Crystal Structure of Triphenyltin Fluoride†

David Tudela,*[,a] **Enrique Gutiérrez-Puebla**[b] **and Angeles Monge**[b]
[a] *Departamento de Química, Universidad Autónoma de Madrid, 28049-Madrid, Spain*
[b] *Instituto de Ciencias de los Materiales, sede D, CSIC, Serrano 113, 28006-Madrid, Spain and Laboratorio de Rayos-X, Facultad de Ciencias Químicas, Universidad Complutense, Ciudad Universitaria, 28040-Madrid, Spain*

Triphenyltin fluoride has been studied by powder and single-crystal X-ray diffraction. Powder studies show that the polymeric chain of $SnPh_3F$ propagates along the *c* axis with a repeat distance of *ca.* 4.29 Å. The colourless crystals are trigonal, space group $P\bar{3}c1$ (no. 165), with a = 10.358(1), c = 8.583(1) Å and Z = 2. The F atom lies at an inversion centre, giving rise to a crystallographically imposed rod (class 1) polymer with identical Sn–F distances of 2.1458(3) Å. X-Ray powder diffraction and variable-temperature Mössbauer spectroscopy fail to distinguish between rod (class 1) and zigzag (class 2) triorganotin(IV) polymers.

Tin-119 variable-temperature Mössbauer spectroscopy has been widely used in the investigation of the lattice dynamics and lattice structure of organotin compounds,[1] and in recent years several workers have attempted to obtain structural information from the temperature dependence of the recoil-free fraction, f.[2–10] For thin absorbers f is proportional to the area under the Mössbauer spectrum and, according to the Debye model, plots of ln A *vs.* temperature should be linear in the high-temperature limit. The temperature coefficient of f, $a = -\mathrm{d}(\ln A)/\mathrm{d}T$, is a measure of the mean-square amplitude of vibration for the tin atom. Therefore, it is expected that a should decrease as the degree of intermolecular association increases, and the lattice becomes more tightly bound.[1] Indeed, it was initially thought that solids composed of non-interacting monomeric molecules had a values of *ca.* 1.8×10^{-2} K^{-1}, while strongly hydrogen-bonded lattices and one-, two- and three-dimensional polymeric lattices exhibited a values of *ca.* 0.9×10^{-2} K^{-1}.[11] Nevertheless, when more data became available it was clear that such a simple generalization is not valid because the ranges of a values for monomers and associated compounds strongly overlap, and several polymeric species show a values higher than those of other monomeric compounds.[1,12,13] While efficiently packed non-associated molecules can exhibit low a values, the wide range found for polymeric organotin compounds has been accounted for by considering that not all polymeric structures constrain the vibrational motion of the tin atom in the same way, and that the vibrational freedom that characterizes monomeric compounds is also present in some polymeric structures.[14]

According to their tertiary structure, organotin polymers have been classified into four groups: class 1, rod-like polymers with linear Sn–X–Sn linkages; class 2, zigzag polymers with a bent Sn–X–Sn arrangement; class 3, S-shaped polymers with larger, more flexible bridging groups; and class 4, helical polymers with very flexible bridging groups. It is assumed that flexible arrangements such as those of class 3 and 4 polymers afford a vibrational freedom to the tin atom similar to that of a non-polymeric structure, giving rise to high a values, while class 2 polymers should display a lower temperature coefficient and class 1 compounds should have the lowest a values.[14] In agreement with this, the lower temperature coefficient for triphenyltin formate compared to triphenyltin acetate is consistent with the known crystal structures for both compounds which show greater linearity in the formate chain.[15] On the other hand, the temperature coefficient for $SnPh_3F$ (a = 1.49×10^{-2} K^{-1}) has led to the proposal of a class 2 polymeric structure with a relatively weak intermolecular bond (anisobidentate bridging) for this compound.[14] However, recent high-resolution solid-state ^{119}Sn NMR studies of $SnPh_3F$ have shown that the ^{119}Sn nucleus is apparently equally coupled to two fluorine atoms.[16] Therefore, the crystal structure determination of $SnPh_3F$ would be a major test of the usefulness and limitations of structural methods which can give information in the absence of a full X-ray structure determination.

The repeat distance in carboxylate-bridged triorganotin(IV) carboxylate polymers has been defined as the ratio of the unit-cell length parallel to the axis of propagation of the polymer to the number of monomeric units this length encompasses.[17] This concept can be applied to other types of organotin polymers, and the repeat distance of ten class 2 triorganotin(IV) polymers with second-row bridging atoms lies in a narrow range, with an average value of *ca.* 4.25 Å.[18] On the other hand, the repeat distance for the class 1 polymeric triorganotin(IV) fluoride $Sn(CH_2SiMe_3)_3F$ is 5.13 Å.[19] It is therefore interesting to check whether unit-cell constants obtained from X-ray powder diffraction data can be used to distinguish between class 1 and 2 polymeric triorganotin(IV) fluorides. Consequently, we have studied $SnPh_3F$ by powder and single-crystal X-ray diffraction. The study of this compound is particularly interesting because of its use as a biocide in antifouling paints.[20–22]

Experimental

Triphenyltin fluoride was a gift from M & T Chemicals. Colourless crystals with hexagonal prismatic shape were obtained by vapour diffusion of diethyl ether into a dimethylformamide solution. IR (Nujol): 374s (br) [ν(SnF)] and 281vs cm^{-1} [ν_{asym}(SnC)]. X-Ray powder diffraction data were obtained with a Siemens D500 diffractometer using Cu-Kα radiation. Unit-cell constants were calculated from X-ray powder data,[23] yielding a trigonal or hexagonal lattice with a = 10.369 and c = 4.294 Å, although we suspected that the c axis could be twice the refined value.

Crystal Data.—$C_{18}H_{15}FSn$, M = 369.0, trigonal, space group $P\bar{3}c1$ (no. 165), a = 10.358(1), c = 8.583(1) Å, U =

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

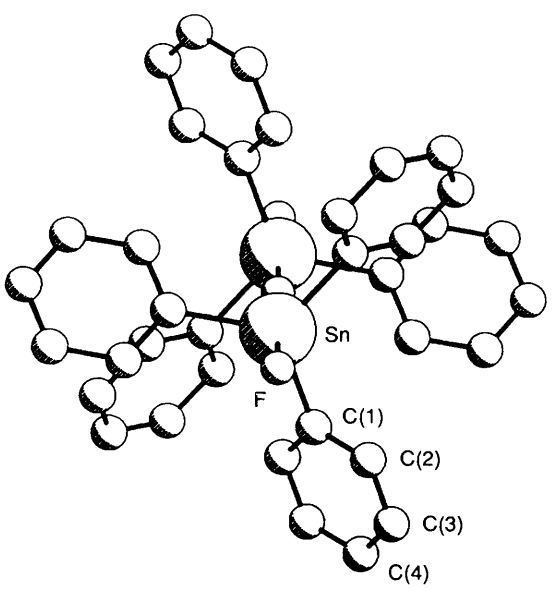

Fig. 1 A PLUTO plot of the polymeric chain in $SnPh_3F$

Table 1 Fractional atomic coordinates (× 10^4) for $SnPh_3F$

Atom	*x*	*y*	*z*
Sn	0	0	2500
F	0	0	0
C(1)	2042(6)	0	2500
C(2)	3197(5)	951(6)	3477(6)
C(3)	4535(6)	954(7)	3469(8)
C(4)	4712(6)	0	2500

Table 2 Bond distances (Å) and angles (°) in $SnPh_3F$

Sn–F	2.1458(3)	Sn–F′	2.1458(3)
Sn–C(1)	2.115(6)	C–C (average)	1.381(7)
F–Sn–F′	180	Sn–F–Sn″	180
F–Sn–C(1)	90	C(1)–Sn–C(1‴)	120
Sn–C(1)–C(2)	120.5(3)	C–C–C (average)	120.0(6)

Symmetry codes: (′) $y, x, \frac{1}{2} - z$; (″) $\bar{x}, \bar{y}, \bar{z}$; (‴) $\bar{y}, x - y, z$.

797.4(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 1.54$ g cm^{-3}, $F(000) = 364$. Colourless prisms. Crystal dimensions: 0.3 × 0.3 × 0.2 mm, μ(Mo-Kα) = 16.04 cm^{-1}, $T = 293$ K.

Data Collection and Processing.[24]—CAD4 diffractometer, ω–2θ mode with ω scan width = 0.80 + 0.35 tan θ, variable scan speed with maximum recording time 50 s, graphite-monochromated Mo-Kα radiation; 599 reflections measured ($1 \leqslant \sigma \leqslant 25°$, $+h$, $+k$, $+l$), 475 unique (merging $R = 0.013$), giving 327 with $I \geqslant 2\sigma(I)$. No significant crystal decay was observed.

Structure Analysis and Refinement.—Heavy-atom method. Empirical absorption correction applied at the end of isotropic refinement. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens fixed in calculated positions with a common isotropic thermal parameter. Final R and R' values were 0.021 and 0.023 for 327 unique observed reflections (number of variables = 33); maximum shift/e.s.d. = 0.005; no trend in ΔF *vs.* F_o or (sin θ)/λ was observed. The final difference map revealed a peak of 2.3 e Å^{-3} at the tin atom position; all the remaining peaks were $\leqslant$0.2 e Å^{-3}. Programs used and sources of scattering factor data are given in ref. 24. Final positional parameters for the non-hydrogen atoms are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

On the basis of Mössbauer[14] and ^{119}Sn solid-state NMR data,[16] $SnPh_3F$ is known to have a polymeric structure with a five-co-ordinated, *trans*-Ph_3SnF_2 geometry at tin. The unit-cell constants, calculated from X-ray powder diffraction data, indicate that the polymeric chain must propagate along the *c* axis with a repeat distance[17,18] of *ca.* 4.29 Å. This value is in the range found for zigzag (class 2) triorganotin(IV) polymers with second-row bridging atoms,[18] but shorter than the repeat distance (5.13 Å) in the rod (class 1) polymer $Sn(CH_2SiMe_3)_3F$.[19] Therefore, if X-ray powder diffraction data can be used to distinguish between class 1 and 2 organotin(IV) polymers, $SnPh_3F$ should be a class 2 polymer as predicted from a variable-temperature ^{119}Sn Mössbauer study.[14] Nevertheless, the X-ray single-crystal study showed some unexpected results.

As suggested by the unit-cell constants, the polymeric chain of $SnPh_3F$ propagates along the *c* axis. A plot of the structure is shown in Fig. 1 and selected bond lengths and angles are collected in Table 2. The F atom lies at an inversion centre, giving rise to a crystallographically imposed rod (class 1) polymer with identical Sn–F distances. The environment of the Sn atom is also highly symmetrical with a perfect trigonal-bipyramidal geometry (see Table 2). The intermolecular Sn ••• F bond is very strong and the shortest so far reported for a polymeric triorganotin fluoride,[19,25–27] only *ca.* 0.18 Å longer than the Sn–F single-bond distance in monomeric four-co-ordinated triorganotin fluorides (*ca.* 1.96 Å).[28–30] In the light of the structural results, we can check the usefulness and limitations of physical techniques which can give structural information in the absence of a full X-ray structure determination.

Solid-state ^{119}Sn NMR data for $SnPh_3F$[16] show that the ^{119}Sn nucleus is apparently equally coupled to two fluorine atoms in accord with the equality of the Sn–F distances (Table 2). Only a few polymeric triorganotin fluorides have been studied by solid-state ^{119}Sn NMR spectroscopy,[16,31,32] and presently no distinction can be made between rod (class 1) and zigzag (class 2) chains. Nevertheless, when more crystallographic and solid-state NMR data become available, it should be checked whether there is a correlation between the $^1J(^{119}Sn–^{19}F)$ coupling constant and the Sn–F distance or the Sn–F–Sn angle.

The suggestion that the unit-cell constants obtained from X-ray powder diffraction data could be useful to distinguish between class 1 and 2 triorganotin(IV) fluorides[18] is not supported by the present results. While the repeat distance for the class 1 polymer $Sn(CH_2SiMe_3)_3F$ is 5.13 Å,[19] the value for the present compound (4.292 Å) is in the range previously found for class 2 polymers.[18] It is clear that the repeat distance is more sensitive to the bond lengths than to the Sn–F–Sn angle, and X-ray powder diffraction data cannot be used to distinguish between both types of polymers.

On the basis of the temperature coefficient of the Mössbauer recoil-free fraction (a = 1.49 × 10^{-2} K^{-1}), a class 2 polymeric structure with unequal Sn–F and Sn ••• F distances has been proposed for $SnPh_3F$.[14] Nevertheless, this compound is a class 1 polymer with identical Sn–F bond distances (Table 2), which indicates that structure assignments from *a* values should be considered with caution. For example, class 1 polymeric $SnPh_3F$ has a higher *a* value (1.49 × 10^{-2} K^{-1}) than the class 2 polymer $SnPh_3(OH)$ (1.10 × 10^{-2} K^{-1}), the class 3 polymer $SnPh_3(O_2CH)$ (1.15 × 10^{-2} K^{-1}), or monomeric $SnPh_4$ (1.37 × 10^{-2} K^{-1}).[14] It is assumed that, in terms of the variable-temperature Mössbauer spectroscopy experiment, the lattice

Table 3 Structural and variable-temperature Mössbauer data for $SnPh_3X$ (X = F or OH)

	$SnPh_3F$	$SnPh_3(OH)$
$M/\mathrm{g\ mol^{-1}}$	369.0	367.0
Sn–X/Å	2.1458(3)[a]	2.197(5)[b]
X ··· Sn/Å	2.1458(3)[a]	2.255(5)[b]
Sn–X ··· Sn/°	180(–)[a]	137.8(3)[b]
$10^2 a/\mathrm{K^{-1}}$	1.49[c]	1.10[c]

[a] This work. [b] Ref. 33. [c] Ref. 14.

rigidity decreases as (*i*) the strength of the bridging bond (X ··· Sn) decreases or (*ii*) as the bridging mass is progressively displaced away from the Sn ··· Sn vector.[14] Table 3 shows data for the isoelectronic compounds $SnPh_3F$ and $SnPh_3(OH)$, and we can conclude that *a* values are not a reliable guide to the strength of the intermolecular interactions or the tertiary structure of the polymeric chain. Therefore, although there is a general trend towards lower *a* values as the degree of intermolecular association increases,[1] our current understanding of the *a vs.* structure systematics for organotin compounds needs to be improved before we can use it to obtain unambiguous structural information.

It is interesting that while $SnMe_3F$ is a zigzag (class 2) polymer,[25] bulkier substituents on the tin atom lead to rod (class 1) polymers or monomers. So, $SnPh_3F$, $Sn(CH_2Ph)_3F$,[27] and $Sn(CH_2SiMe_3)_3F$[19] are class 1 polymers, while $Sn(C_6H_{11})_3F$ is intermediate between a class 1 polymer and a monomer,[26] and $Sn[C(SiMe_3)_3]Me_2F$,[28] $Sn[C(SiMe_3)_3]Ph_2F$,[28] $Sn[C(SiMe_2Ph)_3]Me_2F$[28] and $Sn(C_6H_2Me_3\text{-}2,4,6)_3F$[29] are monomeric compounds.

Acknowledgements

We thank M & T Chemicals for a gift of $SnPh_3F$, and the Spanish Comisión Interministerial de Ciencia y Tecnología (Project MAT88-0250-C02) and Dirección General de Investigación Cientifica y Técnica (Project PS90-0023) for financial support.

References

1 P. G. Harrison, in *Chemistry of Tin*, ed. P. G. Harrison, Blackie, Glasgow, 1989, p. 97.
2 P. G. Harrison, N. W. Sharpe, C. Pelizzi, G. Pellizi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1983, 1687.
3 F. A. K. Nasser and J. J. Zuckerman, *J. Organomet. Chem.*, 1984, **266**, 225.
4 D. Tudela, V. Fernández and J. D. Tornero, *Inorg. Chem.*, 1985, **24**, 3892.
5 K. C. Molloy, K. Quill, S. J. Blunden and R. Hill, *J. Chem. Soc., Dalton Trans.*, 1986, 875.
6 R. Barbieri, G. Alonzo and R. H. Herber, *J. Chem. Soc., Dalton Trans.*, 1987, 789.
7 T. Birchall, R. Faggiani, C. J. L. Lock and V. Manivannan, *J. Chem. Soc., Dalton Trans.*, 1987, 1675.
8 K. C. Molloy, G. Tagliavini, P. Ganis and D. Furlani, *Inorg. Chim. Acta*, 1988, **141**, 7.
9 K. C. Molloy, K. Quill, D. Cunningham, P. McArdle and T. Higgins, *J. Chem. Soc., Dalton Trans.*, 1989, 267.
10 S. W. Ng and V. G. Kumar Das, *J. Organomet. Chem.*, 1991, **409**, 143.
11 P. G. Harrison, R. C. Philips and E. W. Thornton, *J. Chem. Soc., Chem. Commun.*, 1977, 603.
12 R. V. Parish, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, ed. G. J. Long, Plenum, New York, 1984, p. 549.
13 J. J. Zuckerman, in *Chemical Mössbauer Spectroscopy*, ed. R. H. Herber, Plenum, New York, 1984, p. 282.
14 K. C. Molloy and K. Quill, *J. Chem. Soc., Dalton Trans.*, 1985, 1417.
15 K. C. Molloy, K. Quill and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 1987, 101.
16 H. Bai, R. K. Harris and H. Reuter, *J. Organomet. Chem.*, 1991, **408**, 167.
17 S. W. Ng, Chen Wei and V. G. Kumar Das, *J. Organomet. Chem.*, 1988, **345**, 59.
18 D. Tudela, *Struct. Chem.*, 1990, **1**, 437.
19 L. N. Zakharov, Yu. T. Struchkov, E. A. Kuz'min and B. I. Petrov, *Kristallografiya*, 1983, **28**, 271.
20 A. G. Davies and P. J. Smith, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, New York, 1982, vol. 2, p. 613.
21 C. J. Evans and S. Karpel, *J. Organomet. Chem. Library*, 1985, **16**, 1.
22 S. J. Blunden, P. A. Cusack and R. Hill, *The Industrial Uses of Tin Chemicals*, The Royal Society of Chemistry, London, 1985, p. 3.
23 J. W. Visser, *J. Appl. Crystallogr.*, 1969, **2**, 89.
24 E. Carmona, L. Contreras, E. Gutiérrez-Puebla, A. Monge and L. J. Sánchez, *Organometallics*, 1991, **10**, 71.
25 H. C. Clark, R. J. O'Brien and J. Trotter, *J. Chem. Soc.*, 1964, 2332; K. Yasuda, Y. Kawasaki, N. Kasai and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1216.
26 S. Calogero, P. Ganis, V. Peruzzo, G. Tagliavini and G. Valle, *J. Organomet. Chem.*, 1981, **220**, 11.
27 H. Reuter, Ph.D. Thesis, University of Bonn, 1986.
28 S. S. Al-Juaid, S. M. Dhaher, C. Eaborn, P. B. Hitchcock and J. D. Smith, *J. Organomet. Chem.*, 1987, **325**, 117.
29 H. Reuter and H. Puff, *J. Organomet. Chem.*, 1989, **379**, 223.
30 U. Kolb, M. Dräger and B. Jousseaume, *Organometallics*, 1991, **10**, 2737.
31 R. K. Harris, P. Reams and K. J. Packer, *J. Mol. Struct.*, 1986, **141**, 13.
32 R. K. Harris, K. J. Packer and P. Reams, *Chem. Phys. Lett.*, 1985, **115**, 16.
33 C. Glidewell and D. C. Liles, *Acta Crystallogr., Sect. B*, 1978, **34**, 129.

Received 11*th October* 1991; *Paper* 1/05171G