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# THE CRYSTAL AND MOLECULAR STRUCTURE AND $^{119}$Sn NMR INVESTIGATIONS OF 2,2,3,3,5,5,6,6-OCTAPHENYL-2,3,5,6-TETRASTANNACYCLOHEXANE

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## Summary

The crystal and molecular structures of 2,2,3,3,5,5,6,6-octaphenyl-2,3,5,6-tetrastannacyclohexane were determined from three-dimensional X-ray data. The crystals are triclinic, space group $P\bar{1}$. The unit-cell, with dimensions $a$ 9.490(2), $b$ 10.202(2), $c$ 12.260(3) Å, $\alpha$ 103.43(2), $\beta$ 78.09(2), $\gamma$ 93.06(2)°, contains one molecule. The structure was solved by the Patterson method and refined to a final $R$ value of 0.032 for 3190 independent reflections. The tetrastannacyclohexane ring has a chair conformation. The tin–tin bond length is 2.78 Å.

## Introduction

X-ray data of compounds containing tin–tin bond are relatively rare [1]; the title compound is the first example of a tetrastannacyclohexane.

## Experimental

*Structural data.* The title compound was prepared as described elsewhere [2]. Colourless crystals were obtained by recrystallisation from $CH_2Cl_2/CH_3OH$. The $^{119}$Sn NMR data were measured with a Bruker WP 200 spectrometer with saturated $CDCl_3$ solutions, and with $SnMe_4$ as external reference. The crystal structure determination was based on X-ray intensity data measured on a Syntex diffractometer. 3190 reflections were collected using graphite-monochromatized Mo-$K_\alpha$ ($\lambda$ 0.71069 Å) radiation with $\omega$-scan technique to $2\theta = 47°$. 2818 reflections ($I >$

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TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$, $\times 10^3$ for hydrogen atoms), with e.s.d.'s in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn(1) | 5168(0) | −1749(0) | 3365(0) |
| Sn(2) | 4163(0) | 847(0) | 3653(0) |
| C(O) | 6468(7) | −1874(7) | 4582(5) |
| C(1) | 3375(6) | −3126(6) | 3475(5) |
| C(2) | 3616(8) | −4455(7) | 3399(7) |
| C(3) | 2509(9) | −5383(8) | 3469(7) |
| C(4) | 1130(9) | −4985(8) | 3592(7) |
| C(5) | 866(9) | −3697(9) | 3626(10) |
| C(6) | 1962(8) | −2774(8) | 3576(8) |
| C(7) | 6510(7) | −2501(6) | 1728(5) |
| C(8) | 7994(9) | −2456(9) | 1549(7) |
| C(9) | 8840(12) | −2991(11) | 512(9) |
| C(10) | 8246(13) | −3611(11) | −384(9) |
| C(11) | 6814(14) | −3688(12) | −248(8) |
| C(12) | 5947(11) | −3130(10) | 797(7) |
| C(13) | 5706(6) | 2109(6) | 2818(6) |
| C(14) | 5991(9) | 1977(11) | 1646(8) |
| C(15) | 6918(11) | 2828(13) | 1136(10) |
| C(16) | 7567(10) | 3856(11) | 1783(11) |
| C(17) | 7325(9) | 3995(9) | 2917(11) |
| C(18) | 6389(7) | 3130(7) | 3454(8) |
| C(19) | 2259(7) | 740(6) | 2921(6) |
| C(20) | 2287(11) | 361(11) | 1787(8) |
| C(21) | 1042(14) | 363(14) | 1356(11) |
| C(22) | −235(13) | 764(11) | 2076(12) |
| C(23) | −287(9) | 1107(9) | 3189(11) |
| C(24) | 914(8) | 1110(8) | 3626(9) |
| H(O1) | 654(8) | −282(7) | 453(6) |
| H(O2) | 729(8) | −131(7) | 443(6) |
| H(2) | 453(9) | −469(7) | 339(6) |
| H(3) | 255(8) | −621(7) | 355(6) |
| H(4) | 44(8) | −555(7) | 369(6) |
| H(5) | −6(8) | −332(7) | 366(6) |
| H(6) | 176(8) | −173(7) | 382(6) |
| H(8) | 823(8) | −211(7) | 201(6) |
| H(9) | 973(9) | −289(7) | 45(6) |
| H(10) | 862(8) | −389(7) | −115(6) |
| H(11) | 640(8) | −423(7) | −78(6) |
| H(12) | 508(9) | −329(7) | 91(6) |
| H(14) | 593(8) | 110(7) | 135(6) |
| H(15) | 709(8) | 251(7) | 37(7) |
| H(16) | 822(8) | 435(7) | 134(6) |
| H(17) | 773(8) | 463(7) | 340(6) |
| H(18) | 618(8) | 324(7) | 427(6) |
| H(20) | 308(8) | 4(7) | 139(6) |
| H(21) | 118(8) | 34(7) | 67(6) |
| H(22) | −102(8) | 74(7) | 177(6) |
| H(23) | −100(9) | 153(7) | 380(6) |
| H(24) | 85(8) | 148(7) | 450(6) |

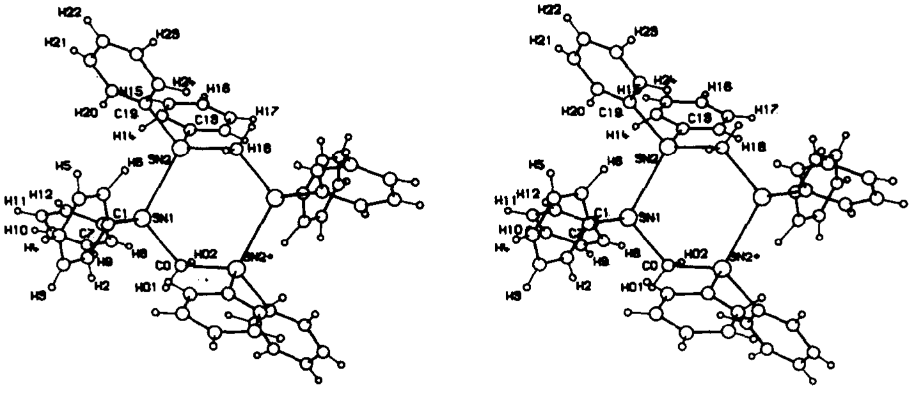

Fig. 1. Stereoscopic view of the molecular structure, numbering of the atoms.

2.5$\sigma(I)$) were used in the structure determination who was solved by the heavy atom method. The refinement was carried out by the SHELX [3] program with anisotropic thermal parameters for the non-hydrogen atoms. The final conventional $R$ value is 0.032 (with the 3190 independent reflections). The final atomic positional parameters are listed in Table 1, using the numbering indicated in Fig. 1.

Tables of observed and calculated structure factors may be obtained from the authors.

## Results and discussion

The molecular structure of the compound is illustrated in Fig. 1. The molecule has a crystallographic inversion centre and the packing is shown in Fig. 2.

The bond lengths and the bond angles are listed in Tables 2 and 3.

The tin–tin bond length is nearly the same as that in hexaphenyldistannane [4] and dodecaphenylhexastannacyclohexane [5]. The tin–carbon distances are in the expected range for a Sn–C-single bond [4]. Noteworthy is the variation, between 1.319 to 1.402 Å, of the carbon–carbon distances in the benzene rings, reflecting the distortion of the $\pi$-electron density by replacement of a hydrogen by a tin atom.

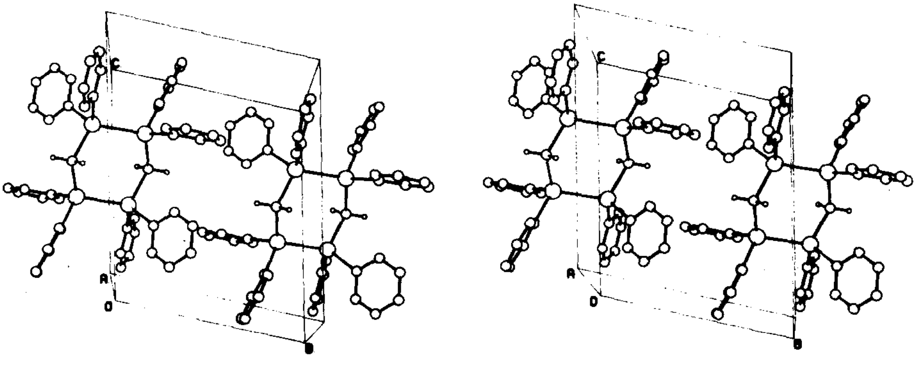

Fig. 2. The unit-cell of $Sn_4C_{50}H_{44}$, $Z = 1$.

TABLE 2

BOND LENGTHS (Å) WITH STANDARD DEVIATIONS (coordinates of C(O)$^{\star}$ are $1-X$, $-Y$, $1-Z$)

| | |
|---|---|
| Sn(2)–Sn(1) | 2.783(1) |
| C(O)–Sn(1) | 2.151(5) |
| C(1)–Sn(1) | 2.151(5) |
| C(7)–Sn(1) | 2.139(6) |
| C(O)$^{\star}$–Sn(2) | 2.149(5) |
| C(13)–Sn(2) | 2.155(5) |
| C(19)–Sn(2) | 2.164(5) |
| C(2)–C(1) | 1.366(8) |
| C(6)–C(1) | 1.380(9) |
| C(3)–C(2) | 1.379(9) |
| C(4)–C(3) | 1.359(11) |
| C(5)–C(4) | 1.341(10) |
| C(6)–C(5) | 1.367(10) |
| C(8)–C(7) | 1.379(9) |
| C(12)–C(7) | 1.369(9) |
| C(9)–C(8) | 1.364(10) |
| C(10)–C(9) | 1.349(13) |
| C(11)–C(10) | 1.335(14) |
| C(12)–C(11) | 1.385(11) |
| C(14)–C(13) | 1.382(9) |
| C(18)–C(13) | 1.369(9) |
| C(15)–C(14) | 1.364(11) |
| C(16)–C(15) | 1.362(13) |
| C(17)–C(16) | 1.336(13) |
| C(18)–C(17) | 1.395(10) |
| C(20)–C(19) | 1.348(10) |
| C(24)–C(19) | 1.402(9) |
| C(21)–C(20) | 1.391(12) |
| C(22)–C(21) | 1.363(15) |
| C(23)–C(22) | 1.319(13) |
| C(24)–C(23) | 1.356(10) |

The tetrastannacyclohexane adopts a somewhat flattened chair conformation similar to that in dodecaphenylhexastannacyclohexane [5]; the torsion angles in the cycle are given in Table 4. The high value of 120.6° for the Sn–C(O)–Sn angles compared with the Sn–Sn–Sn angle of 109° in the hexastannacyclohexane [5] reflects the increasing ring strain upon introduction of the two carbon atoms into the six-membered ring. The angles around the tin atoms are consistent with a slightly distored tetrahedral environment similar to that in $Ph_6Sn_2$ [4].

The relative orientations of the phenyl groups are indicated in Table 5.

The $^{119}$Sn NMR spectrum shows one signal at $\delta$ − 109.32 ppm with three satellites of 4159, 95 and 51 Hz. The first can be assigned to the $^{1}J(^{119}\mathrm{Sn}-^{117}\mathrm{Sn})$ coupling constant. Similar values were found in other hexaalkyl distannanes [6]. The two other ones are the $^{2}J(^{119}\mathrm{Sn}-\mathrm{C}-^{117}\mathrm{Sn})$ and $^{3}J(^{119}\mathrm{Sn}-\mathrm{Sn}-\mathrm{C}-^{117}\mathrm{Sn})$ coupling constants. Due to the complex dependence on steric and electronic factors of the $^{2}J(\mathrm{Sn}-\mathrm{C}-\mathrm{Sn})$ coupling constants [7], an unambiguous assignment of the two small coupling constants is not yet possible.

Further studies of this class of compound are in progress.

TABLE 3
BOND ANGLES (°) WITH STANDARD DEVIATIONS (coordinates of C(O)* and Sn(2)* = $1-X, -Y, 1-Z$)

| | |
|---|---|
| C(O)–Sn(1)–Sn(2) | 112.4(2) |
| C(1)–Sn(1)–Sn(2) | 109.5(1) |
| C(1)–Sn(1)–C(O) | 110.7(2) |
| C(7)–Sn(1)–Sn(2) | 113.7(2) |
| C(7)–Sn(1)–C(O) | 104.8(2) |
| C(7)–Sn(1)–C(1) | 105.4(2) |
| C(13)–Sn(2)–Sn(1) | 113.0(1) |
| C(19)–Sn(2)–Sn(1) | 109.1(1) |
| C(19)–Sn(2)–C(13) | 107.2(2) |
| Sn(1)–Sn(2)–C(O)* | 113.3(2) |
| C(13)–Sn(2)–C(O)* | 107.6(2) |
| C(19)–Sn(2)–C(O)* | 106.3(2) |
| Sn(1)–C(O)–Sn(2)* | 120.6(1) |
| C(2)–C(1)–Sn(1) | 119.5(4) |
| C(6)–C(1)–Sn(1) | 124.3(4) |
| C(6)–C(1)–C(2) | 116.1(6) |
| C(3)–C(2)–C(1) | 122.1(6) |
| C(4)–C(3)–C(2) | 119.7(7) |
| C(5)–C(4)–C(3) | 119.5(7) |
| C(6)–C(5)–C(4) | 120.6(7) |
| C(5)–C(6)–C(1) | 121.8(7) |
| C(8)–C(7)–Sn(1) | 122.7(5) |
| C(12)–C(7)–Sn(1) | 121.8(5) |
| C(12)–C(7)–C(8) | 115.4(6) |
| C(9)–C(8)–C(7) | 122.2(8) |
| C(10)–C(9)–C(8) | 120.7(9) |
| C(11)–C(10)–C(9) | 119.1(9) |
| C(12)–C(11)–C(10) | 120.5(9) |
| C(11)–C(12)–C(7) | 122.0(8) |
| C(14)–C(13)–Sn(2) | 122.4(5) |
| C(18)–C(13)–Sn(2) | 120.1(5) |
| C(18)–C(13)–C(14) | 117.4(6) |
| C(15)–C(14)–C(13) | 121.6(9) |
| C(16)–C(15)–C(14) | 120.2(9) |
| C(17)–C(16)–C(15) | 119.4(8) |
| C(18)–C(17)–C(16) | 121.2(9) |
| C(17)–C(18)–C(13) | 120.1(8) |
| C(20)–C(19)–Sn(2) | 123.3(5) |
| C(24)–C(19)–Sn(2) | 120.3(5) |
| C(24)–C(19)–C(20) | 116.3(6) |
| C(21)–C(20)–C(19) | 121.0(10) |
| C(22)–C(21)–C(20) | 120.4(10) |
| C(23)–C(22)–C(21) | 119.3(8) |
| C(24)–C(23)–C(22) | 121.2(9) |
| C(23)–C(24)–C(19) | 121.7(8) |

TABLE 4
TORSION ANGLES (°)

| | |
|---|---|
| C(O)–Sn(1)–Sn(2)–C(O)* | −39.1 |
| Sn(1)–Sn(2)–C(O)*–Sn(1)* | 42.7 |
| Sn(2)–C(O)*–Sn(1)*–Sn(2)* | 42.3 |

TABLE 5

DIHEDRAL ANGLES (°) BETWEEN LEAST-SQUARES PLANES THROUGH SELECTED ATOMS

| | | | |
|---|---|---|---|
| plane 1-plane 2 | 107.6 | 1 | C(1) to C(6) |
| plane 1-plane 3 | 90.2 | 2 | C(7) to C(12) |
| plane 1-plane 4 | 94.9 | 3 | C(13) to C(18) |
| plane 1-plane 5 | 125.1 | 4 | C(19) to C(24) |
| plane 2-plane 3 | 129.7 | 5 | Sn(1),Sn(2),C(O) |
| plane 2-plane 4 | 17.8 | | |
| plane 2-plane 5 | 64.2 | | |
| plane 3-plane 4 | 119.4 | | |
| plane 3-plane 5 | 67.0 | | |
| plane 4-plane 5 | 61.1 | | |

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