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THE CRYSTAL AND MOLECULAR STRUCTURE OF DIPHENYLADAMANT-1-YLMETHYLSTANNANE: $Sn(C_6H_5)_2(C_{10}H_{15})(CH_3)$

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Summary

The crystal and molecular structure of diphenyladamant-1-ylmethylstannane, $Sn(C_6H_5)_2(C_{10}H_{15})(CH_3)$ has been determined by X-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$, a 12.658(3), b 21.773(5), c 7.255(1) Å, $Z = 4$; $R = 0.0551$, $R_w = 0.0561$ for 2056 unique reflections. The long Sn–ad bond length, (2.175(9) Å) suggests a steric interaction between the adamant-1-yl and neighbouring phenyl groups. This is upheld by a distortion in the tetrahedral geometry about the tin atom when compared to the structures of other tetra-substituted stannanes containing phenyl groups.

Introduction

We have recently been interested in compounds where a tin atom is bound to large organic groups and in particular the effects these groups have on the geometry of the tin environments [1,2]. Of the series of compounds studied, one in particular, tetraadamant-1-yl-stannane ($Sn(ad)_4$) *, gave a large quadrupole splitting in its ^{119}Sn Mössbauer spectrum, 2.70(2) mm s^{-1}. The magnitude of this splitting was explained in terms of a distortion of the tetrahedral environment where the tin atom moves directly down a three-fold axis, from **A** to **B** as depicted in Scheme 1. This would result in the lengthening of one of the Sn–ad bonds, leaving the tin atom in an effective three-fold coordination.

Molecular models have shown that four ad groups, tetrahedrally spaced around the tin atom with normal Sn–C bond lengths results in an extremely sterically hindered structure. However, the environment **B** postulated above would allow the tin atom to fit more easily between the three ad ligands. Moreover, the ^{119}Sn NMR shift, $\delta(^{119}Sn)$ of $Sn(ad)_4$, −73.5 ppm *, was observed approximately 45 ppm upfield from its calculated ** value thus supporting the formation of a distorted

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* ad = adamant-1-yl = tricyclo[3.3.1.1^{3,7}]dec-1-yl.

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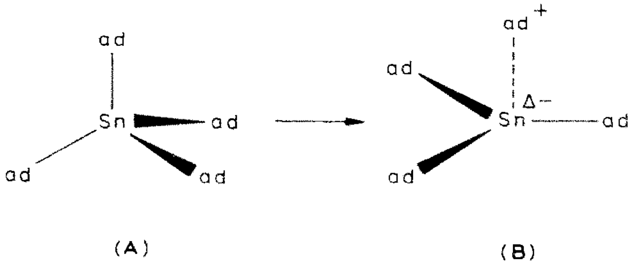

SCHEME 1

structure in solution as well as the solid state. However, since it proved impossible to crystallize Sn(ad)$_4$ (even on very slow cooling only an amorphous powder was obtained), it was necessary to study a material that contained at least one adamant-1-yl ligand and some ligands of approximately compatible size. The title compound was thus chosen for structural determination. Diphenyladamant-1-ylmethylstannane is similar to Sn(ad)$_4$ in that it contains large organic groups bound to the tin. To our knowledge this is the first structural determination of an adamantane ligated to a metal, and only the second for a tetrasubstituted stannane containing three different ligands [9].

Experimental

The title compound was prepared according to literature methods [1], and was recrystallized from diethyl ether/ethanol to give clusters of white needles, m.p. 109–111°C. Found: C, 64.5; H, 6.4. $C_{23}H_{28}Sn$ calcd.: C, 65.2; H, 6.6%.

Crystal data

$C_{23}H_{28}Sn$, M 423.07, orthorhombic, a 12.658(3), b 21.773(5), c 7.255(1) Å, U 1999.5 Å^3, $Z = 4$, D_c 1.405 g cm^{-3}, $(F000) = 864$, Mo-K_α (graphite monochromated) (λ 0.71069 Å), space group, $P2_12_12_1$ no-19 [3], was determined from precession photographs (Cu-K_α radiation, λ 1.5405 Å, Ni filter) systematic absences: $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd, μ(Mo-K_α) 11.87 cm^{-1}.

Data collection [4]

Data were measured on an Enraf–Nonius CAD4 diffractometer using a crystal ca. $0.25 \times 0.25 \times 0.4$ mm^3. Final unit cell parameters were calculated by a least-squares refinement of the setting angles for a series of reflections with $\theta \approx 15°$. Intensities for h, k, $l > 0$ relfections with $1.5 < \theta < 25°$ were measured by an ω–2θ scan technique with a scan width $\Delta\theta = (0.8 + 0.35 \tan \theta)°$. The overall scan rate was variable between 1.3 and 6.7° min^{-1}. Two standard reflections were recorded approximately every 1 h, their intensities showed no significant change over the duration of the data collection. The data were corrected for Lp effects but not for absorption 2056 reflection with $F_o > 3\sigma(F_o)$ were used in the structure refinement.

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* Value rel. Sn(Me)$_4$, have values high field.

** Values calculated from additivity factors.

Structure determination

The structure solution and refinement was carried out on the University of Essex D.E.C. PDP-10 computer using a set of programs for crystal structure determination written by G.M. Sheldrick. Scattering factors for neutral atoms were taken from ref. 5.

The structure was solved using routine heavy atom methods from which the coordinates of the tin atom were assigned. The coordinates of the remaining carbon atoms were located from subsequent Fourier maps. Full matrix least-squares refinement with individual anisotropic temperature factors converged at $R = 0.059$ where $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. Refinement was continued using a weighting scheme of $w = 1$ for $| F_o | \leq A$ and $w = (A/| F_o |)^2$ for $| F_o | > A$ and at convergence R and R_w were 0.0551 and 0.0561 respectively where $R_w = [\Sigma w(\| F_o | - | F_c \|)^2 / \Sigma \omega | F_o |^2]^{1/2}$. The final numerical value of A was set at 20.

The space group $P2_12_12_1$ is non-centrosymmetric and the Sn atom has an appreciable anomalous scattering factor. Although we could have refined the structure in both absolute configurations, as this was not thought likely to affect the positional coordinates, this exercise was not carried out.

From subsequent difference maps peaks were found at positions attributable to some of the hydrogen atoms of the two phenyl rings. However, the remaining hydrogen atoms had to be geometrically estimated. The coordinates of the hydrogen

TABLE 1

ATOMIC POSITIONAL PARAMETERS FOR Sn AND C ($\times 10^5$) FOR $Sn(C_6H_5)_2(C_{10}H_{15})(CH_3)$ [a]

Atom	x	y	z
Sn	16416(5)	36728(3)	20896(9)
C(11)	05780(91)	27486(57)	94342(186)
C(12)	04552(108)	21944(61)	84854(192)
C(13)	10950(95)	17059(63)	88115(174)
C(14)	18891(88)	17691(52)	01292(192)
C(15)	20243(80)	23023(49)	10480(181)
C(16)	13752(73)	28101(43)	07585(141)
C(21)	28557(112)	31273(73)	54473(210)
C(22)	36758(148)	30792(102)	67487(203)
C(23)	45229(146)	34792(101)	66534(276)
C(24)	45268(118)	39279(89)	53613(267)
C(25)	37487(90)	39713(78)	40170(238)
C(26)	28961(86)	35847(51)	40581(156)
C(3)	02528(66)	40217(42)	34997(121)
C(31)	05148(80)	46645(51)	42208(182)
C(32)	99681(99)	35887(51)	51607(158)
C(33)	92798(79)	40651(53)	51607(158)
C(34)	83228(84)	43153(55)	22289(157)
C(35)	85981(96)	49586(60)	40071(229)
C(36)	80672(89)	38927(75)	49015(253)
C(37)	90045(108)	38530(91)	61945(216)
C(38)	92758(121)	45186(89)	69172(184)
C(39)	95259(111)	49320(71)	52948(252)
C(4)	21099(109)	43144(63)	99644(218)

[a] The e.s.d's are given in parentheses.

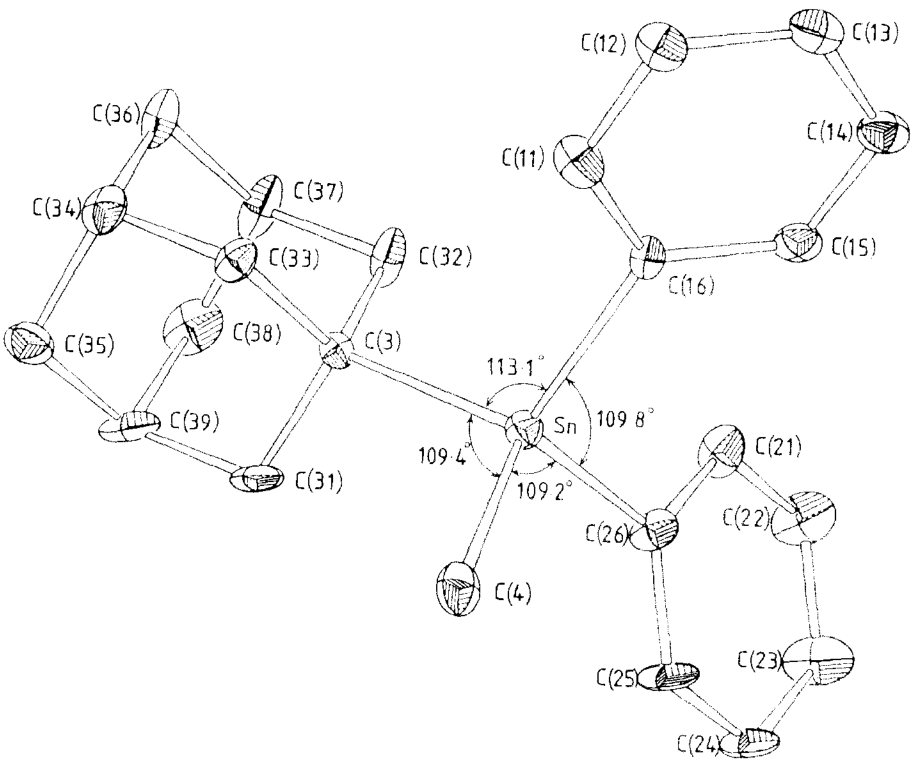

Fig. 1. Molecular structure of $Sn(C_6H_5)_2(C_{10}H_{15})(CH_3)$ [8].

atoms were not refined. The maximum peak in the final difference map was less than 1 e Å^{-3}. The final atomic coordinates are listed in Table 1.

The positional parameters for hydrogen atoms, together with the anisotropic temperature factors and the structure factors, are available from the authors upon request.

Results and discussion

The overall molecular structure with atom numbering scheme and selected bond angles is illustrated in Fig. 1. Bond distances and bond angles are listed in Tables 2 and 3 respectively. As can be seen from Fig. 1 the tin atom lies in a distorted four-coordinate tetrahedral environment. The tin–ad bond length of 2.175(9) Å; although about average for a tin–carbon bond is, however, in relation to the rest of the structure, significantly larger than two other tin–carbon bonds. These are Sn–C(16) and Sn–C(26) (the two Sn–phenyl bonds). This difference in bond length can be accounted for in two ways. Either it is due to the difference between sp^3 hybridization at C(3) and C(4) and the sp^2 hybridization at C(16) and C(26), or it could be, we believe, attributed to a steric interaction between the adamantyl and neighbouring phenyl groups. The variation in bond angles at Sn is, we definitely believe, a steric effect. This is upheld by a distortion in the tetrahedral geometry about the tin atom, when compared to the structures of other phenyl containing

(*Continued on p. 279*)

TABLE 2

BOND LENGTHS (Å) FOR $\mathrm{Sn(C_6H_5)_2(C_{10}H_{15})(CH_3)}$ [a]

Sn–C(16)	2.139(10)	C(3)–C(31)	1.531(14)
Sn–C(26)	2.144(10)	C(3)–C(32)	1.571(14)
Sn–C(3)	2.175(9)	C(3)–C(33)	1.546(12)
Sn–C(4)	2.163(10)	C(31)–C(39)	1.585(17)
		C(32)–C(37)	1.543(18)
C(11)–C(12)	1.398(18)	C(33)–C(34)	1.532(15)
C(12)–C(13)	1.358(18)	C(34)–C(35)	1.531(17)
C(13)–C(14)	1.394(18)	C(34)–C(36)	1.516(19)
C(14)–C(15)	1.350(15)	C(35)–C(39)	1.502(21)
C(15)–C(16)	1.393(14)	C(36)–C(37)	1.515(22)
C(16)–C(11)	1.400(15)	C(37)–C(38)	1.579(26)
		C(38)–C(39)	1.515(24)
C(21)–C(22)	1.407(21)		
C(22)–C(23)	1.383(30)		
C(23)–C(24)	1.354(31)		
C(24)–C(25)	1.389(20)		
C(25)–C(26)	1.369(19)		
C(26)–C(21)	1.418(19)		

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[a] The e.s.d.'s are given in parentheses.

TABLE 3

BOND ANGLES (°) FOR $\mathrm{Sn(C_6H_5)_2(C_{10}H_{15})(CH_3)}$ [a]

C(16)–Sn–C(26)	109.8(4)		
C(16)–Sn–C(3)	113.1(3)		
C(16)–Sn–C(4)	106.8(5)		
C(26)–Sn–C(3)	108.5(4)		
C(26)–Sn–C(4)	109.2(5)		
C(3)–Sn–C(4)	109.4(5)		
C(16)–C(11)–C(12)	120.1(10)	Sn–C(16)–C(15)	122.4(7)
C(13)–C(12)–C(14)	121.6(11)	Sn–C(16)–C(11)	120.5(8)
C(14)–C(13)–C(12)	118.2(11)		
C(15)–C(14)–C(13)	121.0(10)		
C(16)–C(15)–C(14)	122.2(11)		
C(11)–C(16)–C(15)	116.9(10)		
C(26)–C(21)–C(22)	120.2(15)	Sn–C(26)–C(25)	121.0(10)
C(23)–C(22)–C(24)	119.4(17)	Sn–C(26)–C(21)	120.6(9)
C(24)–C(23)–C(22)	119.5(13)		
C(25)–C(25)–C(23)	122.2(17)		
C(26)–C(25)–C(24)	120.1(17)		
C(21)–C(26)–C(25)	118.4(12)		
Sn–C(3)–C(31)	107.7(6)	C(33)–C(34)–C(36)	109.9(10)
Sn–C(3)–C(32)	109.6(6)	C(35)–C(34)–C(36)	110.9(10)
Sn–C(3)–C(33)	112.9(6)	C(34)–C(35)–C(39)	110.5(10)
C(31)–C(3)–C(32)	109.6(9)	C(34)–C(36)–C(37)	110.0(9)
C(32)–C(3)–C(33)	108.2(8)	C(32)–C(37)–C(36)	109.8(14)
C(33)–C(3)–C(31)	108.8(8)	C(32)–C(37)–C(38)	109.4(12)
C(3)–C(31)–C(39)	109.4(9)	C(36)–C(37)–C(38)	108.9(12)
C(3)–C(32)–C(37)	109.2(8)	C(37)–C(38)–C(39)	109.4(10)
C(3)–C(33)–C(34)	110.3(8)	C(38)–C(39)–C(31)	109.2(12)
C(33)–C(34)–C(35)	108.4(10)	C(38)–C(39)–C(35)	110.0(12)
		C(31)–C(39)–C(35)	109.0(12)

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[a] The e.s.d.'s are given in parentheses.

TABLE 4

^{119}Sn MÖSSBAUER AND NMR DATA FOR DIPHENYLADAMANT-1-YLMETHYLSTANNANE [1]

^{119}Sn Mössbauer [a]			^{119}Sn NMR [b]	
δ	Γ [c]	Δ	δ [d](^{119}Sn)	δ(^{119}Sn)
1.34(2)	1.39(2)	CaO	−73	−92.14

[a] Values relative to SnO_2 in mm s^{-1}. [b] Values relative to $Sn(Me)_4$, negative values high field, in ppm. [c] Γ, full width at half length. [d] Value calculated using additivity factors of substituents.

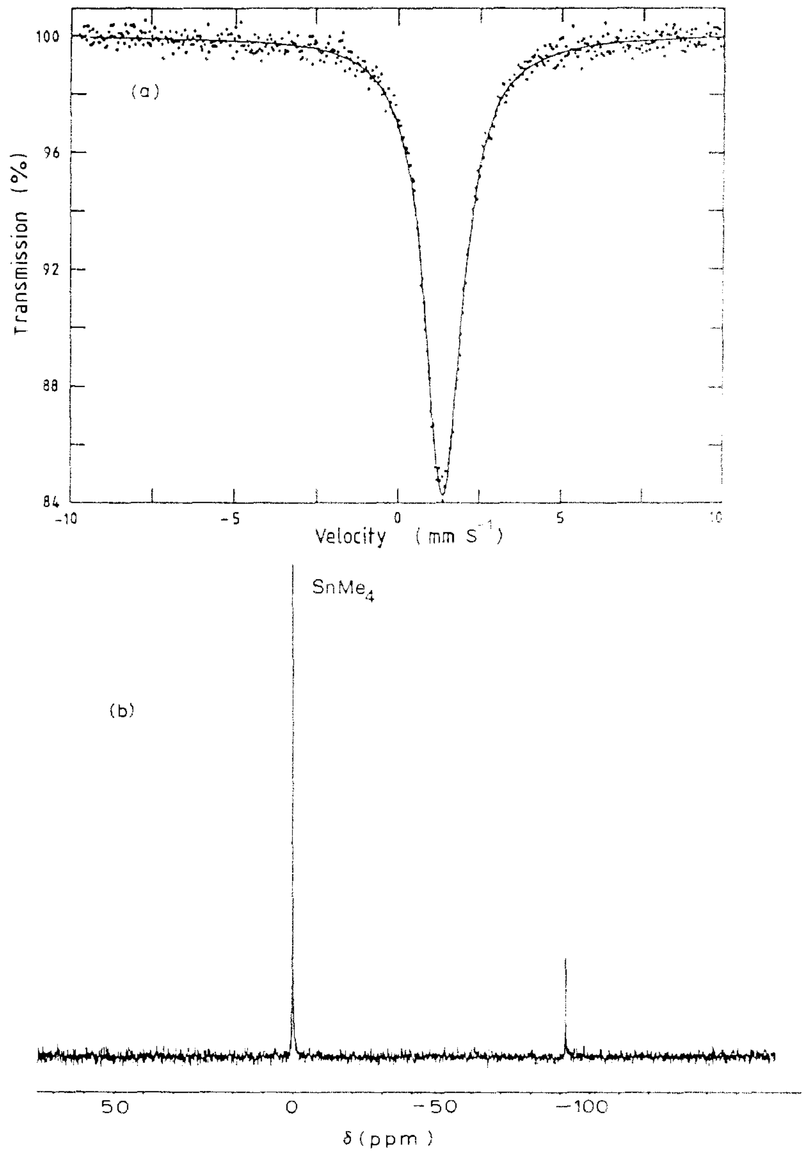

Fig. 2. (a) ^{119}Sn Mössbauer and (b) ^{119}Sn NMR spectra of $SnPh_2(ad)Me$.

tetra-substituted stannanes [6]. The two tin–phenyl bond lengths, mean distance 2.14 Å are comparable with the tin–phenyl bond lengths found in tetraphenylstannane [7].

The ^{119}Sn Mössbauer and NMR parameters for the title compound are shown in Table 4. The Mössbauer linewidth (Fig. 2a) is broad (1.39(2) mm s^{-1}) probably reflecting some unresolved quadrupole splitting due to the distortion in the electronic environment of the tin nucleus. The ^{119}Sn NMR resonance, (Fig. 2b), $\delta(^{119}Sn)$, is observed ~ 20 ppm upfield from its calculated value thus supporting the formation of a distorted structure in solution as well as in the solid, cf. $Sn(ad)_4$.

Although this structure is not totally commensurate with our suggestions for $Sn(ad)_4$ there is nevertheless some evidence of steric effects causing distortion from perfect tetrahedral geometry around the tin atom. It could be expected that the inclusion of three more adamantyl groups would generate even greater distortion.

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