

Tetrakis(3,5-dichlorophenyl)tin(IV)

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Key indicators

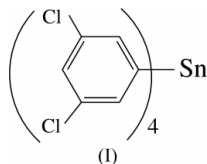
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$
 R factor = 0.050
 wR factor = 0.123
Data-to-parameter ratio = 17.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[\text{Sn}(\text{C}_6\text{H}_3\text{Cl}_2)_4]$, crystallizes in the monoclinic space group $C2/c$, with the molecules having no symmetry. In contrast, its isostere $[3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3]_4\text{Sn}$, (II), crystallizes in the tetragonal space group $P\bar{4}21c$.

Comment

The crystal structures of most of the tetraaryltin(IV) compounds reported to date (Lloyd & Brock, 1997; Schürmann *et al.*, 1999; Wharf & Bélanger-Gariépy, 2003) are in close-packed tetragonal space groups, *viz.* $P\bar{4}21c$, $I\bar{4}$ and $P\bar{4}2/n$. In these structures, the Ar_4Sn molecules are located on sites of $\bar{4}$ symmetry, the molecular conformation with the lowest energy, as determined previously for Ar_4Si analogues (Hutchings *et al.*, 1975). This is also the case for $(\text{C}_6\text{F}_5)_4\text{Sn}$ (Karipides *et al.*, 1974) and $(m\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$ (Karipides & Oertel, 1977), both of which crystallize in $I4_1/a$. Deviations from tetragonal symmetry appear to require larger, more obtrusive, ring substituents, examples being $[p\text{-CH}_3\text{S}(\text{O}_2)\text{C}_6\text{H}_4]_4\text{Sn}$ (Wharf *et al.*, 1990) and $(p\text{-CH}_3\text{CH}_2\text{C}_6\text{H}_4)_4\text{Sn}$ (Wharf & Lebuis, 2000), which both crystallize in $C2/c$ with molecules having 2 symmetry, and others having no molecular symmetry, such as $(p\text{-CH}_3\text{CH}_2\text{OC}_6\text{H}_4)_4\text{Sn}$ in $P2_1/c$ (Wharf & Simard, 1991), and both $(m\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Sn}$ in $C2/c$ and $(o\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Sn}$ in $P\bar{1}$ (Wharf & Simard, 1995).

Desiraju & Jagarlapudi (1986) have proposed that since the Cl atom and the methyl group have almost the same volume, they act as isosteres, with chlorine/methyl analogues being effectively isomorphous. One such example is the toluene and chlorobenzene solvates of 2,3,7,8-tetraphenyl-1,9,10-anthryridine (Madhavi *et al.*, 1997). However, Ng (1997) found that $(p\text{-ClC}_6\text{H}_4)_4\text{Sn}$ crystallizes in $P\bar{1}$, with no molecular symmetry, and is clearly not isomorphous with $(p\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$ in $I\bar{4}$ (Karipides & Wolfe, 1975). We present here the crystal structure of the title compound, (I), which has been investigated for comparison with its methyl analogue $[3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3]_4\text{Sn}$, (II) (Wharf & Bélanger-Gariépy, 2003).



Compound (I) crystallizes in space group $C2/c$ with the molecules having no symmetry and in this way resembles $(m\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Sn}$. However, here the Sn—C distances are identical [2.134 (6)–2.135 (6) Å], and the distortion from tetrahedral geometry at the Sn atom is small [105.9 (2)–

Received 29 July 2003
Accepted 18 August 2003
Online 23 August 2003

113.8 (2)°; Fig. 1 and Table 1]. Intermolecular contacts are all greater than the van der Waals distances, the shortest Cl···Cl distance being 3.60 Å and the shortest H···Cl distance being 3.03 Å.

Violations of the chloro–methyl exchange rule are observed when intermolecular directional forces or weak ‘bonds’ are present (Desiraju & Jagarlapudi, 1986). Schürmann *et al.* (1999) have proposed weak C–H···Cl interactions – still greater than the van der Waals distances – as a possible rationale for the different packing of (*p*-ClC₆H₄)₄Sn and (*p*-CH₃C₆H₄)₄Sn. For (I), the packing diagram (Fig. 2) does not show any clear set of such directed interactions, meaning a more detailed comparison of the structures of (I) and (II) is required for the basis of the crystal structure differences to be determined.

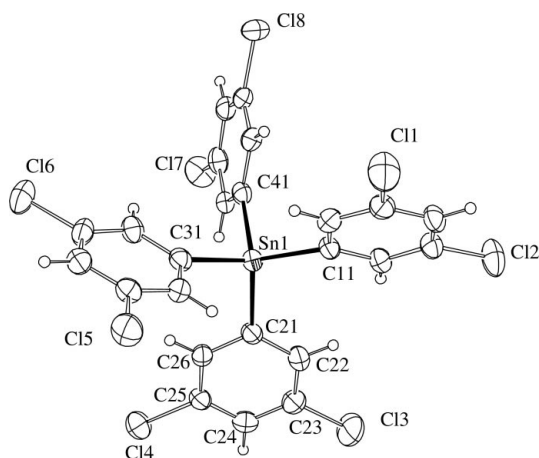


Figure 1
ORTEP (SHELXTL; Sheldrick, 1997) drawing of (I). Displacement ellipsoids correspond to 30% probability.

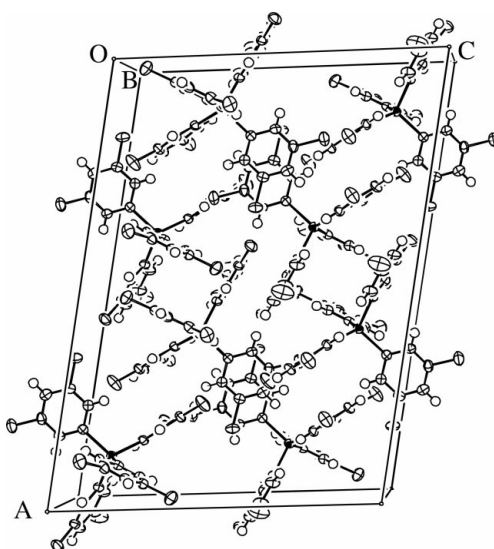


Figure 2
Packing diagram for (I), viewed along the *b* axis. H atoms have been omitted for clarity.

Experimental

The title compound was prepared as described by Wharf & Simard (1997). Suitable crystals for X-ray analysis were obtained by recrystallization from acetone.

Crystal data

[Sn(C₆H₃Cl₂)₄]
 $M_r = 702.63$
 Monoclinic, C_2/c
 $a = 24.861$ (8) Å
 $b = 11.908$ (3) Å
 $c = 18.139$ (4) Å
 $\beta = 100.16$ (2)°
 $V = 5286$ (2) Å³
 $Z = 8$

$D_x = 1.766$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.5$ – 15.5°
 $\mu = 1.79$ mm⁻¹
 $T = 293$ (2) K
 Irregular shape, colourless
 0.55 × 0.47 × 0.45 mm

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (ABSN in NRCVAX; Gabe *et al.*, 1989)
 $T_{\min} = 0.354$, $T_{\max} = 0.449$
 19 754 measured reflections
 5195 independent reflections
 3632 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.099$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -31 \rightarrow 31$
 $k = -15 \rightarrow 15$
 $l = -22 \rightarrow 22$
 3 standard reflections
 every 250 reflections
 intensity decay: 2.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.123$
 $S = 1.13$
 5195 reflections
 299 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0767P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.70$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.94$ e Å⁻³
 Extinction correction: SHELXL96
 Extinction coefficient: 0.00069 (9)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------------|------------|-----------------|------------|
| Sn1–C31 | 2.134 (6) | Sn1–C41 | 2.135 (6) |
| Sn1–C11 | 2.135 (5) | Sn1–C21 | 2.135 (6) |
| C31–Sn1–C11 | 111.0 (2) | C26–C21–C22 | 118.2 (6) |
| C31–Sn1–C41 | 105.9 (2) | C26–C21–Sn1 | 118.2 (4) |
| C11–Sn1–C41 | 108.7 (2) | C22–C21–Sn1 | 123.6 (5) |
| C31–Sn1–C21 | 109.6 (2) | C36–C31–C32 | 118.8 (6) |
| C11–Sn1–C21 | 113.8 (2) | C36–C31–Sn1 | 120.1 (5) |
| C41–Sn1–C21 | 107.5 (2) | C32–C31–Sn1 | 121.1 (4) |
| C16–C11–C12 | 118.4 (5) | C46–C41–C42 | 119.3 (5) |
| C16–C11–Sn1 | 121.2 (4) | C46–C41–Sn1 | 121.2 (4) |
| C12–C11–Sn1 | 120.0 (4) | C42–C41–Sn1 | 119.5 (4) |
| C31–Sn1–C11–C16 | 164.0 (5) | C11–Sn1–C31–C36 | 135.8 (5) |
| C41–Sn1–C11–C16 | –79.9 (5) | C41–Sn1–C31–C36 | 18.0 (5) |
| C21–Sn1–C11–C16 | 39.8 (6) | C21–Sn1–C31–C36 | –97.6 (5) |
| C31–Sn1–C11–C12 | –22.7 (6) | C11–Sn1–C31–C32 | –45.4 (5) |
| C41–Sn1–C11–C12 | 93.4 (5) | C41–Sn1–C31–C32 | –163.2 (5) |
| C21–Sn1–C11–C12 | –146.9 (5) | C21–Sn1–C31–C32 | 81.1 (5) |
| Sn1–C11–C12–C13 | –174.2 (5) | Sn1–C31–C32–C33 | –178.1 (4) |
| Sn1–C11–C16–C15 | 172.2 (5) | Sn1–C31–C36–C35 | 175.9 (4) |
| C31–Sn1–C21–C26 | 30.8 (5) | C31–Sn1–C41–C46 | –103.2 (5) |
| C11–Sn1–C21–C26 | 155.8 (4) | C11–Sn1–C41–C46 | 137.4 (4) |
| C41–Sn1–C21–C26 | –83.8 (5) | C21–Sn1–C41–C46 | 13.8 (5) |
| C31–Sn1–C21–C22 | –150.0 (6) | C31–Sn1–C41–C42 | 75.7 (5) |
| C11–Sn1–C21–C22 | –25.0 (6) | C11–Sn1–C41–C42 | –43.7 (5) |
| C41–Sn1–C21–C22 | 95.3 (6) | C21–Sn1–C41–C42 | –167.3 (4) |
| Sn1–C21–C22–C23 | –177.1 (6) | Sn1–C41–C46–C45 | 178.7 (4) |
| Sn1–C21–C26–C25 | 176.9 (4) | | |

H atoms were constrained to the parent site using a riding model, with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}$ (parent atom).

Data collection: *MSC/AFSC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSC/AFSC Diffractometer Control Software*; data reduction: *DARTD2* in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996); molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *NRCVAX* and *SHELXL96*.

The financial support from the Fonds FCAR du Ministère de l'Éducation du Québec is gratefully acknowledged.

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