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DFT Calculations of the Electric Field Gradient at the Tin Nucleus as a Support of Structural Interpretation by ^{119}Sn Mössbauer Spectroscopy

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Abstract: DFT calculations, using an all-electron basis set and with full geometry optimization, were performed on 34 Sn^{II} and Sn^{IV} compounds of known structure and ^{119}Sn Mössbauer parameters, to obtain the theoretical values of the electric field gradient components, V_{xx}, V_{yy}, and V_{zz}, at the tin nucleus. These were used to determine the quantity $V=V_{zz}\left[1+\frac{1}{3}\left(\frac{V_{xx}-V_{yy}}{V_{zz}}\right)^2\right]^{1/2}$, for each investigated compound, which is related to the quadrupole splitting (ΔE) parameter according to $\Delta E={}^1\!/_2 eQV$, where e is the electronic charge and Q is the quadrupole moment of the tin nucleus. The linear fitting of the correlation plot of the experimental ΔE, versus the corresponding calculated V values, produced a slope that is equal to 0.93 ± 0.03 and a correlation coefficient $R=0.982$. The value of Q obtained, 15.2 ± 4.4 fm^2, is in agreement with that previously experimentally determined or calculated by analogous procedures. The calculation method is able to establish the sign of the electric field gradient component V_{zz}, in agreement with the sign of ΔE determined experimentally by Mössbauer–Zeeman spectroscopy. The calculated structural parameters are in good agreement with the corresponding experimental data, determined by X-ray crystallography in the solid state, with average structural deviations of about 3% for bond lengths and angles in the tin environment. Calculated values of ΔE were obtained from the calibration fitting constant and from the values of V. By comparing experimental and calculated ΔE parameters, the structure assignment of configurational isomers was successful in two test cases, in agreement with the experimental X-ray crystallographic structures. These results indicate that the method can be used as a tool to support the routine structure interpretation of tin compounds by ^{119}Sn Mössbauer spectroscopy.

Keywords: density functional calculations · Mössbauer spectroscopy · nuclear quadrupole splitting · tin

Introduction

Mössbauer spectroscopy[1] is a valuable tool to obtain information about the valency state and the symmetry of the local environment of particular isotopes in solid-state systems, and involves nuclear transitions occurring in the gamma rays energy range. Specifically, in ^{119}Sn Mössbauer spectroscopy, the value of the isomer shift (IS) parameter, which is related to the electron density at the tin nucleus and is observed in clearly separated energy ranges for Sn^{II} and Sn^{IV}, is normally used as a fingerprint criterion to assign the oxidation state of the metal atom. Moreover, information about the geometry of tin compounds can be extracted from the nuclear quadrupole splitting (ΔE) parameter, which is related to the geometrical environment of tin.[2] In particular, ΔE is dependent on the configuration of tin in organotin(IV) compounds,[2] and is related to the electronic properties of the organic groups.[3]

The nuclear quadrupole splitting indicates the presence at the nucleus of an electric field gradient (EFG), according to Equation (1),[1–9] where $\eta=(V_{xx}-V_{yy})/V_{zz}$ is the so-called asymmetry parameter, e is the electronic charge, and Q is the quadrupole moment of the first excited nuclear state that can be experimentally determined.

$$\Delta E = {}^1\!/_2 eQV_{zz}(1 + {}^1\!/_3\eta^2)^{1/2} = {}^1\!/_2 eQV \qquad (1)$$

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V_{xx}, V_{yy}, and V_{zz} are the diagonal components of the diagonalized EFG tensor matrix, chosen such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.[1–9]

The magnitude and the sign of ΔE, which depend upon the components of the diagonalized EFG tensor matrix, mainly the one along the z axis of the molecule (V_{zz}), are influenced by the stereochemistry of the considered compound and by the nature of the tin–ligand bonding.[1–3]

Information about the hyperfine parameters IS and ΔE can be combined with data obtained from computational chemistry. In fact, quantum-chemical methods, nowadays implemented in commercial packages, provide support for structure interpretation of data obtained by most of the spectroscopic techniques.[10a] In particular, DFT methods that partly take into account electron correlation contributions are able to furnish molecular structures in good agreement with the corresponding experimental data, even for large-size systems at reasonable computational effort.[10b]

Previous theoretical studies[4–9] have dealt with the calculation of the EFG and of the electron density at the tin nucleus, to produce linear correlation plots with the experimental ΔE and IS values, respectively, providing a physical interpretation of the ^{119}Sn Mössbauer spectroscopy parameters. In particular, the calculation of 1) the EFG components and of 2) the electron density at the tin nucleus permitted the theoretical evaluation of 1) the nuclear quadrupole moment of tin and 2) the fractional change of the nuclear charge radius of tin following the nuclear excitation, respectively. However, only simple model systems, such as metallic tin and tin alloys, or small molecules, such as halides, chalcogenides, and methyltin compounds, have been considered so far,[4–9] and semiempirical[4–8] or ab initio methods, the latter with minimal basis sets,[9] have been used.

The qualitative interpretation of ^{119}Sn Mössbauer spectra of organotin(IV) compounds, regardless of their size and structural complexity, has been made possible up to now by the empirical point charge method. This has been used successfully in the assignment of coordination number and configuration of the tin environment, and also provides the possibility to study the interaction of organotin(IV) with biological macromolecules.[2] Following this approach, for a given coordination geometry, each coordinated ligand atom contributed to ΔE, in agreement with Equation (1), by way of a partial quadrupole splitting (pqs) value.[2,3] The comparison between the experimental and the calculated ΔE values was then used as a tool to discriminate among structural hypotheses for the tin environment.[2]

However the point charge model has, inter alia, the following three serious limitations:[2,3] 1) it can be applied to Mössbauer atoms where the nonbonding metal electrons do not influence the EFG, ruling out, for example, the application to Sn^{II} compounds; 2) the tabulated pqs values have been determined taking into account nearly symmetric geometries, so that structural distortions (the norm rather than the exception) cannot be unambiguously estimated; 3) the method does not furnish detailed values of structural parameters for the tin environment, in particular with regard to the tin–ligand coordination distances.

Quantum-chemical calculations of the EFG should be able to overcome the limitations inherent to the point charge model formalism and, by exploiting the present computational hardware and software resources, it should be possible to obtain an up to date routine tool for detailed structure analysis of any kind of tin compounds by ^{119}Sn Mössbauer spectroscopy.

To test the capabilities of DFT methods as an improved support for the structural characterization of tin compounds by ^{119}Sn Mössbauer spectroscopy, we performed full geometry optimizations at the B3LYP level[11] with the all-electron DZVP basis set[12] (see Computational details) on 34 selected tin compounds containing up to 94 atoms, which showed various coordination numbers and regular or distorted geometries (see below), whose structures were previously determined by X-ray crystallography in the solid state and whose ^{119}Sn Mössbauer ΔE parameters were known. The correlation of the experimental ΔE with the calculated EFG components was then used to obtain a calibration function [Eq. (1)] to evaluate the theoretical ΔE value for the considered structures.

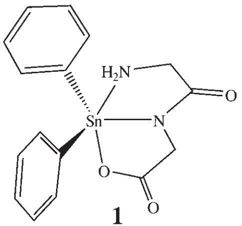
The comparison of the calculated with the experimental structural parameters, the analysis of correlation plot, and the application of this procedure to three isomers of two investigated tin compounds, allowed us to discuss the advantages and limitations of such a procedure.

Results and Discussion

Statistical analysis of the results obtained: Compounds **1**–**34** are tin and organotin complexes, neutral or anionic, with coordination numbers ranging from 3 to 7, and with tin oxidation states 4 and 2 (the latter for example, in **2**, **4**, **16**, **17**, **22**, **25**). Their solid-state structures, which were previously determined by X-ray crystallography,[13–38] were compared with the in vacuo structures obtained in the present work after geometry optimization. The 34 tin compounds investigated were mainly selected on the basis of their experimental ΔE values,[13–38] regularly covering the range analyzed (see Figure 1).

The ^{119}Sn Mössbauer parameters η, V_{zz}, and V, obtained by the DFT calculations (see Computational Details), and the experimental ΔE values, are reported in Table 1. The correlation plot of the experimental ΔE versus the corresponding values of V of the compounds **1**–**34** investigated is shown in Figure 1.

The comparison of experimental and theoretical geometrical parameters, that is, bond lengths and angles involving the tin atom, is given in the Supporting Information Table S1 (except in the case of compound **30**, whose detailed experimental data are not given[37a]). Average deviations of 3.1 ± 0.2 % and 3.3 ± 0.2 % were observed for distances and angles, respectively, as determined by a statistical analysis performed considering 156 distance and 327 angle values,



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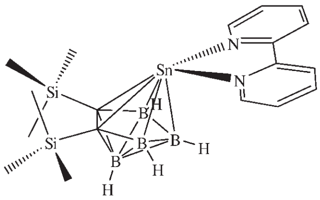

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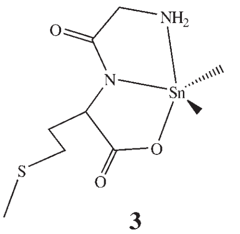

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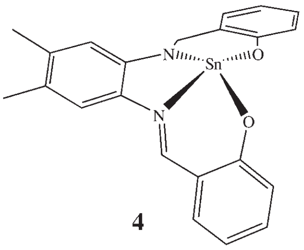

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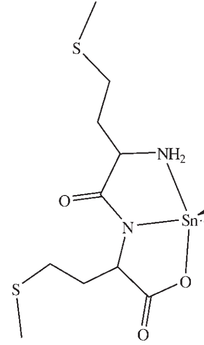

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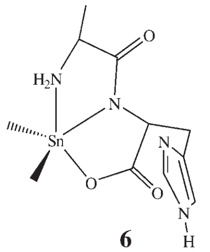

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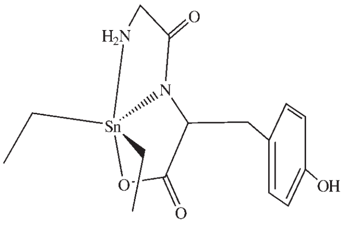

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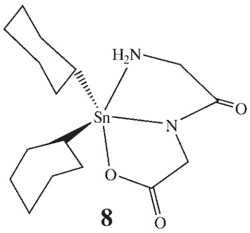

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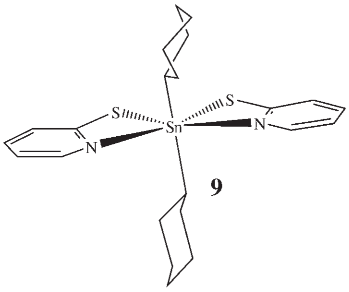

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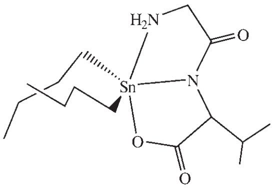

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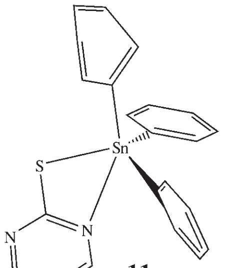

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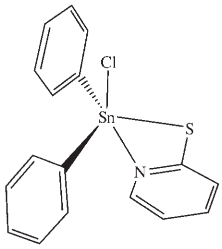

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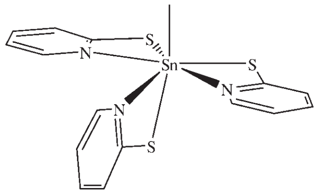

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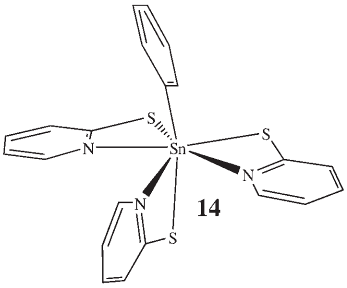

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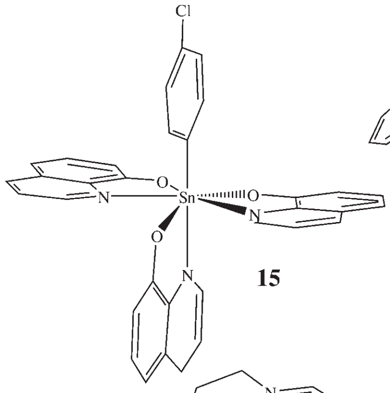

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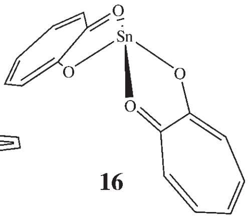

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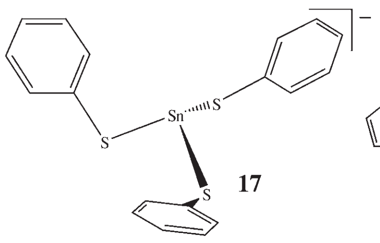

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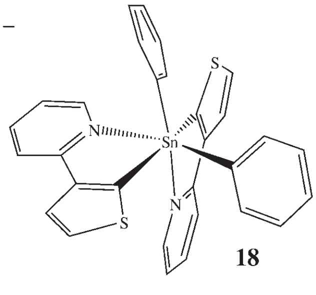

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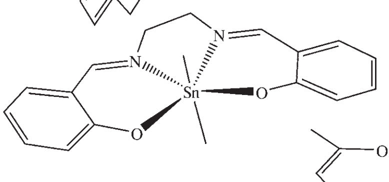

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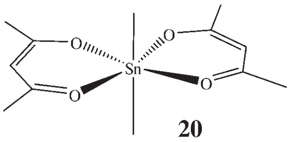

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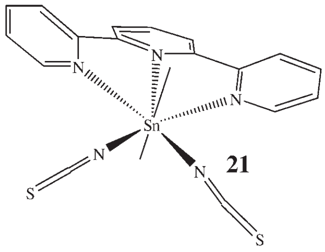

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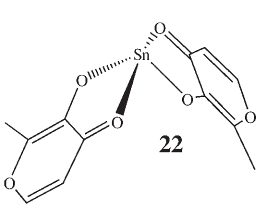

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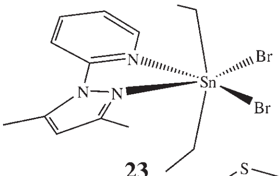

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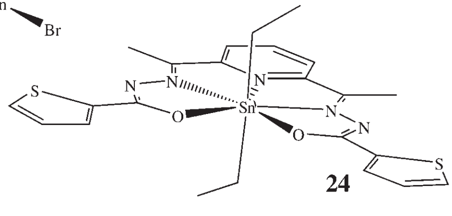

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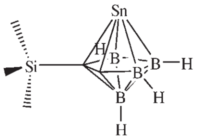

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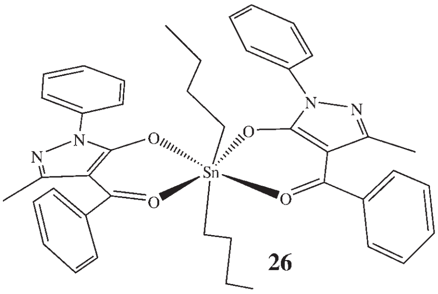

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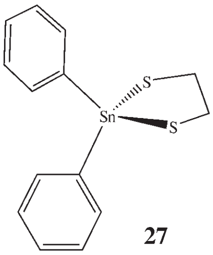

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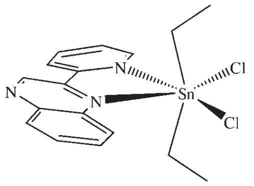

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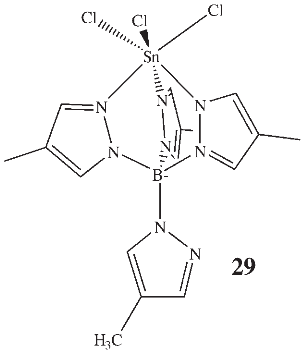

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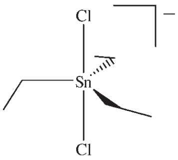

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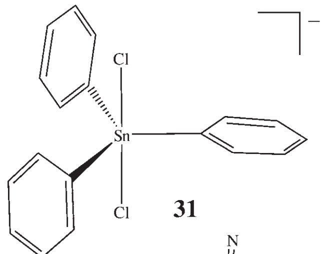

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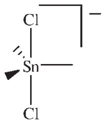

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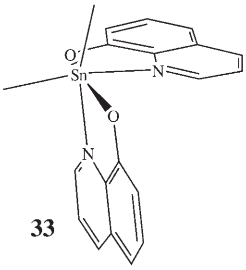

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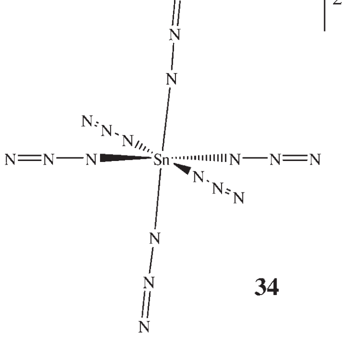

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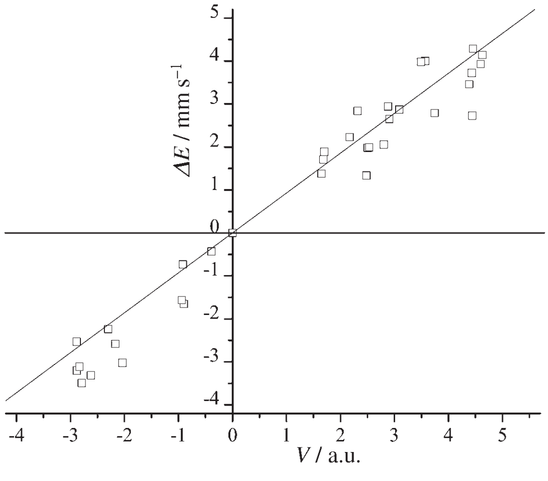


Figure 1. Correlation plot of the experimental ΔE values versus the corresponding calculated values of V for compounds **1**–**34** (see Table 1).

with structural difference maxima of 17 % and 19 %, for the Sn–N distances in **21** and **23**, respectively, and of 18 %, for the C-Sn-C angle of **6**. The observed deviations between calculated and experimental geometrical parameters, larger with respect to those observed in structures containing atoms lighter than tin, can be attributed to the fact that we decided to neglect the relativistic effects[39] in our calculations (see Computational details). Evidently, the V_{xx}, V_{yy}, and V_{zz} components of the EFG summed to zero for **34** and generally for all the spherically symmetric systems considered, like SnX_6^{2-} ($X=F$, Cl, Br and I), in conformity with literature data.[38b] The sign of V_{zz} calculated for five compounds, **1**, **30**–**33**, was equal to the sign of ΔE experimentally determined from Mössbauer–Zeeman spectroscopy measurements.[13,37] This result provides the possibility to predict the sign of V_{zz}, which is known to be affected by subtle effects of the geometrical disposition of the ligands around the tin atom (see for example reference [37a]).

As a consequence of such a result, we attributed positive and negative signs, not experimentally determined, to the ΔE of the compounds investigated, both in the plot in Figure 1 and in Table 1. This possibility was not considered in previous studies,[4–9] in which absolute values were assumed in the comparison of the calculated EFG components with the experimental ΔE values

From a linear regression analysis, by imposing the condition of zero intercept, we obtained $0.93 \pm 0.03\,\mathrm{mm\,s^{-1}\,au^{-1}}$ for the slope, with a linear correlation coefficient $R=0.982$. Using the slope as a calibration constant, it was possible to obtain calculated values of ΔE (Table 1) from the calculated values of V for each of the compounds **1**–**34** by using Equation (2).

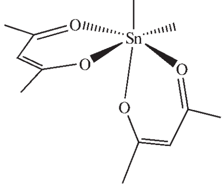
Table 1. Asymmetry parameter, η, V_{zz} component (in atomic units) of the diagonalized EFG tensor and the quantity *V*, obtained from DFT calculations for **1**–**34**, together with the corresponding experimental and calculated Δ*E* values. *V* and Δ*E* are plotted in Figure 1.

Compound	η[a]	V_{zz}[a]	V[b]	ΔE[c]	ΔE_{calcd}[d]	Reference[e]
1	0.84	−2.07	−2.30	−2.24	−2.14	[13a,b]
2	0.70	4.11	4.44	(+)2.73	4.12	[14a]
3	0.98	−2.51	−2.88	(−)2.53	−2.68	[15a,b]
4	0.38	2.42	2.48	(+)1.34	2.31	[16]
5	0.97	2.52	2.88	(+)2.94	2.68	[17a,b]
6	0.93	−2.54	−2.88	(−)3.20	−2.67	[17a,b]
7	0.95	2.71	3.09	(+)2.87	2.87	[18]
8	0.99	−2.46	−2.83	(−)3.11	−2.63	[19]
9	0.76	2.12	2.32	(+)2.84	2.15	[20]
10	0.98	2.53	2.91	(+)2.65	2.70	[15a,b]
11	0.15	−0.90	−0.90	(−)1.65	−0.83	[21]
12	0.71	−2.00	−2.17	(−)2.58	−2.01	[22]
13	0.16	2.16	2.17	(+)2.23	2.02	[23]
14	0.16	1.70	1.70	(+)1.89	1.58	[23]
15	0.18	1.68	1.69	(+)1.71	1.57	[24]
16	0.41	2.43	2.50	(+)1.98	2.32	[25]
17	0.00	1.65	1.65	(+)1.38	1.53	[26]
18	0.51	−0.88	−0.92	(−)0.73	−0.85	[27]
19	0.15	4.37	4.39	(+)3.46	4.07	[28a,b]
20	0.19	4.57	4.60	(+)3.93	4.27	[29a,b]
21	0.18	4.43	4.45	(+)4.29	4.14	[30a,b]
22	0.42	2.46	2.53	(+)1.99	2.35	[25]
23	0.18	3.55	3.57	(+)4.00	3.31	[31]
24	0.16	4.42	4.43	(+)3.72	4.12	[32]
25	0.75	3.43	3.74	(+)2.79	3.48	[14a,b]
26	0.16	4.61	4.63	(+)4.14	4.30	[33]
27	0.21	−0.93	−0.94	(−)1.56	−0.87	[34]
28	0.14	3.48	3.49	(+)3.98	3.24	[35]
29	0.20	−0.38	−0.39	(−)0.43	−0.36	[36]
30	0.00	−2.79	−2.79	−3.49	−2.59	[37a]
31	0.00	−2.04	−2.04	−3.02	−1.89	[37a,b]
32	0.00	−2.62	−2.62	−3.31	−2.43	[37a,c]
33	0.63	2.63	2.80	+2.06	2.60	[37a,d]
34	–	0.00	0.00	0.00	0.00	[38a,b]

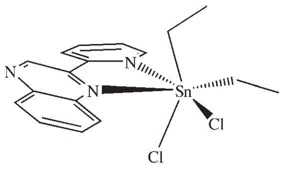
[a] $\eta = (V_{xx}-V_{yy})/V_{zz}$ with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. [b] $V = V_{zz}(1 + \frac{1}{3}\eta^2)^{1/2}$, in atomic units, see Equation (1). [c] Experimental values of the nuclear quadrupole splitting parameter (in mm s^{-1}), obtained from the corresponding references; the sign in parentheses is added to Δ*E* following the sign of *V* obtained from theoretical calculations. [d] See Equation (2), ΔE_{calcd} is the quadrupole splitting parameter calculated from the slope obtained by the linear fitting of Figure 1. [e] The quoted literature refers both to the ^{119}Sn Mössbauer and X-ray crystallographic experimental data.

$$\Delta E_{calcd} = 0.93V \pm 0.58\,\text{mm}\,\text{s}^{-1} \tag{2}$$

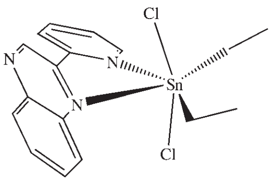
The nuclear quadrupole moment of tin obtained from the value of the slope from Equation (2) was $Q = 15.2 \pm 4.4$ fm^2. This value is in agreement both with the experimental, $|Q| = 10.9 \pm 0.8$ fm^2,[40] and with recently calculated[4,7] values of *Q*. Such result, together with the prevision of the sign of Δ*E*, supports the DFT method used in the present study, compared to previous theoretical approaches,[4–9] for the satisfactory evaluation of the EFG in systems of medium to large dimensions.



20 a



28 a



28 b

The scattering of data points in Figure 1 was analyzed in terms of the differences between the experimental and the calculated structures considered. The largest deviations from the fitted straight line of Figure 1 were observed for **2** and **31** (see Table 1), for which $|\delta\Delta E|$ is within the range 1.0–1.40 mm s^{-1}, where $\delta\Delta E = \Delta E - \Delta E_{calcd}$. The analysis of the structural data of these two compounds (see Table S1 in the Supporting Information) showed that their calculated structure was in reasonable agreement with the corresponding experimental one, with deviations less than 6%. On the other hand, some of the compounds showing significant differences between calculated and experimental structural parameters, such as **21** (see Table S1 in the Supporting Information), exhibited $\delta\Delta E$ values within the associated error (see Equation (2)).

These results allowed us to conclude that the departures of the data from the linear trend in Figure 1 do not depend on the observed discrepancies between the solid-state and the calculated structures. In our opinion the scattering of the data points observed in Figure 1 should be attributable to the difficulty associated with the numerical calculation of second-order quantities like the EFG components. Relativistic effects should also be considered for a better description of the electronic structure of tin compounds. However, we have point out that the aim of the present study was not to quantitatively determine the value of Δ*E* of the considered compounds. Instead, the comparison of the ΔE_{calcd} values, estimated for a series of trial structures, with the experimental Δ*E*, has to be used as a supporting tool for establishing the structural features of the tin compounds investigated.

Determination of the configuration of organotin(IV) compounds: To verify the possibility of applying the method described in the previous section for structural assignment purposes, the calculated values of the quadrupole splitting [Eq. (2)] relative to some exemplary structures, fully optimized at the same level of theory (see Computational Details), were compared with the corresponding experimental Δ*E* values, to address the choice among possible structural hypotheses. The compounds selected, **20a**, **28a** and **28b** are geometrical isomers of **20**[29] and **28**,[35] respectively, and the results obtained were collected in Table 2.

Compounds 20 and 20a: The energy values of the two isomers are very close (see Table 2), **20** being slightly higher in energy than **20a**. Therefore it is not possible to decide which structure is actually the dominant one in the solid

Table 2. Values of relative energy and of V, obtained from DFT calculations for the compounds considered, of ΔE, calculated from the linear fitting parameters ([Eq. (2)]) and difference between experimental and calculated ΔE values.

Compound	Energy[a]	V[b]	ΔE_{calcd}[c]	$\delta\Delta E$[d]
20	0.0	4.60	4.27	−0.34
20a	−1.2	3.13	2.90	1.03
28	0.0	3.49	3.24	0.74
28a	34.2	2.75	2.55	1.43
28b	37.2	2.94	2.73	1.25

[a] Energy difference, in kJ mol^{-1}, of **20a** relative to **20** and of **28a** and **28b** relative to **28**. [b] $V = V_{zz}(1 + \frac{1}{3}\eta^2)^{1/2}$, in atomic units, see Equation (1). [c] See Equation (2), ΔE_{calcd} is the quadrupole splitting parameter calculated from the slope obtained by the linear fitting of Figure 1. [d] $\delta\Delta E$ is the difference between the experimental (see Table 1) and the calculated ΔE values (see footnote c).

phase, because the perturbation due to the solid-state packing may well affect the equilibrium. In this case, the experimental value of the quadrupole splitting along with its theoretical evaluation on **20** and **20a** helps to determine which is the predominant isomer in the solid state. In fact the copresence of tin compounds with different structures is easily detected by ^{119}Sn Mössbauer spectroscopy.[2,3]

The value of $\delta\Delta E$ obtained for **20** is below the uncertainty associated with ΔE_{calcd}, implying that the calculated ΔE value for the structure **20** is consistent with the experimental one,[29] whereas the same analysis performed on **20a** allows us to conclude that this structure, characterized by a $|\delta\Delta E|$ value larger than the associated error, has to be unequivocally discharged.

Compounds 28, 28a and 28b: The results reported in Table 2 show that compound **28** is more than 30 kJ mol^{-1} more stable than the isomers **28a** and **28b**. In this case, solid-state packing factors can with confidence be considered negligible for determining the stability order, **28** being by far the most stable among the three isomers.

It is important to outline that the value of $\delta\Delta E$ observed for **28** can by itself not allow an unambiguous assignment of the involved structure. However, the far larger values of $\delta\Delta E$ obtained for **28a** and **28b** enable us to rule out a significant number of these isomers, confirming the conclusions reached by the energetic considerations.

The cases here presented outline that the theoretical evaluation of the quadrupole splitting on the optimized structures of an isomeric mixture of tin compounds, along with the corresponding experimental evaluation, are able to provide a correct evaluation of the stability order in the solid phase, even if the involved isomers are approximately isoenergetic when considered in vacuo.

Conclusions

DFT-calculated values of the electric field gradient components at the tin nucleus, on the optimized structures of 34 tin compounds, with a standard all-electron basis set and without considering relativistic effects, were correlated to the corresponding ^{119}Sn Mössbauer quadrupole splitting values. This approach proved to be a valid tool for obtaining detailed structural information on tin and organotin derivatives, being more suitable than the point charge model for structure assignment. This method can provide useful information concerning the structural characterization and the determination of the most stable configurations of any type of tin compound by ^{119}Sn Mössbauer spectroscopy. Such a computational method is useful, in particular, for the structural analysis of tin compounds for which X-ray crystallography cannot be performed, for example when it is not possible to obtain suitable crystalline structures.

This work provides further evidence of the ability of DFT methods to support structural interpretations obtained by spectroscopic techniques.

Computational Details

DFT calculations, by using the hybrid Becke's three-parameter method with the Lee–Yang–Parr correlation functional (B3LYP),[11] were performed on the systems **1**–**34**, **20a**, **28a** and **28b**, using the all-electron double-zeta valence plus polarization (DZVP) basis set,[12] with full optimization of the geometry, by using the Gaussian03W[41] program package.

The DZVP basis set has been optimized for DFT calculations,[12] and has been reported to produce structures and energies comparable to those obtained using the better tested basis sets, like 6-31+G(d), for the study of metal compounds,[42] in particular for the study of tin compounds.[43,44] Concerning the importance of relativistic effects for the tin atom, we outline that all-electron relativistic calculations, even at scalar level, are extremely costly.[43] Moreover, the use of relativistic effective core potential basis sets[43] in our calculations was ruled out by the importance, in our study, of the core electrons, as we have verified in preliminary investigations. In fact, the choice of an all-electron basis set was fundamental for obtaining a reliable estimate of the EFG at the tin nucleus.

The eigenvalues of the diagonalized EFG components, V_{ii}, where $i = x, y, z$, calculated at the same level of theory, were used to derive the quantity V, which is related to the theoretical ΔE, in accord with Equation (1). Here V_{ii} is the negative value of the second derivative of the electrostatic potential with respect to the tin coordinates.[1–9]

The experimental ΔE values[13–38] of the compounds **1**–**34** investigated, spanning the range $0 \leq |\Delta E| < 4.5$ mm s^{-1}, were plotted in Figure 1 versus the corresponding values of V (see Table 1). The starting coordinates of **1**–**34** were taken from X-ray crystallography structural data.[13–38] To minimize structural contributions due to the solid-state packing, only tin compounds producing monomer units in the crystalline unit cell have been selected in the present investigation.

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