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THE CRYSTAL STRUCTURE OF 1,4-BIS(IODODIPHENYLTIN)BUTANE

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SUMMARY

The solid state structure of 1,4-bis(iododiphenyltin)butane, $(C_6H_5)_2ISn-(CH_2)_4-SnI(C_6H_5)_2$, has been determined by single crystal X-ray diffraction techniques at room temperature. The monoclinic crystals are in the space group $P2_1/c$ with $a = 10.06 \pm 0.02$, $b = 11.36 \pm 0.02$, $c = 14.36 \pm 0.03$ Å and $\beta = 119° \, 40' \pm 18'$. The final isotropic conventional R factor is 9.6% based on 1537 photographically observed data. The calculated and observed densities are 1.95 g/cm^3 and 1.93 g/cm^3 respectively based on two molecules per unit cell. The molecule is symmetrical and resides on a crystallographic center of symmetry. The coordination about each tin atom is approximately tetrahedral. The average Sn–C phenyl bond length is 2.15 ± 0.02 Å, the average methylene bond length is 1.55 ± 0.03 Å, and the Sn–I bond distance is 2.729 ± 0.003 Å.

INTRODUCTION

1,4-Bis(iododiphenyltin)butane, $(C_6H_5)_2ISn-(CH_2)_4-SnI(C_6H_5)_2$ has been synthesized[1] to make available a difunctional tin compound of the type $XR_2Sn-(CH_2)_n-SnR_2X$. 1,4-Bis(iododiphenyltin)butane is prepared by the reaction of iodine with 1,4-bis(triphenyltin)butane:

$$(C_6H_5)_3Sn-(CH_2)_4-Sn(C_6H_5)_3 + I_2 \rightarrow \underset{\text{(I)}}{(C_6H_5)_2SnI-(CH_2)_4-SnI(C_6H_5)_2}$$

$$\text{or} \quad \underset{\text{(II)}}{(C_6H_5)_3Sn-(CH_2)_4-Sn(C_6H_5)I_2} \qquad (1)$$

The purified reaction product has an experimentally measured dipole moment in benzene solution of 5.24 Debye[1,2]. This evidence seems to indicate that the reaction product is the unsymmetrical isomer (II). However, this X-ray structure determination shows the compound to be the symmetrical isomer (I). To explain the apparent anomaly in these results, it has been proposed that the symmetrical isomer (I) forms an

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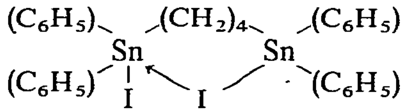
intramolecular complex in solution in which one tin atom is pentacoordinate[2]. It is also possible that in solution the numerous degrees of freedom which the molecule undoubtedly possesses lead to a variety of conformations and a residual dipole moment*.



EXPERIMENTAL

Crystals of 1,4-bis(iododiphenyltin)butane were supplied by Dr. J. J. Miller. The compound crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters of $a = 10.06 \pm 0.02$, $b = 11.36 \pm 0.02$, $c = 14.36 \pm 0.03$ Å and $\beta = 119^\circ 40' \pm 18'$.

Systematic absences of $h0l$ reflections for $l = 2n+1$ and $0k0$ reflections for $k = 2n+1$ indicate the unique space group $P2_1/c$. An experimental density of 1.93 ± 0.02 g/cm^3 determined by flotation in a mixture of methanol and bromoform agrees well with a calculated density of 1.95 g/cm^3 based on two molecules per unit cell. The crystal used for data collection measured 0.30 mm × 0.42 mm × 0.30 mm; the latter dimension was colinear with the rotation axis. The crystal has a linear absorption coefficient, μ, of 40.8 cm^{-1}. No absorption corrections were made**.

Multiple film equiinclination Weissenberg data were collected at room temperature for the reciprocal levels $0kl$ through $9kl$ with zirconium-filtered molybdenum K_α radiation ($\lambda = 0.7107$ Å). The intensities of 1537 independent reflections were estimated visually by comparison with a standard intensity strip and were corrected for Lorentz-polarization effects.

STRUCTURE DETERMINATION AND REFINEMENT

A three-dimensional Patterson function was computed and provided trial coordinates for the tin and iodine atoms***.

A structure factor calculation with the coordinates for the tin and iodine atoms gave an unweighted R factor, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ of 23%. The scattering factor curves for tin and iodine were taken from Hanson *et al.*[9] while those for carbon were taken from the International Tables[10]. The phases from this calculation were used to compute a three-dimensional electron density map which revealed the positions of all other non-hydrogen atoms. The addition of these atomic coordinates to the structure factor calculation reduced the discrepancy index, R_1, to 12.2%.

After several cycles of full matrix isotropic least-squares refinement of the 16

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* The authors thank one of the referees for this comment.

** It has been demonstrated that failure to make absorption corrections does not result in errors in the atomic positional parameters appreciably larger than the assigned standard deviations[3–5]. In this study the maximum dimensions of an irregularly shaped crystal have been reported.

*** Calculations were performed with programs[6–8] which were modified for an IBM 7040 16K computer.

TABLE 1

ATOMIC PARAMETERS FOR $(C_6H_5)_2ISn-(CH_2)_4-SnI(C_6H_5)_2$ WITH ESTIMATED STANDARD DEVIATIONS[a]

Atom	x	y	z	B (Å^2)
I	0.8027(1)	0.1781(2)	0.0996(1)	3.40(5)
Sn	0.8706(2)	0.3930(1)	0.1953(1)	2.03(4)
C_2	0.674(3)	0.441(2)	0.209(2)	2.4(4)
C_3	0.635(3)	0.384(3)	0.276(2)	4.4(6)
C_4	0.506(4)	0.418(3)	0.284(2)	4.8(6)
C_5	0.423(4)	0.509(3)	0.225(3)	5.2(7)
C_6	0.459(4)	0.572(3)	0.149(2)	4.6(6)
C_7	0.586(3)	0.534(3)	0.151(2)	4.1(5)
C_8	0.916(3)	0.511(2)	0.098(2)	2.9(4)
C_9	0.986(2)	0.453(2)	0.034(2)	2.1(4)
C_{10}	0.058(3)	0.353(2)	0.346(2)	2.5(4)
C_{11}	1.047(3)	0.365(2)	0.439(2)	3.1(5)
C_{12}	1.175(4)	0.345(3)	0.545(3)	5.8(8)
C_{13}	1.311(4)	0.319(3)	0.545(2)	4.8(6)
C_{14}	1.324(4)	0.312(3)	0.455(2)	4.9(6)
C_{15}	1.202(3)	0.325(2)	0.354(2)	3.8(5)

[a] Numbers in parentheses here and in succeeding Tables are standard deviations in the least significant digits.

non-hydrogen atoms in the asymmetric unit, the final discrepancy index, R_1, was 9.6% and the weighted discrepancy index $R_2 = [\Sigma w \cdot |\,|F_o| - |F_c|\,|^2 / \Sigma w \cdot |F_o|^2]^{\frac{1}{2}} \times 100$, was 11.7%. Variable weights were assigned as follows: $\sqrt{w} = 20/F_o$ if $I_o > (\sqrt{}20) \cdot I_{min}$; $\sqrt{w} = I_o^2/F_o \cdot I_{min}^2$ if $I_o < (\sqrt{}20) \cdot I_{min}$. Individual scale factors were used for each reciprocal layer of data throughout the refinement.

Final atomic parameters with estimated standard deviations are given in Table 1. Table 2 lists the observed and calculated structure factors scaled to $F(000) = 804$.

DISCUSSION

1,4-Bis(iododiphenyltin)butane exists in the solid state as discrete molecules

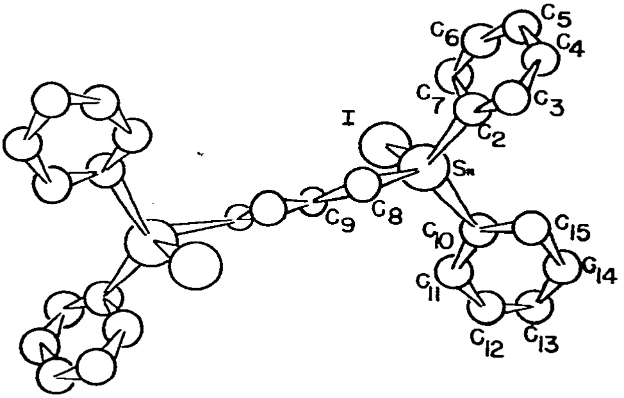

Fig. 1. The molecular configuration of $(C_6H_5)_2ISn-(CH_2)_4-SnI(C_6H_5)_2$.

TABLE 2

STRUCTURE FACTORS FOR $(C_6H_5)_2ISn{-}(CH_2)_4{-}SnI(C_6H_5)_2$ SCALED TO $F(000)$

L	FO	FC
[illegible]	[illegible]	[illegible]

TABLE 3

BOND LENGTHS IN $(C_6H_5)_2ISn{-}(CH_2)_4{-}SnI(C_6H_5)_2$ WITH ESTIMATED STANDARD DEVIATIONS[a]

Bond	Distance (Å)	Bond	Distance (Å)
Sn–I	2.729(2)	C_8–C_9	1.54(3)
Sn–C_2	2.16(2)	C_9–$C_{9'}$	1.56(3)
Sn–C_{10}	2.14(2)		
Sn–C_8	2.14(2)		
C_2–C_3	1.35(4)	C_{10}–C_{11}	1.40(3)
C_3–C_4	1.40(5)	C_{11}–C_{12}	1.47(4)
C_4–C_5	1.35(4)	C_{12}–C_{13}	1.40(5)
C_5–C_6	1.48(5)	C_{13}–C_{14}	1.36(4)
C_6–C_7	1.34(4)	C_{14}–C_{15}	1.39(4)
C_7–C_2	1.38(4)	C_{15}–C_{10}	1.43(4)

[a] A primed number refers to the atom related by inversion through the center of symmetry.

TABLE 4

INTERATOMIC BOND ANGLES IN $(C_6H_5)_2ISn{-}(CH_2)_4{-}SnI(C_6H_5)_2$ WITH ESTIMATED STANDARD DEVIATIONS

Atoms	Angles (°)	Atoms	Angles (°)
C_2–Sn–C_{10}	111.6(9)	Sn–C_8–C_9	115(1)
C_2–Sn–C_8	113.3(9)	C_8–C_9–$C_{9'}$	110(2)
C_{10}–Sn–C_8	115.8(9)		
C_2–Sn–I	104.6(6)		
C_8–Sn–I	108.1(6)		
C_{10}–Sn–I	102.1(6)		
C_2–C_3–C_4	121(3)	C_{10}–C_{11}–C_{12}	123(3)
C_3–C_4–C_5	119(3)	C_{11}–C_{12}–C_{13}	114(3)
C_4–C_5–C_6	122(3)	C_{12}–C_{13}–C_{14}	123(3)
C_5–C_6–C_7	117(3)	C_{13}–C_{14}–C_{15}	123(3)
C_6–C_7–C_2	126(3)	C_{14}–C_{15}–C_{10}	118(3)
C_7–C_2–C_3	119(2)	C_{15}–C_{10}–C_{11}	119(2)

of crystallographically required $\bar{1}$ (C_i) symmetry (Fig. 1). Intramolecular bond lengths and angles are given in Tables 3 and 4.

The coordination about the tin atom is that of a slightly distorted tetrahedron with maximum and minimum angles of 115.8(9) and 102.1(6) degrees respectively. The C–Sn–I angles are all smaller than the tetrahedral value of 109.5°, while the C–Sn–C angles are all greater than the tetrahedral value. The average C–Sn–I angle is 104.9° and the average C–Sn–C angle is 113.6°. This observation is in agreement with increased p character in the hybrid orbitals used by tin in bond formation to the more electronegative iodine ligand[11].

The average Sn–C phenyl bond distance is 2.15(2) Å and agrees well with similar Sn–C distances from other systems. The average tin–phenyl carbon distances in the compounds $(C_6H_5)_3Sn[\pi\text{-}C_5H_5Fe(CO)_2]$[12], $(C_6H_5)_3SnMn(CO)_5$[13], $(C_6H_5)_3Sn[(C_6H_5)_3PMn(CO)_4]$[14], and $(CO)_4CoSn(C_6H_5)_2Mn(CO)_5$[15] are 2.13, 2.15, 2.17 and 2.18 Å respectively. The C–C distances about the phenyl rings have an aver-

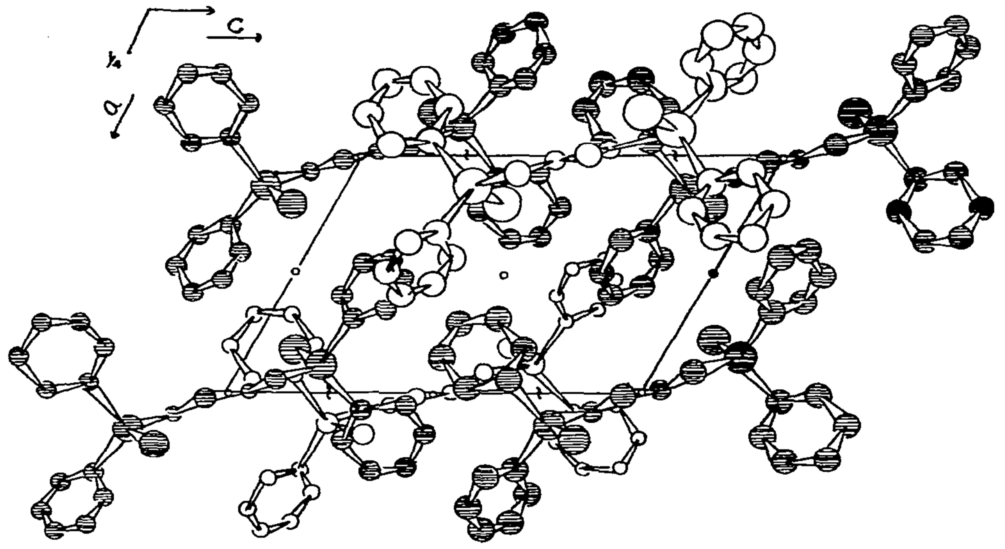

Fig. 2. [010] projection of the unit cell.

age value of 1.40 Å (Range: 1.34–1.48 Å) in good agreement with the accepted C–C phenyl distance of 1.397 Å. The average C–C bond length in the methylene chain is 1.55 Å which is normal for this type of bond.

Fig. 2 shows the [010] projection of the unit cell. The shortest nonhydrogen atom interatomic approach is 3.7 Å between carbon atoms of two adjacent phenyl rings.

The centrosymmetric structure of 1,4-bis(iododiphenyltin)butane present in the solid state does not explain the large dipole observed for this molecule in solution; however, an intramolecular interaction may exist when the molecule is dissolved in nonpolar solvents or a residual dipole may result because of a variety of conformations in solution.

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