dichloromethane. X-ray photographs were taken with Cu Kα radiation. A Picker 4-circle diffractometer automated by a PDP-11 computer, with Zr-filtered Mo K$\bar{\alpha}$ X-rays (λ = 0.71069 Å) was then used. The unit cell was refined by least-squares methods employing 21 pairs of centering measurements (obtained at $\pm 2\theta$) in the range $|2\theta|$ = 21–44°. The crystal was mounted along the *b* axis. The crystal data at 25 °C are as follows: space group $P\bar{1}$; a = 8.331 (3), b = 9.794 (4), c = 7.840 (2) Å; α = 96.19 (5), β = 99.65 (3), γ = 111.92 (4)°; (Delaunay reduced cell) V(cell) = 574.8 (3) Å^3; D_m = 2.113 (5) g cm^{-3} (flotation in $CCl_4/CHBr_3$) D_c = 2.105 g cm^{-3}; Z = 1; formula $C_8H_{24}B_2F_4O_{12}P_4Pt$; M_r = 728.75. One reciprocal space hemisphere of intensity measurements ($h \geq 0$) were done up to 2θ = 60°. A $\theta/2\theta$ step scan was used with 50 steps of 0.04° in 2θ, counting for 1 s per step. Background measurements were for 25 s at each end of the scan. Three standards, −2,−2,0, 4,−1,−4, and 0,−4,0, preceded each batch of 50 intensity measurements and were used to correct the intensities for instrument instability and beam variations. The intensities were corrected with the Lorentz and polarization factors. Absorption corrections were applied with a numerical integration procedure utilizing a Gaussian grid (4 × 12 × 12). The crystal shape was defined by perpendicular distances to crystal faces from a central origin as follows: {100}, 0.0517 mm; {010}, 0.222 mm; {001}, 0.187 mm. The absorption coefficient was 68.1 cm^{-1}, and the range of correction factors was 0.12–0.52. The computer program has been tested.[20] The final file contained 3124 independent reflections.

(C) Crystal Structure Solution and Refinement. The structure was solved by standard heavy-atom methods. The refinement was by least squares, using a full matrix, and minimizing $\sum w(|F_o| - |F_c|)^2$. The atomic scattering factors were from ref 21 with Pt treated as an anomalous scatterer. A weighting scheme was used in the final stages of refinement: $w = (A + Bx + Cx^2 + Dx^3)^{-1}$, where $x = |F_o|$ and A = 17.1221, B = −1.52881, C = 5.2126 × 10^{-2}, D = −1.96 × 10^{-4}. The positions of the methyl hydrogen atoms were calculated with the assumption that the POCH torsion angles are consistent with staggered geometry as seen along the O–C bond directions and that the C–H bond lengths were 1.09 Å. The final two cycles of least squares gave convergence at R = 0.050 with a maximum change/error ratio of 0.47. The final difference map was satisfactory. The errors in bond lengths and angles were calculated from all components of the variance/covariance matrix. The main computer programs used for this work were supplied by Penfold[22] and are modified versions of ORFLS, FORDAP, ORFFE, and ORTEP. The diffractometer programs were written in this laboratory. The determined atomic coordinates are given in Table I. The hydrogen atom coordinates, the temperature factors, intermolecular contacts, and the structure factor tables have been deposited.

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Registry No. $Pt((POMe)_2O)_2BF_2)_2$, 80041-62-9; $Pt((P(OMe)_2O)_2H)_2$, 30053-63-5; $BF_3 \cdot OEt_2$, 109-63-7.

Supplementary Material Available: Tables of calculated fractional atomic coordinates of the hydrogen atoms (Table S1), interatomic distances (Table S2), anisotropic temperature parameters (Table S3), and observed and calculated structure factor amplitudes (Table S4) (13 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Oklahoma, Norman, Oklahoma 73019

Oxy and Thio Phosphorus Acid Derivatives of Tin. 10. Crystal and Molecular Structure of Triphenyltin(IV) Diphenyl Phosphate, a Cyclic Hexamer[1]

K. C. MOLLOY, F. A. K. NASSER, C. L. BARNES, D. VAN DER HELM, and J. J. ZUCKERMAN*[2]

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(Diphenyl phosphato)triphenyltin(IV), $C_{30}H_{25}O_4PSn$, forms colorless crystals, mp = 178–180 °C, in the triclinic space group $P\bar{1}$ with a = 21.814 (16) Å, b = 20.724 (9) Å, c = 10.117 (5) Å, α = 99.25 (3)°, β = 92.70 (3)°, γ = 114.52 (4)°, V = 4073.9 Å^3, Z = 6, and ρ_{calcd} = 1.465 g cm^{-3}. The structure was solved by three-dimensional Patterson and difference Fourier techniques from 9953 reflections measured at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer using monochromated Mo Kα radiation to a final R value of 0.048 for the 8336 reflections included in the least-squares sums. The molecular units associate to form a centrosymmetric, cyclic hexamer in which planar triphenyltin(IV) groups are axially bridged by –O–P–O– linkages of the diphenyl phosphate ligand to form almost perfect trigonal bipyramids at tin. The structure of the ring is linear at tin but bent through an average O–P–O angle of 118.5°. The intrachain tin–oxygen and phosphorus–oxygen bonds are virtually symmetrical, indicating extensive delocalization of the P=O double bond. The ring is slightly puckered into a chair conformation with the phenoxy groups at each phosphorus pointing out from the center in an eclipsed array of phosphorus connections. However, one of the phenyl groups on each tin atom protrudes toward the center of the ring, with such phenyls lying alternately above and below the ring plane to produce a staggered array of triphenyltin groups. The adjacent hexameric unit along the *c* axis then nestles into the stack to fill space efficiently. A pentameric ring would be the smallest that could accommodate the axially bridged triphenyltin trigonal bipyramids, but expansion to the hexamer is necessary to accommodate the phenyl rings in the interior of the ring. No other examples of small oligomeric rings containing axially bridged trigonal-bipyramidal tin(IV) of any size are known.

We have been investigating the syntheses[1,3,4] and structures[5–8] of organotin(IV) derivatives of oxy and thio phosphorus acids in which biocidal activity is a property of both the tin and phosphorus portions of the molecule. As part of this

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[1] For the previous paper in this series see: Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J. *Inorg. Chem.*, in press.

[2] To whom correspondence should be addressed.

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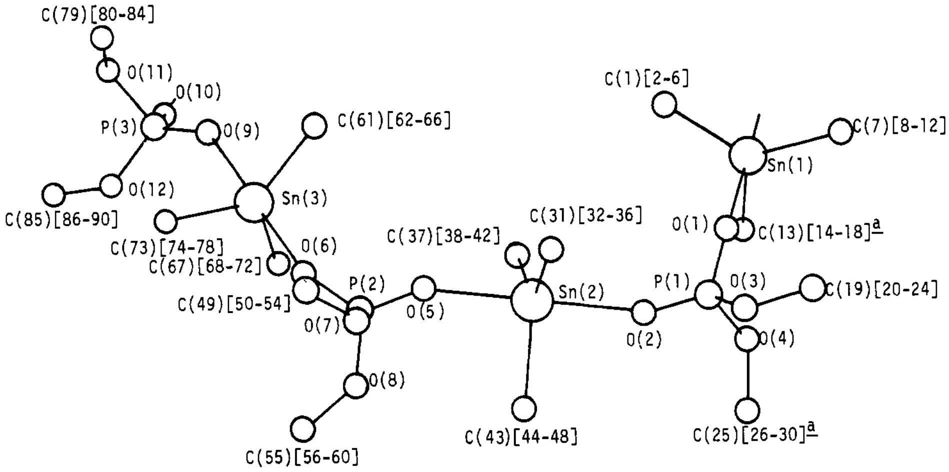

Figure 1. Three-molecule asymmetric unit drawn schematically to indicate the atomic labeling. The α-carbon of each phenyl ring is numbered in parentheses, with the remaining carbons, which are omitted for clarity, given in cyclic order in brackets following. Rings footnoted *a* are disordered (see Figures 2 and 3 and text).

program we have prepared a series of triorganotin derivatives of the diphenyl phosphate ligand.[1] Kubo showed in the early 1960s that triphenyltin(IV) diphenyl phosphate possessed fungicidal and phytotoxic properties.[9] The title compound is a white solid, melting at 178–180 °C, which has been synthesized by the action of triphenyltin(IV) chloride on ammonium diphenyl phosphate:[9]

$$(C_6H_5)_3SnCl + NH_4^+[OP(O)(OC_6H_5)_2]^- \rightarrow (C_6H_5)_3SnOP(O)(OC_6H_5)_2 + NH_4Cl \quad (1)$$

or by splitting out water in the condensation of triphenyltin(IV) hydroxide with diphenyl phosphate:[1]

$$(C_6H_5)_3SnOH + HOP(O)(OC_6H_5)_2 \rightarrow (C_6H_5)_3SnOP(O)(OC_6H_5)_2 + H_2O \quad (2)$$

The spectral parameters of the doublet tin-119m Mössbauer spectrum [isomer shift (IS) = 1.26 ± 0.03; quadrupole splitting (QS) = 3.54 ± 0.06 mm s^{-1}] are indicative of a coordination number greater than 4 at the tin atom.[10] This can be achieved through chelation or bridging by the diphenyl phosphate ligand. The absence of a resolvable Mössbauer resonance at ambient temperatures is negative evidence and cannot be used to rule out an associated lattice. This possibility as well as whether the chelation or bridging is symmetrical or anisobidentate in the solid can only be settled with respect to X-ray diffraction data, and we report the unexpected result in this paper.

Experimental Section

Crystal Data. Colorless crystals of the title compound were obtained by slow cooling of a toluene solution and were stable to both atmospheric moisture[1] and X-rays. Crystal data are listed in Table I.

Details of our diffractometer and methods of data collection and data reduction have been outlined previously.[5] Specific data collection parameters are listed in Table II. Structure factors for each reflection were assigned individual weights.[5]

Table I. Crystal Data for $(C_6H_5)_3SnO_2P(OC_6H_5)_2$

a, Å^a	21.814 (16)	formula	$C_{30}H_{25}O_4PSn$
b, Å^a	20.724 (9)	crystal class	triclinic
c, Å^a	10.117 (5)	fw	599.2
α, deg^a	99.25 (3)	space group	$P\bar{1}$
β, deg^a	92.70 (3)	ρ_{calcd}, g cm^{-3}	1.463
γ, deg^a	114.52 (4)	*F*(000)	1812
V, Å^3	4073.9	μ(Mo Kα), cm^{-1}	10.41
Z	6		

[a] On the basis of ±2θ values of 48 reflections and with Mo Kα_1 radiation (λ = 0.709 26 Å).

Table II. Data Collection Parameters

diffractometer	Enraf-Nonius CAD/4
temp	138 ± 2 K
radiation	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å)
scan technique	θ–2θ
limit	1 ≤ 2θ ≤ 44°
max scan time	40 s
scan angle	0.7 + 0.2 tan θ
aperture width	2.50 + 0.86 tan θ
aperture height	6 mm
aperture dist	173 mm
monitor reflctns	$4\bar{1}3$, 720, $5\bar{5}4$
intens monitor frequency	7200 s
max fluctuation in monitor	<2.5%
orientation monitors	150 reflctns
no. of unique data	9953
no. of obsd data^a	8590
corrections	Lorentz, polarization, anomalous dispersion (Sn, P)

[a] $I > 2\sigma(I)$.

Structure Determination and Refinement. The structure was solved by conventional Patterson and Fourier techniques. Refinement[11] was anisotropic for tin, phosphorus, and oxygen and isotropic for carbon. Anomalous dispersion corrections were made for the two heaviest elements. Two of the phenyl rings exhibited disorder at the 2-,3- and 5-,6-positions (the 1,4-carbon atoms being common to both disordered halves in each case). Accordingly, C(14), C(14*), C(15), C(15*), C(17), C(17*), C(18), C(18*), C(26), C(26*), C(27, C(27*), C(29), C(29*), C(30), and C(30*) were all assigned an occupancy factor of 0.5, on the basis of the relative intensities of peaks in the Fourier map.

Refinement was concluded at a final *R* value of 0.048 (for the 8336 reflections included in the least-squares sums) or 0.064 (over all data). Final shifts in both positional and thermal parameters were less than one-quarter of their corresponding estimated standard deviation. Scattering factors were for neutral atoms and were taken from ref 12.

Final atomic parameters, both positional and thermal, and intramolecular distances and angles are listed in Tables III–VI, respectively. The asymmetric unit is diagramed schematically in Figure 1 to indicate

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Table III. Final Positional ($\times 10^4$) and Isotropic[a] Thermal Parameters for $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$[b]

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
Sn(1)	7971.9 (3)	5067.9 (4)	5420.8 (7)		C(33)	5508 (6)	2354 (7)	9360 (13)	3.0 (3)
Sn(2)	5497.8 (3)	2264.0 (4)	4977.6 (7)		C(34)	6074 (7)	2222 (7)	9758 (14)	3.5 (3)
Sn(3)	2695.7 (3)	2351.3 (4)	5571.4 (7)		C(35)	6473 (6)	2123 (7)	8766 (13)	3.2 (3)
P(1)	7328.4 (14)	3124 (2)	4775 (3)		C(36)	6327 (6)	2157 (6)	7419 (12)	2.6 (2)
P(2)	3718.4 (14)	1339 (2)	5249 (3)		C(37)	5387 (5)	3122 (5)	4260 (10)	1.5 (2)
P(3)	1585.6 (14)	3191 (2)	5300 (3)		C(38)	5098 (6)	3522 (6)	5043 (11)	2.1 (2)
O(1)	7614 (4)	3900 (4)	5446 (8)		C(39)	4994 (6)	4065 (6)	4549 (12)	2.7 (2)
O(2)	6581 (4)	2679 (4)	4560 (8)		C(40)	5147 (6)	4198 (7)	3291 (13)	2.8 (2)
O(3)	7633 (4)	3111 (4)	3398 (7)		C(41)	5435 (6)	3797 (6)	2506 (12)	2.5 (2)
O(4)	7622 (3)	2709 (4)	5619 (8)		C(42)	5561 (5)	3260 (6)	2998 (11)	1.7 (2)
O(5)	4415 (3)	1915 (4)	5318 (7)		C(43)	5272 (5)	1275 (6)	3603 (11)	1.7 (2)
O(6)	3159 (3)	1568 (4)	5473 (7)		C(44)	5469 (6)	780 (7)	4042 (13)	2.9 (2)
O(7)	3573 (4)	817 (4)	3830 (7)		C(45)	5285 (7)	93 (8)	3199 (14)	3.8 (3)
O(8)	3728 (4)	844 (4)	6287 (8)		C(46)	4911 (7)	−78 (7)	1935 (14)	3.4 (3)
O(9)	2221 (3)	3127 (4)	5716 (7)		C(47)	4722 (7)	427 (7)	1538 (14)	3.4 (3)
O(10)	1636 (3)	3735 (4)	4482 (7)		C(48)	4906 (6)	1103 (6)	2373 (12)	2.5 (2)
O(11)	1079 (3)	2414 (4)	4495 (8)		C(49)	2987 (6)	160 (6)	3525 (11)	2.1 (2)
O(12)	1220 (4)	3349 (4)	6541 (7)		C(50)	3054 (7)	−469 (7)	3742 (14)	3.4 (3)
C(1)	7150 (5)	5062 (5)	6475 (10)	1.5 (2)	C(51)	2475 (7)	−1117 (8)	3443 (15)	4.0 (3)
C(2)	6806 (6)	4500 (6)	7138 (11)	2.1 (2)	C(52)	1848 (7)	−1147 (7)	2980 (14)	3.5 (3)
C(3)	6274 (6)	4504 (6)	7866 (12)	2.5 (2)	C(53)	1804 (6)	−526 (7)	2753 (13)	3.2 (3)
C(4)	6085 (6)	5058 (7)	7919 (13)	2.8 (2)	C(54)	2377 (6)	139 (6)	3021 (12)	2.4 (2)
C(5)	6429 (6)	5644 (6)	7271 (12)	2.6 (2)	C(55)	3317 (5)	697 (6)	7329 (11)	1.9 (2)
C(6)	6954 (6)	5631 (6)	6555 (11)	2.0 (2)	C(56)	2618 (6)	384 (6)	7064 (12)	2.2 (2)
C(7)	7867 (5)	4832 (6)	3279 (11)	1.7 (2)	C(57)	2242 (6)	244 (7)	8139 (13)	2.8 (2)
C(8)	8428 (6)	4972 (6)	2578 (12)	2.4 (2)	C(58)	2571 (7)	404 (7)	9439 (14)	3.3 (3)
C(9)	8328 (6)	4750 (7)	1166 (13)	3.1 (3)	C(59)	3283 (6)	713 (7)	9684 (13)	3.0 (3)
C(10)	7686 (7)	4412 (8)	483 (14)	3.8 (3)	C(60)	3660 (6)	856 (6)	8621 (12)	2.2 (2)
C(11)	7129 (8)	4264 (8)	1171 (16)	4.7 (3)	C(61)	2782 (5)	2329 (6)	3482 (11)	1.8 (2)
C(12)	7216 (7)	4492 (7)	2595 (14)	3.4 (3)	C(62)	3405 (6)	2444 (6)	3030 (11)	2.2 (2)
C(13)	8917 (5)	5304 (6)	6533 (11)	1.6 (3)	C(63)	3463 (6)	2382 (7)	1651 (13)	2.9 (3)
C(14)	9543 (12)	5742 (13)	6071 (24)	2.5 (5)	C(64)	2898 (7)	2202 (7)	745 (14)	3.5 (3)
C(15)	10174 (12)	5900 (13)	6772 (24)	2.4 (5)	C(65)	2280 (7)	2087 (7)	1206 (14)	3.5 (3)
C(16)	10177 (7)	5681 (7)	7991 (14)	3.7 (3)	C(66)	2225 (6)	2154 (6)	2563 (12)	2.3 (2)
C(17)	9621 (15)	5234 (16)	8333 (30)	4.2 (6)	C(67)	3466 (5)	3089 (5)	7138 (10)	1.3 (2)
C(18)	8989 (14)	5072 (15)	7633 (28)	3.6 (6)	C(68)	3595 (6)	3821 (6)	7422 (11)	2.1 (2)
C(14*)[c]	8984 (11)	5552 (12)	7953 (22)	1.9 (4)	C(69)	4074 (6)	4292 (6)	8535 (12)	2.7 (2)
C(15*)	9611 (12)	5765 (13)	8716 (25)	2.6 (5)	C(70)	4440 (6)	4032 (6)	9285 (11)	2.2 (2)
C(17*)	10048 (13)	5448 (14)	6735 (26)	3.0 (5)	C(71)	4311 (5)	3313 (6)	9006 (11)	1.9 (2)
C(18*)	9421 (11)	5215 (12)	5953 (23)	2.2 (4)	C(72)	3829 (5)	2834 (6)	7947 (11)	1.8 (2)
C(19)	7576 (5)	2502 (6)	2469 (11)	1.8 (2)	C(73)	1812 (5)	1549 (6)	6113 (11)	1.6 (2)
C(20)	8001 (6)	2666 (6)	1449 (12)	2.3 (2)	C(74)	1443 (6)	901 (6)	5176 (12)	2.3 (2)
C(21)	7979 (6)	2086 (7)	481 (13)	2.9 (3)	C(75)	869 (6)	356 (7)	5519 (13)	3.2 (3)
C(22)	7541 (7)	1378 (7)	511 (14)	3.4 (3)	C(76)	659 (7)	465 (7)	6771 (14)	3.7 (3)
C(23)	7122 (6)	1231 (7)	1561 (13)	3.2 (3)	C(77)	1010 (6)	1101 (7)	7686 (13)	3.0 (3)
C(24)	7132 (6)	1801 (6)	2524 (12)	2.4 (2)	C(78)	1594 (6)	1659 (6)	7356 (12)	2.3 (2)
C(25)	8302 (5)	3023 (6)	6253 (11)	1.9 (2)	C(79)	387 (5)	2208 (6)	4062 (11)	1.9 (2)
C(26)	8397 (13)	3162 (14)	7624 (26)	3.1 (5)	C(80)	−75 (6)	1638 (6)	4556 (12)	2.5 (2)
C(27)	9053 (15)	3386 (16)	8264 (31)	4.0 (6)	C(81)	−768 (7)	1391 (7)	4094 (13)	3.3 (3)
C(28)	9597 (7)	3525 (8)	7510 (15)	4.0 (3)	C(82)	−974 (7)	1716 (8)	3166 (14)	3.9 (3)
C(29)	9526 (15)	3417 (16)	6213 (30)	4.0 (6)	C(83)	−492 (7)	2292 (7)	2719 (14)	3.4 (3)
C(30)	8866 (14)	3214 (15)	5550 (28)	3.5 (6)	C(84)	208 (6)	2545 (6)	3174 (12)	2.6 (2)
C(26*)	8472 (15)	3491 (16)	7429 (30)	3.9 (6)	C(85)	1321 (6)	3255 (6)	7863 (11)	2.1 (2)
C(27*)	9152 (14)	3773 (15)	8075 (29)	3.7 (6)	C(86)	776 (6)	2787 (7)	8368 (13)	3.1 (3)
C(29*)	9399 (11)	3112 (12)	6215 (23)	2.5 (4)	C(87)	872 (7)	2744 (8)	9733 (15)	4.3 (3)
C(30*)	8746 (11)	2854 (12)	5599 (23)	2.3 (4)	C(88)	1485 (8)	3157 (9)	10482 (17)	4.9 (3)
C(31)	5757 (5)	2279 (6)	7036 (10)	1.6 (2)	C(89)	2020 (7)	3618 (8)	9981 (15)	4.0 (3)
C(32)	5354 (6)	2374 (6)	8011 (12)	2.5 (2)	C(90)	1943 (6)	3670 (7)	8609 (13)	2.8 (2)

[a] Carbon atoms only. [b] Estimated standard deviations in parentheses. [c] Asterisks represent disordered atoms.

the atomic labeling. The disordered phenyl rings are shown in Figures 2 and 3 (supplementary materials).

Description and Discussion of the Structure

Triphenyltin(IV) diphenyl phosphate crystallizes in a centrosymmetric, cyclic hexamer modestly puckered into a chair conformation as shown in Figures 4 and 5 (supplementary material) in which planar triphenyltin(IV) units are axially bridged by symmetrical, three-atom –O–P–O– linkages of the diphenyl phosphate ligand.

There are three molecules in each asymmetric unit, and two asymmetric units make up the contents of the unit cell as shown in Figure 6. Each unit cell thus consists of six triphenyltin(IV) diphenyl phosphate molecules. Three adjacent molecules are centrosymmetric with another three molecules whose atoms are distinguished by primed numbers.

The coordination geometry at the tin atoms as shown in Figure 7 is almost perfectly trigonal bipyramidal, with the average axial O–Sn–O angle = 177.0° and equatorial C–Sn–C angle = 120.0°. The planarity of the SnC_3 system in this class of compounds could not be deduced from the vibrational spectra in the $\nu(Sn-C_3)$ region since absorptions in the infrared and Raman spectra of the parent diphenylphosphoric acid obscure the 600–500-cm^{-1} region for the triorganotin(IV) derivatives.[1]

These axial tin–oxygen distances are nearly equal [average d(Sn–O) = 2.234 ± 0.015 Å] and the bridging –O–P–O–

Table V. Final Intramolecular Bond Distances (Å) in $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$[a]

Sn(1)-O(1)	2.219 (8)	Sn(1)-C(7)	2.123 (11)
Sn(1)-O(10')[b]	2.247 (8)	Sn(1)-C(13)	2.127 (11)
Sn(1)-C(1)	2.125 (11)		
Sn(2)-O(2)	2.241 (8)	Sn(2)-C(37)	2.123 (11)
Sn(2)-O(5)	2.227 (7)	Sn(2)-C(43)	2.135 (11)
Sn(2)-C(31)	2.124 (11)		
Sn(3)-O(6)	2.233 (7)	Sn(3)-C(67)	2.124 (11)
Sn(3)-O(9)	2.237 (8)	Sn(3)-C(73)	2.124 (11)
Sn(3)-C(61)	2.126 (11)		
P(1)-O(1)	1.487 (9)	P(1)-O(4)	1.588 (8)
P(1)-O(2)	1.487 (8)	O(3)-C(19)	1.402 (14)
P(1)-O(3)	1.573 (8)	O(4)-C(25)	1.417 (14)
P(2)-O(5)	1.482 (8)	P(2)-O(8)	1.587 (9)
P(2)-O(6)	1.496 (8)	O(7)-C(49)	1.403 (15)
P(2)-O(7)	1.582 (8)	O(8)-C(55)	1.405 (14)
P(3)-O(9)	1.492 (8)	P(3)-O(12)	1.580 (8)
P(3)-O(10)	1.475 (8)	O(11)-C(79)	1.412 (14)
P(3)-O(11)	1.579 (8)	O(12)-C(85)	1.403 (14)

[a] Estimated standard deviations in parentheses. [b] Primed atoms are related to unprimed atoms (*x*, *y*, *z*) by 1 − *x*, 1 − *y*, 1 − *z*.

Table VI. Final Intramolecular Bond Angles (Deg) in $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$[a, b]

O(1)-Sn(1)-O(10')[c]	176.7 (3)	O(10')-Sn(1)-C(7)[c]	93.0 (4)
O(1)-Sn(1)-C(1)	88.7 (4)	O(10')-Sn(1)-C(13)[c]	86.6 (4)
O(1)-Sn(1)-C(7)	90.0 (4)	C(1)-Sn(1)-C(7)	121.4 (4)
O(1)-Sn(1)-C(13)	90.7 (4)	C(1)-Sn(1)-C(13)	119.4 (4)
O(10')-Sn(1)-C(1)[c]	90.8 (4)	C(7)-Sn(1)-C(13)	119.2 (4)
O(2)-Sn(2)-O(5)	175.7 (3)	O(5)-Sn(2)-C(37)	84.6 (4)
O(2)-Sn(2)-C(31)	93.1 (4)	O(5)-Sn(2)-C(43)	92.2 (4)
O(2)-Sn(2)-C(37)	91.2 (4)	C(31)-Sn(2)-C(37)	124.5 (4)
O(2)-Sn(2)-C(43)	89.5 (4)	C(31)-Sn(2)-C(43)	115.8 (4)
O(5)-Sn(2)-C(31)	89.7 (4)	C(37)-Sn(2)-C(43)	119.5 (4)
O(6)-Sn(3)-O(9)	178.6 (3)	O(6)-Sn(3)-C(73)	87.9 (4)
O(6)-Sn(3)-C(61)	87.9 (4)	O(9)-Sn(3)-C(61)	93.4 (4)
O(6)-Sn(3)-C(67)	91.0 (3)		
O(9)-Sn(3)-C(67)	88.7 (3)	C(61)-Sn(3)-C(73)	117.8 (4)
O(9)-Sn(3)-C(73)	91.1 (4)	C(67)-Sn(3)-C(73)	118.3 (4)
C(61)-Sn(3)-C(67)	123.7 (4)		
Sn(3)-O(9)-P(3)	142.9 (5)	O(9)-P(3)-O(11)	105.5 (4)
Sn(1')-O(10)-P(3)[c]	142.9 (5)	O(9)-P(3)-O(12)	112.8 (5)
C(79)-O(11)-P(3)	124.4 (7)	O(10)-P(3)-O(11)	109.5 (4)
C(85)-O(12)-P(3)	127.6 (8)	O(10)-P(3)-O(12)	105.4 (5)
O(9)-P(3)-O(10)	117.9 (5)	O(11)-P(3)-O(12)	105.0 (4)
Sn(1)-O(1)-P(1)	152.7 (5)	O(1)-P(1)-O(3)	105.6 (5)
Sn(2)-O(2)-P(1)	158.8 (5)	O(1)-P(1)-O(4)	109.4 (5)
C(19)-O(3)-P(1)	127.5 (7)	O(2)-P(1)-O(3)	110.7 (5)
C(25)-O(4)-P(1)	122.7 (7)	O(2)-P(1)-O(4)	104.9 (4)
O(1)-P(1)-O(2)	119.9 (5)	O(3)-P(1)-O(4)	105.5 (4)
Sn(2)-O(5)-P(2)	150.7 (5)	O(5)-P(2)-O(7)	105.9 (4)
Sn(3)-O(6)-P(2)	153.8 (5)	O(5)-P(2)-O(8)	108.6 (4)
C(49)-O(7)-P(2)	120.0 (7)	O(6)-P(2)-O(7)	111.4 (4)
C(55)-O(8)-P(2)	125.4 (7)	O(6)-P(2)-O(8)	109.2 (4)
O(5)-P(2)-O(6)	117.7 (4)	O(7)-P(2)-O(8)	103.1 (4)

[a] Estimated standard deviations in parentheses. [b] Angles O–C–C and C–C–C are given in Table VIII (supplementary material). [c] Primed atoms are related to unprimed atoms (*x*, *y*, *z*) by 1 − *x*, 1 − *y*, 1 − *z*.

linkages are likewise almost equal [average *d*(P–OSn) = 1.487 ± 0.012 Å], indicating extensive delocalization of the P═O double bond and obviating the question of which of the P–O–Sn connections is double bonding and dative and which is the single bonding and ester linkage. The bonds that phosphorus makes with the phenoxy oxygen atom [average *d*(P–OC) = 1.582 ± 0.009 Å] are longer, as expected, and the angles SnO–P–OSn [average = 118.5°], CO–P–OSn (average = 108.2°), and CO–P–OC (average = 104.5°) lie in the order predicted by isovalent hybridization for the stannoxy group being less electronegative than the phenoxy group.

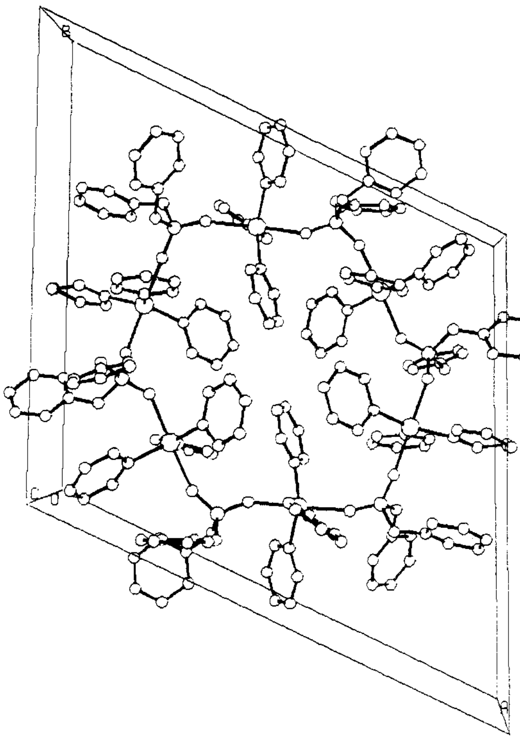

Figure 6. Unit cell contents of triphenyltin(IV) diphenyl phosphate.

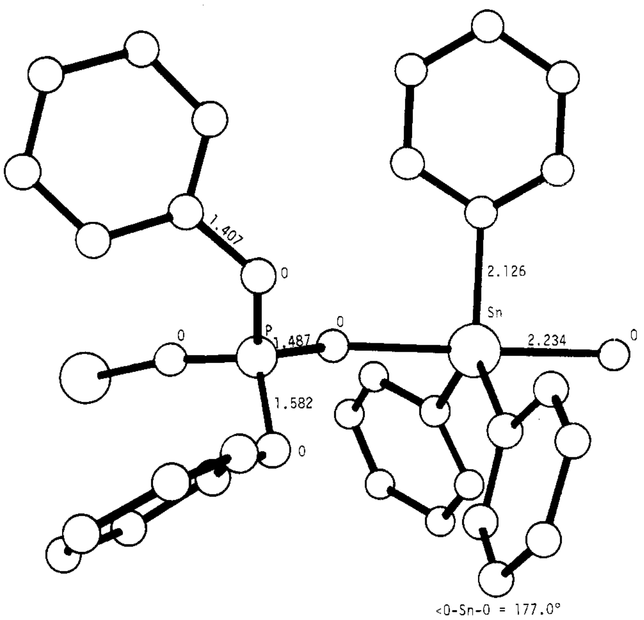

Figure 7. Coordination geometry at the tin and phosphorus atoms in triphenyltin(IV) diphenyl phosphate. Mean bond distances label the appropriate bonds.

In general we expect that our P—O distances will be longer than those in localized P═O systems forming dative bonds to tin, and shorter than in true P—O—Sn ester linkages. Unfortunately, direct comparisons are not available, since even in the most directly analogous system we have studied, $(CH_3)_3SnOP(O)(OH)C_6H_5$, the P═O distance is lengthened through additional hydrogen bonding. However, the ester P–OSn linkage is longer at 1.492 Å[8] than our delocalized one.

Likewise, our Sn–O distances should be longer than those in true ester P–O–Sn linkages but shorter than in dative P═O→Sn bonds. By comparison with the internuclear distances in the analogous (phenylphosphonato)trimethyltin(IV), the O→Sn bond contiguous to the P═O double bond is longer than our Sn—O bond at 2.319 Å, but the ester linkage is within experimental error at 2.240 Å.[8] In the related (nitrato)triphenyl(triphenylphosphine oxide)tin(IV) system which also involves a trigonal-bipyramidal triphenyltin(IV) center axially coordinated by oxygen, the O→Sn distance of 2.29 Å[13] is, on the other hand, longer than ours as well.

Although the linearity of the O–Sn–O bonds requires linearity of the hexamer in the vicinity of the tin atoms, the chains are bent into rings through the tetrahedrally coordinated phosphorus atoms of the diphenyl phosphate ligand at an average SnO–P–OSn angle = 118.5°. In the structure of the analogous (α-phenylphosphonato)trimethyltin(IV), $(CH_3)_3SnOP(O)(OH)C_6H_5$, the chains continue to propagate through the crystal in a 4_1 helical fashion, establishing hydrogen bonds between the P—OH and P═O units of adjacent helices. The stacks of helices, held at regular intervals by hydrogen bonds, create infinite, two-dimensional sheets.[8] On the other hand, in the divalent tin series the tin(II) atoms in the hydrogen phosphate $(SnHPO_4)$,[14-16] bis(dihydrogen phosphate) $[Sn(H_2HPO_4)_2]$,[17] phosphite $(SnHPO_3)$,[16] $Sn_2(OH)PO_4$,[16,18] $Sn_3(PO_4)_2$,[16,19] $Sn_3(O)(OH)PO_3$,[16,20] the two halophosphites $Sn_3PO_4F_3$[16,21] and $SnFPO_3$[16,22] and $ClSnH_2PO_2$[23] are all bridged by O–P–O linkages in polymeric lattices. In our title compound, by contrast, the chains lock together to form a hexamer incorporating a 24-atom ring rather than to propagate linearly or helically through the crystal. Ring formation is found for tin(IV) in two other examples involving phosphate moieties. In the dimeric $[Cl_3SnPO_2Cl_2{\cdot}POCl_3]_2$, eight-membered centrosymmetric rings are formed by dichloro phosphate groups doubly bridging two $Cl_3Sn \leftarrow O{=}PCl_3$ units to form an octahedral geometry at tin,[24] and tris(dimethyltin(IV)) bis(orthophosphate) octahydrate, $[(CH_3)_2Sn]_3(PO_4)_2{\cdot}8H_2O$, consists of infinite ribbons in which octahedral, *trans*-dimethyltin(IV), *cis*-diaquo groups are cis linked by PO_4 tetrahydra to form eight-membered rings in chair conformations.[25] However, in these examples the rings do not accommodate axially bridged trigonal bipyramids at tin. From the position of the adjacent hexamer shown in Figure 8 (supplementary material), it is apparent that more atoms can be packed into less space by the cyclic system than by any other arrangement. It is also apparent that the pentamer is the smallest unstrained ring capable of being formed incorporating axially bridged trigonal-bipyramidal triphenyltin groups. The average O–P–O angle would then be 108°. However, in our triphenyltin(IV) solid the need to accommodate the one phenyl group on each tin atom that is thrust into the center of the oligomeric ring expands the system to the hexamer.

The hexameric rings are puckered into a chair conformation with Sn(1′) slightly above (by 1.022 Å) and the symmetry-related Sn(1) slightly below (by 1.022 Å) the least-squares plane formed by the other four tin atoms ($0.1103x + 0.0143y + 0.9938z = 6.0184$). The phenoxy groups on each phosphorus atom point out from the center of the ring and are thus eclipsed by one another. However, one of the phenyl groups on each tin atom protrudes alternately above and below the ring plane to produce a staggered arrangement of the triphenyltin groups around the ring. The hexameric units nestle together in a stack along the *c* axis as shown in Figure 8 where the downward tilting phenyl groups of one hexamer fit between the upward tilting phenyls of the hexamer below to give the *c* axis spacing of 10.117 (5) Å. The arrangement of the stack viewed down the *c* axis is shown in Figure 9 (supplementary material). The utilization of available space is thus very efficient, and no doubt contributes to the choice of structure over the alternative chelated monomer, larger oligomer, or helical or linear polymer. We are unaware of any other axially bridged, trigonal-bipyramidal tin(IV) systems that form oligomeric rings.[26]

Finally, as stated above, there is a disordered region consisting of phenyl rings attached to Sn(1) [C(13)–C(18)] and to O(4) [C(25)–C(30)]. In both ring systems the disorder can be described as a rotation about the axis of attachment to the molecule [Sn(1)–C(13) → C(16) and O(4)–C(25) → C(28)], the magnitude of the rotation being 49° for the ring attached to Sn(1) and 34° for the ring attached to O(4), as determined by calculation of the dihedral angles between the respective least-squares planes. The disordered ring at Sn(1) is not the one directed into the interior of the hexamer. The disordered rings interact only with each other.

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Supplementary Material Available: Tables of final anisotropic temperature factors (Table IV), interatomic C–C distances in the phenyl groups (Table VII), and interatomic bond angles in the phenyltin and phenoxy systems (Table VIII), Figures 2–5, 8, and 9 (showing views of the disordered phenyl ring, the cyclic, hexameric triphenyltin(IV) diphenyl phosphate, and the stacking of the hexameric units), and a listing of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

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