

## Tetrakis(3,5-dimethylphenyl)tin(IV)

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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$ 

R factor = 0.038

wR factor = 0.099

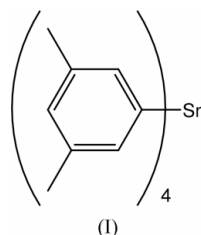
Data-to-parameter ratio = 17.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{Sn}(\text{C}_8\text{H}_9)_4]$ , with Sn located at a site of symmetry  $\bar{4}$ , crystallizes close-packed in the same tetragonal space group ( $P\bar{4}2_1c$ ) as tetraphenyltin. Both molecules may be considered quasi-spherical.

## Comment

Tetraaryl group 14 derivatives have long been used as models to test various paradigms describing the rules by which molecules are assembled in periodic ordered arrays, *i.e.* crystal packing (Lloyd & Brock, 1997). Much earlier, Kitaigorodskii (1961) had shown that symmetrical  $\text{Ar}_4\text{M}$  molecules prefer to crystallize in tetragonal space groups, with molecules having  $\bar{4}$  symmetry. Moreover, such quasi-spherical molecules should use certain space groups allowing close packing,  $P\bar{4}2_1c$ ,  $I\bar{4}$  and  $P4_2/n$ . Pertinent examples are:  $(\text{C}_6\text{H}_5)_4\text{Sn}$  in  $P\bar{4}2_1c$  (Engelhardt *et al.*, 1982), and  $(p\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$  (Karapides & Wolfe, 1975) and  $(p\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Sn}$  (Wharf & Simard, 1987) in  $I\bar{4}$ . In addition, he predicted that, as *para*-substituents became larger and more obtrusive, the packing effectiveness of these tetragonal space groups would decrease, resulting in the use of less symmetric space groups, with the molecules losing  $\bar{4}$  symmetry. Such is the case for  $(p\text{-CH}_3\text{CH}_2\text{OC}_6\text{H}_4)_4\text{Sn}$  in  $P2_1/c$  (Wharf & Simard, 1991) and  $(p\text{-CH}_3\text{CH}_2\text{C}_6\text{H}_4)_4\text{Sn}$  in  $C2/c$  (Wharf & Lebuis, 2000).



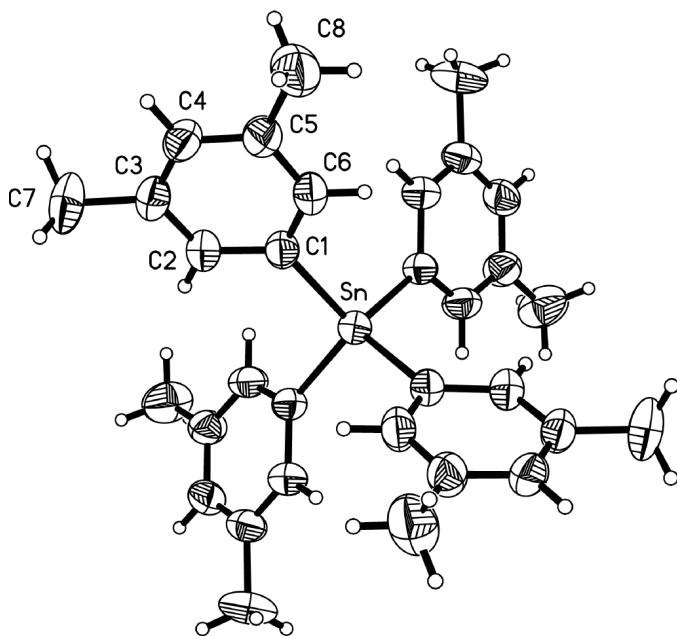
The effects of *meta*- and *ortho*-substituents on crystal packing have received less attention. Thus,  $(o\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$  is isomorphous with  $(\text{C}_6\text{H}_5)_4\text{Sn}$  (Belsky *et al.*, 1983), but  $(m\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$  crystallizes in the non-close-packing tetragonal space group,  $I4_1/a$  (Karipides & Oertel, 1977). Here, the title compound, (I), has been investigated to determine the effect of two methyl groups in the *meta*-positions.

Compound (I) crystallizes in the same space group ( $P\bar{4}2_1c$ ) as the unsubstituted phenyl analogue. The geometry around tin, which lies on a site of symmetry  $\bar{4}$ , is almost tetrahedral (Table 1 and Fig. 1), while the packing (Fig. 2) is the same as in  $(\text{C}_6\text{H}_5)_4\text{Sn}$ , with the *exo-m*- $\text{CH}_3$  groups assisting the translational quadruple phenyl embrace (Dance & Scudder, 1996). The effect of the *endo-m*- $\text{CH}_3$  groups is to keep the closely

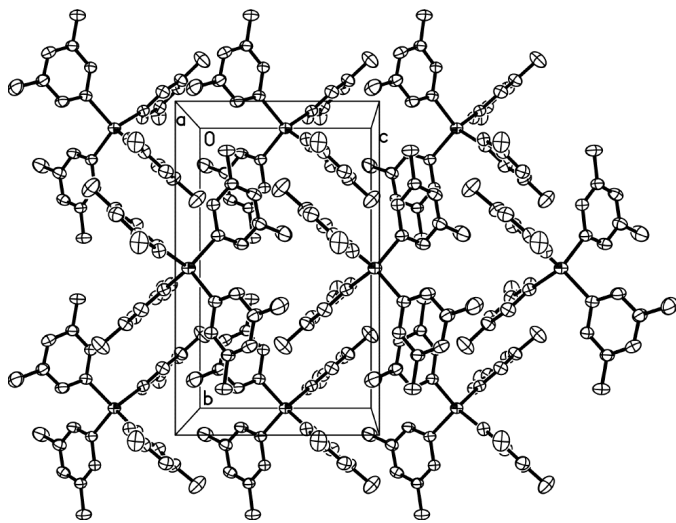
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**Figure 1**  
View of the molecule perpendicular to the  $\bar{c}$  axis. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
Packing diagram for the title compound, viewed along the  $a$  axis. H atoms have been omitted for clarity.

packed columns parallel to the  $c$  axis slightly further apart than in tetraphenyltin.

The relationship of molecular shape and crystal design is normally discussed in terms of the asymmetry of the molecules, enabling them to pack in a complementary fashion (Brock & Dunitz, 1994), thus fulfilling Kitaigorodskii's Principle of Close Packing (1961). In an earlier era, possible crystal structures were predicted on the basis of the best close-packing of spheres and ellipsoids (Kitaigorodskii, 1945; Nowacki, 1948). Thus  $(m\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$ , with all *meta*-methyl groups *exo*, is somewhat ellipsoidal (quasi-prolate spheroid) and will not pack in the same manner as the quasi-spherical  $(\text{C}_6\text{H}_5)_4\text{Sn}$ . In (I), with both *exo* and *endo* methyl groups, the

molecule is more spherical and the crystal packing can now revert to that of  $(\text{C}_6\text{H}_5)_4\text{Sn}$ . We also note that for  $(p\text{-XC}_6\text{H}_4)_4\text{Sn}$  [ $X = (\text{CH}_3)_3\text{C}$ ], the large umbrella-like *para*-substituents render this molecule quasi-spherical and it also crystallizes in a close-packing tetragonal space group,  $P4_2/n$  (Wharf & Lebus, 2000).

## Experimental

The title compound was prepared earlier (Wharf & Simard, 1997). Suitable crystals were obtained from ethanol.

### Crystal data

$[\text{Sn}(\text{C}_6\text{H}_9)_4]$   
 $M_r = 539.30$   
 Tetragonal,  $P\bar{4}2_1c$   
 $a = 13.4000$  (19) Å  
 $c = 8.2000$  (16) Å  
 $V = 1472.4$  (4) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.216$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 17.0\text{--}20.0^\circ$   
 $\mu = 7.00$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Needle, colourless  
 $0.53 \times 0.11 \times 0.07$  mm

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega$  scans  
 Absorption correction: by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)  
 $T_{\min} = 0.289$ ,  $T_{\max} = 0.659$   
 20587 measured reflections  
 1390 independent reflections

1182 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.071$   
 $\theta_{\text{max}} = 70.0^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -16 \rightarrow 16$   
 $l = -9 \rightarrow 9$   
 5 standard reflections  
 frequency: 60 min  
 intensity decay: 1.6%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.099$   
 $S = 1.19$   
 1390 reflections  
 78 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.1298P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.58$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.42$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL96*  
 Extinction coefficient: 0.0055 (6)  
 Absolute structure: Flack (1983), 581 Friedel pairs  
 Flack parameter =  $-0.01$  (3)

**Table 1**

Selected geometric parameters (Å, °).

|                             |             |                             |            |
|-----------------------------|-------------|-----------------------------|------------|
| Sn—C1                       | 2.134 (5)   |                             |            |
| C1 <sup>i</sup> —Sn—C1      | 109.6 (2)   | C6—C1—Sn                    | 121.7 (3)  |
| C1 <sup>ii</sup> —Sn—C1     | 109.40 (12) | C2—C1—Sn                    | 120.8 (4)  |
| C6—C1—C2                    | 117.6 (5)   |                             |            |
| C1 <sup>i</sup> —Sn—C1—C6   | 53.4 (4)    | C1 <sup>ii</sup> —Sn—C1—C2  | 111.9 (5)  |
| C1 <sup>ii</sup> —Sn—C1—C6  | −66.5 (3)   | C1 <sup>iii</sup> —Sn—C1—C2 | −8.2 (4)   |
| C1 <sup>iii</sup> —Sn—C1—C6 | 173.4 (4)   | Sn—C1—C2—C3                 | −179.4 (3) |
| C1 <sup>i</sup> —Sn—C1—C2   | −128.2 (4)  | Sn—C1—C6—C5                 | 178.9 (5)  |

Symmetry codes: (i)  $1 - x, 1 - y, z$ ; (ii)  $y, 1 - x, -z$ ; (iii)  $1 - y, x, -z$ .

H atoms were constrained to the parent site using a riding model; C—H = 0.93–0.96 Å. The  $U_{\text{iso}}$  values were set to  $1.5U_{\text{eq}}$  of the parent atom for methyl H atoms and  $1.2U_{\text{eq}}$  for other H atoms. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 1995).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRC-2* and *NRC-2A* (Ahmed *et al.*, 1973); program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL96*.

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