

Syntheses, crystal structures, and quadratic nonlinear optical properties in four “push–pull” diorganotin derivatives

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Abstract

Four “push–pull” diorganotin compounds obtained by reaction of methoxysalicylaldehyde or 4-diethylaminosalicylaldehyde, 2-amino-5-nitrophenol and dibutyltin or diphenyltin oxide are reported. The molecular structures for the diphenyl derivatives, in the solid state, show a tin in a distorted trigonal bipyramid geometry with the oxygen atoms in axial positions and the organic moieties and iminic nitrogen in equatorial ones. For the dibutyl derivative, a dimeric structure was favored due to intermolecular interactions between the tin and oxygen atoms, in this case, the tin atom shows a distorted octahedral geometry. A computational study of the diethyl derivatives constructed from the available dibutyl structure, at DFT level, revealed that the main differences between the solid and gas phases are the geometry around the tin atom and the π -conjugated organic backbone which is nearly planar in the solid state and distorted in the gas phase. The electric field induced second-harmonic (EFISH) of the nonlinear optical (NLO) response for the dibutyl derivatives revealed that the change from boron to tin increases 1.5 times the hyperpolarizabilities (β).

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Keywords: Diorganotin; Multinuclear NMR; X-ray structure; NLO properties; DFT

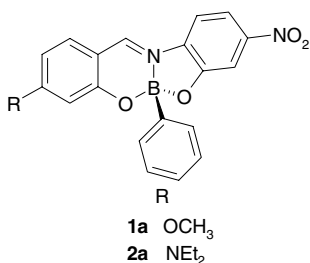
1. Introduction

Recently, diorganotin (IV) complexes have attracted considerable attention due to potential application in homogeneous catalysis [1] and medicinal chemistry, as anti-cancer agents [2]. In particular, diorganotin (IV) complexes have shown higher antitumor activity *in vitro* and *in vivo*, as well as lower toxicity than other well-known drugs like *cis*-platin [3]. An important class of diorganotin (IV) complexes are derived from Schiff bases, in this respect we have reported a series of diorganotin complexes containing aminoacid fragments in which different correlations were found between the spectroscopic data and the X-ray structures [4].

Moreover, there has been considerable interest in the introduction of metal [5] or organometallic [6] fragments in molecules with nonlinear optical properties (NLO) with the aim to improve properties such as: increased thermal stability [7], increased NLO response [8], to introduce chiral moieties which are important for bulk response [9], or to offer the possibility of switching such properties [10]. In a previous paper, we reported a series of “push–pull” boronates (Scheme 1) in which the possibility of switching NLO properties taking advantage of the rotation of the phenyl ring attached to the boron atom was studied using a semiempirical approach [11]. However, the NLO skeleton in the boron derivatives was found to be invariably bent, leading to chromophores with reduced NLO response. In order to overpass this difficulty and to extend the range of metal organic NLO materials, we report in the present investigation on the syntheses of four “push–pull” diorganotin derivatives, their spectroscopic characterization,

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Scheme 1.

X-ray diffraction studies as well as DFT calculations of geometry and NLO response in solution.

2. Results and discussion

2.1. Synthetic aspects

The most common route for the synthesis of this kind of complexes is the reaction of SnX₂R₂ (X = halogen, R = alkyl, phenyl) with a tridentate ligand in the presence of a strong base, a procedure which requires two steps. In a recent paper, a one step synthesis of tin complexes from Schiff bases that involves the reaction of salicylaldehyde, an amino acid and a diorganotin oxide, under reflux of an adequate solvent was reported [4]. In this case the Schiff base is formed *in situ* and then reacted with tin to form the complex. The previous methodology was followed for the preparation of the derivatives reported herein (**1b**, **1c**, **2b** and **2c**). Thus, SnOR₂ (R = Ph, Bu) was reacted with 2-amino-5-nitrophenol and the corresponding salicylaldehyde in acetonitrile under reflux, as shown in Scheme 2. The reactions were considered completed when all the diorganotin oxide was dissolved (3 h for dibutyltin oxide and 48 h for diphenyltin oxide).

2.2. Spectroscopic properties

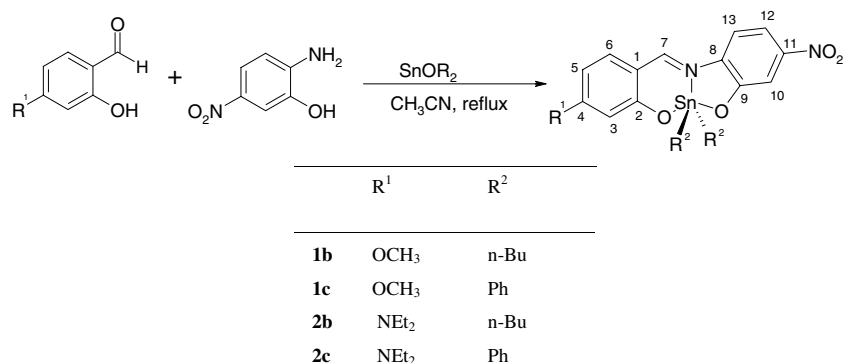
The ¹H NMR data for all compounds is reported in Section 4, the presence of a signal for the iminic proton

(H-7) between 8.29 and 8.58 ppm confirms formation of the product, in general, complexes with a Et₂N group appear at higher frequencies than CH₃O derivatives. The iminic signal shows a ³J(Sn–H) coupling with the ¹¹⁷Sn and ¹¹⁹Sn nuclei in the range between 45 and 60 Hz, this fact is indicative of Sn–N coordination, as shown in the solid state. The individual rings in the complexes were differentiated based on their COSY spectra which allow correlation between the protons in the ring containing the electron-withdrawing group and those of the ring with the electron-donating group. The COSY spectra were necessary because the multiplicity and chemical shifts of some signals are almost identical. In the case of the diphenyl derivatives, correct assignment of the signals to a particular ring is not trivial due to the presence of three different aromatic rings.

An important data that allows to estimate the C–Sn–C angle in solution is the ¹J(¹¹⁹Sn–¹³C), which in the case of dibutyl derivatives shows values of 600 and 621 Hz for **1b** and **2b**, respectively. These values allowed to calculate the C–Sn–C angle using the equation proposed by Holeček et al. [12] (134.8° for **1b** and 136.8° for **2b**). For the diphenyl derivatives, the coupling constants were 1007 Hz for **1c** and 1022 Hz for **2c** while the Ph–Sn–Ph angle were 122.5° and 127.0°, respectively [4].

The ¹¹⁹Sn NMR spectra for the four compounds show a single sharp signal at –176.6 and –178.0 ppm for the dibutyl derivatives (**1b**, **2b**) and –320.6 and –319.3 ppm for the diphenyl derivatives (**1c**, **2c**), characteristic for diorganotin complexes with a pentacoordinated geometry. It is well known also that the ¹¹⁹Sn signals shift to lower frequencies upon substitution of a butyl for a phenyl group [13].

The experimental UV–Vis data for the tin and boron derivatives are summarized in Table 1. In addition to the well-documented shift to higher wavelengths and intensities as the donor–acceptor strength is increased, it is important to notice that an additional red shift and increased intensity is achieved on going from boron to tin. This observation is consistent with an increased planarity in the tin compounds, as discussed in the next section.



Scheme 2.

Table 1

Comparison of the experimental low lying intense transitions (λ_{\max} in nm) and intensities (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) for organotin and boron chromophores

	λ_{\max}	ϵ
1a [11]	452	16 400
1b	464	27 700
1c	459	24 800
2a [11]	475	43 300
2b	486	55 700
2c	477	48 200

2.3. Molecular structure of tin derivatives

An important issue when comparing the NLO response of the tin and boron chromophores is related to the change in molecular geometry. We reported previously that boron-based chromophores are strongly bent as a result of the tetrahedral coordination sphere around the boron atom, leading to reduced NLO responses when compared to the related and well-known stilbene-based chromophores. In the case of the diphenyl tin chromophores, the tin atom shows a distorted trigonal bipyramid geometry, the axial positions being occupied by the oxygen atoms and the equatorial ones by organic moieties and the iminic nitrogen, in the solid state. The distances and angles around the tin atom are shown in Table 2. The distances are comparable with those previously reported in similar complexes [14]. However, in dibutyl derivative **1b**, the compound is a dimer with Sn–O intermolecular interactions. This fact modifies the coordination around the tin atom which show a distorted octahedral geometry with Sn–O interaction distances of 3.033(4) Å. The dimeric structure is assembled through the formation of a four-membered Sn–O(2)–Sn–O(2) ring.

Table 2

Selected bond lengths (Å) and angles (°) around the tin atom for **1b**, **1c**, **2c** (e.s.d's are in parentheses)

	1b	1c	2c
C(14)–Sn(1)	2.122(4)	2.118(3)	2.125(6)
C(14a)–Sn(1)	2.146(5)	2.110(3)	2.119(6)
N(1)–Sn(1)	2.208(3)	2.180(2)	2.155(5)
O(2)–Sn(1)	2.119(3)	2.0943(18)	2.106(4)
O(1)–Sn(1)	2.137(3)	2.0879(19)	2.079(4)
O(2)–Sn(1)–C(14)	95.76(15)	96.03(9)	93.4(2)
O(2)–Sn(1)–O(1)	156.29(12)	160.66(7)	162.21(16)
C(14)–Sn(1)–O(1)	86.86(15)	94.53(10)	93.4(2)
O(2)–Sn(1)–C(14a)	96.30(19)	95.32(9)	94.6(2)
C(14)–Sn(1)–C(14a)	140.8(2)	122.01(10)	125.7(2)
O(1)–Sn(1)–C(14a)	96.4(2)	92.74(9)	94.7(2)
O(2)–Sn(1)–N(1)	76.03(10)	77.24(7)	76.84(18)
C(14)–Sn(1)–N(1)	115.12(13)	114.35(9)	123.64(19)
O(1)–Sn(1)–N(1)	81.52(11)	83.66(8)	85.71(18)
C(14a)–Sn(1)–N(1)	104.00(18)	114.35(9)	110.43(19)

The change in coordination geometry when the boron atom is substituted by tin is indicative that the π -conjugated organic backbone is changed from a bent system in boron chromophores to nearly planar in the tin derivatives, as evidenced by the crystal structures of **1b**, **1c** and **2c** (Figs. 1–3). This increased planarity would be expected to increase considerably the intramolecular charge transfer properties, and hence the hyperpolarizability. However, recent combined theoretical-crystallographic studies have shown differences in conformational and geometrical parameters for diorganotin systems in the solid and gas phases which can be attributed to crystal packing effects [15]. This observation raises the issue of whether the planarity of the molecule is due to packing factors or to an intrinsic stability of the molecular geometry. To clarify this question, a theoretical study at the DFT level was performed. Initially calculations were run on the butyl derivative, however, they showed no minimum. Thus, the gas-phase structures of the analogous diethyl derivatives constructed from the available X-ray data for the dibutyl complex were calculated within the framework of DFT theory, to avoid the effect of the environment. An important difference between the solid and gas phase structures is a sizeable reduction of the C–Sn–C angle, as illustrated in Fig. 4. This difference is consistent with the presence of intermolecular Sn–O interactions with a neighbouring molecule, which pushes the hydrocarbon chains apart from one another. It is important to notice that the angles in the gas phase are significantly smaller than those based on coupling constant values determined in solution. More importantly, the crystal struc-

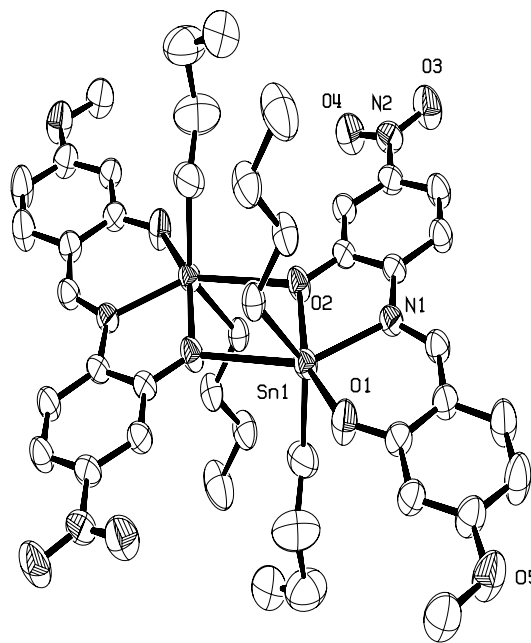


Fig. 1. Dimeric structure of **1b**. H atoms were omitted for clarity (thermal ellipsoids at 30%).

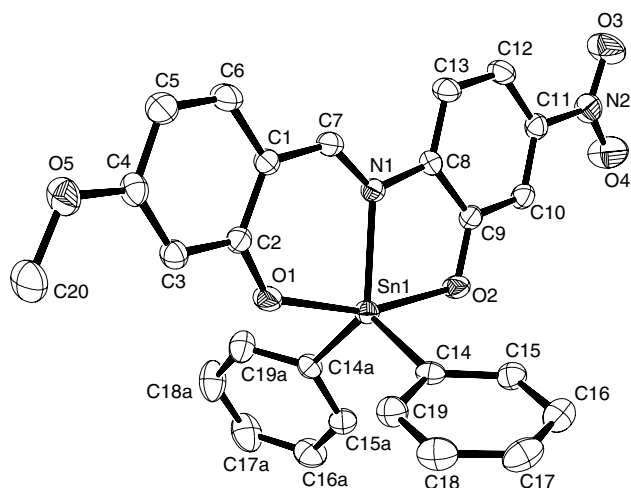


Fig. 2. Molecular structure of **1c**. H atoms were omitted for clarity (thermal ellipsoids at 30%).

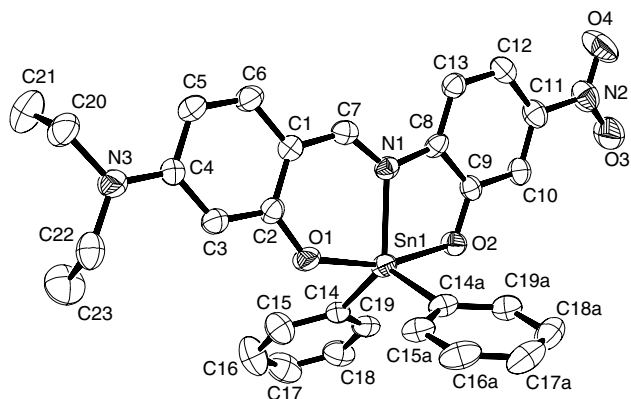


Fig. 3. Molecular structure of **2c**. H atoms and one disorder molecule of CHCl_3 were omitted for clarity (thermal ellipsoids at 30%).

ture shows an angle of 8.1° between the methoxyphenyl and the nitrophenyl moieties, as a result of a nearly planar geometry. By comparison, the calculated structures reveal angles of 22.8° and 22.0° between the phenyl rings in **1b** and **2b**, respectively. Therefore, even if the planarity is partially explained by crystal packing effects, the large torsion angle observed in the boron derivatives is undoubtedly reduced in the tin analogues. This tendency will favour a better charge transfer delocalization,

which is expected to red shift the electronic transitions, and finally to enhance the NLO response.

2.4. NLO response

Analysis of the spectroscopic data, in particular the UV and the molecular structures, reveals that one can expect almost the same NLO response for dibutyl or diphenyl-based chromophores. Since the dibutyl derivatives are more soluble in common organic solvents they were selected for the NLO studies. The electric field induced second-harmonic (EFISH) data for **1b** and **2b** are summarized in Table 3 and compared to those of the boron derivatives previously investigated. Before discussing the NLO response for both families of organometallic chromophores, it is important to observe that the agreement between experimental and calculated data is satisfactory, within the formalism of the DFT method. On the other hand, the ZINDO (Zerner intermediate neglect of differential overlap) method [16], which has been successfully used in connection with the sum-over-state (SOS) formalism [17] for the description of numerous organometallic chromophores cannot be employed in the present case since tin is not parametrized in the ZINDO releases commercially available. As a major consequence, it is not possible to establish precisely the relationship between the NLO responses, and the optical spectra for the tin derivatives. Nevertheless, the effect of the experimental red shift and increased intensity evidenced on the electronic spectra on going from boron to tin derivatives may tentatively be analysed within the framework of the two-level quantum description of the NLO response.

Table 3

Experimental EFISH data (β in $\text{cm}^5 \text{esu}^{-1}$ and μ in D) for **1b**, **2b** recorded at $1.907 \mu\text{m}$, and DFT calculated values

	Experimental data		DFT calculated values	
	β	μ	β	μ
1a [11]	27.0	10.2	40.2	
1b	48.9	10.2		9.64
2a [11]	46.4	13.6	73.8	
2b	63.5	12.6		12.8

The NLO responses of the boron-based chromophores **1a**, **2a** are shown for reference.

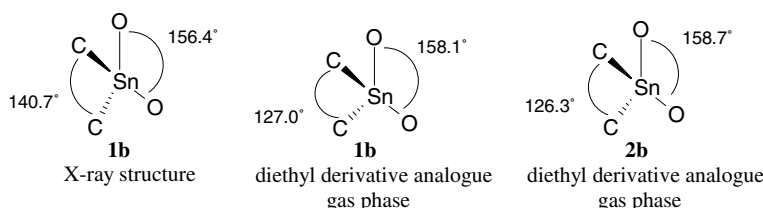


Fig. 4. Gas-phase coordination sphere of the tin atom compared to that of the available crystal structure data.

In “push–pull” stilbene-based chromophores, a simple two-level model is a widely used guideline, this assumes that the low-lying electronic transition is responsible for most of the NLO response. In this model, β is described in terms of a ground and a first excited-state having a charge-transfer character and related to the energy of the optical transition (E), its oscillator strength (f), and the difference between the ground and excited state dipole moment ($\Delta\mu$) through the relation [18]

$$\beta_{zzz} = \frac{3e^2\hbar^2 f(\Delta\mu)_z}{2mE^3} \frac{E^4}{(E^2 - (2\hbar\omega)^2)(E^2 - (\hbar\omega)^2)}. \quad (1)$$

In this equation, $\hbar\omega$ is the energy of the incident laser beam. Owing to the pseudo-stilbene type of the organic skeleton, and “push–pull” character of the molecules, we will assume that, to a large extent, the two-level model can lead to a rationale for the origin of the NLO response. For the methoxy-containing chromophores, the red shift and increased intensity obtained on going from boron to tin (Table 1) leads to a β value 1.8 time larger for **1b** than for the parent boron derivative, through the estimation provided by Eq. (1). In the case of **2b**, there is an enhancement of 1.4 times. Both estimations are fully consistent with the experimentally determined β value summarized in Table 3, providing a satisfactory understanding for the modulation of the NLO properties in these organometallic NLO chromophores.

3. Conclusion

The work described herein shows that this kind of “push–pull” diorganotin complexes can be easily prepared and have better NLO properties than the boron derivatives previously reported. The increase in β is in the order of 1.5 times and can be attributed to the fact that the tin derivatives are more planar than the corresponding boron complexes, as established by X-ray diffraction studies. However, crystal packing effects are partially responsible for this planarity, as shown by DFT calculations, which revealed that in the gas phase the structure of the organic π backbone is less planar than in the solid state. Moreover, in the solid state, the geometry of the tin atom in the dibutyl derivatives is affected by neighboring molecules due to formation of Sn–O intermolecular interaction. These interactions are not present in the gas phase and the most important consequence is the modification in the C–Sn–C angle, which is close to 13°. In our opinion, the fact that diethyl derivatives were used for geometry optimizations instead of the dibutyl derivative, which did not show a minimum, should have no effect in the planarity of the molecule in the gas phase or the geometry around the tin

atom. The results show that metal organic tin derivatives, which up to now have not been investigated that much in molecular electronics might be envisioned as good candidates for NLO due to excellent planarity. In this respect, chiral tin-based Schiff bases complexes have recently been reported [4]. This route could allow to engineer tin-based chromophores in various acentric environments, which is an requisite for a bulk NLO response.

4. Experimental

All starting materials were commercially available. Solvents were used without further purification. Melting points were recorded on a Gallenkamp MFB-595 apparatus and are uncorrected. Infrared spectra were measured on a Perkin–Elmer 16F-PC FT-IR spectrometer. ^1H , ^{119}Sn and ^{13}C -NMR spectra were recorded on a Bruker avance DPX 300 spectrometer. Chemical shifts (ppm) are relative to $(\text{CH}_3)_4\text{Si}$ for ^1H and ^{13}C and to $\text{Sn}(\text{CH}_3)_4$ for ^{119}Sn . UV spectra were obtained with a Perkin–Elmer Lambda 12 UV/Vis spectrophotometer. Mass spectra were recorded on a HP 5989A spectrometer. Elemental analyses were carried out on a Thermo Finnigan Flash 1112 elemental microanalyzer.

4.1. Syntheses

The following procedure was used in the syntheses of the four compounds studied herein. Equimolecular amounts of 4-diethylaminosalicylaldehyde (or 4-methoxysalicylaldehyde), 2-amino-5-nitrophenol and dibutyltin oxide (or diphenyltin oxide) were refluxed in acetonitrile for 3 h for the dibutyl derivatives and 48 h for the diphenyl derivatives. The solvent was removed under vacuo and the products recrystallized from chloroform–hexane to yield the products.

4.1.1. 2,2-Di-*n*-butyl-6-aza-1,3-dioxo-11-methoxy-16-nitro-2-stannabenzocyclononene (**1b**)

Compound **1b** was obtained from 0.30 g (2.0 mmol) of methoxysalicylaldehyde, 0.30 g (2.0 mmol) of 2-amino-5-nitrophenol and 0.49 g (2.0 mmol) of dibutyltin oxide. The product was obtained as a red solid (0.90 g, 1.7 mmol), m.p. 102–103 °C, yield: 86%. ^1H NMR (300 MHz, CDCl_3): δ , 0.86 (t, $J = 7.3$, 6H, H-17), 1.32 (sx, $J = 7.3$, 4H, H-16), 1.53 (m, 4H, H-14), 1.67 (m, 4H, H-15), 3.86 (s, 3H, OCH_3), 6.23 (d, $J = 2.4$, 1H, H-3), 6.39 (dd, $J = 2.4$, 8.9, 1H, H-5), 7.17 (d, $J = 8.9$, 1H, H-6), 7.33 (d, $J = 8.9$, 1H, H-13), 7.56 (dd, $J = 2.5$, 8.9, 1H, H-12), 7.62 (d, $J = 2.5$, 1H, H-10), 8.56 (s, $^3J^{119/117}\text{Sn}-^1\text{H} = 45.3$ Hz, 1H, H-7); ^{13}C NMR (75.4 MHz, CDCl_3): δ , 13.6 (C-17), 22.3 ($^1J^{119}\text{Sn}-^{13}\text{C} = 600.0$, C-14), 26.6 (C-16), 26.9 (C-15), 55.7 (OCH_3), 103.5 (C-3), 109.5 (C-5), 111.4 (C-12), 112.5 (C-1), 112.6 (C-10), 114.2 (C-13),

137.5 (C-6), 138.4 (C-11), 147.5 (C-8), 159.0 (C-9), 162.6 (C-7), 168.9 (C-4), 173.7 (C-2); ^{119}Sn NMR (111.9 MHz, CDCl_3): δ , -176.6 ppm; IR (KBr): ν , 2956, 2920, 1614, (C=N), 1588, 1564, 1514, 1486, 1308, 1256, 1210, 1174; MS m/z (%): 520 (58) [M^+ , (^{120}Sn)], 518 (42) [M^+ , (^{118}Sn)], 516 (23) [M^+ , (^{116}Sn)], 463 (100), 461 (86), 459 (48), 407 (74), 405 (65), 403 (40), 361 (8), 359 (7), 357 (5). Elemental Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_5\text{Sn}$: C, 50.90; H, 5.44; N, 5.40. Found: C, 51.08; H, 5.44; N, 5.63%.

4.1.2. 2,2-Di-*n*-butyl-6-aza-1,3-dioxo-11-diethylamino-16-nitro-2-stannabenzocyclononene (**2b**)

Compound **2b** was obtained from 0.38 g (2.0 mmol) of 4-diethylaminosalicylaldehyde, 0.30 g (2.0 mmol) of 2-amino-5-nitrophenol and 0.49 g (2.0 mmol) of dibutyltin oxide. The product was obtained as a red solid (1.00 g, 1.9 mmol), m.p. 127–129 °C, yield: 90%. ^1H NMR (300 MHz, CDCl_3): δ , 0.84 (t, $J=7.3$, 6H, H-17), 1.23 (t, $J=7.3$, 6H, CH_3), 1.33 (sx, $J=7.3$, 4H, H-16), 1.47 (m, 4H, H-14), 1.64 (m, 4H, H-15), 3.42 (q, 4H, NCH_2), 5.90 (d, $J=2.4$, 1H, H-3), 6.24 (dd, $J=2.4$, 9.0, 1H, H-5), 7.03 (d, $J=9.0$, 1H, H-6), 7.23 (d, $J=8.9$, 1H, H-13), 7.53 (dd, $J=2.5$, 8.9, 1H, H-12), 7.58 (d, $J=2.5$, 1H, H-10), 8.30 (s, $^3J^{119/117}\text{Sn}-^1\text{H}=48.7$, 1H, H-7); ^{13}C NMR (75.4 MHz, CDCl_3): δ , 13.1 (CH_3), 13.8 (C-17), 22.1 ($^1J^{119}\text{Sn}-^{13}\text{C}=621.7$, C-14), 26.8 (C-16), 27.1 (C-15), 45.1 (NCH_2), 100.3 (C-3), 106.1 (C-5), 110.2 (C-12), 111.6 (C-10), 111.9 (C-1), 113.3 (C-13), 138.4 (C-6), 139.8 (C-11), 146.5 (C-8), 156.1 (C-9), 158.6 (C-4), 159.3 (C-7), 172.2 (C-2); ^{119}Sn NMR (111.9 MHz, CDCl_3): δ , -178.0 ppm; IR (KBr): ν , 2956, 2920, 2870, 1614 (C=N), 1586, 1560, 1492, 1306, 1142, 828; MS m/z (%): 561 (41) [M^+ , (^{120}Sn)], 559 (30) [M^+ , (^{118}Sn)], 557 (17) [M^+ , (^{116}Sn)], 504 (81), 502 (60), 500 (32), 447 (100), 445 (74), 443 (38). Elemental Anal. Calc. for $\text{C}_{25}\text{H}_{35}\text{N}_3\text{O}_4\text{Sn}$: C, 53.60; H, 6.30; N, 7.50. Found: C, 53.30; H, 6.17; N, 7.95%.

4.1.3. 2,2-Diphenyl-6-aza-1,3-dioxo-11-methoxy-16-nitro-2-stannabenzocyclononene (**1c**)

Compound **1c** was obtained from 0.30 g (2.0 mmol) of methoxysalicylaldehyde, 0.30 g (2.0 mmol) of 2-amino-5-nitrophenol and 0.56 g (2.0 mmol) of diphenyltin oxide. The product was obtained as orange solid (1.06 g, 1.7 mmol), m.p. 259–262 °C, yield: 94%. ^1H NMR (300 MHz, CDCl_3): δ , 3.96 (s, 3H, OCH_3), 6.45 (dd, $J=2.4$, 8.9, 1H, H-5), 6.56 (d, $J=2.4$, 1H, H-3), 7.17 (d, $J=8.9$, 1H, H-6), 7.34 (d, $J=9.0$, 1H, H-13), 7.43–7.48 (m, 6H, H_{meta} , H_{para}), 7.58 (dd, $J=2.6$, 9.0, 1H, H-12), 7.89–7.94 (m, 5H, H-10, H_{ortho}), 8.58 (s, $^3J^{119/117}\text{Sn}-^1\text{H}=56.2$, 1H, H-7); ^{13}C NMR (75.4 MHz, CDCl_3): δ , 56.1 (OCH_3), 104.3 (C-3), 110.2 (C-5), 112.3 (C-12), 112.9 (C-1), 113.6 (C-10), 114.5 (C-13), 129.3 (C_{meta}), 131.07 (C_{para}), 136.8 (C_{ortho}), 137.7 (C-11), 137.9 (C-6), 139.3 ($^1J^{119}\text{Sn}-^{13}\text{C}=1007.0$, C_{ipso}), 147.8 (C-8), 158.5 (C-9), 162.3 (C-7), 169.3 (C-4), 173.8 (C-2); ^{119}Sn NMR (111.9 MHz,

CDCl_3): δ , -320.6 ppm; IR (KBr): ν , 3051, 1733, 1613 (C=N), 1514, 1487, 1438, 1410, 1380, 1334, 1305, 1075, 863; MS m/z (%): 560 (94) [M^+ , (^{120}Sn)], 558 (71) [M^+ , (^{118}Sn)], 556 (40) [M^+ , (^{116}Sn)], 483 (100), 437 (15), 406 (26), 255 (22), 240 (23), 212 (63). Elemental Anal. Calc. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_5\text{Sn}$: C, 55.89; H, 3.60; N, 5.01. Found: C, 56.07; H, 3.60; N, 5.10%.

4.1.4. 2,2-Diphenyl-6-aza-1,3-dioxo-11-diethylamino-16-nitro-2-stannabenzocyclononene (**2c**)

Compound **2c** was obtained from 0.38 g (2.0 mmol) of diethylaminosalicylaldehyde, 0.30 g (2.0 mmol) of 2-amino-5-nitrophenol and 0.56 g (2.0 mmol) of diphenyltin oxide. The product was obtained as a red solid (0.98 g, 1.6 mmol), m.p. 281–282 °C, yield: 82%. ^1H NMR (300 MHz): δ , 1.31 (t, $J=7.0$, 6H, CH_3), 3.50 (q, $J=7.0$, 4H, CH_2), 6.21 (d, $J=2.2$, 1H, H-3), 6.26 (dd, $J=2.2$, 9.2, 1H, H-5), 7.02 (d, $J=9.2$, 1H, H-6), 7.23 (d, $J=8.8$, 1H, H-13), 7.36–7.44 (m, 6H, H_{meta} , H_{para}), 7.55 (dd, $J=2.2$, 8.8, 1H, H-12), 7.84 (d, $J=2.2$, 1H, H-10), 7.91–7.93 (m, 4H, H_{ortho}), 8.29 (s, $^3J^{119/117}\text{Sn}-^1\text{H}=59.7$, 1H, H-7); ^{13}C NMR (75.4 MHz, CDCl_3): δ , 13.3 (CH_3), 45.5 (CH_2), 100.8 (C-3), 106.7 (C-5), 110.4 (C-1), 112.4 (C-12), 112.7 (C-10), 113.3 (C-13), 129.1 (C_{meta}), 130.7 (C_{para}), 136.9 (C_{ortho}), 138.7 (C-6), 139.3 ($^1J^{119}\text{Sn}-^{13}\text{C}=1022.1$, C_{ipso}), 140.4 (C-11), 146.5 (C-8), 156.6 (C-9), 157.9 (C-4), 158.9 (C-7), 172.4 (C-2); ^{119}Sn NMR (111.9 MHz, CDCl_3): δ , -319.3; IR (KBr): ν , 3052, 2972, 2927, 1615 (C=N), 1588, 1558, 1491, 1432, 1328, 1242, 1070, 732; MS m/z (%): 601 (100) [M^+ , (^{120}Sn)], 599 (77) [M^+ , (^{118}Sn)], 597 (41) [M^+ , (^{116}Sn)], 586 (21), 524 (53), 432 (27), 312 (16), 253 (42), 209 (42); Elemental Anal. Calc. for $\text{C}_{29}\text{H}_{27}\text{N}_3\text{O}_4\text{Sn}$: C, 58.02; H, 4.53; N, 7.00. Found: C, 57.73; H, 4.51; N, 6.85%.

4.2. X-ray data collection and structure determination

X-ray diffraction studies were determined on an Enraf Nonius-CAD4 area detector diffractometer (Mo $\text{K}\alpha$; $\lambda = 0.71073$ Å, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan mode) the crystals were mounted in LIND-EMAN tubes. Absorption correction was performed with SHELX-A procedure [19]. Corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-97) for structure solution and SHELXL-97 ver. 34 for refinement and data output [19] were applied using the WIN-GX program set [20], the corresponding images were prepared with the ORTEP 3 program [21]. Hydrogen atoms were determined by difference Fourier maps and systematically model situation and calculation, as well as one overall isotropic thermal parameter for refinement, the other nonhydrogen atoms were refined anisotropically. Crystallographic data for the four diorganotin complexes are summarized in Table 4.

Table 4
Crystal data for **1b**, **1c** and **2c**

	1b	1c	2c
Chemical formula	C ₂₂ H ₂₈ N ₂ O ₅ Sn	C ₂₆ H ₂₀ N ₂ O ₅ Sn	C ₂₉ H ₂₇ N ₃ O ₄ Sn · CHCl ₃
Formula weight	519.15	559.15	719.59
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>a</i>	<i>Pbca</i>
<i>a</i> (Å)	10.5496(12)	8.79270(10)	13.6099(2)
<i>b</i> (Å)	10.7909(18)	25.8907(4)	16.1739(3)
<i>c</i> (Å)	11.535(2)	10.1291(2)	28.1345(6)
α (°)	81.477(15)	90	90
β (°)	74.103(12)	91.7840(10)	90
γ (°)	63.567(11)	90	90
<i>V</i> (Å ³)	1130.4(3)	2304.76(6)	6193.1(2)
<i>T</i> (K)	293(2)	293(2)	293(2)
<i>Z</i>	2	4	8
Collected reflections	4195	5224	11 144
Independent reflections	3693	5224	6066
<i>R</i> ^a	0.0367	0.0322	0.0637
<i>R</i> _w ^b	0.0413	0.0475	0.1913
Variables	323	388	407

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b R_w(F_o)^2 = [\sum_w (F_o^2 - F_c^2)^2 / \sum_w F_o^4]^{1/2}.$$

4.3. Computational details

All geometries for diethyl analogues of **1b** and **2b** were fully optimized using the GAUSSIAN-98 program package within the framework of DFT at the B3PW91/6-31G*/LANL2DZ(Sn) level [22], in which relativistic effects are included for Sn. In addition, we checked that the geometry calculated using an all electron basis set for Sn (B2PW91/6-31G*/DZVP(Sn)) [23] is very similar to the one obtained with the pseudo-potential basis set LANL2DZ(Sn). The starting point for DFT calculations was derived from the crystal structure of **1b**, by substituting butyl moieties by ethyl groups, and eventually MeO– by Me₂N–. Vibrational analysis was performed at the same level in order to establish the presence of a minimum on the potential energy surface. Static hyperpolarizabilities (β_0) of the calculated structures were evaluated at the B3PW91/6-31G*/LANL2DZ(Sn) level, using the numerical finite field procedures included in GAUSSIAN-98. A field strength (*E*) of 0.001 au was chosen for the calculation of β_0 .

4.4. NLO properties

The principle of the EFISH technique is reported elsewhere [24]. The data were recorded using a picosecond Nd:YAG pulsed (10 Hz) laser operating at $\lambda = 1.064 \mu\text{m}$. The outgoing Stokes-shifted radiation at 1.907 μm generated by Raman effect in a hydrogen cell (1 m long, 50 atm.) was used as the fundamental beam for second harmonic generation. The compounds were dissolved in chloroform at various concentration and the centrosymmetry of the solution was broken by

dipolar orientation with a high voltage pulse (6 kV) synchronized with the laser pulse. The SHG signal was selected through a suitable interference filter, detected by a photomultiplier, and recorded on an ultrafast Tektronic TDS 620 B oscilloscope. With the NLO response being induced by dipolar orientation of the chromophores, the EFISH signal is therefore proportional to the dipole moment (μ) and to β_{vec} , the vector component of β along the dipole moment direction. Due to the pseudo-one-dimensional character of the charge transfer process, β and μ are nearly parallel and, therefore β and β_{vec} are assumed to be equivalent. The dipole moments were measured independently by a classical method based on the Guggenheim theory [25].

5. Supplementary material

Crystallographic data for **1b**, **1c** and **2c** have been deposited at the Cambridge Crystallographic Data Centre with deposition numbers CCDC 229405 for **1b**, CCDC 229406 for **1c** and CCDC 229407 for **2c**, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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