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Note

The crystal structure of 3-butenyltriphenylstannane. Crystal disorder and thermodynamic properties

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Abstract

The tin derivative 3-butenyltriphenylstannane [$Ph_3Sn–CH_2–CH_2–CH=CH_2$] (**A**) has been prepared; the crystal and molecular structure has been determined by X-ray analysis. The compound crystallizes in the tetragonal space group $P\bar{4}2_1c$ with $a=b=11.860(3)$, $c=6.839(2)$ Å, $Z=2$. Refinement converged to the final R index 0.044. The crystal and physical data are compared with those of tetraphenyltin (**B**); the relevant differences are explained in terms of structural disorder.

Keywords: Crystal structures; Phenylalkylstannanes

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1. Introduction

Compounds of general formula R_4M (M = C, Si, Ge, Sn or Pb) have the potential molecular symmetry $\bar{4}$ [1,2], which in some cases has been proved to be retained in the crystal, as they mostly belong to the tetragonal space group $P\bar{4}2_1c$ [3–7]. It has been inferred that the complex $Ph_3GeCOPh$ [5,6] crystallizes in the same space group; this implies that its apparent $\bar{4}$ symmetry derives from a disorder arrangement of the molecules in the crystal. Yet, no data have been reported so far for a detailed description of this feature which is also expected to control some physical properties. Here we report the crystal structure of 3-butenyltriphenylstannane (**A**), which is revealed as belonging to the space group $P\bar{4}2_1c$, albeit corresponding to the general formula Ph_3MR. This fact re-proposes the same structural characteristics found, but not discussed, for $Ph_3GeCOPh$, and affords the opportunity to clear up the problem.

2. Experimental

2.1. Material

3-Butenyltriphenylstannane was prepared by treatment of 3-butenyl magnesium bromide with triphenyltin chloride in the ratio 2:1 in anhydrous ether following the procedure for analogous compounds [8]. The product was crystallized from petroleum ether (40–60°), m.p. 99–100°C. *Anal.* Calc. for $C_{22}H_{22}Sn$: C, 65,23; H, 5,47. Found: C, 65.15; H, 5.61%. IR (Nujol) (cm^{-1}): ν(C=C) 1630m. ^{119}Sn NMR ($CDCl_3$) (ppm): δ −100.7; literature: −100.9 [9].

2.2. X-ray data collection and structure determination

A needle-shaped colorless crystal, of proper dimensions, was mounted on a Philips four-circle automated diffractometer (Mo Kα radiation, $3.0 \leq 2\theta \leq 45°$, θ–2θ scan method). No absorption corrections were made. The structure was solved by Patterson methods using 329 reflections with $I \geq 2\sigma(I)$. The parameters of the complete structure could be refined by anisotropic least-squares cycles including variable occupancy factors for the carbon atoms, to the conventional R index of 0.044 ($w = 1/\sigma^2(F) + 0.002F$). Only the hydrogens of the phenyl groups were geometrically positioned and included in the calculations, but not refined. The scattering factor for the tin atom was corrected for the real and imaginary parts of anomalous dispersion by use of Cromer's value [10]. All the computations were carried out using the SHELX-76 program [11]. Crystal and intensity data are summarized in Table 1.

3. Results and discussion

Compound **A** crystallizes in the tetragonal space group $P\bar{4}2_1c$ with $a=b=11.860(3)$, $c=6.839(2)$ Å, $Z=2$, $D_c = 1.40$ g cm^{-3}, $\mu = 12.1$ cm^{-1}.

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Table 1
Crystal data and details of intensity measurements for $Ph_3Sn–CH_2–CH_2–CH=CH_2$ (**A**); some data are compared with those of Ph_4Sn (**B**)

	A	**B** [a]
Formula	$C_{22}H_{22}Sn$	$C_{24}H_{20}Sn$
Formula weight	405.1	427.1
Crystal dimensions (mm)	0.30×0.25×0.25	
T (K)	298	
Radiation, (Å)	graphite monochromatized, Mo Kα (0.7107)	
Space group	$P\bar{4}2_1c$	$P\bar{4}2_1c$
a (Å)	11.860(2)	12.058(1)
b (Å)	11.860(2)	12.058(1)
c (Å)	6.839(1)	6.568(1)
Cell volume (Å^3)	961.97	954.96
Z	2	2
D_c (g cm^{-3})	1.40	1.48
F(000)	400	428
μ (cm^{-1})	12.12	13.5
Scan speed (° min^{-1})	2.0 in 2θ scan mode	
Scan width (°)	1.2	
Take off angle (°)	3	
2θ Range (°)	$3.0 \leq 2\theta \leq 45$	
Total reflections [b]	686	
Reflection used for refinement with $I \geq 2\sigma(I)$	326	366
Solution method	Patterson	
R_c (on F_o) [c]	0.044	0.078
R_w [d]	0.051	
Goodness of fit [e]	1.1	
Highest map residual (e Å^{-3})	0.70	0.50

[a] See Ref. [6].
[b] $F_o^2 > 2\sigma(F_o^2)$.
[c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.
[e] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(ND - NV)^2]^{1/2}$.

The atomic parameters, and bond distances and angles are listed in Tables 2 and 3, respectively, according to the atom labels of Fig. 1.

The space group $P\bar{4}2_1c$ with $Z = 2$ imposes a $\bar{4}$ symmetry of the molecular unit which in turn requires a lattice disorder. The unsaturated alkyl group alternates statistically with a phenyl group in the same site with a weight ratio 1:3, assuming conformations as indicated in Scheme 1.

Calculations, performed using variable occupancy factors, show a predominance, or probably the sole presence, of the conformations (a) and (b) which are almost isosteric with the corresponding tetra-atomic sequence of the phenyl group. Also the thermal parameters are in agreement with this assumption (see Table 2 and Section 4). Likely, the conformations (c) and (d) are inhibited by their very different steric encumbrance, which would destroy the group symmetry $\bar{4}$ as found in the crystal structure of the complex $Ph_3Sn–CH_2–CH=CH–CH_3$ present with both *cis* and *trans* isomers [12]. The resulting geometrical parameters about Sn are not invalidated by this disorder, thus the coordination about the metal

Table 2
Fractional atomic coordinates of non-hydrogen atoms with equivalent isotropic thermal parameters (Å^2) for $Ph_3Sn–CH_2–CH_2–CH=CH_2$ (**A**)

Atom	x	y	z	U_{eq} [a]
Sn	0.0000	0.0000	0.0000	0.071(3)
C(1)	0.0175(11)	0.1492(7)	0.8206(11)	0.082(5)
C(2)	0.1052(8)	0.1555(9)	0.6781(12)	0.093(4)
C(3)	0.1260(10)	0.2507(10)	0.5565(11)	0.110(7)
C(4)	0.0470(12)	0.3368(11)	0.5715(12)	0.125(6)
C(5)	−0.0432(11)	0.3310(11)	0.6994(14)	0.104(5)
C(6)	−0.0643(9)	0.2356(9)	0.8233(12)	0.117(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected geometrical parameters for $Ph_3Sn–CH_2–CH_2–CH=CH_2$ (**A**)

Bond lengths (Å)			
Sn–C(1)	2.160(4)	C(3)–C(4)	1.390(7)
C(1)–C(2)	1.430(8)	C(4)–C(5)	1.381(9)
C(2)–C(3)	1.421(8)	C(5)–C(6)	1.440(8)
C(1)–C(6)	1.410(9)		
Bond angles (°)			
C(1′)–Sn–C(1)	108.7(2)	C(1)–C(6)–C(5)	116.4(3)
Sn–C(1)–C(2)	120.0(4)	C(2)–C(3)–C(4)	115.1(4)
Sn–C(1)–C(6)	121.4(5)	C(6)–C(5)–C(4)	123.1(4)
C(1)–C(2)–C(3)	124.5(3)	C(3)–C(4)–C(5)	122.1(3)
Torsion angles (°)			
Sn–C(1)–C(2)–C(3)	−178		
Sn–C(1)–C(6)–C(5)	179		
C(1)–C(2)–C(3)–C(4)	−6		
C(1)–C(6)–C(5)–C(4)	5		

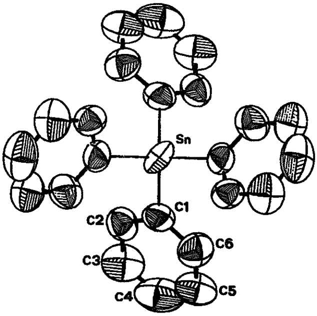
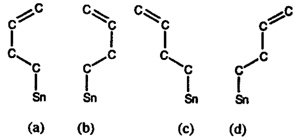


Fig. 1. ORTEP view of 3-butenyltriphenylstannane (thermal ellipsoids at 30% probability level), with atom numbering for the non-hydrogen atoms. Due to the disorder character of the structure each six-membered ring of this figure is the apparent result of a weighted overlapping of a phenyl group and a 3-butenyl group, in the conformations (a) and (b) of Scheme 1, nearly in the ratio 3/4:1/8:1/8.



Scheme 1.

is almost exactly tetrahedral (the bond angles C–Sn–C are all ~109(1)°). A comparison with the data of Ph_4Sn (**B**) [6] shows that the crystal parameters are almost identical (see Table 1); the small changes are in line with the different chemical structure. Also the average distribution of diffracted intensity is quite similar except for the expected overall lower values due to the lower number of diffracting electrons. The only exception in this regard is shown by the inversion of the observed intensities for the strong reflections 021 and 121 which are approximately 8550 and 12 450 for **A** and 10 140 and 9600 for **B**, respectively (see Section 4 and Ref. [6]). The density values reveal that an identical mode of packing is operative in both cases.

In contrast, there are striking differences in the physical properties of the two compounds: the melting point $T_m = 372$–373 K for **A** (499–500 K for **B**) and the melting enthalpy $\Delta H_m = 6450$ cal mol^{-1} for **A** ($\Delta H_m = 9740$ cal mol^{-1} for **B**)[1]. These substantial differences can be explained only in terms of a structural disorder of **A** with respect to **B**, in the solid state, the other parameters being virtually identical. The melting entropies ΔS_m for **A** and **B** (~18 and 19 e.u., respectively) are almost the same and confirm the assumption that the entropy of fusion for most of the compounds is mainly due to the change of libration in the solid state to free rotation in the liquid [13]. The present analysis affords an example for which it is possible to quantify the influence of structural disorder on thermodynamic properties.

4. Supplementary material

The anisotropic thermal parameters of the non-hydrogen atoms, the positional parameters of the hydrogen atoms, and a list of calculated and observed structure factors are available from the authors on request.

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