Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Isomorphous dichloro- and dibromo(2-methyl-2-phenylpropyl)phenylstannane, both displaying the same intramolecular π–π interaction at 120 K

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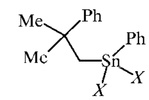
Received 25 September 2003
Accepted 22 October 2003
Online 8 November 2003

The title compounds, dichloro- and dibromoneophylphenyltin, $[SnCl_2(C_6H_5)(C_{10}H_{13})]$ and $[SnBr_2(C_6H_5)(C_{10}H_{13})]$, respectively, are remarkable for the 'U' shape of the molecules, whereby the two phenyl groups are brought face-to-face in an arrangement that permits intermolecular C—H$\cdots\pi$ bonds to connect the molecules into layers parallel to (100). Intermolecular Sn–halide bonds are notably absent from the structures.

Comment

Numerous entries in the Cambridge Structural Database (CSD; Allen, 2002) reveal that simple non-functionalized diorganodihalotins, $RR'SnX_2$, exist in the solid state as molecular compounds, sometimes exhibiting various types of intermolecular interaction. Regardless of the involvement of the tin centre in these intermolecular interactions [such as that noted for a series of compounds (with X = Cl) by Amini *et al.* (1987)], they are generally weak. The interactions and conformations of the title compounds, (I) and (II), have been investigated. Fig. 1 shows the molecule of (I); this figure, with Br atoms substituted for Cl atoms, is equally appropriate for the molecule of (II). Selected bond lengths and angles for (I) and (II) are given in Table 1. The C—C distances and internal angles in the benzene rings of (I) and (II) (not given in Table 1) are in the ranges 1.346 (12)–1.406 (8) Å and 117.3 (10)–122.6 (11)°, respectively, and are not discussed further. The Sn—C bond lengths and the angles at the Sn atom are similar for the two molecules. More significant, however, is the similarity of the intramolecular Sn—X bond lengths [X = Cl for (I) and Br for (II)]; as discussed in greater detail later, such a similarity is not observed in other formally similar compounds. The torsion angles in Table 1 clearly demonstrate that, while (I) and (II) are isomorphous the sample crystals are, by chance, enantiomeric, *i.e.* of opposite polarity.



(I) X = Cl
(II) X = Br

Totally unexpected, however, is the overall 'U' shape of the molecules of (I) and (II), which brings the two benzene rings in the molecule face-to-face. The intramolecular interaction between the rings [designated as ring 1, with centroid $Cg1$, forming part of the 2-methyl-2-phenylpropyl (also known as neophyl) ligand, and ring 2, with centroid $Cg2$, bonded directly to the Sn atom] is characterized as now described [values for (II) are given in parentheses]. The distance between the ring centroids ($Cg1\cdots Cg2$, vector A) is 3.94 Å. The perpendicular distances from $Cg1$ to the plane of ring 2 (vector B), and from $Cg2$ to the plane of ring 1 (vector C), are 3.3 and 3.76 Å, respectively. The dihedral angle between the planes, the angle between vectors A and B at $Cg1$, and the angle between vectors A and C at $Cg2$ are, respectively, 14.0 (2) [11.1 (2)], 17.5 (17.7) and 31.3° (28.8°). The intramolecular separation between these planes, the only face-to-face separation between them of any significance, is roughly comparable to that normally associated with π–π stacking (*ca* 3.4 Å; Pauling, 1960). For both (I) and (II), this conformation results in the C—H$\cdots\pi$ interactions given in Table 2. These connect the molecules to form layers parallel to (100) (Fig. 2) and related to one another by cell translation. Each C—H$\cdots\pi$ interaction is confined to a single ring type (see Fig. 2 and Table 2), which provides both the donated H atom and the benzene-ring acceptor. Ring 1 is employed in the connection of molecules related to one another by the operation of a crystallographic twofold screw axis with equation $\frac{1}{2}$, y, $\frac{1}{2}$, in which interaction the donor-to-acceptor polarity in (I) is in the $+b$ direction. For ring 2, the equation of the twofold screw axis is $\frac{1}{2}$, y, 0, and the polarity of the interaction in (I) is now in the $-b$ direction. Thus, in each case, the C—H$\cdots\pi$ interaction can be considered to connect chains of molecules propagating in the b direction, but the participation of the molecules in both chains connects them and completes the connectivity of the layer. Clearly, it is the orientations of the molecules and the resulting polarity of the C—H$\cdots\pi$ interactions that determine the polarity of the structure as a whole, which is compatible with the non-centrosymmetric space group $P2_1$. The layer surfaces are populated primarily by methyl groups, the edges of the phenyl groups and Cl atoms. There is, however, no evidence of C—H$\cdots$Cl or any other form of intermolecular interaction other than van der Waals interactions across the interlayer boundary. Indeed, the shortest intermolecular Sn–halide distances in (I) and (II) are of the order of 5.4 and 5.6 Å, respectively. The situation in (I) is in striking contrast to that found in the formally analogous compounds dichloro-

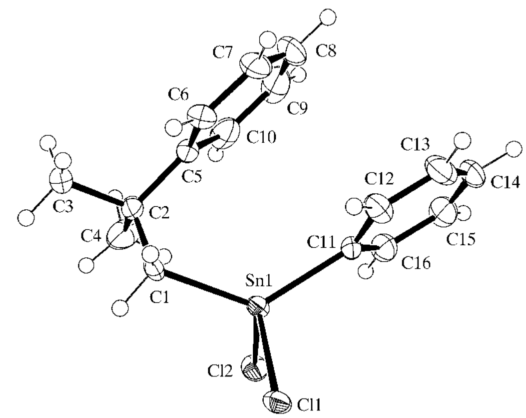


Figure 1
The molecule of (I), showing the atom-labelling scheme. This figure, with Br atoms substituted for Cl atoms, applies equally well to (II). Non-H atoms are shown with 50% probability displacement ellipsoids and H atoms are shown as spheres of arbitrary radii.

(diphenyl)tin, Ph_2SnCl_2, (III) (CSD, Version 5.24, refcode DCDPSN; Greene & Bryan, 1971), and methylphenyltin(IV) dichloride, (IV) (CSD refcode GIJYAZ; Amini *et al.*, 1987). Bokii *et al.* (1972), in re-evaluating the published results of Greene & Bryan (1971), showed that intermolecular Sn$\cdots$Cl contacts [lengths now computed as being in the range 3.7697 (18)–3.8724 (19) Å] are present, inducing significant distortion of the Sn coordination and, in particular, accounting for the comparatively wide range [2.336 (2)–2.357 (2) Å] in the primary Sn—Cl bond lengths in (III). Likewise, for (IV), Amini *et al.* (1987) report primary Sn—Cl bonds in the range 2.36 (1)–2.39 (1) Å associated with intermolecular Sn$\cdots$Cl contacts now computed to be in the range 3.422 (9)–3.806 (11) Å. Similar weak intermolecular Sn$\cdots$I bonds have

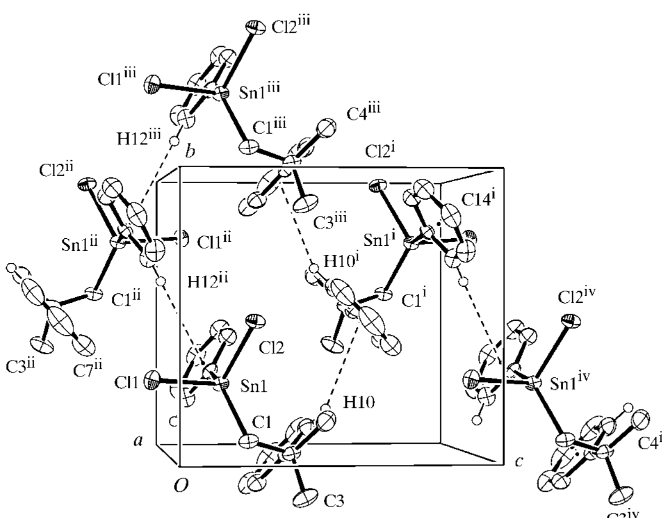


Figure 2
C—H$\cdots\pi$ interactions (dashed lines) between molecules of (I) in a layer parallel to (100). Non-H atoms are shown with 50% probability displacement ellipsoids and those H atoms involved in the contacts are shown as spheres of arbitrary radii. Selected atoms are labelled. [Symmetry codes: (i) $1-x, \frac{1}{2}+y, 1-z$; (ii) $1-x, \frac{1}{2}+y, -z$; (iii) $x, 1+y, z$; (iv) $x, y, 1+z$.]

been invoked by Howie & Wardell (1996) to explain features of the coordination of the Sn atom in diphenyltin diiodide (CSD refcode HIHCUW). Also present in (III), with no equivalent in the structures of (I) and (II), are aryl C—H$\cdots$Cl hydrogen bonds, with C$\cdots$Cl distances in the range 3.449 (6)–3.825 (7) Å and, for C—H set at 1.08 Å, H$\cdots$Cl distances and C—H$\cdots$Cl angles in the respective ranges 2.80–2.81 Å and 118–156°. Pairwise π–π and C—H$\cdots\pi$ contacts are present in all three structures, but in (III), the former are in the form of intermolecular contacts between centrosymmetrically related pairs of only one of the two molecules present in the asymmetric unit, as distinct from the intramolecular contact of this type present in (I) and (II). The presence of intermolecular Sn$\cdots$Cl bonds in (III) and (IV) is clearly consistent with the differences in the lengths of the primary Sn$\cdots$Cl bonds in these structures, and the absence of these intermolecular bonds is consistent with the equivalence of the intramolecular bonds in (I). The fact that the Sn$\cdots$Cl bonds are longer in (I) than in (III) or (IV) is, however, surprising.

Experimental

Compound (I) was obtained by reaction of $[PhC(Me)_2CH_2]Ph_3Sn$, (V), with $HgCl_2$ in acetone. Recrystallization from ethanol provided crystals suitable for analysis (m.p. 328–330 K). IR (Nujol mull, cm^{-1}): ν 344 (*s br*, Sn—Cl); ^{1}H NMR (200 MHz, Me_2CO-d_6): δ 1.53 [*s*, 6H, $J(^{119,117}Sn–^1H)$ = 10.7 Hz, Me], 2.67 [*s*, 2H, $J(^{119,117}Sn–^1H)$ = 78.4, 75.3 Hz, CH_2Sn], 7.3–7.7 (*m*, 10H, Ph); ^{13}C NMR (50 MHz, Me_2CO-d_6): δ 32.7 [$J(^{119,117}Sn–^{13}C)$ = 67.2, 64.2 Hz, Me], 39.1 [$J(^{119,117}Sn–^{13}C)$ = 22 Hz, CMe_2], 49.1 [$J(^{119,117}Sn–^{13}C)$ = 548, 524 Hz, CH_2], 126.1 (C_m, Ph_{neo}), 127.5 (C_p, Ph_{neo}), 129.7 [$J(^{119,117}Sn–^{13}C)$ = 22 Hz, C_o, Ph_{neo}], 129.8 [$J(^{119,117}Sn–^{13}C)$ = 82.2, 78.4 Hz, C_m, PhSn], 131.6 [$J(^{119,117}Sn–^{13}C)$ = 16.7 Hz, C_p, PhSn], 135.4 [$J(^{119,117}Sn–^{13}C)$ = 65.0, 62.3 Hz, C_o, PhSn], 142.9 [$J(^{119,117}Sn–^{13}C)$, C_{ipso}, PhSn], 150.5 [$J(^{119,117}Sn–^{13}C)$ = 55.5, 52.5 Hz, C_{ipso}, Ph_{neo}]; ^{119}Sn NMR (75 MHz, Me_2CO-d_6): δ −32.3. Compound (II) was obtained by reaction of (V) with Br_2 in acetone solution [the (V)/Br_2 molar ratio was 1:2] and recrystallized from heptane (m.p. 318–320 K). IR (polythene film, cm^{-1}): ν 252 (*br*, Sn—Br); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.58 [*s*, 6H, $J(^{119,117}Sn–^1H)$ = 10.4 Hz, Me], 2.84 [*s*, 2H, $J(^{119,117}Sn–^1H)$ = 73.6, 70.8 Hz, CH_2Sn], 7.3–7.7 (*m*, 10H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.4 [$J(^{119,117}Sn–^{13}C)$ = 69.4, 66.5 Hz, Me], 38.8 [$J(^{119,117}Sn–^{13}C)$ = 19.9 Hz, CMe_2], 49.4 [$J(^{119,117}Sn–^{13}C)$ = 475.7, 455.2 Hz, CH_2], 125.1 (C_m, Ph_{neo}), 127.0 (C_p, Ph_{neo}), 129.0 [$J(^{119,117}Sn–^{13}C)$ = 22.2 Hz, C_o, Ph_{neo}], 129.1 [$J(^{119,117}Sn–^{13}C)$ = 78.7, 75.6 Hz, C_m, PhSn], 130.8 [$J(^{119,117}Sn–^{13}C)$ = 16.4 Hz, C_p, PhSn], 134.2 [$J(^{119,117}Sn–^{13}C)$ = 65.0, 62.3 Hz, C_o, PhSn], 139.4 [$J(^{119,117}Sn–^{13}C)$ 637, 604 Hz, C_{ipso}, PhSn], 148.5 [$J(^{119,117}Sn–^{13}C)$ = 38 Hz, C_{ipso}, Ph_{neo}].

Compound (I)

Crystal data

$[SnCl_2(C_6H_5)(C_{10}H_{13})]$	D_x = 1.618 Mg m^{-3}
M_r = 399.89	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 4852 reflections
a = 9.1673 (3) Å	θ = 2.9–27.5°
b = 9.0698 (2) Å	μ = 1.87 mm^{-1}
c = 9.8939 (3) Å	T = 120 (2) K
β = 93.8823 (17)°	Block, colourless
V = 820.75 (4) Å^3	0.24 × 0.22 × 0.14 mm
Z = 2	

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer	3239 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)	$\theta_{max} = 27.5°$
$T_{min} = 0.668$, $T_{max} = 0.692$	$h = -11 \rightarrow 10$
6614 measured reflections	$k = -10 \rightarrow 11$
3375 independent reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{max} = 0.78$ e Å^{-3}
$wR(F^2) = 0.063$	$\Delta\rho_{min} = -0.72$ e Å^{-3}
$S = 1.05$	Absolute structure: Flack (1983), 1386 Friedel pairs
3375 reflections	Flack parameter = 0.07 (3)
174 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.81P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Compound (II)

Crystal data

$[SnBr_2(C_6H_5)(C_{10}H_{13})]$	Mo $K\alpha$ radiation
$M_r = 488.81$	Cell parameters from 7897 reflections
Monoclinic, $P2_1$	$\theta = 2.9–27.5°$
$a = 9.2966$ (3) Å	$\mu = 6.24$ mm^{-1}
$b = 9.3763$ (3) Å	$T = 120$ (2) K
$c = 9.6898$ (3) Å	Slab, colourless
$\beta = 93.010$ (2)°	$0.30 \times 0.18 \times 0.08$ mm
$V = 843.47$ (5) Å^3	
$Z = 2$	
$D_x = 1.925$ Mg m^{-3}	

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer	3618 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.034$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)	$\theta_{max} = 27.5°$
$T_{min} = 0.528$, $T_{max} = 0.861$	$h = -12 \rightarrow 10$
9872 measured reflections	$k = -12 \rightarrow 11$
3772 independent reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$wR(F^2) = 0.061$	$\Delta\rho_{min} = -1.27$ e Å^{-3}
$S = 1.08$	Absolute structure: Flack (1983), 1735 Friedel pairs
3772 reflections	Flack parameter = 0.006 (7)
174 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

In the final stages of the refinement of (I), H atoms were introduced in calculated positions and treated as riding, with C—H distances of 0.95, 0.99 and 0.98 Å, and U_{iso}(H) values of 1.2, 1.2 and 1.5 times U_{eq} of the parent C atom for, respectively, phenyl, methylene and methyl H atoms. The rotational orientation of the rigid-body methyl groups was also refined. Subsequent to the initial independent solution and refinement of the structure of (II), the structure was re-refined in an identical manner with the coordinates found for (I) as starting parameters, but with Br atoms substituted for Cl atoms.

Table 1
Selected bond lengths, bond angles and torsion angles (Å, °) for compounds (I) and (II).

	(I), X = Cl	(II), X = Br
Sn1—C11	2.121 (4)	2.122 (3)
Sn1—C1	2.141 (5)	2.151 (4)
Sn1—X2	2.3727 (12)	2.4895 (4)
Sn1—X1	2.3740 (8)	2.4963 (4)
C1—C2	1.516 (6)	1.534 (5)
C2—C3	1.520 (6)	1.531 (5)
C2—C4	1.527 (6)	1.530 (5)
C2—C5	1.538 (6)	1.517 (5)
C11—Sn1—C/1	127.53 (16)	127.04 (14)
C11—Sn1—X2	104.91 (10)	105.57 (10)
C1—Sn1—X2	110.36 (13)	110.13 (10)
C11—Sn1—X1	107.15 (10)	106.84 (9)
C1—Sn1—X1	102.62 (14)	102.38 (10)
X2—Sn1—X1	101.31 (5)	102.183 (13)
C2—C1—Sn1	115.0 (3)	114.5 (3)
C1—C2—C3	109.0 (4)	108.1 (3)
C1—C2—C4	109.1 (4)	108.6 (3)
C3—C2—C4	107.1 (4)	106.9 (3)
C1—C2—C5	108.5 (3)	109.0 (3)
C3—C2—C5	110.3 (3)	110.7 (3)
C4—C2—C5	112.8 (4)	113.3 (3)
C11—Sn1—C1—C2	52.5 (4)	52.1 (3)
X2—Sn1—C1—C2	−76.7 (3)	77.3 (3)
X1—Sn1—C1—C2	176.1 (3)	−174.6 (2)
Sn1—C1—C2—C3	−172.9 (3)	−172.8 (2)
Sn1—C1—C2—C4	70.4 (4)	−71.5(4)
Sn1—C1—C2—C5	−52.8 (4)	52.3 (3)
C1—C2—C5—C10	116.2	−115.6 (4)
C3—C2—C5—C10	−124.5 (4)	125.6 (4)
C4—C2—C5—C10	−4.8 (5)	5.5 (5)
C1—C2—C5—C6	−61.2 (4)	62.2 (4)
C3—C2—C5—C6	58.2 (5)	−56.6 (4)
C4—C2—C5—C6	177.9 (4)	−176.8 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

H_{perp} is the perpendicular distance of the H atom from the plane of the benzene ring. Cg1 and Cg2 are defined in the *Comment*.

	Compound	C—H	H···Cg	H_{perp}	X—H···Cg	X···Cg
C10—H10···Cg1^{i}	(I)	0.95	3.32	2.97	140	4.10
	(II)	0.95	3.41	2.91	137	4.15
C12—H12···Cg2^{ii}	(I)	0.95	3.17	2.79	171	4.12
	(II)	0.95	3.24	2.79	166	4.12

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $1 - x, y - \frac{1}{2}, -z$.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

The authors acknowledge the use of both the EPSRC's Chemical Database Service (Fletcher *et al.*, 1996) at Daresbury Laboratory, Warrington, England, for access to the Cambridge Structural Database, and X-ray crystallographic service at Southampton, England, for data collection. We thank CNPq, FUJB and CAPES, Brazil, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1033). Services for accessing these data are described at the back of the journal.

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