A Novel Configuration of a Benzoylacetonato-Diorganotin Species is Modified by an Electron-Withdrawing Substituent on Tin − Synthesis, IR and NMR Spectroscopy, Structure, and ab initio Studies

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Diorganotin(IV) complexes of the β-diketonato benzoylacetonato ligand were synthesized and characterized with IR and multinuclear (H, C, Sn) NMR spectroscopy. The X-ray diffraction study of bis(benzoylacetonato)di-*tert*-butyltin(IV) shows two independent molecules in the crystallographic unit cell. The metal polyhedron is a distorted octahedral (Skewed Trapezoidal Bipyramidal) with the *trans* angle C–Sn–C of 151.5(5)°. Each ligand chelates the metal with different donor abilities [Sn–O bond lengths of 2.423(8) Å and 2.135(8) Å in one ligand, and 2.107(9) Å and 2.357(8) Å in the other]; results for the 2nd molecule are similar. The coordination arrangement differs from those of related bis(β-diketonato)diorganotin derivatives containing asymmetric ligands, which are characterized by an approximate C_s symmetry, in that both benzoylacetonato ligands point their methyl (and phenyl) substituents across (*anti*) the metal atom. Chelate planarity and some phenyl-chelate coplanarity was observed. Hartree–Fock (HF) and Density Functional Theory (DFT) calculated structures are in good agreement with those obtained using X ray analysis. DFT and HF calculated structures of bis(benzoylacetonato)diphenyltin(IV), having a similar connectivity as bis(benzoylacetonato)di-*tert*-butyltin(IV), differ markedly: the phenyls subtend a C–Sn–C bond angle of 180°, all Sn–O bond lengths are equal and the tin coordination sphere is a regular octahedron with the ligand bzac being isobidentate. This arrangement is caused by the phenyl electronic withdrawal effect. However, IR data for this compound show several Sn–O bands inconsistent with this configuration and suggest a different connectivity. Additional DFT structural calculations for $(bzac)_2SnPh_2$, performed on the connectivity resembling the "normal" *syn* geometry, show a conformational energy slightly lower than that of the centrosymmetric arrangement. Low temperature NMR spectra illustrate the possible rearrangements in solution.

Introduction

The acetylacetonato-like donors represent one of the most important classes of chelating ligands in the field of coordination chemistry, not only because of their technological applications,[1−4] but also for theoretical structural studies performed on their metal complexes.[5,6] Several studies have appeared in the literature regarding structural and spectroscopic features of tin(II)[7−11] and tin(IV) acetylacetonates,[12−23] including their catalytic properties in the formation of polyurethane in foams,[24] their promising antineoplastic activity,[25−27] and more recently, their use as molecular precursors in LAD (laser ablation and subsequent deposition) technology.[28]

Diorganotin(IV) acetylacetonates adopt a *trans* regular octahedral geometry[12] (Figure 1), whereas dihalotin(IV) acetylacetonates prefer the *cis*-dihalo octahedral configuration.[18]

Subsequent studies on monothioacetylacetonatotin[29] derivatives revealed the possibility of large deviations from ideal geometries in accordance with the Zahrobsky[30] and Kepert models.[31] Other studies on asymmetric β-diketonates have appeared recently, including our own systematic

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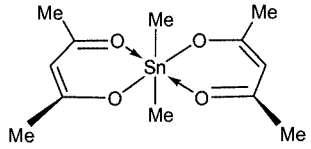
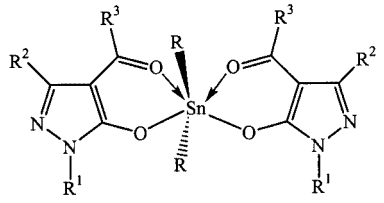
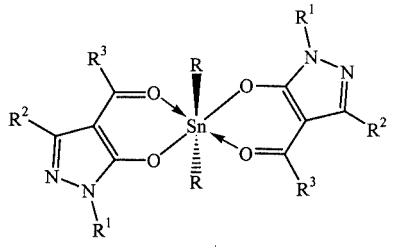


Figure 1. $(acac)_2Sn(CH_3)_2$

investigations on the structural aspects of tin(II)[32] and tin(IV)[33] derivatives containing 4-acyl-5-pyrazolonato ligands, which are β-diketonates fused to a pyrazole ring[34] containing three substituent groups. In these asymmetric ligands, the carbonyl nearest the heterocyclic ring is a better donor than the 4-acyl carbonyl group, and the diorganotin derivatives posses strongly deformed octahedral structures (Figure 2a) with both ligands pointing their equivalent arms in a *syn* configuration.



(a) *syn* configuration



(b) *anti* configuration

Figure 2. (a) *syn* configuration (b) *anti* configuration

Our studies have revealed the following geometrical features of these tin complexes: i) the *trans* C−Sn−C bond angle can be as small as 150°, and ii) the R groups are folded towards the O(acyl) atoms. The O(pyrazolonato) atom (that is, the oxygen closest to the pyrazole ring) forms a short, covalent, Sn−O bond (range 2.09−2.14 Å), whereas the O(acyl) atom forms a long, coordinative, Sn−O bond (range 2.22−2.46 Å).[33b] The asymmetric binding of these ligands reflects the different electronic donating ability of the oxygen atoms and is responsible for the octahedral deformation described earlier. In contrast, the dimethyltin derivative of the symmetrical β-diketonato acac has maximum electronic delocalization in the chelate moiety and is a perfect octahedron[12] (Figure 1). We have also found, however, that an appropriate choice of peripheral substituents on N1 allows the synthesis of isomers with a centrosymmetrical (*anti*) configuration (see **b** in Figure 2).[35]

It seems that the features determining the *syn* and *anti* configurations are subtle and more factors than those first hypothesized are responsible. For example, in octahedral diphenyltin compounds, *cis*-diphenyl species are also known. Specifically, in the case of bis(4-acyl-5-pyrazolonato)diphenyltin compounds, the *cis* arrangement has been observed with Mössbauer spectroscopy.[33c] Subtle molecular changes can also induce the *trans* form in related compounds such as Ph_2SnCl_2(2,2′-bipyridine), which is a *trans*-diphenyl *cis*-dichloro species, whereas (*p*-tolyl)$_2SnCl_2$(2,2′-bipyridine) is a *cis*-ditolyl *trans*-dichloro isomer.[36] Therefore, we decided to reinvestigate the field of diorganotin(IV) classical β-diketonates giving special attention to the asymmetric donor 1-phenylbutane-1,3-dionato, also known as benzoylacetonato (bzac), to derive some fundamental principles from the stereochemistry of these compounds.

Results and Discussion

Synthesis of the Diorganotin(IV) Derivatives 1−6

Derivatives $(bzac)_2SnR_2$ **1−6** were synthesized by interaction of two mmoles of bzacH and one mmole of the appropriate diorganotin(IV) acceptor in methanol in the presence two mmoles of $NaOCH_3$ (Scheme 1).

$$2bzacH + 2NaOCH_3 + R_2SnX_2 \rightarrow (bzac)_2SnR_2 + 2NaX + 2CH_3OH$$

	R	X		R	X
1	Me	Cl	**4**	*t*Bu	Br
2	Et	Cl	**5**	Cy	Cl
3	*i*Bu	Cl	**6**	Ph	Cl

Scheme 1

The reactions were performed according to methods previously employed with 4-acyl-5-pyrazolonato donors,[33] since they avoid hydrolysis. The yields of the reactions were higher when a large excess of bzacH was employed.

Spectroscopic Characterization

The infrared spectra of derivatives **1−6** show the carbonyl ν(C=O) shifted to lower frequencies upon complex formation, as expected for coordination of the β-diketonato ligand through both the oxygen atoms.[37] In the far-IR region several strong Sn−O bands[37] can be seen in the range 390−460 cm^{-1}. In the spectra of derivatives **1−5**, some medium to weak absorptions between 450 and 600 cm^{-1} were assigned to the ν(Sn−C) on the basis of literature reports.[38] In the spectrum of **6**, three strong bands in the range 250−310 cm^{-1} are due to ν(Sn−C).[39] In the spectra of **1−6**, the presence of several ν(Sn−O) and ν(Sn−C) modes indicates either distortion from ideal *trans*-octahedral geometry in the solid state (confirmed for **4** by the diffraction study, see below) or the presence of *cis* isomers.

The ^1H NMR spectra of derivatives **1** and **2** show one set of resonances for each magnetically equivalent group of protons. On cooling the samples, each signal splits into sev-

eral signals, two of which are very intense with respect to the others. We have measured the $^2J_{Sn,H}$ coupling constants and related them to the C−Sn−C angle.[40] From the empirical relation derived by Lockhart[40a] a C−Sn−C angle for compound **1** of ca. 160°, typical of skewed *trans*-octahedral species,[40] was found. For this reason, the two main resonances observed at low temperature for the CH_{bzac} and Me_{bzac} protons can be attributed to *syn* and *anti* isomers. The less intense signals are likely due to either *cis* isomers or four- to five-coordinate species involved in the interconversion mechanism between *syn* and *anti* isomers.

The ^{119}Sn NMR spectra of **1** and **2** further support our hypothesis: at room temperature only one resonance was detected, which split into two at 218 K.

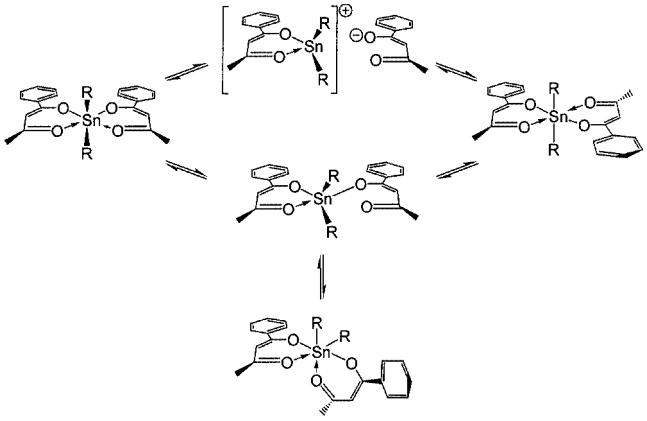
A similar situation was found for the derivatives **3**−**6** containing bulky or electron-withdrawing organic groups bonded to tin. In these compounds, the fluxionality is lost at higher temperature with respect to **1** and **2**. They show more than one set of resonances at room temperature, thus indicating that the energy required for the interconversion mechanism is a function of steric hindrance and electronegativity of the R groups coordinated to tin. At low temperatures, the ^{119}Sn NMR spectra of **5** and **6** show three resonances, two of which are dominant and are likely to be due to *syn* and *anti* isomers; the third is assigned to one *cis* $(bzac)_2SnR_2$ complex.[41]

Reports in the literature on possible mechanisms for configurational rearrangements of $(\beta\text{-diketonato})_2SnX_2$ complexes[39b,42] include: complete dissociation of one β-diketonato donor, to give a four coordinate intermediate; breaking of one M−O bond to give a five coordinate intermediate with a monodentate β-diketonato donor; and twisting mechanisms with subsequent rearrangement without any metal−ligand bond breaking.

To better understand the mechanism operating in solution for derivatives **1**−**6**, we carried out a ^{1}H NMR variable-temperature study of a mixture containing derivative **1** and the equivalent amount of free neutral bzacH proligand in $CDCl_3$. At room temperature, only one set of signals was observed, in accordance with ligand exchange in the complex, whereas at 218 K all resonances due to **1** and to the neutral bzacH in both enolic and ketonic forms were found. It seems that the twisting mechanism is excluded and the *syn-anti* conversion proceeds with breaking and re-formation of $Sn-O_{bzac}$ bonds through four- or five-coordinate intermediate species (Scheme 2). In the case of four coordinate intermediates the absence of conductivity in chlorohydrocarbon solvents could be attributed to ion pairing effects.

The variable-temperature ^{1}H NMR spectra indicate the following coalescence temperatures: 273 K (compounds **1** and **2**), 303 K (**3**), 323 K (**4** and **6**). These results further confirm the role of R groups on the configurational rearrangements.

The ^{119}Sn chemical shift is typical of six-coordinate SnC_2O_4 species, and is a function of steric and electronic features of R groups on tin. This is in agreement with previous studies on related $(4\text{-acyl-5-pyrazolonato})_2SnR_2$ derivatives.[33] The donating ability of $bzac^-$ is higher than that of 4-acyl-5-pyrazolonates, as the signals are generally high-field shifted with respect to that of 4-acyl-5-pyrazolonato complexes.



Scheme 2

The ^{13}C NMR spectra of **1**, **3**, and **4** show one broad set of resonances at room temperature. The magnitude of the $^1J(^{119}Sn-^{13}C)$ coupling constant of **1** (934 Hz) further supports the presence of *trans* isomers in solution.[40] The ^{13}C NMR spectrum of **6**, on the other hand, exhibits more than one set of resonances for each magnetically equivalent carbon atom, in accordance with the ^{1}H and ^{119}Sn NMR spectra.

X-ray Structural Discussion of Derivative $(bzac)_2Sn(tBu)_2$ (4)

The crystals of $(bzac)_2Sn(tBu)_2$ are formed by well separated molecules with no imposed crystallographic symmetry. Each asymmetric unit contains 2 molecules related by a local (non-crystallographic) inversion center at approximately [0.625, 0.0, 0.75] [see also Exp. Sect. and related Figure S1 (Supporting Information)]. Besides the inverted configuration only minor geometrical differences between these 2 molecules are observed, probably due to packing forces; one of these molecules is shown in Figure 3. The metal is six coordinate and surrounded by 4 O atoms from 2 bzac ligands, and 2 C atoms from the *tert*-butyl groups, which are almost eclipsed, as shown in Figure 4. Table 1 shows a selection of the structural data. The C−Sn−C bond angles [151.5(5)° for C11−Sn1−C15 in one molecule and 152.1(5)° for C51−Sn2−C55 in the other] are of the order found in bis(4-acyl-5-pyrazolonato)dialkyltin[33b] *syn* structures, as are the marked differences in Sn−O bonds in each ligand. The carbonyl closest to the methyl substituent in one ligand has the short Sn−O bond [Sn1−O2 = 2.135(8) Å], whereas in the other ligand the short bond is close to the phenyl substituent [Sn1−O21 = 2.107(9) Å]. This feature is uncommon for bzac compounds {but it does exist[43] in the anion $[(bzac)_4Eu]^-$} and contrasts with bis(4-acyl-5-pyrazolonato)diorganotin derivatives, where the short bond only appears in the carbonyl fused to the pyrazole ring, The ligand asymmetry differs from that of $(bzac)_2Sn^{II}$, which shows a short Sn−O bond for the

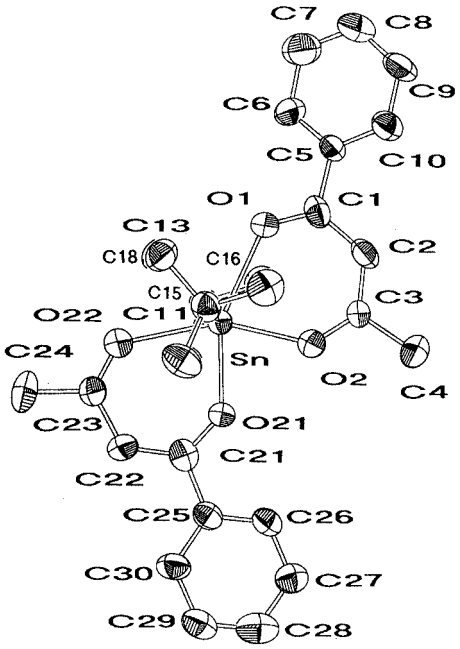


Figure 3. X-ray structure of $(bzac)_2Sn(tBu)_2$ (**4**). In this view, *tert*-butyl group C15−C18 (C15, C16, and C18 have small labels) is below the other *tert*-butyl C11−C14 (only C11 and C13 are labeled); H atoms are omitted.

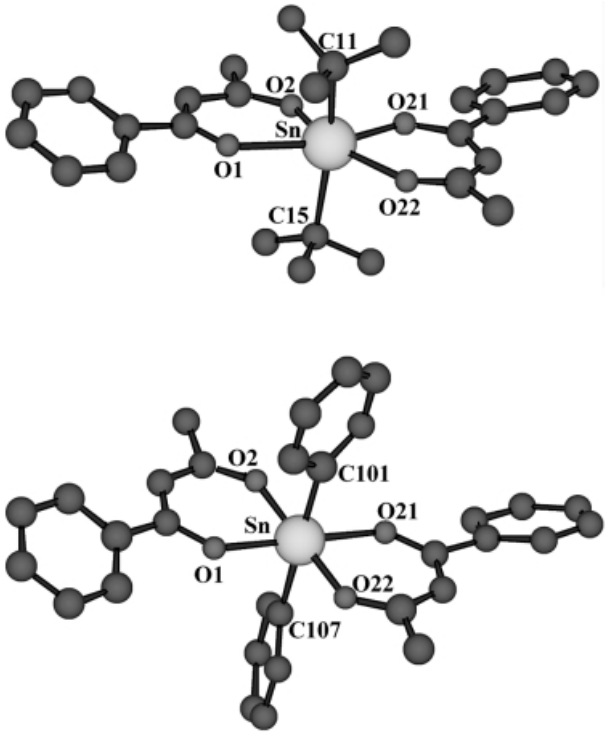


Figure 4. DFT structures of $(bzac)_2Sn(tBu)_2$ (**4**) and *anti* $(bzac)_2SnPh_2$ (**6**).

phenyl-carbonyl (2.13 Å) and a long Sn−O bond (2.29 Å) for the methyl-carbonyl, in both ligands.[10]

In analyzing the molecular arrangement, we see that the title compound has its bzac equivalent substituents (for instance both Ph groups) opposite each other. This is in contrast with *syn* bis(4-acyl-5-pyrazolonato)diorganotin derivatives that have the equivalent ligand substituents facing each other (see **a** in Figure 2). This opposite arrangement is reminiscent of the *anti* bis(4-acyl-5-pyrazolonato)diorganotin geometry[35] (see **b** Figure 2), although the latter also differs from the title compound and has a regular octahedral configuration with the C−Sn−C bond angle of 180°. Therefore, the structural form of the title compound is different from those so far observed.

X-ray data show planar chelate moieties. Thus, the least-square C1−C2−C3−O1−O2 plane has all atoms within 0.01 Å, and the C21−C22−C23−O21−O22 plane has all atoms within 0.04 Å; in the 2nd molecule these parameters are both 0.03 Å. The metals are contained in these chelate planes within 0.05 and −0.02 Å (for the 1st molecule) and −0.02 and 0.00 Å (for the 2nd molecule); therefore the molecule has a skewed trapezoidal bipyramidal (STB) configuration.[31] In addition, the dihedral angles between the two chelate planes are 2.4(2)°, in one molecule and 3.1(3)° in the other. Further, each phenyl substituent shows some co-planarity with its chelate moiety as seen by torsion angles O1−C1−C5−C6 [−19(2)°] and O21−C21−C25−C26 [−16(1)°].

There are two X-ray structures of di-*tert*-butyltin compounds containing four additional O atoms in the coordination sphere in the CSD database. These are di-*tert*-butyl-bis{[(*E*)-2-(2-hydroxy-5-methylphenyl)diazenyl]-benzoato-*O*,*O*′}tin(IV)[44] and di-*tert*-butyl-bis(1-phenyl-3-methylbenzoyl-pyrazolon-5-ato-*O*,*O*′)tin(IV).[45] In both complexes the oxygen ligands chelate the metal, as occurs in compound **4**. Comparison with compound **4** shows the former having a smaller C−Sn−C bond angle (141.0°) and a more deformed octahedron; the latter (containing a β-diketonato ligand) shows more similar features because its C−Sn−C bond angle is 150° and both *t*Bu groups are eclipsed as in compound **4** (see Figure 3).

Theoretical Study

The molecular structure of $(bzac)_2Sn(tBu)_2$ was also studied using theoretical methods. The starting coordinates were those obtained from the X-ray structure determination and were optimized by energy-minimization with the Hartree−Fock (HF) and Density-Functional Theory (DFT) methods. Structural data are included in Table 1. There is excellent agreement for the data obtained experimentally from the X-ray diffraction study for the deformed metal polyhedron including the sum of the *cis* O−Sn−O bond angles of 360°. The co-planarity in the chelate moieties resembles that observed with X-rays as shown by torsion angles in Table 1. The DFT structure is shown in Figure 4.

In previous studies on (4-acyl-5-pyrazolonato)organotin derivatives, we showed that an electron-withdrawing group on tin, such as Ph, behaves differently from alkyl groups.[33c] Due to the electron-withdrawing effect, phenyl groups pull electron density away from the metal and consequently induce more electron donation from the chelating ligands. Therefore, the normally weakly coordinated acyl carbonyl provides more electronic donation and this results in de-

Table 1. Selected structural data of $(bzac)_2Sn(tBu)_2$ (**4**)

Distances					
Method[a]	XR	HF	DFT	XR (2nd molecule)	
Sn−O1	2.423(8)	2.439	2.418	Sn2−O41	2.408(8)
Sn−O2	2.135(8)	2.137	2.092	Sn2−O42	2.138(8)
Sn−O21	2.107(9)	2.110	2.141	Sn2−O61	2.145(8)
Sn−O22	2.357(8)	2.360	2.390	Sn2−O62	2.367(7)
Sn−C11	2.19(1)	2.193	2.194	Sn2−C51	2.20(1)
Sn−C15	2.18(1)	2.177	2.194	Sn2−C55	2.18(1)
Angles					
Method	XR	HF	DFT	XR (2nd molecule)	
C11−Sn−C15	151.5(5)	151.3	155.3	C51−Sn2−C55	152.1(5)
O1−Sn−O2	78.6(3)	76.7	78.8	O41−Sn2−O42	78.9(3)
O21−Sn−O22	79.2(3)	76.7	78.8	O61−Sn2−O62	79.0(3)
O1−Sn−O22	126.2(3)	126.7	124.7	O41−Sn2−O62	127.4(3)
O21−Sn−O2	76.0(3)	79.9	77.7	O61−Sn2−O42	74.7(3)
Torsion angles					
Method	XR	HF	DFT		
O1−C1−C2−C3	3(2)	−3.5	−4.0		
O2−C3−C2−C1	0(2)	−1.3	−2.0		
C4−C1−C2−C3	−1(2)	−1.2	−2.6		
C5−C1−C2−C3	−173(1)	177.4	177.1		
O1−C1−C5−C6	−19(2)	−22.7	−20.0		
O21−C21−C22−C23	3(2)	−2.4	−1.1		
O22−C23−C22−C21	3(2)	−0.3	0.9		
C24−C21−C22−C23	1(2)	−0.1	1.6		
C25−C21−C22−C23	−178(1)	178.8	179.9		
O21−C21−C25−C26	−16(1)	−21.1	−18.1		

[a] Methods, X-ray diffraction (XR); Hartree−Fock (HF); Density Functional Theory (DFT).

creased octahedral deformation.[33c] For this reason, we wanted to see if replacing the *tert*-butyl groups with phenyl groups resulted in some structural change, and so we also studied $(bzac)_2SnPh_2$ (**6**) theoretically. Therefore, the *tert*-butyl groups from $(bzac)_2Sn(tBu)_2$ were replaced by phenyls and the energy minimized as above (Figure 4 also depicts this calculated DFT molecule and Table 2 includes selected geometric data). This resulted in a dramatic variation on the molecular structure: the C−Sn−C bond angle became 180° and a regular octahedron was found. In addition, increased involvement in binding to tin by O1 and O22 was observed and all Sn−O bonds were equal (about 2.14 Å for HF or 2.19 Å for DFT).

Therefore, replacing the *tert*-butyl groups on tin with phenyls while keeping the $(bzac)_2Sn(tBu)_2$ connectivity, modified the skewed trapezoidal bipyramidal arrangement to regular octahedral. Moreover, the phenyl groups on tin caused the asymmetric binding of the ligand bzac to disappear, e.g. the ligand bzac became isobidentate. Co-planarity between phenyl substituents and chelate moieties was less marked than in the *tert*-butyl derivative, as seen from the corresponding torsion angles in Table 1 and 2.

However, IR data for $(bzac)_2SnPh_2$ show several Sn−O bands that are inconsistent with the symmetrical tin environment found using ab initio methods. IR results could imply either a *cis*-diphenyl structure or a *syn* STB structure with equivalent ligand arms (methyls or phenyls) facing each other. In other words, the theoretical study shows that the $(bzac)_2Sn(tBu)_2$ connectivity is not possible for $(bzac)_2SnPh_2$.

Table 2. Selected ab initio structural data of *anti* $(bzac)_2SnPh_2$ (**6**)

Distances		
Method	HF	DFT
Sn−O1	2.149	2.189
Sn−O2	2.142	2.186
Sn−O21	2.147	2.191
Sn−O22	2.143	2.185
Sn−C101	2.138	2.146
Sn−C107	2.138	2.144
Angles		
C101−Sn−C107	179.8	179.1
O1−Sn−O2	84.9	85.5
O21−Sn−O22	85.0	85.6
O1−Sn−O22	95.3	94.1
O21−Sn−O2	94.8	94.9
Torsion angles		
O1−C1−C2−C3	−1.5	0.2
O2−C3−C2−C1	−1.0	0.3
C4−C1−C2−C3	−1.6	−0.3
C5−C1−C2−C3	179.9	−178.9
O1−C1−C5−C6	−26.9	−22.1
O21−C21−C22−C23	−1.5	0.1
O22−C23−C22−C21	−0.8	0.4
C24−C21−C22−C23	−1.2	−0.2
C25−C21−C22−C23	179.8	−178.9
O21−C21−C25−C26	−26.8	−22.4

We then performed an additional DFT structural calculation for $(bzac)_2SnPh_2$, with a connectivity resembling the common *syn* geometry (see Figure 5). From the coordinates of *anti* $(bzac)_2SnPh_2$, obtained above, the methyl and the Ph groups belonging to the O1···O2 chelate were exchanged

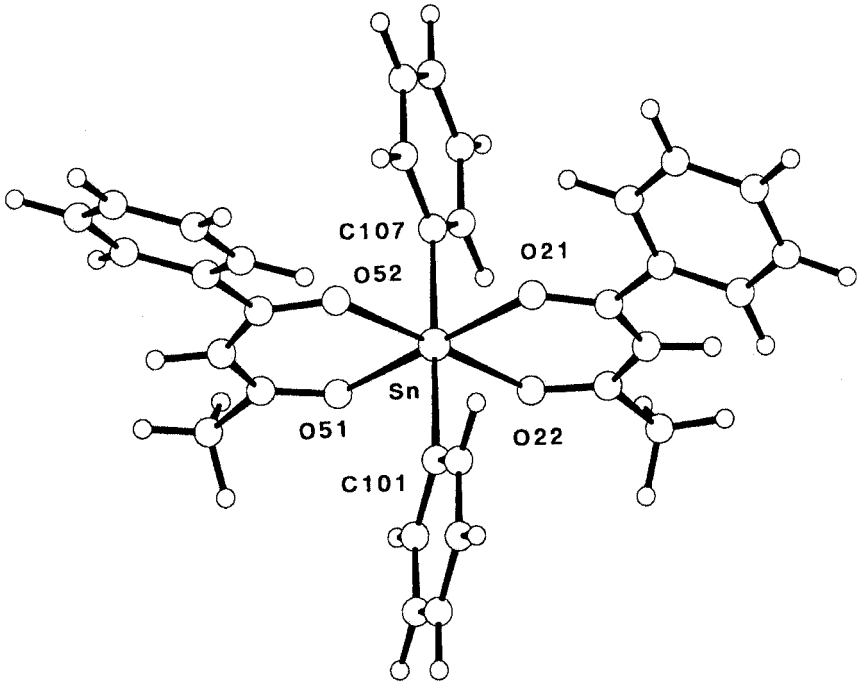


Figure 5. DFT structure of *syn* $(bzac)_2SnPh_2$ (**6**)

(this chelate is labeled O51···O52 in Figure 5), and a minimization process was performed as above. The resulting molecule posses a slight octahedral deformation characterized by a C−Sn−C bond angle of 178.3° and Sn−O bond lengths differ less in each ligand than in other *syn* (β-diketonato)SnR_2 compounds[33] (Sn−O21 = 2.198 Å and Sn−O22 = 2.176 Å in one ligand; Sn−O52 = 2.193 Å and Sn−O51 = 2.178 Å in the other ligand). From these results, the methyl carbonyl seems to be a slightly stronger donor that the phenyl carbonyl, which agrees with the phenyl electron-withdrawing and the methyl electron releasing effects. The Sn atom is included in the equatorial plane defined by the 4 oxygen atoms as expected for a STB geometry. Each chelate plane forms a similar dihedral angle with the corresponding attached phenyl ring (23.8 and 23.9°). The conformational energy of this *syn* structure is slightly lower than the one calculated with the *anti* geometry (0.03 kcal/mol). The experimental IR data seem consistent with the former option.

Conclusions

The already versatile stereochemistry of bis(β-diketonato)-diorganotin derivatives has been further enriched with the use of the ligand 1-phenylbutane-1,3-dionato (bzac). Derivative $(bzac)_2Sn(tBu)_2$ has a skewed trapezoidal bipyramidal (STB) configuration with methyl (and phenyl) ligand arms pointing opposite each other whereas in previously studied bis(β-diketonato)diorganotin derivatives,[33] the ligand arms were facing each other. The new structural form is ascribed to ligand asymmetry that induces different metal−O bond lengths.

The diffraction study shows that structural features of $(bzac)_2Sn(tBu)_2$ agree with HF and DFT calculated structures, including overall ligand planarity.

The molecular structure of $(bzac)_2Sn(tBu)_2$ contrasts with that of $(bzac)_2SnPh_2$ (calculated theoretically and *bearing the same connectivity*). The latter shows a regular octahedral configuration otherwise seen with the symmetric ligand acac. The phenyl groups on tin thus negate bzac ligand asymmetry, but since IR data for $(bzac)_2SnPh_2$ show several Sn−O bands indicating an asymmetrical Sn environment, the ab initio *anti* structure cannot be realistic. The *syn* structure, also calculated theoretically, agrees with IR results, though the energy difference between the *syn* and *anti* structures is small (0.03 kcal/mol) and comparison may be rather speculative. However, a *cis*-diphenyl structure is also an isomer that could explain the observed IR data. Further studies are planned to try to determine which is the actual isomer experimentally obtained.

It is concluded that a delicate balance of factors governs bis(β-diketonato)diorganotin stereochemistry. Several configurations are allowed dependent on a) tin's capacity for octahedral deformation; b) the interplay of electronic effects of the tin substituents; c) the intrinsic ligand asymmetry; and d) peripheral ligand modifications.

In closing, the NMR study shows that in the case of diorganotin(IV) complexes containing asymmetric β-diketonato ligands, a mixture of isomers is present in solution. Generally, the *trans* isomers are the most abundant and the conversions *cis-trans, syn-anti*, are strongly dependent on the temperature, and the bulkiness and electronegativity of the R groups. An asymmetric ligand demonstrates a completely different behavior in R_2Sn^{IV} species compared to symmetric

donors such as acac,[35] at least when electron-withdrawing substituents such as Ph are present.

Experimental Section

General Remarks: The organotin(IV) halides and benzoylacetone were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried under vacuum to constant weight (20 °C, about 0.1 Torr). Elemental analyses (C, H) were performed in house with Fisons Instruments 1108 CHNS-O Elemental Analyzer. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin−Elmer System 2000 FT-IR instrument. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at 300 MHz for ^1H, 75 MHz for ^{13}C, and 111.9 MHz for ^{119}Sn, referred to TMS (^1H and ^{13}C) and $(CH_3)_4Sn$ (^{119}Sn). Relative intensities of signals are given in square brackets. The ^{119}Sn NMR experiments were carried with a spectral width of 900 ppm. Melting points were taken on an IA 8100 Electrothermal Instrument. The electrical conductances (reported as Ω^{-1} cm^2 mol^{-1}) of dichloromethane (M = mol/L) were measured with a Crison CDTM 522 conductimeter at room temperature.

Synthesis of the Complexes

Bis[1-phenylbutane-1,3-dionato]dimethyltin(IV) [(bzac)$_2$SnMe$_2$] (1): To a methanol solution (30 mL) of bzacH (2 mmol) was added $NaOCH_3$ (2 mmol) and $(t\text{Bu})_2SnCl_2$ (1 mmol). A precipitate slowly formed after stirring the mixture for 36 h. The precipitate was then filtered, washed with methanol (ca 10 mL), and dried under reduced pressure at room temperature. This was re-crystallized from chloroform/*n*-hexane. Yield 74%. m.p. 138−139 °C. $C_{22}H_{24}O_4Sn$: calcd. C 56.09, H 5.13; found C 56.34, H 5.04. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1587 s, 1555 vs, 1540 sh, 1507 vs, ν(C=O) + ν(C=C), 573 s, 521 s, 436 s, 408 s, 323 m, 280 m, ν(Sn−C) + ν(Sn−O) + δ(bzac). ^1H NMR ($CDCl_3$, 295 K): δ = 0.74 [s, $^2J(^{119}Sn\text{-}^1H)$ = 98.7, $^2J(^{117}Sn\text{-}^1H)$ = 94.8 Hz, 6 H, Sn−Me], 2.13 (s, 6 H, Me_{bzac}), 6.01 (s br, 2 H, CH_{bzac}), 7.4 (m), 7.88 (d, 10 H, Ph_{bzac}). ^1H NMR ($CDCl_3$, 273 K): δ = 0.75 [s, $^2J(Sn\text{-}^1H)$ = 97.5 Hz, 6 H, Sn−Me,), 2.14 (s, 6 H, Me_{bzac})], 6.01 [5], 6.2 [1] (s br, 2 H, CH_{bzac}), 7.4 (m), 7.9 (d, 10 H, Ph_{bzac}). ^1H NMR ($CDCl_3$, 248 K): δ = 0.76 [s, $^2J(Sn\text{-}^1H)$ = 97.8 Hz, 6 H, Sn−Me)], 2.15 [5], 2.21 [1] (s, 6 H, Me_{bzac}), 6.02 [5], 6.21 [1] (s, 2 H, CH_{bzac}), 7.4 (m), 7.88 (d, 10 H, Ph_{bzac}). ^1H NMR ($CDCl_3$, 218 K): δ = 0.76 [4], 0.77 [5] [s, 6 H, Sn−Me, $^2J(Sn\text{-}^1H)$ = 98 Hz], 2.17 [5], 2.22 [1] (s, 6 H, Me_{bzac}), 6.01 [5], 6.03 [4], 6.22 [2] (s, 2 H, CH_{bzac}), 7.4 (m), 7.88 (d, 10 H, Ph_{bzac}). ^1H NMR ($CDCl_3$, 326 K): δ = 0.75 [s, $^2J(Sn\text{-}^1H)$ = 97.5 Hz, 6 H, Sn−Me], 2.14 (s, 6 H, Me_{bzac}), 6.01 (s br, 2 H, CH_{bzac}), 7.4 (m), 7.88 (d, 10 H, Ph_{bzac}). ^1H NMR ($CDCl_3$+ equimolar quantity of bzac, 295 K): δ = 0.74 [s, $^2J(Sn\text{-}^1H)$ = 97.8 Hz, 6 H, Sn−Me], 2.15 [2], 2.19 [10], 2.23 [2] (s, 12 H, Me_{bzac}), 4.08 (s, 1 H, CH_{2bzac}), 6.00 [2], 6.20 [1], 6.20 [5], 6.24 [2] (s, 4 H, CH_{bzac}), 7.4 (m), 7.88 (d, 20 H, Ph_{bzac}), 16.4 (br, 3 H, OH_{bzac}). ^1H NMR ($CDCl_3$+ equimolar quantity of bzac, 223 K): δ = 0.75 [9], 0.79 [1] [s, $^2J(Sn\text{-}^1H)$ = 122 Hz, 6 H, Sn−Me], 2.16 (s, 12 H, Me_{bzac}), 6.11 (s br, 4 H, CH_{bzac}), 7.4 (m), 7.88 (d, 20 H, Ph_{bzac}). ^{13}C NMR ($CDCl_3$, 295 K): δ = 7.7 [s, $^1J(^{119}Sn\text{-}^{13}C)$ = 934, $^1J(^{117}Sn\text{-}^{13}C)$ = 886 Hz, Sn−Me] 28.9 (s, Me_{bzac}), 97.1 (s br, CH_{bzac}), 127.4, 128.3, 131.4, 138.8 (4s, Ph_{bzac}), 183.4 (s, CO_{bzac}), 193.0 (s, CO_{bzac}). ^{119}Sn ($CDCl_3$, 295 K): δ = −355. ^{119}Sn ($CDCl_3$, 273 K): δ = −356. ^{119}Sn ($CDCl_3$, 248 K): δ = −355 [4], 359 [5]. ^{119}Sn ($CDCl_3$, 218 K): δ = −356 [4], 361 [5]. Λм (10^{-3} м) = 0.05.

Derivatives **2**−**6** were synthesized in a similar way, **2** formed after stirring the solution for 36 h, **3** and **4** formed after 24 h, and **5** and **6** precipitated immediately upon mixing the reactants at 273 K.

Bis[1-phenylbutane-1,3-dionato]diethyltin(IV) [(bzac)$_2$SnEt$_2$] (2): Yield 80%. m.p. 157 °C dec. $C_{24}H_{28}O_4Sn$: calcd. C 57.75, H 5.65; found C 57.32, H 5.71. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1596 s, 1574 s, 1557 sh, 1519 m, ν(C=O) + ν(C=C); 568 m, 546 m, 531 m, 515 m, ν(Sn−C) + δ(bzac), 448 m, 413 m, ν(Sn−O). ^1H NMR ($CDCl_3$, 295 K): δ = 1.16 [t, $^3J(Sn\text{-}^1H)$ = 170 Hz, 6 H, Sn-Et], 1.47 [q, $^2J(Sn\text{-}^1H)$ = 98 Hz, 4 H, Sn−Et], 2.15 (s br, 6 H, Me_{bzac}), 6.0 (br, 2 H, CH_{bzac}), 7.4 (m), 7.87 (dd, 10 H, Ph_{bzac}). ^1H NMR ($CDCl_3$, 243 K): δ = 1.13 [t, $^3J(Sn\text{-}^1H)$ = 170 Hz, 6 H, Sn−Et], 1.47 [q, $^2J(Sn\text{-}^1H)$ = 98 Hz, 4 H, Sn−Et], 2.16 [5], 2.21 [4] (s, 6 H, Mebzac), 5.97 [5], 6.21 [4] (br, 2 H, CH_{bzac}), 7.78 (m), 7.87 (d, 10 H, Ph_{bzac}). ^{119}Sn ($CDCl_3$, 295 K): δ = −392, ^{119}Sn ($CDCl_3$, 243 K): δ = −390.5 [4], 392.5 [5]. Λм (10^{-3} м) = 0.1.

Bis[1-phenylbutane-1,3-dionato]diisobutyltin(IV) [(bzac)$_2$Sn(*i*Bu$_2$)] (3): Yield 55%. m.p. 209 °C (dec). $C_{28}H_{36}O_4Sn$ (555): calcd. C 60.57, H 6.53; found C 60.43, H 6.72. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1594 s, 1573 s, 1552 m, 1509 sh, ν(C=O) + ν(C=C); 599 br, 568 br, 550 m, 531 m, 517 m, 505 w, 493, 467 w, 440 br, ν(Sn−C) + ν(Sn−O). ^1H NMR ($CDCl_3$, 295 K): δ = 0.78 (t, 6 H, Sn-*i*Bu), 1.27 (m, 6 H, Sn-*i*Bu), 1.49 (m, 6 H, Sn-*i*Bu), 2.15 (s, 6 H, Me_{bzac}), 6.02 (br, 2 H, CH_{bzac}), 7.4 (m), 7.87 (dd, 10 H, Ph_{bzac}). ^{13}C NMR ($CDCl_3$, 295 K): δ = 13.78 (s, Sn-*i*Bu), 26.34 [s, $^1J(^{119}Sn\text{-}^{13}C)$ = 893, $^1J(^{117}Sn\text{-}^{13}C)$ = 810 Hz, Sn-*i*Bu], 27.14 (s, Sn-*i*Bu), 27.88 (s, Sn-*i*Bu), 28.0 (s, Me_{bzac}), 96.9 (s, CH_{bzac}), 127.25, 128.41, 131.81, 139.22 (s, Ph_{bzac}), 182.24 (s, CO_{bzac}), 193.31 (s, CO_{bzac}). ^{119}Sn NMR ($CDCl_3$, 295 K): Λ−389.8 [15], −392.4 [1]. Λм (10^{-3} м) = 0.1.

Bis[1-phenylbutane-1,3-dionato]di-*tert*-butyltin(IV) [(bzac)$_2$Sn(*t*Bu)$_2$] (4): Yield 71%. m.p. 151−153 °C. $C_{28}H_{36}O_4Sn$: calcd. C 60.57, H 6.53; found C 60.51, H 6.62. IR (nujol, cm^{-1}): 1592 s, 1558 s, ν(C=O) + ν(C=C); 575 s, 566 s, 528 s, 509 m, 447 m, 432 m, ν(Sn−C) + δ(bzac); 415 vs, 394 s, ν(Sn−O); 317 m, 305 m, 289 m, 261 s. ^1H NMR ($CDCl_3$, 295 K): δ = 1.20 [br, $^3J(^{119}Sn-^1H)$ = 131.7 Hz, $^3J(^{117}Sn-^1H)$ = 128.0 Hz, 18 H, Sn-*t*Bu], 2.13 [1], 2.16 [1] (s, 6 H, Me_{bzac}), 6.03 [1], 6.10 [1] (s, 2 H, CH_{bzac}), 7.38−7.52 (m, 6 H, Ph_{bzac}), 7.92 (d, 4 H, Ph_{bzac}). ^1H NMR($CDCl_3$, 218 K): δ = 1.16 [100], ($^3J(Sn-^1H)$ = 140.6 Hz), 1.24 [1], 1.28 [2], 1.40 [5] (br, 18 H, Sn-*t*Bu), 2.17 [7], 2.18 [7], 2.21 [3], 2.24 [1] (s, 6 H, Me_{bzac}), 6.03 [8], 6.07 [12], 6.14 [1], 6.17 [1], 6.21 [1], 6.23 [1] (s, 2 H, CH_{bzac}), 7.43−7.60 (m, 6 H, Ph_{bzac}), 7.84−8.02 (m, 4 H, Ph_{bzac}). ^{13}C NMR ($CDCl_3$, 295 K): δ = 29.4, 29.7, 29.9, 30.0 (4s, *t*Bu + Me_{bzac}), 49.4 (br, Sn−C), 97.7, 98.0, 98.1 (3s br, CH_{bzac}), 127.8, 128.8, 131.6, 132.2 (4s br, Ph_{bzac}), 183.8 (s, CO_{bzac}), 193.8 (s, CO_{bzac}). ^{119}Sn NMR ($CDCl_3$, 295 K): δ = −485.6. ^{119}Sn NMR ($CDCl_3$, 218 K): δ = −485.4 [1], −486.5 [2]. Λм (10^{-3} м) = 0.2.

Bis[1-phenylbutane-1,3-dionato]dicyclohexyltin(IV) [(bzac)$_2$SnCy$_2$] (5): Yield 56%. m.p. 150 °C (dec). $C_{32}H_{40}O_4Sn$: calcd. C 63.28, H 6.64; found C 63.36, H 6.71. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1593 s, 1575 m, 1560 m, 1558 vs, ν(C=O) + ν(C=C); 590 m, 580 m, 564 m, 546 m, 530 sh, 514 m, 500 m, 489 m, 474 m, 450 w, 440 m, 432 m, 419 m, 373 m, 328 m, ν(Sn−C) + ν(Sn−O) + δ(Ph). ^1H NMR ($CDCl_3$, 295 K): δ = 1.3 (br, 84 H, Sn-Cy), 1.6 (br, 10 H, Sn-Cy), 2.0 [2], 2.1 [1] (s br, 2 H, Sn-Cy), 6.0 [2], 6.11 [1], 6.13 [1], 6.20 [2] (s br, 2 H, CH_{bzac}), 7.5 (m, 6 H, Ph_{bzac}), 7.9 (d br, 4 H, Ph_{bzac}). ^{119}Sn NMR ($CDCl_3$, 295 K): δ = −466 [1], −467 [1] −468 [2]. Λм (10^{-3} м) = 0.3.

Bis[1-phenylbutane-1,3-dionato]diphenyltin(IV) [(bzac)$_2$SnPh$_2$] (6): Yield 74%. m.p. 130−132 °C. $C_{32}H_{28}O_4Sn$: calcd. C 64.57, H 4.74;

found C 64.34, H 4.66. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1592 s, 1564 vs, 1553 vs, ν(C=O) + ν(C=C); 580 s, 524 m, 455 s, 450 s, 430 m, 402 w, ν(Sn−O) + δ(bzac); 309 m, 267 vs, 253 s, ν(Sn−C); 237 m, 230, 223 m. ^{1}H NMR ($CDCl_3$, 295 K): δ = 2.12 [10], 2.16 [1], 2.19 [1] (s, 6 H, Me_{bzac}), 6.10 [5]. 6.17 [1] (s, 6 H, CH_{bzac}), 6.8−7.2 (m), 7.30−7.45 (m), 7.75 (dd), 7.90 (d, 20 H, Ph_{bzac} + Sn-Ph). ^{1}H NMR ($CDCl_3$, 325 K): δ = 2.12 (s br, 6 H, Me_{bzac}), 6.09 (s, 2 H, CH_{bzac}), 6.8−7.2 (m), 7.30−7.45 (m), 7.72 (d), 7.86 (d, 20 H, Ph_{bzac} + Sn-Ph). ^{1}H NMR ($CDCl_3$, 218 K): δ = 2.03 [10], 2.12 [10], 2.21 [1], 2.22 [10], 2.23 [12], 2.26 [2] (s, 6 H, Me_{bzac}), 6.14 [5]. 6.18 [4], 6.21 [4], 6.24 [4] (s, 6 H, CH_{bzac}), 6.9−8.0 (m, 20 H, Ph_{bzac} + Sn-Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ = 26.4, 27.5, 28.6, 28.8 (4s, Me_{bzac}), 96.7, 97.8, 98.1 (3s br, CH_{bzac}), 127.0, 127.6, 127.9, 128.3, 128.5, 131.7, 132.3, 135.5, 135.9, 138.0, 148.5, 150.2 (s br, Ph_{bzac}), 184.0 (s, CO_{bzac}), 194.2, 194.6 (s, CO_{bzac}). ^{119}Sn NMR ($CDCl_3$, 296 K): δ = −509.9 [4], −510.5 [1]. ^{119}Sn NMR ($CDCl_3$, 218 K): δ = −503.8 [3], −504.3 [2], −504.7 [6]. ^{119}Sn NMR ($CDCl_3$, 325 K): δ = −511.2. Λм (10^{-3} м) = 0.4.

X-ray Crystallographic Studies

The structure was solved using direct methods with SIR.[46] Psi-scan showed no absorption anisotropy.

Crystals were obtained directly from the reaction mixture. Crystal data were collected with a Syntex P21 diffractometer. A diffraction quality crystal was selected and mounted on the diffractometer. The search subroutine showed orthorhombic axes and symmetry was the orthorhombic confirmed by taking rotation photograph about the 3 axes. Psi-scan showed no absorption anisotropy. Cell volume implies 8 molecules/cell and systematic extinctions indicated 2 possible space groups, *Pnma* and $Pna2_1$ (Table 3). Attempts to solve the structure in the centrosymmetric *Pnma* space group (which implies one molecule/asymmetric unit) failed, whereas using $Pna2_1$ space group (corresponding to 2 molecules in the asymmetric unit) allowed structure resolution with SIR.[46] The two independent molecules in the asymmetric unit show the [*x*,*y*,*z*] coordinates of corresponding atoms (for instance atoms named Sn and Sn2) add to [1.24, 0.02, 1.49]. Therefore an approximate local inversion point [0.625, 0.0, 0.75] relating the two independent molecules exists. Figure S1 depicts the cell packing approximately along axis *b*.

Table 3. Summary of crystal data

Empirical formula	$C_{28}H_{36}O_4Sn$
Formula mass	555.28
Cryst habit	hexagonal plate
Cryst size (mm)	0.40 × 0.25 × 0.10
Cryst system	orthorhombic
Space group	$Pna2_1$ (no. 33)
Crystal color	colorless
a (Å)	18.156(4)
b (Å)	10.012(2)
c (Å)	29.739(7)
V (Å^3)	5406(3)
Z	8
T (K)	298
$D_{calcd.}$ (Mg m^{-3})	1.365
$2\theta_{max}$ (°)	56
μ (mm^{-1})	0.983
Wavelength (Å) (graph monchr)	Mo-K_α
Scan speed (°min^{-1})	2
Transmission factors	0.99−1.00
Scan range (°)	1.2
Measured reflections	8713
Unique reflections	8039
Refined reflections $F>1.5\sigma(F)$	5773
Refined parameters	595
R,[a] R_w	0.043, 0.056
S[b]	0.82

[a] $R(F) = \Sigma|(Fo - Fc)|/\Sigma Fo$. [b] $S = [\Sigma\{w(F_0^2 - F_c^2)^2\}/(n - p)]^{0.5}$, *n* = no. of data and *p* = no. of refined parameters.

Each of the 4 pairs of molecules forming the cell is located approximately in each quarter of the picture and darker atoms are closest to the viewer. The four local inversion centers are evident. A further attempt to refine the structure in the *Pnma* space by shifting tin atom coordinates such that the inversion center found in $Pna2_1$ became the origin in *Pnma* was unsuccessful. This could be expected because there is no mirror plane evident (required for *Pnma*) in Figure S1; also the existence of only 4 inversion centers is coherent with 4 positions in $Pna2_1$ whereas a truly *Pnma* space group would require 8 inversion centers. The existence of local (non-crystallographic) centers of symmetry has been discussed by Marsh et al. who found that this feature accounts for at least 70% of all $Pna2_2$ structures explored in the CSD database.[47] Reflections collected: *h* [0−25], *k* [0−14], *l* [0−41]. H atoms riding on attached C atoms at 0.96 Å and hydrogen *B(iso)* fixed. Atomic scattering factors were taken from the literature.[48]

CCDC-171306 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical Studies

All computations were carried out with the MULLIKEN program[49] package on an IBM/SP2 supercomputer. Hartree−Fock and MB3LYPDFT (Density-Functional Theory)[50] methods were used. The basis set used with both methods was 6−31G*. For the tin atom an ECP approximation[51−59] was applied, as implemented within MULLIKEN, using a double zeta basis. The MULLIKEN default convergence criteria were used in computations of energies and geometries.

Supporting Information (see also footnote on the first page of this article): HF and DFT Cartesian coordinates for $(bzac)_2Sn(tBu)_2$ and *anti* $(bzac)_2SnPh_2$, DFT Cartesian coordinates of *syn* $(bzac)_2SnPh_2$.

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