set employed. It is observed that Δ*E* between the *S*;*O*–*S*;*S* and the *S*;*S*–*S*;*S* conformations for (**1**) increases with the quality of basis functions employed, which means that it takes more energy to break the secondary interactions that make the coordination polyhedron around tin. It also may be observed that with the exception of the RPES calculated with the all-electron 3-21G** basis set, which does not include any kind of relativistic effect, all calculations yield the same trend: The *S*;*S*–*S*;*S* coordination pattern is more stable than *S*;*O*–*S*;*S*.

Due to the prochirality of tin atom in (**2**), two scans for the conversion from the experimental coordination pattern *S*;*S*–*S*;*S* to *S*;*O*–*S*;*S* were performed. One where the methoxyl group passes near the methyl residue on tin, with an energy barrier of 35.05 kJ/mol, and a second one where the methoxyl group passes near the phenyl residue with a lower energy barrier of 30.98 kJ/mol, despite the larger steric hindrance of the phenyl group compared to the methyl substituent. In all our calculations the highest energy conformation is reached at half the turn of the ligand, i.e. DA1 = 90°.

The energy barrier for the conversion from *S*;*S*–*S*;*S* to the *S*;*O*–*S*;*S* conformer for compound (**3**) is 25.39 kJ/mol. Both phenyl groups rotate in opposite directions during the scan ease this interconversion.

It must be stressed that for compound (**3**) the energy differences between conformers are not sensitive towards the relative orientation of the two phenyl groups. A RPES scan at the experimental conformation was performed varying the orientation of the plane from one of the phenyl groups (TZ/SDD for tin; cc-pVDZ else) over a range of 45°. While scanning one of the phenyl residues the other one moved in the opposite direction as a consequence of the repulsion with the first aromatic group. The energy barrier for this process is 0.8 kJ/mol while the energy difference between the initial and the final structures is less than 0.1 kJ/mol. The relative orientation of the phenyl groups in the experimental conformation of (**3**) causes it to be chiral, therefore the change of the orientation of one of them and the respective response of the other one to face the opposite side yields the optical isomer of the original structure.

The energy barrier for the change from the *S*;*O*–*S*;*S* to the *S*;*S*–*S*;*S* conformation for compound (**1**) was also calculated (TZ-SDD for Sn, cc-pVDZ for the rest of the molecule at the RHF level of theory). This energy barrier has a value of 29.52 kJ/mol, which is smaller than the value of 37.91 kJ/mol calculated in the same manner for the conversion from *S*;*O*–*S*;*S* to the *S*;*O*–*S*;*O* conformer. Since the former barrier is smaller it would be expected that the *S*;*O*–*S*;*S* conformer changes into the *S*;*S*–*S*;*S* rather than to the *S*;*O*–*S*;*O* conformer. Furthermore the energy difference $\Delta E = E_{S;O\text{–}S;O} - E_{S;O\text{–}S;S} = 11.23$ kJ/mol is positive while $\Delta\ E = E_{S;S\text{–}S;S} - E_{S;O\text{–}S;S} = -9.87$ kJ/mol is negative, which indicates that the latter conversion yields a more stable geometry than the experimental conformation [1].

The value of the energy difference between two given conformations calculated in the RPES procedure is equal to the value that is obtained by subtracting the final energies calculated separately in the geometry optimizations described above.

A striking feature was observed throughout the scans that stress the importance of secondary interactions in the total molecular stabilization. While scanning DA1 the DA{S11, Sn1, S10, C12} (hereafter named DA2) changed in such a way that the local geometry around the tin atom was preserved leaving the four donor atoms lying on the same plane. Only when DA1 = 90° this local geometry was broken and the highest energy conformation was reached. Thus the system oppose to the change in geometry around the metallic centre. This local geometry conserva-

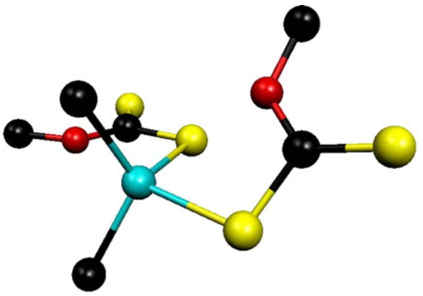


Fig. 3. Anomalous structure calculated with SDD ECP and its non-augmented basis set (hydrogen atoms were omitted for clarity).

tion is a result of the large stabilization effect provided by the secondary bonding which at all times increases the coordination number of tin as it is expected.

Nevertheless for the RPES where the non-augmented basis set for the SDD R-ECP was employed DA2 changed dramatically placing the donor atoms far from tin at the transition state conformation. The ligand was placed out of position and the original geometry around the tin atom was lost (see Fig. 3).

4. Conclusions

The inclusion of correlation consistent basis sets along with a R-ECP provides a complete description of bonding in heavy-atom-containing molecules such as the diorganotin(IV) compounds studied herein. Table 1 shows that bond lengths calculated with the TZ and cc-pVDZ basis sets are closer to the experimental values than the ones calculated with a 3-21G** basis set. We have shown that in this small group of tin(IV) xanthates the order of relative energy is *S*;*S*–*S*;*S* < *S*;*O*–*S*;*S* < *S*;*O*–*S*;*O*; opposite to the previously reported and in agreement with the known fact that the *S*;*S* coordination pattern is the most commonly observed for tin(IV) xanthates whenever the ligand acts in a bidentate manner [24]. The atomic charge on tin increases both with the number of oxygen atoms present in the coordination sphere reflecting the weaker interaction with these than with sulfur atoms.

The energy differences between the various conformers of each compound vary with the alkyl groups bonded to tin in the order: $Me_2 > Me$, $Ph > Ph_2$. For the largest of the three compounds, bis(dimethylxanthate)diphenyltin(IV) (**3**), the energy differences between conformers are almost negligible. The contribution to the total stabilization by the secondary interactions becomes lower in compound (**3**) due to the large resonance stabilization provided by the phenyl groups as it may be observed from the low energy differences between conformers for this compound.

The inclusion of post Hartree–Fock corrections to account for the correlation energy at the MP4/STO3G level, using the MP2/STO3G optimized geometries, is not enough to promote a change in the relative order of stability with respect to that calculated at the RHF/3-21G** level of theory. The inversion of the order of relative stability is only accomplished with the use of a large basis set and the consideration of relativistic effects, included in the SDD ECP, with which a better description of the bonds in the coordination polyhedron is accomplished.

A comparison between the Wiberg bond indices for (**1**) calculated both with TZ/cc-pVDZ and 3-21G** shows that the former level gives a better description of the secondary bonding in the molecule since significant differences may be observed for the bond index values for the Sn–S and Sn–O bonds, while in the latter there is practically no difference between having oxygen or sulfur secondarily bonded to tin.

The RPES scans show that for compound (**1**) the change from the *S*;*O*–*S*;*S* to the *S*;*S*–*S*;*S* coordination is more favorable than to the *S*;*O*–*S*;*O* pattern, since the energy barrier of the former process is smaller and the resultant conformer is more stable than for the latter. While scanning DA1, the molecule tends to twist in order to conserve the skewed trapezoidal bipyramid geometry around tin defined by the organic substituents and the plane of the four donor atoms. This local geometry conservation is a consequence of the large effect that the secondary interactions have on the total molecular stabilization energy.

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