THEORETICAL STUDY OF THE STRUCTURE OF METHYLTIN(IV) DERIVATIVES OF 2-MERCAPTOPYRIDINE COMPLEXES

Renato Barbieri[1], Giampaolo Barone[2], Dario Duca[2] and Gianfranco La Manna*[3]

[1] Dipartimento di Chimica Inorganica, Università, Viale delle Scienze, 90128 Palermo, Italy
<barbieri@unipa.it>
[2] Dipartimento di Scienze Farmaceutiche, Università, Via Ponte Don Melillo, 84084 Fisciano (SA), Italy
<dduca@unisa.it>
[3] Dipartimento di Chimica Fisica, Università, Viale delle Scienze, 90128 Palermo, Italy
<lamanna@unipa.it>

The geometrical structure of some complexes formed by methyltin(IV) and 2-mercaptopyridine moieties was determined by using an ab initio pseudopotential method. Different conformers were found in two cases, with low differences of energy values, suggesting possible interactions with biological receptors.

INTRODUCTION

Organotin(IV) derivatives of 2-mercaptopyridine (HSPy) show some interesting properties as stabilizing agents for polymers, and a number of them have been synthetized for possible applications[1]. At the same time, some interest on the structure of such compounds has been developed[2-10], also considering the biological implications of the high affinity of mercapto groups for tin atom.

The determination of the geometrical structures of organotin compounds is generally made by diffraction studies in the solid phase. Semiempirical and ab initio calculations allow to obtain reliable structures of substances containing heavy atoms, often giving rise to different conformers.

In this paper we report a theoretical study on the geometrical and electronic structure of $(CH_3)_aSn(IV)Cl_b(SP_y)_c$, where a,c=1,2, with the constraint a+b+c=4. Experimental data in the solid phase, when available, are compared with the theoretical findings.

The main goal of the present study is to explore the possibility of obtaining different conformers for the considered systems, with low energy differences allowing a conformational mobility which can play an important role for assuming a biological activity.

COMPUTATIONAL METHOD

The geometries of the four considered systems were optimized by the pseudopotential LANL2DZ method [11], that is largely used when heavy atoms are present. In all cases, different starting geometries were adopted and preliminary optimizations were carried out by the semiempirical PM3 method[12]. The existence of minimum energy structures was confirmed by examining the hessian matrix eigenvalues. All the calculations were performed with the Gaussian98W package[13] on a PC-Pentium 400 Mhz platform. Pictures were obtained by using the Chem3D Pro package[14].

RESULTS AND DISCUSSION

$(CH_3)_2Sn(SP_y)_2$ dimethylbis-2-(pyridinethiolato)tin(IV)

The geometrical optimization led to four minimum energy structures, that are depicted in Fig.1. The structure labelled as **a2** corresponds to the absolute minimum, whose energy is lower by 0.3, 2.4 and 6.1 $kcal\,mol^{-1}$ with respect to the conformers called **a4**, **a1** and **a3**, respectively. The obtained geometrical parameters are reported in Table I.

The four conformers here obtained can be characterised through their symmetry properties. While the structure **a1** shows two symmetry planes containing the tiopyridinic moieties and the C,Sn,C atoms, respectively, the conformer **a2** shows a twofold rotation around an axis crossing the tin atom. In the other two conformers, the two thiopyridinic moieties do not show any symmetry properties, as pointed out from the different values of Sn-N and Sn-S interatomic distances.

In all the four conformers, the value of the Sn-N distance is in the range 2.3-2.7 Å, with the exceptions of the shorter value of 2.17 Å in the case of conformer **a4** and of 3.20 Å in the **a3** conformer. In these cases we have to consider the tin atom as coordinated to only three of the four possible ligand sites, because only one nitrogen atom is actually bound to the central tin in the case of the conformer **a3** and only one sulphur atom in the **a4** structure.

Table I. Geometrical parameters of the optimised structure of $(CH_3)_2Sn(SP_y)_2$ (Bond lengths in Å, bond angles and torsional angles in degrees).

	a1	**a2**	**a3**	**a4**	exp. [3]
C-Sn	2.112	2.134	2.122, 2.112	2.109, 2.109	2.133,2.13
S-Sn	2.557	2.684	2.526, 2.527	3.032, 2.581	2.487
S-C	1.803	1.793	1.809, 1.803	1.767, 1.802	1.751
C_4-N	1.341	1.348	1.334, 1.341	1.365, 1.341	1.36
N-Sn	2.661	2.302	3.199, 2.563	2.167, 2.623	2.702
C-Sn-S	107.1	97.4	96.3, 117.6	84.9, 104.3	108.8, 110.3
Sn-S-C	88.6	79.4	101.4, 87.2	70.6, 87.6	---
S-C-N	114.6	113.0	117.6, 113.4	118.0, 114.4	114.4
S_3-Sn-N_{13}	61.2	63.2	54.8, 62.5	59.7, 61.3	60.5
C-Sn-C	130.1	108.4	119.1	137.7	125.1
S-Sn-S	91.8	145.9	100.2	150.8	86.9
N-Sn-N	145.8	78.2	121.8	152.4	152.1
C-Sn-S-C	71.5	-167.8	179.4, 70.9	110.6, -74.3	---
S-Sn-S-C	180.	-42.5	-67.3, -173.0	0., 180.	---
ΔE (kcal mol^{-1})	+2.4	0.	+3.6	+0.3	

The structure **a1**, having a C_{2v} symmetry, shows a very good agreement with the geometrical data in the solid phase[3] (mean square deviations 0.03 Å for bond lengths and 2.2° for bond angles). The Sn environment in this compound was described as a skew trapezoidal bipyramid or as a bicapped tetrahedron in Ref. 3, because of the presence of tetrahedral angles C-Sn-S. In the structure **a1**, as from the experimental data, the thiolato moieties lie in a plane. If the methyl groups are substituted by chlorine atoms, the experimental data report that the ligands lie at 90° to each other [15]. So, we made an attempt to verify if our method of calculation is able to reproduce this finding. The obtained result confirmed that the two thiolato species lie in perpendicular planes in the case of $Cl_2Sn(SP_y)_2$.

$(CH_3)SnCl(SP_y)_2$ methylbis-2-(pyridinethiolato)chlorotin(IV)

In this case five conformations corresponding to local minima were found (Fig.2), with the compounds labelled as **b2** and **b3** isoenergetic absolute minima, and the other conformers **b4**, **b5** and **b1** more energetic by 4.4, 4.6 and 11.0 $kcalmol^{-1}$, respectively. The main geometrical parameters are shown in the Table II.

Table II. Geometrical parameters of the optimised structure of $Sn(CH_3)SnCl(SP_y)_2$ (Bond lengths in Å, bond angles and torsional angles in degrees).

	b1	b2	b3	b4	b5
C-Sn	2.109	2.118	2.118	2.121	2.115
Cl-Sn	2.407	2.479	2.450	2.445	2.474
S-Sn	2.540	2.718, 2.610	2.615, 2.658	2.584, 2.667	2.722, 2.623
S-C	1.802	1.784, 1.790	1.798, 1.791	1.797, 1.781	1.786, 1.784
C_4-N	1.340	1.357, 1.350	1.350, 1.352	1.348, 1.353	1.357, 1.352
N-Sn	2.513	2.188, 2.205	2.267, 2.203	2.279, 2.215	2.174, 2.223
Cl-Sn-S	106.5	152.4, 102.6	96.5, 103.5	101.3, 92.3	156.7, 91.2
S_3-Sn-N_{13}	62.7	64.0, 65.2	64.7, 64.5	65.3, 64.1	64.2, 64.7
Cl-Sn-C	126.4	96.6	98.7	96.3	93.7
S-Sn-S	90.9	97.9	147.0	94.1	89.6
N-Sn-N	143.5	89.6	83.5	92.3	153.0
Cl-Sn-S-C	69.7, -69.7	-19.6, -80.4	-170.8, 79.6	-174.5, -97.3	-1.0, 102.7
S-Sn-S-C	177.2, -177.2	-157.5, 81.0	-43.5, -46.1	-81.3, 161.2	-93.2, -100.6
C-Sn-S-C	70.6, -70.6	98.7, 179.8	88.6, 180.8	86.3, 16.9	104.9, -3.0
ΔE (kcal mol^{-1})	11.0	0.0	0.0	4.4	4.6

Sn Mössbauer and IR data [7] in solid phase give indication of a distorted octahedral environment of the tin atom with the chlorine and the alkyl groups in pseudo-axial positions. Among the local minima here obtained, the geometry above is found only in the structure **b1** (bond angle Cl-Sn-C = 126.4°). The two thiopyridinic moieties lie approximately in a plane (deviation of 2.8° from the planarity) with an overall structure approximately belonging to the C_{2v} group. In the other conformers the tin environment is more distorted and it is unlikely to assign axial positions to both methyl groups and chlorine atoms.

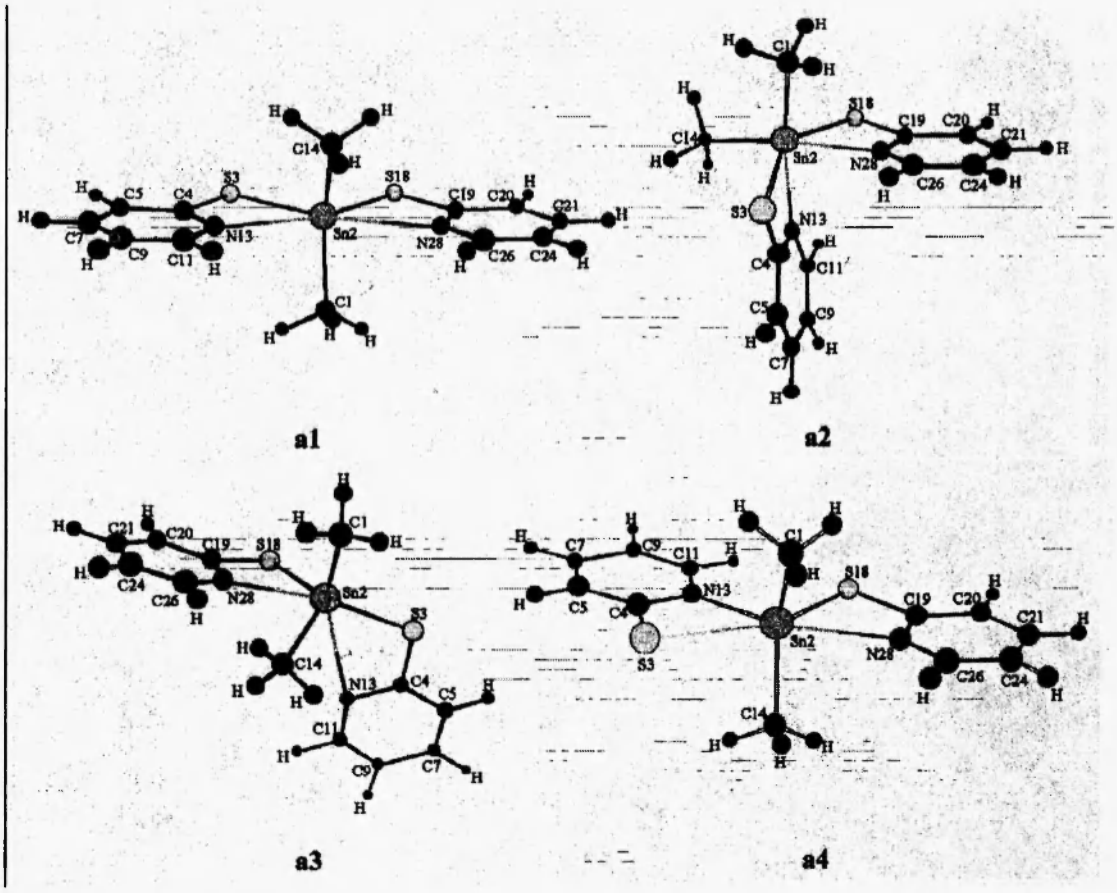

Figure 1: Optimized geometries and atom numbering of the isomers of $(CH_3)_2Sn(Sp_y)_2$

$(CH_3)_2SnCl(SP_y)$ dimethyl-2-(pyridinethiolato)chlorotin(IV)

Two local minima were found in this case, that are shown in Fig.3. The isomer labelled as **c2** has an energy value lower by 3.6 kcal mol^{-1}. The main geometrical differences between the two conformers are observed for the S-Sn-Cl and N-Sn-Cl bond angles, and for the torsional angles (see Table III). In particular, the values of S-Sn-Cl and N-Sn-Cl angles are approximately exchanged when passing from one conformer to another and the Cl-Sn and C-S bonds are in trans or in cis positions depending on the considered isomer. A comparison is possible with the X-ray data on the crystals of the similar compound, where the methyl groups are substituted by phenyl groups [5,6]. A similarity of the experimental geometrical parameters with those of the isomer **c1** is apparent, with the largest difference in the case of the dihedral angle Cl-Sn-N-C. The distorted trigonal-bipyramidal environment about the tin atom, determined by X-ray diffraction, is confirmed from the calculations, that give an apical N-Sn-Cl angle 158.4°, to be compared with the experimental value 156.1°.

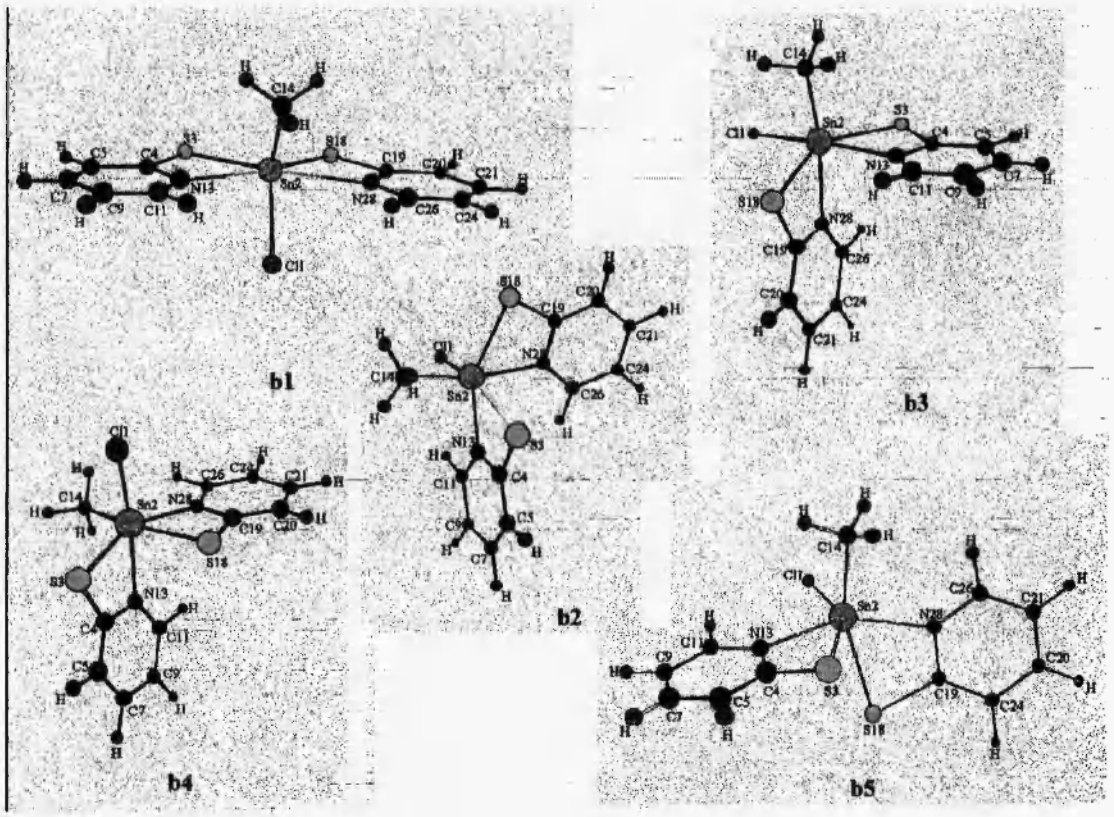

Figure 2: Optimized geometries and atom numbering of the isomers of $(CH_3)_2SnCl(Sp_y)$

Table III. Geometrical parameters of the optimised structure of $(CH_3)_2SnCl(SP_y)$ and $(CH_3)SnCl_2(SP_y)$. Experimental values, referring to the **c** isomers, are taken from Ref. 5; values in parenthesis from Ref. 6. (Bond lengths in Å, bond angles and torsional angles in degrees).

	c1	**c2**	exp.	**d1**	**d2**
C-Sn	2.111	2.108	---	2.104	2.116
S-Sn	2.528	2.823	2.431(2.447)	2.517	2.579
S-C	1.802	1.775	1.741	1.804	1.797
C_4-N	1.345	1.349	---	1.345	1.349
N-Sn	2.436	2.136	2.413	2.308	2.218
Cl-Sn	2.459	2.488	2.451(2.458)	2.391,2.421	2.410
C-Sn-S	115.7	94.2	---	120.6	100.2
Sn-S-C	84.5	73.6	85.6(84.6)	82.2	79.7
S-C-N	112.6	114.8	113.4	111.1	110.8
S-Sn-N	63.9	62.9	64.8	65.3	65.2
C-Sn-C	123.1	128.1	---		
S-Sn-Cl	94.5	153.1	91.6(90.7)	120.6,94.6	120.0
N-Sn-Cl	158.4	90.2	156.1	86.4,158.6	87.3
C-Sn-S-C	77.3,-77.3	115.6,-115.6	---	-80.5	180.
Cl-Sn-S-C	180.	0.	---	70.4,173.1	71.0,-71.0
N-Sn-S-C	0.	0.	3.6(0.8)	1.9	0.
Cl-Sn-N-C	-23.2	180.	5.3(-3.5)	-23.4,-127.6	124.9,-124.9
ΔE (kcal mol^{-1})	3.6	0.0		0.0	0.9

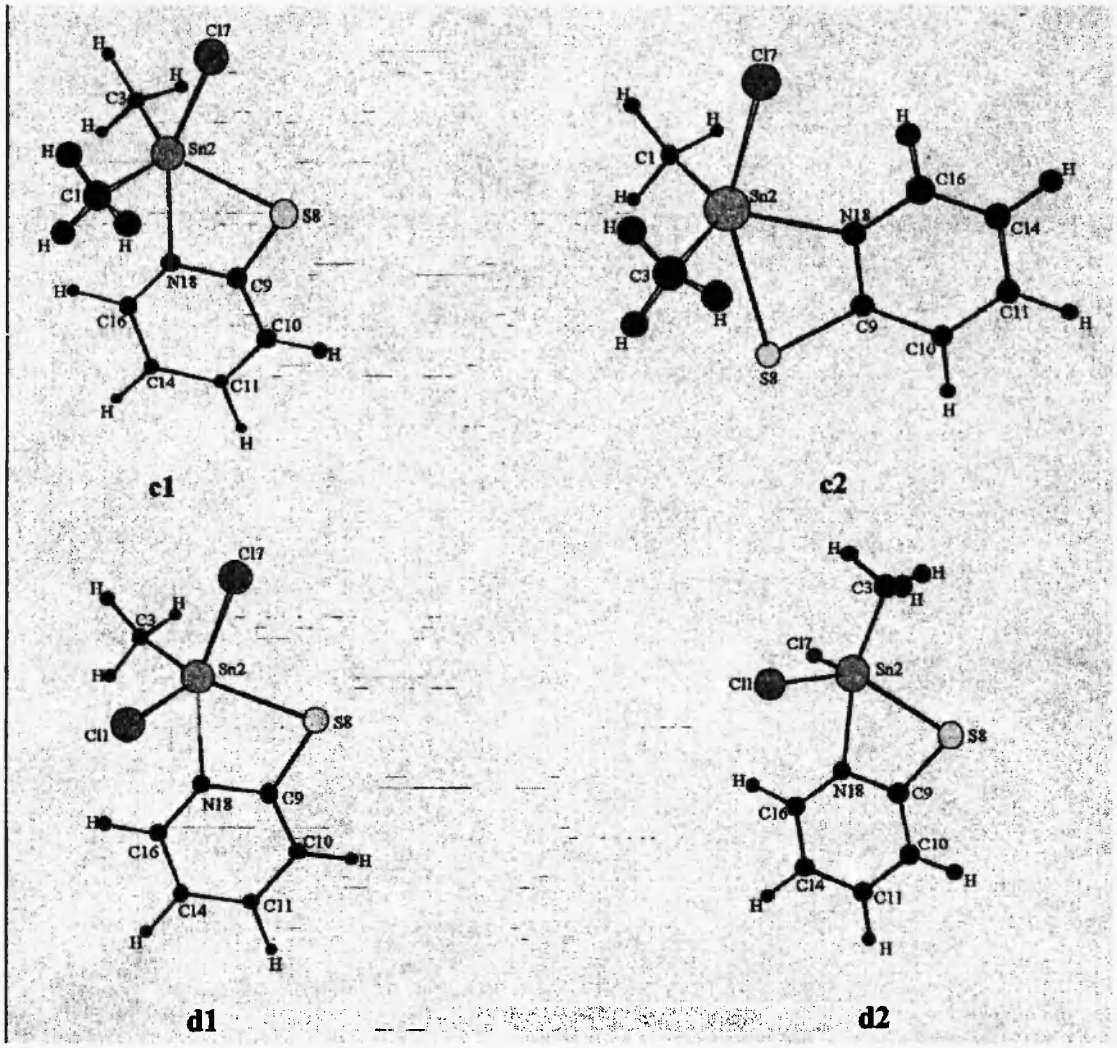

Figure 3: Optimized geometries and atom numbering of the isomers of of $(CH_3)_2Sn(Sp_y)_2$ (top) and $(CH_3)_2Sn(Sp_y)_2$ (bottom)

$(CH_3)SnCl_2(SP_y)$ methyl-2-(pyridinethiolato)dichlorotin(IV)

As in the previous case, two minimum energy conformers were found, differing in energy by 0.9 kcal mol^{-1}. Mössbauer data on the solid indicate a trigonal bipyramidal environment around the tin [7].
The structural data here obtained , shown in the Table IV and in Fig.3, are compatible with the geometry of the isomer **d2**, with the methyl carbon and the nitrogen atom are in apical position (C-Sn-N = 165.4°).

A general consideration on the results obtained on the four considered systems allows to deduce that a noticeable conformational flexibility was found for the compounds here labelled as **a** and **b**. In particular, in these cases, a certain number of conformers lie within a few kilocalories of the global minimum. These results indicate that more that one accessible conformation may be available for interaction with a receptor site suggesting a possible biological activity.

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