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Evaluation of PM3 calculations applied to organotin compounds: crystal structure of [Ph_2SnCl_2 (1,10-phenanthroline-5,6-dione)]·$2Me_2CO$[†]

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PM3 calculated geometries of a set of mainly organotin compounds covering different coordination numbers at tin were compared with published experimental results, obtained either by electron or X-ray diffraction. In addition, data for the previously unreported acetone solvated Ph_2SnCl_2·1,10-phenanthroline-5,6-dione complex, [Ph_2SnCl_2(pdon)]·$2Me_2CO$, are included. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: organotin compounds; PM3 calculations; crystal structure; 1,10-phenanthroline-5,6-dione

INTRODUCTION

The development of ever-improving computing systems enables more and more elaborate calculations to be undertaken by increasingly more elaborate programs. The more complex the computational package used, the longer the time and/or the more powerful the computing system required to arrive at a conclusion. A question to answer is what level of theory, and hence what time and computing system, is necessary to arrive at a suitable conclusion.

Various computational methods have been employed on calculations on tin compounds. In some cases, comparisons of experimental and calculated data have been made. For example, Tiekink and coworkers carried out a combined crystallographic and theoretical studies of the structures of some organotin compounds and complexes. Their calculations[1–3] were performed at the HF/LanL2DZ level of theory, on a Silicon Graphics Workstation, and gave results in good agreement with experimental geometric parameters for complexes such as [$(CH_2{=}CH)_2SnCl_2$]·0.5PhH and [Me_2SnCl_2(phen)].

However, very convenient semi-empirical calculation packages are available, including Dewar and coworkers' MNDO[4,5] and AM1[6] methods and the PM3 method,[7,8] which can be used on most currently used personal computers, with relatively short computing times. As all of these include parameters for tin, they can be useful tools for tin chemists, even if the calculated results may not be so close to experimental ones. As shown by the various publications, PM3 calculations have been considered for use for various tin-containing systems, including free radicals,[9] radical cations,[10] coordination compounds containing aminocarboxylates,[11] pyridines,[12] mercaptides,[13] DNA–tin interactions,[14] or clusters of tin with fullerenes[15] or cyclic acenes.[16] However, in the main, each of these publications has dealt with a single compound or a small group of closely related compounds.

In order to evaluate the PM3 method further, a range of mainly organotin compounds (see Fig. 1) covering different coordination numbers at tin have been investigated. Comparisons of the calculated geometries and published experimental results, obtained either by electron or X-ray diffraction, have been made. In addition, data for the previously unreported acetone-solvated Ph_2SnCl_2(1,10-phenanthroline-5,6-dione) complex, [**21**]·$2Me_2CO$, are included. Our aim in this study was to see how close the PM3 method came to reproducing diffraction results and to establish whether consistent correction factors could be applied.

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[†] Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

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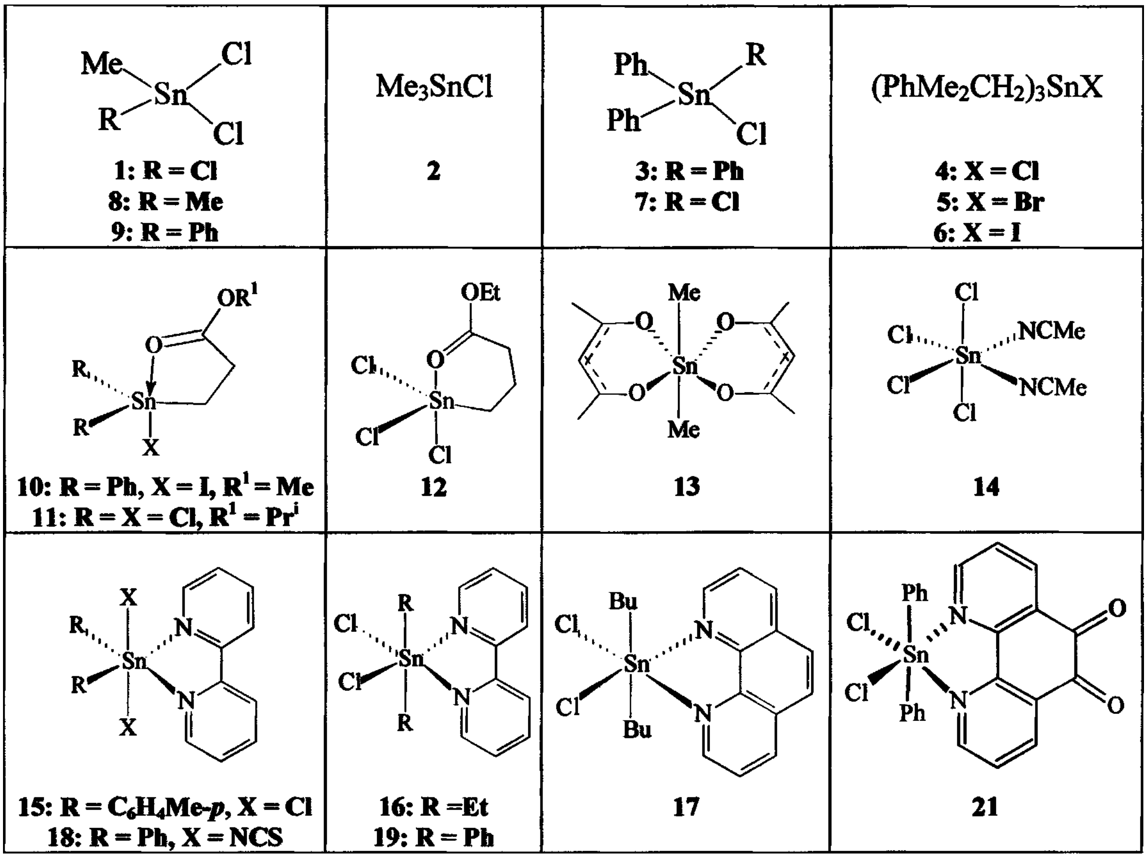

Figure 1. Structures of compounds used in the evaluation.

RESULTS AND DISCUSSION

A set of 19 compounds was selected to include four-, five- and six-coordinate tin compounds, see Figure 1. These compounds included two compounds, Me$_3$SnCl and MeSnCl$_3$, used in Tiekink and coworkers' study; furthermore, both studies included compounds of the type R$_2$SnX$_2$(L–L). Whereas in our calculations different guessed starting geometries were experimented with to avoid local minima and simulate an actual application, those of Tiekink and coworkers started optimization from the diffraction results.

The compounds selected for our study fall into three classes: class **I** contains non-associated four-coordinated tetrahedral compounds; class **II** contains weakly associated organotin halides, i.e. compounds having intermolecular tin–halide interactions much weaker than the intramolecular tin–halide bonds; and class **III** contains clear-cut five and six-coordinated species, all of which exist as molecular species, with no significant intermolecular interactions involving tin. Comparisons of calculated and experimental values for selected bond lengths and angles are provided in Tables 1–3.

As shown in Table 1, calculated geometrical data for the simple four-coordinate, tetrahedral species, **I**, agreed well with the experimental data, whether obtained by electron diffraction or by X-ray diffraction. The greatest differences were shown by the most hindered compound of this group, namely (PhMe$_2$CCH$_2$)$_3$SnI. For this compound, the C–Sn–I bond angles were found experimentally to be larger than the calculated ones, with the reverse findings for the C–Sn–C angles. The results at the PM3 and HF/LanL2DZ levels[1–3] are in close accord.

The calculated structure for compound Me$_3$SnCl (**2**) was compared with available electron and X-ray diffraction data. This compound is monomeric in the gas phase (and thus gaseous **2** is placed in the class **I** compounds) but forms extended chains with weakly chlorine-bridged associated molecules in the solid state[35] (and thus solid **2** is considered a type **II** compound). The results of the PM3 calculations for class **II** compounds are listed in Table 2. Calculations were based on individual molecules and, thus, ignored the weak intermolecular Sn–Cl interactions. However, as can be seen in Table 2, with the exception of data for MePhSnCl$_2$, the calculated bond lengths for the intramolecular Sn–C and Sn–Cl bonds are reasonably close to the experimental values. More significant discrepancies are realized with the bond angle data, as is to be expected from the neglect of the intermolecular interactions. The intermolecular Sn–halide interactions in these class **II** compounds are generally much weaker than the intramolecular ones, but always within the sum of the van der Waals radii for tin and the halogen.

Table 1. Comparison of selected calculated and experimental geometric parameters (Å, °) for tetracoordinate tin compounds

Compound	Geometric parameter	PM3 calculated values[a]	Experimental	Ref.[b] [XRD] or [ED]
1: $MeSnCl_3$[c]	Sn–C	2.11	2.10(2)	[17] [ED]
	Sn–Cl	2.36	2.304(3)	
	C–Sn–Cl	115.5	113.9(7)	
	Cl–Sn–Cl	107.4	104.7(4)	
2: Me_3SnCl[d]	Sn–C	2.12	2.106(6)	[18] [ED]
	Sn–Cl	2.38	2.351(7)	
(gas phase)	C–Sn–C	112.8	114.9(2)	
	C–Sn–Cl	105.8	103.2(6)	
3: Ph_3SnCl	Sn–C	2.07	2.112(4)	[19] [XRD]
	Sn–Cl	2.37	2.374(2)	
	C–Sn–C	114.8	114.4(1)	
	C–Sn–Cl	104.5	103.9(1)	
4: $(PhCMe_2CH_2)_3SnCl$	Sn–C	2.19	2.149(5)	[20] [XRD]
	Sn–Cl	2.39	2.382(3)	
	C–Sn–C	117.4	117.2(1)	
	C–Sn–Cl	99.4	99.67(15)	
5: $(PhCMe_2CH_2)_3SnBr$	Sn–C	2.18	2.163(13)[e]	[21] [XRD]
	Sn–Br	2.46	2.544(2)[e]	
	C–Sn–C	115.8	116.1(9)[e]	
	C–Sn–Br	102.0	101.6(1)[e]	
6: $(PhCMe_2CH_2)_3SnI$	Sn–C	2.19	2.16(1)[e]	[21] [XRD]
	Sn–I	2.68	2.74(1)[e]	
	C–Sn–C	117.3	115.5(5)[e]	
	C–Sn–I	99.1	102.5(2)[e]	

[a] This work.

[b] Reference to experimental data: XRD = X-ray diffraction, ED = electron diffraction.

[c] Calculated data at HF.Lan L2DZ level from Ref. 1: Sn–C 2.098 Å; Sn–Cl 2.358 Å; C–Sn–Cl 111.8°; Cl–Sn–Cl 107.1°.

[d] Calculated data at HF.Lan L2DZ level from Ref 1: Sn–C 2.121 Å; Sn–Cl 2.424 Å; C–Sn–Cl 104.6°; C–Sn–C 113.9°.

[e] Mean value.

Their impact on the bond angles at tin in this group of compounds clearly indicates their significance and that they cannot be ignored. Figures 2 and 3 show plots of calculated and experimental data for bond lengths and angles respectively.

The nature, aggregated or molecular, of a solid-state structure of a class **II** compound has been a matter of conjecture for many years. This is well illustrated by tris(cyclohexyl)tin chloride (**20**). Initial X-ray structural results by Tagliavini and coworkers[36] for **20** were taken to be indicative of a molecular structure with four coordinate tin, i.e. the intermolecular Sn–Cl interactions could be ignored, in contrast to conclusions from Mössbauer spectroscopy of a polymeric structure with five-coordinate tin. Further X-ray and Mössbauer spectral data from the same authors[36] led to the conclusion in favour of the molecular structural model. However, Blunden and Hill[37] argued from their Mössbauer data and solution ^{119}Sn chemical shift values that this compound was indeed a weakly associated species in the solid state but a molecular species in solution. A conflicting conclusion regarding the solid-state structure was reached a few years later by Harris *et al.*,[38] who reported that ^{119}Sn chemical shifts in the solid state (CP-MAS) and in solution were sufficiently similar to indicate a molecular

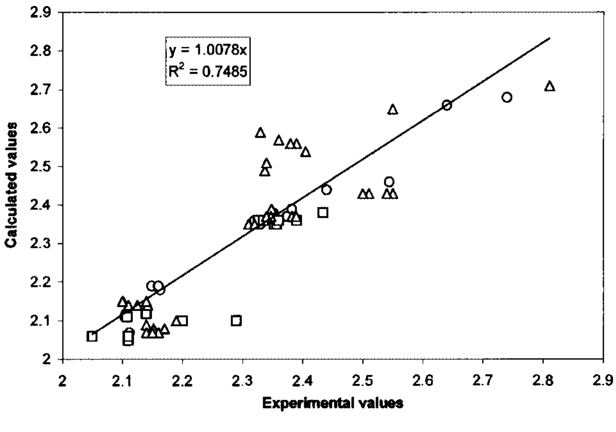

Figure 2. Plot of calculated bond lengths versus experimental values ○: class **I**; □: class **II**; △: class **III**. Major outliers are: for class **II**, $MePhSnCl_2$ parameters (**9**); for class **III**, Sn–X parameters, X being a non-anionic ligand.

Table 2. Comparison of selected calculated and experimental geometric parameters (Å, °) for organotin halides, possessing weak intermolecular tin–halide interactions

Compound	Geometric parameter	PM3 calculated values[a]	X-ray experimental data	Ref.[b]
2: Me_3SnCl[c]	Sn–C	2.12	2.119(10)[d]	22
	Sn–Cl	2.38	2.430(2)	
(solid)	C–Sn–C	112.8	117.1(19)[d]	
	C–Sn–Cl	105.8	99.9(7)[d]	
	Sn···Cl [required]		3.27	
8: Me_2SnCl_2	Sn–C	2.11	2.108	23
	Sn–Cl	2.36	2.327	
	Cl–Sn–Cl	105.9	93.5	
	Sn···Cl[e]		3.54	
9: $MePhSnCl_2$	Sn–C(alkyl)	2.10	2.29(4)/2.20(3)[f]	24
	Sn–C(aryl)	2.06	2.11(6)/2.05(3)[f]	
	Sn–Cl	2.36	2.36(1)[d]	
	Cl–Sn–Cl	105.6	98.6(3)	
	C–Sn–C	117.0	133	
	Sn···Cl[e]		3.442(9)	
7: Ph_2SnCl_2	Sn–C	2.05	2.11	25
	Sn–Cl	2.35	2.355[d]	
	Cl–Sn–C	106.4	101.7	
	C–Sn–C	117.9	127	
	Sn···Cl[e] [required]		3.77	

[a] This work.
[b] Reference to experimental data.
[c] Calculated data at HF.Lan L2DZ level from Ref 1: Sn–C 2.121 Å; Sn–Cl 2.424 Å; C–Sn–Cl 104.6°; C–Sn–C 113.9°.
[d] Mean value.
[e] Intermolecular bond.
[f] Two independent molecules.

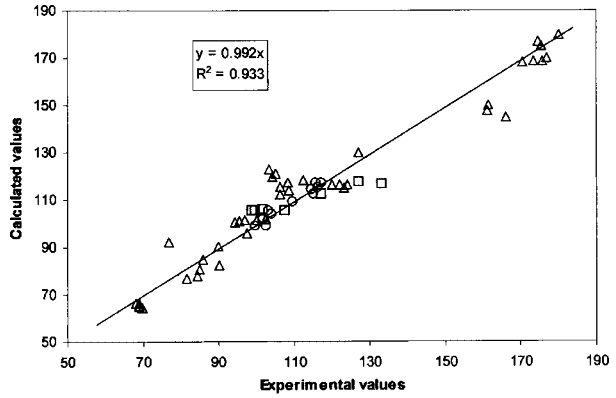

Figure 3. Plot of calculated bond angles versus experimental values ○: class **I**; □: class **II**; △: class **III**.

solid state as well. More recently, Asadi *et al.*[39] investigated the X-ray crystal structure of **20** over the temperature range 120–298 K and clearly revealed the importance of the intermolecular contacts. Of interest is that, as the temperature is reduced, the 'intramolecular' Sn–Cl bond lengths increased and the 'intermolecular' Sn–Cl [Sn–Cl′] distances decreased. The reverse temperature effects on the 'intramolecular' Sn–Cl and 'intermolecular' Sn–Cl′ bond lengths provide clear evidence of the importance of the latter. Of interest is that the bond angle Cl–Sn–Cl′ remains essentially linear.

It is our view that these class **II** compounds should be considered as genuine hypervalent tin compounds, as the results and discussion herein will support.

Results for $MePhSnCl_2$ in Table 2 suggest that its X-ray structure ought to be redetermined: the original structure determination had a poor refinement, $R = 0.085$, with high su values. Particularly noticeable are the long Sn–C(methyl) bond lengths of 2.20 and 2.29 Å (in two independent molecules), which are well above the average Sn–C(methyl) values commonly found for methyltin species.[24]

Data for the penta- and hexa-coordinate tin species (class **III**) are gathered in Table 3. Of the compounds listed in Table 3, hexacoordinate $Me_2Sn(acac)_2$ stands alone, in that, leaving aside the halides and organic groups, the coordinating ligand, acac, is anionic, whereas all the other complexes have either neutral external ligands, such as MeCN, bipyridyl and phen, or contain organic groups with internal donor centres. Calculated data, especially bond angle data, for $Me_2Sn(acac)_2$, are in excellent agreement with the X-ray diffraction data. Of interest is that the calculations for $[SnCl_4{\cdot}2MeCN]$ also

Table 3. Comparison of selected calculated and experimental geometric parameters, (Å, °) for five- and six-coordinate organotin species

Compound: geometry	Geometric parameter	PM3 calculated values[a]	X-ray experimental data	Ref.[b]
(a) five-coordinate tin species				
10: $IPh_2SnCH_2CH_2CO_2Me$	Sn–I	2.71	2.811(2)	26
	Sn–O	2.65	2.55(2)	
[trig. bipy]	Sn–C(aryl)[c]	2.07	2.15(2)	
	Sn–C(alkyl)	2.15	2.10(2)	
	I–Sn–O	168.0	170.5(3)	
	I–Sn–C(alkyl)	96.0	97.6(6)	
	I–Sn–C(aryl)[c]	101.6	98.6(5)	
	C–Sn–C(aryls)	118.4	112.1(7)	
	C(aryl)–Sn–C(alkyl)[c]	116.5	120.8(7)	
12: $Cl_3Sn(CH_2)_3CO_2Et$	Sn–C	2.14	2.125(12)	27
	Sn–Cl_{eq}[c]	2.35	2.31(1)	
[trig. bipy]	Sn–Cl_{ax}	2.37	2.382(4)	
	Sn–O	2.54	2.405(8)	
	Cl_{eq}–Sn–Cl_{eq}	117.4	108.2(1)	
	Cl_{eq}–Sn–Cl_{ax}[c]	101.3	95.4(1)	
	Cl_{eq}–Sn–C[c]	115.3	123.3	
	Cl_{eq}–Sn–O	77.2	81.5	
	Cl_{ax}–Sn–O	176.9	174.4(2)	
11: $Cl_3Sn(CH_2)_2CO_2^iPr$	Sn–C	2.14	2.142(9)	28
	Sn–Cl_{eq}[c]	2.35	2.320(2)	
[trig. bipy]	Sn–Cl_{ax}	2.37	2.389(3)	
	Sn–O	2.49	2.337(5)	
	Cl_{eq}–Sn–Cl_{eq}	115.8	106.4	
	Cl_{eq}–Sn–Cl_{ax}[c]	101.7	97.0	
	Cl_{eq}–Sn–C[c]	116.4	124.2	
	Cl_{eq}–Sn–O	80.7	85.0	
	Cl_{ax}–Sn–O	175.2	175.3	
(b) six-coordinate tin species				
13: $[Me_2Sn(acac)_2]$	Sn–C	2.09	2.14(2)	29
	Sn–O[c]	2.10	2.19(1)	
octahedral	C–Sn–O	90.3	90(1)	
[trans Me groups]	O–Sn–O	85.0	86(1)	
	C–Sn–C	180.0	180.0	
14: $[SnCl_4(MeCN)_2]$	Sn–Cl_{eq}[c]	2.39	2.348(7)	30
	Sn–Cl_{ax}[c]	2.37	2.347(8)	
octahedral	Sn–N[c]	2.37	2.34(3)	
[cis MeCN ligands]	Cl_{eq}–Sn–Cl_{eq}	102.1	102.6(2)	
	Cl_{ax}–Sn–Cl_{ax}	145.1	166.1(3)	
	Cl_{ax}–Sn–Cl_{eq}[c]	100.8	94.2(3)	
	N–Sn–Cl_{ax}[c]	78.0	84.5(6)	
	N–Sn–Cl_{eq}	82.7	90.3(6)	
19: $[Ph_2SnCl_2(bipy)]$	Sn–C[c]	2.08	2.152	31
	Sn–Cl[c]	2.43	2.51	
octahedral	Sn–N[c]	2.57	2.36	
[trans Ph groups]	C–Sn–C	168.4	173.5(3)	
	Cl–Sn–Cl	122.9	103.5(1)	
	N–Sn–N	65.0	69.0(2)	
18: $[Ph_2Sn(NCS)_2(bipy)]$	Sn–C[c]	2.08	2.17	32
	Sn–NCS[c]	2.03		

(*continued overleaf*)

Table 3. (*Continued*).

Compound: geometry	Geometric parameter	PM3 calculated values[a]	X-ray experimental data	Ref.[b]
octahedral	Sn–N_{bipy}[c]	2.59	2.33	
[trans NCS groups]	C–Sn–C	112.5	106.3	
	SCN–Sn–NCS	147.8	161.1	
	N_{bipy}–Sn–N_{bipy}	64.4	69.7	
17: [Bu_2SnCl_2(phen)]	Sn–C[c]	2.14	2.11	33
	Sn–Cl[c]	2.43	2.55	
octahedral	Sn–N[c]	2.56	2.39	
[trans Bu groups]	C–Sn–C	170.0	177(2)	
	Cl–Sn–Cl	121.1	105(1)	
	N–Sn–N	66.4	68(1)	
15: [(*p*-tolyl)$_2SnCl_2$(phen)]	Sn–C[c]	2.07	2.16	34
	Sn–Cl[c]	2.43	2.50	
octahedral	Sn–N[c]	2.51	2.34	
[trans Cl]	C–Sn–C	114.4	108.7(1)	
	Cl–Sn–Cl	149.8	161.4(1)	
	N–Sn–N	66.4	69.1(1)	
16: [Et_2SnCl_2(phen)]	Sn–C[c]	2.14	2.15	35
	Sn–Cl[c]	2.54	2.43	
octahedral	Sn–N[c]	2.38	2.56	
[trans Et groups]	C–Sn–C	175.8	168.8(2)	
	Cl–Sn–Cl	104.2	119.7(3)	
	N–Sn–N	69.0	65.2(1)	

[a] This work.
[b] Reference to experimental data.
[c] Mean value.

provide bond lengths close to the experimental values, but this is not so for bond angles.

It is apparent that PM3 calculations undervalue the strengths of the tin–neutral ligand interactions in the coordination compounds containing neutral nitrogen or oxygen ligands or donor groups. This is shown by the calculated Sn–N or Sn–O bonds being longer and halo–or pseudo-halo–tin bonds being shorter than the corresponding experimental values. The more marked deviations are experienced by the tin–neutral ligand bonds. A consequence of the differences in the calculated/experimental bond length data is that there must also be differences in the bond angle data.

Not surprisingly, the more elaborate calculations at the HF/LanL2DZ level generally provide data closer to the experimental values than do the PM3 calculations for the hypervalent diorganotin dichloride complexes. Calculated Sn–Cl and Sn–N, as well as Sn–C, bond lengths from the HF/LanL2DZ study[1] on [$(H_2C{=}CH)_2SnCl_2$(bipy)]·0.5PhH, [$MePhSnCl_2$(bipy)]·0.5$CHCl_3$, and [Me_2SnCl_2(phen)] are, in all cases, slightly longer, but by *ca* 0.03–0.04 Å, than the corresponding X-ray results. The finding that both the calculated tin–halide and tin–donor atom bond lengths in the HF/LanL2DZ study are longer than experimental values is in contrast to the findings at the PM3 level. Calculated bond angles are also generally closer to the experimental X-ray results in the HF/LanL2DZ calculations than obtained in our PM3 study.

Compound [Ph_2SnCl_2·1,10-phenanthroline-5,6-dione], [Ph_2SnCl_2(pdon)] (21)

The reverse of our usual practice was carried out with this compound. First, the PM3 calculations were carried out on possible structures of **21** and subsequently an X-ray structure determination was performed.

PM3 calculations on octahedral structures for **21** indicated four stationary points, including three local minimum energies: two structures with Ph groups in cis sites (one with a planar pdon ligand [*cis*-planar-**21**] and one with a non-planar-pdon ligand [*cis*-distorted-**21**]) and one with trans Ph groups and a non-planar pdon group [*trans*-distorted-**21**]. One structure with trans Ph groups and a planar pdon ligand was determined to be a local maximum, i.e. a transition state, and was discarded. Relative energies and selected calculated geometric parameters for the three local mimina are shown in Table 4. The ligand distortion arises from the non-aromaticity of the central quinoid ring and is best referenced by the O–C–C–O torsion angle. The planar and distorted forms of the pdon ligand interconvert, as calculated with PM3 for both the free and monoprotonated species. The energetic

Table 4. Comparison of calculated and experimental geometric parameters (Å, °) for **21** and [(**21**)] · $2Me_2CO$

	PM3 calculated data for **21**				
Geometric parameter	*cis*-planar **21**	*cis*-distorted **21**	*trans*-distorted **21**	X-ray data for [(**21**)] · $2Me_2CO$	
Sn–C	2.06	2.06	2.08	Sn–C19	2.151(14)
				Sn–C13	2.164(13)
Sn–N	2.53	2.54	2.59	Sn–N2	2.394(11)
				Sn–N1	2.405(12)
Sn–Cl	2.42	2.42	2.42	Sn–Cl2	2.461(3)
				Sn–Cl1	2.467(4)
C–Sn–C	115.2	115.4	166.8	C13–Sn–C19	169.1(5)
N–Sn–N	65.6	65.9	64.6	N1–Sn–N2	69.9(4)
Cl–Sn–Cl	148.1	147.9	124.0	Cl1–Sn–Cl2	103.0(2)
O–C–C–O	0	34.2	36.0	O1–C5–C6–O2	5(2)
Relative stability (kcal mol^{-1})	0.5	0	6.9		

Table 5. Crystal data and structure refinement for $[Ph_2SnCl_2(pdon)]\cdot 2Me_2CO$[**21**$\cdot 2Me_2CO$]

Empirical formula	$C_{30}H_{28}Cl_2N_2O_4Sn$	θ range for data collection (°)	2.28 to 27.10
Formula weight	670.13	Absorption coefficient (mm^{-1})	1.079
Temperature (K)	120(2)	Abs correction $T_{min/max}$	0.8812/0.9767
Crystal system	Orthorhombic	Reflections collected/unique	29 429/6230
Space group	$Pca2_1$	R_{int}	0.1145
Cell dimensions			
a (Å)	16.7628(14)	Index ranges	$-21 \leq h \leq 21$
b (Å)	10.5501(7)		$-13 \leq k \leq 13$
b (Å)	16.7621(12)		$-21 \leq l \leq 21$
Mo Kα radiation (Å)	0.710 73	Data/restraints/parameters	6230/1/148
V(Å^3)	2964.4	Goodness of fit on F^2	1.146
Z	4	$R_1(I > 2\sigma(I))$	0.1004
D_{calcd}(g cm^{-3})	1.502	wR_2 (all data)	0.2172
F(000)	1352	$(\Delta/\rho)_{min}$(e^- Å^{-3})	−1.468
Crystal size (mm^3)	0.15 × 0.12 × 0.04	$(\Delta/\rho)_{max}$(e^- Å^{-3})	1.067
Crystal description	Orange plates	CCD deposition no.	246 463

barriers were 1.2 kcal mol^{-1} and 0.7 kcal mol^{-1} respectively, with the distorted structure being the more stable in both cases.

Unfortunately, crystals of **21**, grown from acetone solution as a bis-acetone solvate, were of relatively poor quality and only led to an R value of 0.100. However, there is no doubt that the solvate has a trans arrangement of phenyl groups; furthermore, an essentially planar pdon ligand was detected; see Figure 4 and Table 5. Thus, the PM3 calculations did not predict the particular structure found in the solid state. Similar calculations were then carried for cis and trans isomers of compounds **16**–**19**, and in all cases the cis isomer was calculated to be the more stable by 5.2–6.6 kcal mol^{-1}. It is important to pointout that there are successful predictions with PM3 for preferential isomers in more constrained systems, such as chelating dithiocarbamate ligands.[40]

Ubiquitous crystal packing effects, as well as the presence of the acetone solvate molecules in [**21**$\cdot 2Me_2CO$], can also be put forward, partially at least, for the differences in the crystallographic and PM3 findings. Indeed, the major aim in the Tiekink and coworkers studies[1–3] was to study the influence of crystal packing, in particular the effects of such intermolecular interactions as hydrogen bonding and π–π stacking, on molecular structures, using, as criteria, differences between calculated and experimental data. It is apparent that both calculation methods, PM3 and HF/LanL2DZ, produced more symmetric optimized structures than found by experiment.

Present in the crystal structure of [**21**]$\cdot 2Me_2CO$ are several weak hydrogen bonding interactions, including intermolecular C–H$\cdots$O hydrogen bonds involving carbonyl oxygen atoms of the pdon ligands and solvate oxygen atoms. The relative poor refinement prevents any further detailed discussion.

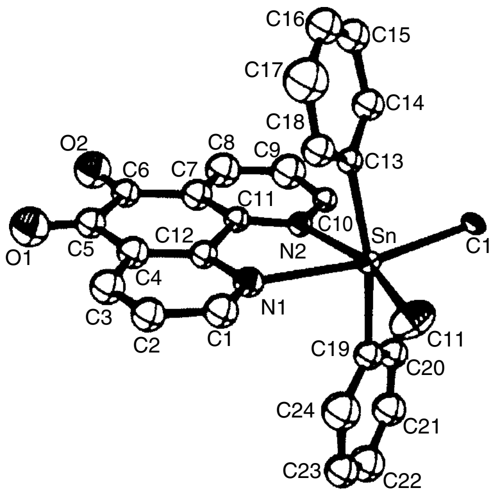

Figure 4. Molecular structure and atom labelling for [Ph_2SnCl_2(pdon)]·$2Me_2CO$; ORTEP plot drawn at the 50% probability level; acetone molecules and hydrogen atoms have been omitted for clarity.

MATERIALS AND METHODS

PM3 calculations

All calculations were performed using the PM3 Hamiltonian as implemented in the GAMESS 6 package[41] running on a 1.0 GHz PC. Structural parameters were obtained using the program ORTEP 3.[42] Global structural optimization was achieved by gradient in successive runs using different starting structures. The calculations were in Cartesian coordinates using standard parameters, and the nature of the stationary points obtained was determined by harmonic frequency analysis.

Instruments

FTIR spectra were obtained with an IR760 Nicolet-Magna spectrophotometer using mineral oil dispersions over PE windows in the 600–50 cm^{-1} range. Solution ^{13}C and ^{119}Sn NMR spectra were obtained using a DRX300 MHz Bruker instrument.

Crystallography

Data collection

Intensity data for **21** were obtained with Mo Kα radiation, $\lambda = 0.710\,73$ Å, by means of the Enraf Nonius KappaCCD area diffractometer of the EPSRC's crystallography service at Southampton. The entire process of data collection, cell refinement and data reduction was accomplished by means of the programs DENZO[43] and COLLECT.[44] Correction for absorption by a semi-empirical method based upon the variation in intensity of equivalent reflections was achieved with the program SORTAV.[45,46]

Structure solution and refinement

The initial solution of the structure was obtained by the heavy-atom technique with the program SHELXS-86[47] and completed and refined by full-matrix least squares on F^2 with SHELXL-97.[48] In the final stages of refinement, hydrogen atoms were introduced in calculated positions and refined with a riding model.

Crystal data

$C_{30}H_{28}Cl_2N_2O_4Sn$, $M = 670.13$, orthorhombic $Pna2_1$, $a = 16.7628(14)$, $b = 10.5501(7)$, $c = 16.7621(12)$ Å, $V = 2964.4$ Å^3, $Z = 4$, 6230 unique reflections ($\theta_{max} = 27.1°$), R(4738 data with $I > 2\sigma(I)) = 0.100$, $wR = 0.217$ (all data), $\rho_{max} = 1.07$ e$^-$ Å^3, Flack parameter = 0.09(7). CCDC deposition number: 246463. The program ORTEP-3 for Windows[49] was used in the preparation of the figures and SHELXL-97 and PLATON[50] for bond length and angle and other molecular geometry calculations.

Diphenyldichloro(1,10-phenanthroline-5,6-dione)stannane

To a solution of pdon[51] (0.230 g, 1.10 mmol) in EtOH (20 ml) was added a solution of Ph_2SnCl_2 (0.390 g, 1.14 mmol) in EtOH (5 ml). A beige solid, which slowly formed, was collected, washed with small portions of EtOH and petroleum ether, and recrystallized from acetone, yielding yellow crystals. ^{13}C NMR (DMSO-d_6 solvent) δ: 155.6 [C_{ipso}], 127.8 [C_m, $^3J(^{119}Sn{-}^{13}C) = 122.6$ Hz], 135.1 [C_o, $^2J(^{119}Sn{-}^{13}C) = 71.9$ Hz], 128.3 [C_p, $^4J(^{119}Sn{-}^{13}C) = 23$ Hz]. ^{119}Sn NMR (DMSO-d_6 solvent) δ: −402. IR (mineral oil, cm^{-1}): 461, 448, 279 (Sn–C); 262 (Sn–Cl). Anal. found: C, 50.9; H, 2.8; N, 4.8. Calc. for $C_{24}H_{16}Cl_2N_2O_2Sn$: C, 52.0; H, 2.9; N, 5.1 %.

CONCLUSIONS

The well-established PM3 semi-empirical method was developed without parameters for d-orbitals (the same applies to AM1 and MNDO), and this accounts for the poorer predictions found for such hypervalent compounds as listed in Table 3 than does the HF/LanL2DZ method, which incorporates the use of the effective core potential[52] approximation in the treatment of the tin atom. Other methods essentially fail with the weakly associated organotin halides. To our knowledge, no semi-empirical method accounting for tin d-orbitals is generally available.

The better correlation found for bond angles, in comparison with bond lengths, may be explained by the coulombic repulsion integrals used to calculate the former, whereas the latter need integrals of coulombic attraction and repulsion, which are more error prone. Another hypothesis would be a larger participation of d-orbitals in determining bond lengths. The more diffuse tin d-electrons would exert less influence on the bond angles.

All in all, despite the orbitals taken into account, we consider that the PM3 predictions are generally satisfactory, especially considering the computing time required, and that they provide suitable structure predictions for those chemists whose interests are in ball-park figures rather than precise values. Furthermore, it is possible to arrive at very good estimates of solid-state bond lengths for certain groups of compounds by making specific additions/subtractions to the PM3 calculated values. For example, for six-coordinate diorganotin complexes with neutral bidentate ligands and for internally chelated penta-coordinate $Cl_3Sn(CH_2)_nCO_2R$ compounds, reductions of *ca* 0.17 Å in the calculated tin–donor atom bond lengths provide values very close to experimental solid-state values. It is of interest to discover whether the same or another correction is needed for other types of organotin species.

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