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THE SYNTHESIS AND CRYSTAL STRUCTURE OF TRIPHENYLVINYLTIN

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Summary

Triphenylvinyltin has been prepared by an improved method. It crystallizes in the $Pbn2_1$ space group; the crystal contains two non-equivalent molecules which have almost the same conformation. The latter are compared with the conformations in tetraphenyl-methane, -silane, -germane, -tin and -lead.

Experimental

Preparation of triphenylvinyltin

The apparatus consisted of an 0.25 l flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel also filled with a reflux condenser. A suspension of 2.8 g of magnesium turnings suspended in 60 ml of anhydrous tetrahydrofuran was introduced into the flask, and a solution of 13 g of vinyl bromide in 20 ml of tetrahydrofuran cooled to 253 K was added dropwise, the reflux condensers being cooled with methanol at 253 K. The mixture was subsequently heated under reflux for 1 h then cooled to 293 K. The solution thus obtained was added dropwise with stirring to a solution of 38.5 g of Ph_3SnCl in 0.1 l of heptane boiling in an 0.5 l flask. The mixture was stirred vigorously and heated for 4 h, cooled to 293 K, and treated with a mixture of ice and solid NH_4Cl. The aqueous layer was separated and extracted with ether. The combined organic solutions were dried over $CaCl_2$. The solvent was partly evaporated and the remaining solution was treated with 25% aqueous KF to remove any unchanged Ph_3SnCl. The organic layer was washed with water and dried over Na_2SO_4. The solvents were evaporated under vacuum and the residual solid was recrystallised from methanol to give 24.9 g of a white product, melting at 312–313 K. The yield was 66% based on the initial Ph_3SnCl and 74% based on the Ph_3SnCl consumed.

Analysis: Found: C, 63.92; H, 4.81; Sn, 31.83. $C_{20}H_{18}SN$ (376.90) calcd.: C, 63.71; H, 4.77; Sn, 31.51%.

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Crystallography

Collection and reduction of X-ray data

A suitable single crystal was mounted in a Lindemann capillary. The cell parameters were determined from Weissenberg and precession photographs. Systematic absences $h0l$ ($h + l = 2n + 1$), $0kl$ ($k = 2n + 1$) indicated two possible space groups *Pbnm* (D_{2h}^{16}, no. 62) and *Pbn*2$_1$ (C_{2v}^{9}, no. 33).

Crystal data. $(C_6H_5)_3(CH{=}CH_2)Sn$ $M = 376.7$. a 7.016(2), b 16.442(6), c 29.75(2) Å. V 3432 Å^3, ρ_{obs} 1480 kg m^{-3} (flotation) ρ_{calc} 1470 kg m^{-3} for $Z = 8$. Crystal dimensions: less than 0.2 mm μ(Mo-K_α) 1356 m^{-1}.

Data collection. Mo-K_α radiation, λ 0.7107 Å, graphite crystal monochromated; θ range 1°–37.5°; $0 \leqslant h \leqslant 8$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 36$. Total number of reflections measured (including systematic absences) 3943. Independent reflections (excluding systematic absences) 3436. Independent reflections with $F_0/\sigma(F_0) > 1$: 2286. No absorption or extinction corrections were made.

Structure solution and refinement

A projection of the Patterson map on the y, z plane showed large peaks forming approximate equilateral triangles (the disposition is similar to that of Sn atoms in Fig. 1) but the x coordinates for the large peaks were not zero. Furthermore many peaks were related by symmetry. Despite the complexity the Patterson map shows roughly how the molecules packed together and this helped considerably in locating the Sn atoms.

An attempt was first made with space group *Pbnm* (because the multiplicity in that group equals $Z = 8$). Although the Patterson map could not be interpreted precisely, plausible coordinates for the Sn atom were tried but refinements proved unsatisfactory.

In space group *Pbn*2$_1$ the multiplicity equals 4 and there should be 2 (crystallographically non-equivalent) molecules in the symmetric unit. Equivalent positions are: x, y, z; $\bar{x}, \bar{y}, 1/2 + z$; $1/2 + x, 1/2 - y, 1/2 + z$; $1/2 - x, 1/2 + y, z$). The Sn

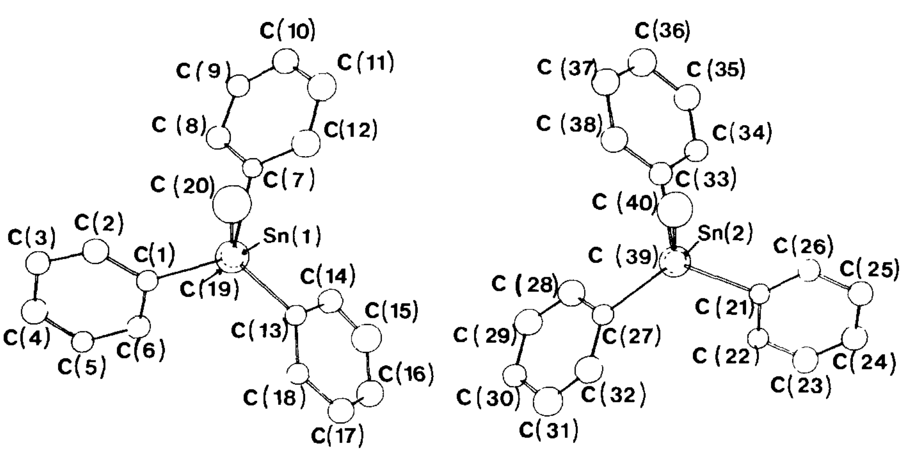

Fig. 1. The two molecules in the asymmetric unit exhibiting their almost exact symmetry after displacement and rotation.

TABLE 1

ATOMIC COORDINATES OF TRIPHENYLVINYLTIN

Atom	*x*	*y*	*z*	*B*
Sn(1)	0.9397(2)	0.4961(1)	0.5	4.05(7)
C(1)	0.755(4)	0.437(2)	0.543(1)	4.0(5)
C(2)	0.624(4)	0.473(2)	0.571(1)	5.4(6)
C(3)	0.498(4)	0.440(2)	0.601(1)	4.7(6)
C(4)	0.499(5)	0.357(2)	0.603(1)	5.7(7)
C(5)	0.617(4)	0.312(2)	0.577(1)	4.2(6)
C(6)	0.749(5)	0.352(2)	0.549(1)	5.0(6)
C(7)	1.114(3)	0.581(2)	0.536(1)	3.2(4)
C(8)	1.130(4)	0.587(2)	0.583(1)	4.8(6)
C(9)	1.246(4)	0.645(2)	0.598(1)	4.2(5)
C(10)	1.352(5)	0.690(2)	0.576(1)	5.7(7)
C(11)	1.346(5)	0.688(2)	0.531(1)	6.4(8)
C(12)	1.224(5)	0.633(2)	0.508(1)	6.5(8)
C(13)	1.113(4)	0.411(2)	0.466(1)	3.8(5)
C(14)	1.301(4)	0.397(2)	0.476(1)	5.3(6)
C(15)	1.404(7)	0.340(2)	0.453(1)	7.8(9)
C(16)	1.318(5)	0.294(2)	0.420(1)	6.0(8)
C(17)	1.147(5)	0.306(2)	0.409(1)	5.5(7)
C(18)	1.026(4)	0.361(2)	0.432(1)	3.8(5)
C(19)	0.770(6)	0.568(2)	0.455(1)	7(1)
C(20)	0.756(9)	0.644(3)	0.457(2)	10(1)
Sn(2)	0.9194(2)	0.2333(1)	0.2766(1)	4.02(7)
C(21)	0.743(4)	0.170(2)	0.229(1)	3.6(5)
C(22)	0.763(4)	0.087(2)	0.225(1)	3.8(5)
C(23)	0.645(5)	0.044(2)	0.198(1)	6.3(7)
C(24)	0.516(5)	0.082(2)	0.174(1)	5.7(7)
C(25)	0.493(4)	0.165(2)	0.176(1)	5.1(6)
C(26)	0.609(4)	0.211(2)	0.207(1)	4.2(5)
C(27)	1.098(4)	0.150(1)	0.314(1)	3.9(5)
C(28)	1.284(5)	0.146(2)	0.304(1)	6.4(7)
C(29)	1.409(6)	0.094(2)	0.326(1)	6.9(8)
C(30)	1.342(4)	0.043(2)	0.359(1)	4.8(6)
C(31)	1.138(5)	0.047(2)	0.368(1)	7.3(8)
C(32)	1.033(5)	0.100(2)	0.346(1)	6.0(7)
C(33)	1.100(4)	0.317(2)	0.244(1)	4.4(5)
C(34)	1.112(4)	0.320(2)	0.199(1)	4.6(6)
C(35)	1.244(5)	0.370(2)	0.174(1)	6.2(7)
C(36)	1.342(5)	0.431(2)	0.200(1)	6.8(8)
C(37)	1.312(5)	0.432(2)	0.247(1)	5.9(7)
C(38)	1.197(4)	0.375(2)	0.268(1)	5.5(6)
C(39)	0.739(6)	0.300(2)	0.322(1)	6.7(8)
C(40)	0.726(6)	0.380(2)	0.324(1)	8.2(9)

ANISOTROPIC THERMAL FACTORS FOR Sn(1) AND Sn(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	0.0547(9)	0.0444(8)	0.0552(9)	0.0023(9)	−0.0017(12)	−0.0067(10)
Sn(2)	0.0534(8)	0.0472(8)	0.0520(8)	−0.0036(10)	−0.0049(12)	−0.0004(9)

atoms were located approximately in the following positions: Sn(1) $x = +0.58$; $y = 0.0$; $z = 0.5$; Sn(2), $x = 0.42$; $y = 0.25$; $z = 0.75$. The z-coordinate of Sn(1) was arbitrarily fixed at 0.5. After refinements the conventional R factor was 0.21. Successive Fourier difference maps and refinements revealed all the heavy atoms and R fell to 0.100. With anisotropic thermal factors for the tin atoms R decreased to 0.0828. Most of the hydrogen atoms were seen on a Fourier difference map but evenso they were placed at calculated positions using the SHELX program [1], except for the methylene hydrogen atoms of the vinyl groups, which were not considered; C–H bond lengths were fixed at 1.08 Å and the H atoms were allowed to ride on the atom to which they are bonded. The R factor was 0.0797.

Description of the structure

The positional and thermal parameters are given in Table 1. The Sn atoms are four-coordinate as shown in Table 2.

The two molecules in the asymmetric unit are almost enantiomers as may be seen in Fig. 1, in which the two molecules are shown, shifted and rotated from their actual dispositions, in such a way that the Sn(1)–C(19) and Sn(2)–C(39) bonds are perpendicular to the figure and Sn(1)C(19)C(20) and Sn(2)C(39)C(40) planes parallel to each other: the symmetry of the molecules is obvious. The torsion angles (Table 3) confirm that both molecules have a symmetrical conformation.

Projected onto the yz plane (Fig. 2) the structure looks like a plane of closed packed molecules but the Sn atoms have different x-coordinates. The stacking is more complicated than for more symmetrical molecules such as tetraphenylmethane [2], tetraphenylsilane [3] tetraphenylgermane [4,5], tetraphenyltin [6] or tetraphenyllead [7].

Molecular conformation

The positions of the vinyl group and of the phenyl groups are considered separately.

The vinyl group. Since the positions of the vinyl groups in the two molecules of triphenylvinyltin are almost equivalent, a detailed investigation of only one molecule is necessary. In molecule 1 (around Sn(1)) the torsion angle C(20)–C(19)–Sn(1)–C(7) is rather small, viz. 5° (Table 3(A)). Its sign is not arbitrary and is related to the

TABLE 2

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Sn(1)–C(1)	2.07(3)	Sn(2)–C(21)	2.15(3)
Sn(1)–C(7)	2.15(3)	Sn(2)–C(27)	2.16(3)
Sn(1)–C(13)	2.12(3)	Sn(2)–C(33)	2.11(3)
Sn(1)–C(19)	2.17(4)	Sn(2)–C(39)	2.15(4)
C(19)–C(20)	1.27(7)	C(39)–C(40)	1.31(5)
C(1)–Sn(1)–C(7)	111(1)	C(21)–Sn(2)–C(33)	111(1)
C(7)–Sn(1)–C(13)	110(1)	C(33)–Sn(2)–C(27)	108(1)
C(13)–Sn(1)–C(1)	110(1)	C(27)–Sn(2)–C(21)	111(0)
C(19)–Sn(1)–C(1)	107(1)	C(39)–Sn(2)–C(21)	109(1)
C(19)–Sn(1)–C(7)	107(1)	C(39)–Sn(2)–C(33)	108(1)
C(19)–Sn(1)–C(13)	112(1)	C(39)–Sn(2)–C(27)	111(1)

rotation of the phenyl group C(7)–C(12): it can be seen from Fig. 1 that C(8) is below C(7) and C(12) above and so C(20) must rotate in the way it does. The position of the vinyl group is thus determined by intramolecular steric effects.

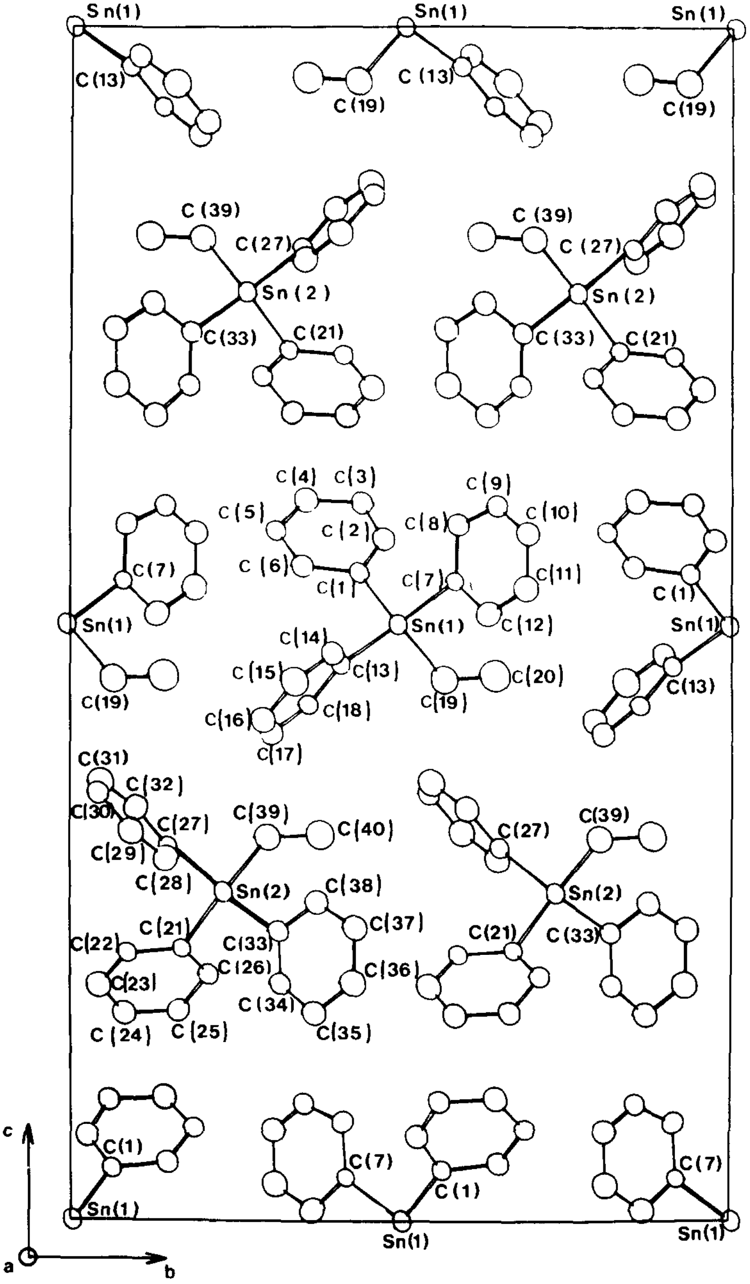

Fig. 2. Projection of the structure on plane (1 0 0). Fully labelled molecules correspond to atoms listed in Table 1.

TABLE 3

TORSION ANGLES (°) INVOLVING (A) THE VINYL AND (B) THE PHENYL GROUPS

(A)	C(20)–C(19)–Sn(1)–C(1)	−112	C(40)–C(39)–Sn(2)–C(21)	111
	C(20)–C(19)–Sn(1)–C(7)	5	C(40)–C(39)–Sn(2)–C(33)	−9
	C(20)–C(19)–Sn(1)–C(13)	127	C(40)–C(39)–Sn(2)–C(27)	−127
(B)	C(19)–Sn(1)–C(1)–Ph(1)	58.1(1.3)		
	C(19)–Sn(1)–C(7)–Ph(7)	54.7(1.8)		
	C(19)–Sn(1)–C(13)–Ph(13)	46.2(1.3)		
	C(39)–Sn(2)–C(21)–Ph(21)	54.5(4.5)		
	C(39)–Sn(2)–C(33)–Ph(33)	48.9(2.7)		
	C(39)–Sn(2)–C(27)–Ph(27)	47.2(0.9)		
	Average value	51.6		

The phenyl groups. We denote by Ph(1), Ph(7), Ph(13), Ph(21), Ph(33) and Ph(27) the phenyl groups linked to tin through the C(1), C(7), C(13), C(21), C(33) and C(27) atoms, respectively. Table 3 includes the torsion angles for these groups with respect to the C(19)–Sn(1) bond; these angles were calculated as an average of the torsion angles for different atoms in the phenyl groups; for example C(19)–Sn(1)–C(1)–Ph(1) has been calculated by taking into account C(2), C(3), C(5) and C(6). Consideration of the e.s.d.'s for both molecules (Table 3(B)) shows that the torsion angles are nearly equal within the margin of error.

The results may be compared with those for tetraphenyl compounds studied by several authors [5,6,8] despite the fact that the crystallographic symmetry is lower in the vinyl compound. Karipides and Haller [5] have shown that the torsion angle α of the phenyl groups around Ge–C can be calculated from intramolecular and intermolecular contacts ($\alpha_{\mathrm{exp.}}$ 54.1, α_{calc} 54 or 49°), and it appears that intermolecular H–H interactions were critical in defining that conformation. For tetraphenyltin the corresponding angle is 56.7° [6].

The average value, α 51.6°, of the torsion angles for the phenyl groups in triphenylvinyltin is smaller than in tetraphenyltin; the decrease in that angle means that a phenyl group is further from perpendicularity to the C(19)–Sn(1) bond. From Table 3(B) it appears that the α angle is changed most for the Ph(13) and Ph(27) groups and this is easily understandable, for these groups are opposite to and away from the vinyl groups they are less sensitive to the steric effect from the fourth substituent. This again is an intramolecular effect. A rather large change in α values would also be expected for Ph(1) and Ph(21) in view of the fact that the interactions with a vinyl group seem to be much smaller than with a fourth phenyl group, but in fact there is a rather small change, if any. This supports Karipides and Haller's view that the conformation cannot be calculated by taking account only of intramolecular interactions; i.e optimisation of the stacking also influences the shape.

It thus appears that the major features of the conformation of the triphenylvinyltin(IV) may be interpreted in terms of intramolecular effects. Thus (a) the vinyl group is rotated by 5° away from the center of a phenyl group and in a direction such that its hydrogen atoms get further away from the phenyl group, and (b) the phenyl group furthest from the vinyl group has apparently more freedom to rotate than the other phenyl groups, and its angle with the Sn vinyl is smaller. But interpretation of other details requires consideration of intermolecular interactions.

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