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THE ABSOLUTE CONFIGURATION OF (+)-2-TRIPHENYLSTANNYLBUTANE

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Summary

The X-ray structural analysis of (+)-2-triphenylstannylbutane was undertaken in order to establish the absolute configuration of the molecule, using the anomalous scatter of Cu-K_α radiation by tin atoms. The configuration of (+)-2-triphenylstannylbutane is *S*.

Introduction

In a preceding paper we described the preparation and reported the maximum optical rotation of a number of 2-triorganostannylbutanes, of which 2-triphenylstannylbutane was chosen as a standard [1]. These compounds are very useful for stereochemical studies related to the formation and the cleavage of the tin—carbon bond [2]. Although the absolute configuration of (+)-2-triphenylstannylbutane could be predicted by semiempirical methods [3], for certainty we decided to make an X-ray determination.

Results and discussion

Crystal data

Suitable colourless crystals of 2-triphenylstannylbutane were grown at room temperature from ethanol by slow evaporation. A prismatic specimen (0.22 × 0.25 × 0.45 mm) was mounted along its elongated axis (*y*) on a glass fibre for X-ray analysis.

The crystal system and space group were obtained from rotation and Weissenberg photographs, and the cell parameters were derived from diffractometer measurements. The results are as follows: monoclinic system, space group

$P2_1$; $a = 12.551(4)$, $b = 20.068(15)$, $c = 7.743(8)$ Å; $\beta = 96.42(4)°$; $V = 1938.3$ Å^3; $Z = 4$ (2 independent molecules in the asymmetric unit); $D_c = 1.394$ g cm^{-3}; $F(000) = 824$.

The intensities of 3679 independent reflections hkl and $\bar{h}kl$ up to $\theta = 70°$ were collected on a Siemens AED automatic four-circle diffractometer with Ni-filtered Cu-K_α radiation ($\lambda = 1.5418$ Å), using the five-value measuring method and the $\theta - 2\theta$ scan technique. The standard reflection recorded twice after every

TABLE 1

FRACTIONAL ATOMIC COORDINATES (X 10^4) WITH ESTIMATED STANDARD DEVIATIONS σ

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$
Sn(1)	2554.9(1)	9918.6(0.5)	1613.2(1.3)
Sn(2)	2352.8(1)	6707.8(0.5)	3270.8(1.0)
C(1)	3748(10)	9379(7)	0.366(19)
C(2)	4836(11)	9561(8)	0749(23)
C(3)	5602(12)	9176(11)	−0029(27)
C(4)	5323(15)	8655(9)	−1124(26)
C(5)	4271(15)	8481(10)	−1485(26)
C(6)	3429(16)	8838(9)	−0720(27)
C(7)	2608(11)	10940(7)	0780(23)
C(8)	3394(14)	11103(9)	−0433(28)
C(9)	3409(14)	11759(9)	−0983(28)
C(10)	2709(15)	12230(8)	−0512(27)
C(11)	1941(14)	12072(9)	0588(28)
C(12)	1922(13)	11411(8)	1220(28)
C(13)	1005(11)	9499(7)	0666(21)
C(14)	0325(12)	9871(9)	−0562(23)
C(15)	−0687(13)	9593(10)	−1096(25)
C(16)	−1017(12)	8994(9)	−0456(25)
C(17)	−0376(12)	8689(7)	0818(24)
C(18)	0673(13)	8917(7)	1412(25)
C(19)	3995(18)	10065(16)	5160(34)
C(20)	2913(10)	9789(7)	4476(21)
C(21)	1988(18)	9816(15)	5394(36)
C(22)	1213(26)	10412(18)	5182(37)
C(51)	1127(12)	7259(7)	4323(20)
C(52)	0041(13)	7070(10)	4042(27)
C(53)	−0756(16)	7416(11)	4807(29)
C(54)	−0464(16)	7961(10)	5780(30)
C(55)	0594(17)	8178(10)	6127(27)
C(56)	1395(14)	7832(8)	5455(23)
C(57)	2362(10)	5731(7)	4456(20)
C(58)	1664(14)	5563(10)	5540(26)
C(59)	1637(17)	4904(11)	6333(28)
C(60)	2342(15)	4439(10)	5971(29)
C(61)	3060(14)	4616(9)	4831(28)
C(62)	3088(12)	5242(8)	3947(22)
C(63)	3909(11)	7134(7)	4054(19)
C(64)	4591(11)	6855(7)	5284(20)
C(65)	5636(14)	7119(10)	5774(26)
C(66)	5934(14)	7689(9)	5052(24)
C(67)	5182(16)	8025(10)	3803(29)
C(68)	4180(14)	7752(9)	3283(25)
C(69)	0994(20)	6985(18)	−0199(33)
C(70)	1930(13)	6614(11)	0449(28)
C(71)	2953(13)	6651(12)	−0508(27)
C(72)	3645(21)	6148(16)	−0156(36)

fifty measurements showed a linear decrease in its intensity; 3274 reflections were considered "observed" ($I > 3\sigma(I)$) and used in the calculations. The intensities were corrected for Lorentz and polarization effects, and readjusted for the observed decrease. No correction was made for absorption ($\mu(\text{Cu-K}_\alpha) = 10.8$ cm^{-1}) or extinction.

Structure determination and absolute configuration

The crystal structure was solved by the heavy atom method. Both scale factor and overall temperature parameter ($\bar{B} = 4.6$ Å^2) were evaluated by Wilson's method. The fractional coordinates of the two independent tin atoms were derived from a three-dimension Patterson map, and their structure factors yielded a conventional reliability index R equal to 0.27 after two block-diagonal least-squares cycles based on the normalized reflections. The corresponding set of phases was used with observed structure factors and forty out of the forty six carbon atoms appeared clearly on the resulting Fourier—Bragg map; R was 0.148; the six missing atoms, that is the carbon atoms of the two methyl and the two ethyl groups, were located from a difference Fourier map.

The refinement of the atomic coordinates and isotropic temperature parameters led to the value $R = 0.130$, which fell to 0.079 when anisotropic temperature parameters were applied to the tin atoms, and converged to 0.068 following complete anisotropic refinement. The final positional shifts were all less than 0.7 σ (σ = estimated standard deviation).

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATION IN THE TWO INDEPENDENT MOLECULES A AND B

(the numbering is that of molecule A; for molecule B, add 1 (tin atom) or 50 (carbon atoms)).

	Mol. A	Mol. B		Mol. A	Mol. B
Sn(1)—C(1)	2.16(1)	2.13(2)	C(20)—Sn(1)—C(1)	108.27(5)	108.69(6)
Sn(1)—C(7)	2.15(1)	2.16(1)	C(20)—Sn(1)—C(7)	113.57(5)	109.47(6)
Sn(1)—C(13)	2.17(1)	2.16(1)	C(20)—Sn(1)—C(13)	111.38(5)	115.09(6)
Sn(1)—C(20)	2.23(2)	2.20(2)	C(7)—Sn(1)—C(13)	108.94(6)	106.14(5)
C(1) ··· C(6)$_{\text{av.}}$	1.40(3)	1.40(3)	C(1)—Sn(1)—C(13)	107.13(5)	110.96(5)
C(7) ··· C(12)$_{\text{av.}}$	1.39(3)	1.39(3)	C(1)—Sn(1)—C(7)	107.26(5)	106.08(5)
C(13 ··· C(18)$_{\text{av.}}$	1.39(2)	1.39(2)	Sn(1)—C(20)—C(19)	112.4(1)	113.6(1)
C(20)—C(19)	1.51(3)	1.43(3)	Sn(1)—C(20)—C(21)	113.9(1)	110.4(2)
C(20)—C(21)	1.43(3)	1.55(2)	C(19)—C(20)—C(21)	124.2(2)	119.7(2)
C(21)—C(22)	1.54(4)	1.34(4)	C(20)—C(21)—C(22)	121.0(2)	114.7(2)
Sn(1)—C(1)—C(2)	118.6(1)	122.0(1)	C(8)—C(9)—C(10)	122.9(2)	119.8(2)
Sn(1)—C(1)—C(6)	119.3(1)	120.7(1)	C(9)—C10)—C(11)	121.0(2)	117.5(2)
C(2)—C(1)—C(6)	122.0(1)	117.2(1)	C(10)—C(11)—C(12)	117.7(2)	124.8(2)
C(1)—C(2)—C(3)	117.1(1)	121.7(2)	C(11)—C(12)—C(7)	122.2(2)	115.1(1)
C(2)—C(3)—C(4)	122.7(2)	118.2(2)	Sn(1)—C(13)—C(14)	118.1(1)	121.7(1)
C(3)—C(4)—C(5)	199.9(2)	123.5(2)	Sn(1)—C(13)—C(18)	119.0(1)	118.4(1)
C(4)—C(5)—C(6)	121.4(2)	119.5(2)	C(14)—C(13)—C(18)	122.5(1)	119.9(1)
C(5)—C(6)—C(1)	116.9(2)	119.7(1)	C(13)—C(14)—C(15)	116.4(1)	122.3(1)
Sn(1)—C(7)—C(8)	116.6(1)	121.9(1)	C(14)—C(15)—C(16)	122.4(2)	119.6(2)
Sn(1)—C(7)—C(12)	123.4(1)	118.6(1)	C(15)—C(16)—C(17)	118.6(2)	119.1(2)
C(8)—C(7)—C(12)	119.9(2)	119.3(1)	C(16)—C(17)—C(18)	123.2(2)	120.9(2)
C(7)—C(8)—C(9)	116.1(2)	123.2(2)	C(17)—C(18)—C(13)	116.5(1)	118.0(2)

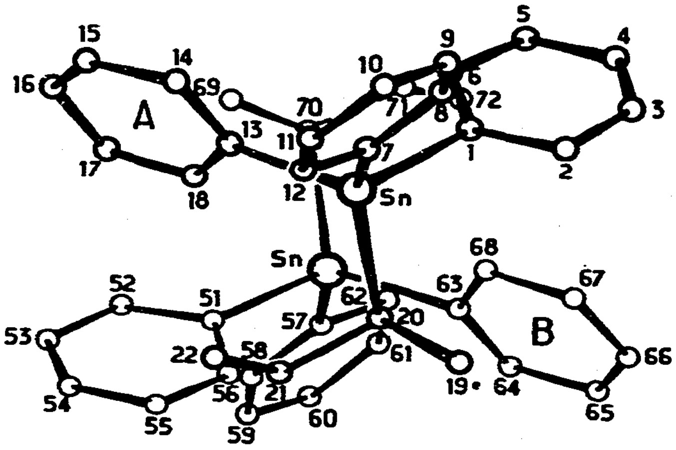

Fig. 1. Crystal conformation of the two independent molecules *A* and B (projected along the *y* axis). The absolute configuration is *S*.

The absolute configuration of the molecule was established during the last calculations. The structure factors were computed for both *R* and *S* configurations of the molecule in a right-handed coordinate system with 854 reflections of $\theta \leqslant 30°$. The best agreement with the experimental values was found for the *S* configuration. The Hamilton test [4] was applied to the reliability indices and the experimental ratio $Q_{\exp} = R(R)/R(S) = 1.047$ was higher than the theoretical value Qth(Qth(1, 589, 0.005) $\simeq$ 1.007), which precludes the *R* configuration. This result was verified by examining 36 Bijvoet pairs of reflections *hkl* and $h\bar{k}l$ measured on a second crystal (no radiation damage, smaller size).

The atomic coordinates are listed in Table 1, and Table 2 gives the main bond lengths and angles for the two independent molecules with *S* configuration. It will be that the discrepancies between experimental and theoretical values result from X-ray damage of the crystal and from the phenomenon of absorption. The higher thermal parameters affect the terminal atoms C(19), C(22), C(69) and C(72). Figure 1 shows the projection of the two independent molecules (which are related by a pseudo-centre of symmetry) along the *y* axis.

All the calculations were carried out on the CII IRIS 80 computer of the University of Bordeaux I. The scattering factors for tin and carbon atoms and the anomalous dispersion factors for tin atoms were taken from ref. 5. Lists of structure factors and final thermal parameters can be obtained from the authors.

Conclusion

This work has established the absolute configuration of the optically active 2-triphenylstannylbutane. Consequently the absolute configurations of all the 2-trialkyl- and 2-triaryl-stannylbutanes can now be derived.

References

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