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Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.052
wR factor = 0.143
Data-to-parameter ratio = 14.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

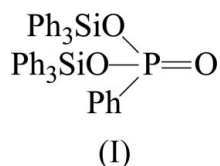
Bis(triphenylsilyl) phenylphosphonate

In the structure of the title monomeric phosphorosilicate, $\text{C}_{42}\text{H}_{35}\text{O}_3\text{PSi}_2$ or $\text{PhP}(\text{=O})(\text{OSiPh}_3)_2$, there are notable differences in the chemically equivalent $\text{P}^{\text{V}}-\text{O}-\text{Si}$ angles [$141.59(16)$ and $152.38(18)^\circ$] and the two $\text{P}-\text{O}(-\text{Si})$ distances [$1.546(3)$ and $1.566(3) \text{ \AA}$]. There is also a significant $\text{C}-\text{H}\cdots\text{O}=\text{P}$ hydrogen bond which links molecules into extended chains along [100].

Received 21 February 2005
Accepted 24 February 2005
Online 4 March 2005

Comment

Compounds containing $\text{P}-\text{O}-\text{Si}$ linkages ('phosphorosilicates', also called 'phosphosiloxanes') are amongst the best known of all heterosiloxane species. Whereas the synthesis and chemical properties of simple phosphosiloxanes have been studied exhaustively (Borisov *et al.*, 1971; Chernyshev & Bugarenko, 1968), the structural properties have not received much attention. This paper addresses the lack of structural information on $\text{P}-\text{O}-\text{Si}$ species in a simple $\text{O}=\text{P}^{\text{V}}-\text{O}-\text{Si}$ -containing compound, *viz.* $\text{PhP}(\text{=O})(\text{OSiPh}_3)_2$, (I).



This colourless crystalline solid is quite air- and moisture-stable; exposure to the atmosphere for *ca* two months produced no discernible changes in the melting point or IR spectrum. However, it was completely hydrolysed after three hours in a water–acetone (3:1) mixture heated under reflux.

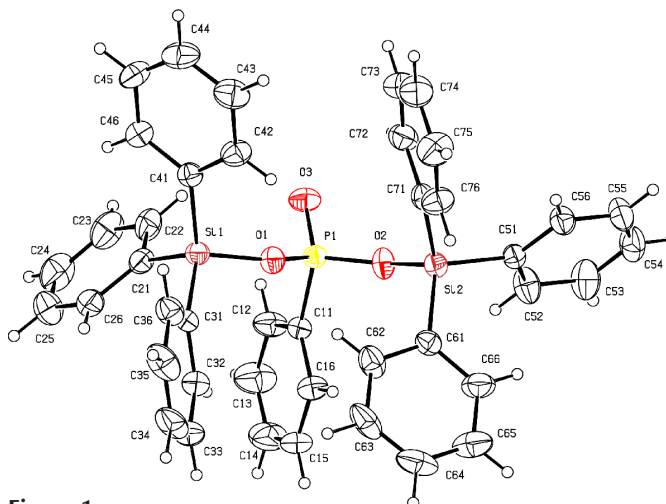


Figure 1
A view of (I) with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

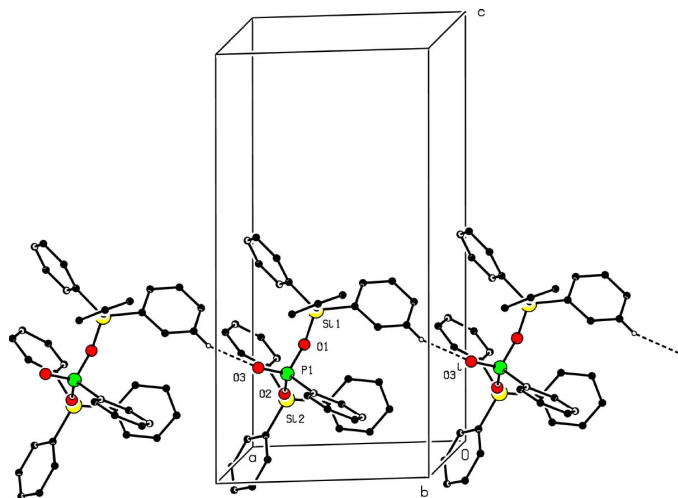


Figure 2
A view showing the C–H...O hydrogen bonding in (I). See Table 2 for symmetry codes.

The central tetrahedral (O=)PO₂C_{Ph} unit in (I) is linked through the two singly bound O atoms to two –SiPh₃ groups with tetrahedrally coordinated silicon (Fig. 1). Principal bond distance and angles for (I) are given in Table 1. The two chemically equivalent P^V–O–Si angles in (I) differ considerably in magnitude, with values of 141.59 (16) and 152.38 (18)°. The two P–O(–Si) distances are also different (at the 3 × s.u. level), with dimensions of 1.546 (3) and 1.566 (3) Å, the latter value corresponding with the smaller P–O–Si angle. The Si–O(–P) distances are 1.651 (3) and 1.661 (3) Å.

Molecules are linked to form chains in the [100] direction by a C–H...O hydrogen bond (Table 2) involving C33–H33 and an adjacent O3 atom of a symmetry-related molecule at (–1 + x, y, z). There are no significant π–π interactions in the crystal structure, but there are three C–H...π interactions which effectively link the molecules to generate a three-dimensional network (see Table 2).

Experimental

Reactions were carried out under an inert atmosphere. Solvents were dried and distilled prior to use. Phenylphosphonic acid and triphenylsilanol were obtained from Aldrich and were used directly. Phenylphosphonic acid (0.636 g, 4.02 mmol) and triphenylsilanol (2.222 g, 8.04 mmol) were refluxed in toluene (50 ml) in a Dean–Stark apparatus for 6 h. Recrystallization of the colourless product from dichloromethane–cyclohexane (1:2) afforded (I) as rectangular crystals [2.452 g, 3.85 mmol, 90.4%; 461–464 K (literature 461–464 K; Chamberlain *et al.*, 1960)]. Analysis found: C 74.4, H 5.25%; C₄₂H₃₅O₃PSi₂ requires: C 74.75, H 5.2%. FT–IR (KBr disc), ν_{\max} /cm^{–1}: 1429 (s), 1255 (s), 1120 (s), 1075 (s), 1008 (vs), 994 (s), 716 (s), 699 (s), 513 (s). ¹H NMR (CDCl₃, p.p.m.): 7.77–7.21 (*m*, 35 H, C₆H₅). ¹³C NMR (CDCl₃, p.p.m.): 135.47, 134.99, 132.38, 131.14, 130.37, 129.65, 128.06, 127.29. MS (EI), *m/z*: 674 (*M*⁺), 597 (*M*⁺ – Ph), 519 (*M*⁺ – 2Ph – H), 259 (Ph₃Si⁺), 77 (Ph⁺).

Crystal data

C₄₂H₃₅O₃PSi₂
M_r = 674.85
 Triclinic, *P* $\bar{1}$
a = 9.420 (6) Å
b = 10.479 (6) Å
c = 19.269 (9) Å
 α = 85.44 (5)°
 β = 89.45 (5)°
 γ = 71.94 (5)°
V = 1802.4 (18) Å³

Z = 2
D_x = 1.243 Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 26 reflections
 θ = 15.3–19.4°
 μ = 0.18 mm^{–1}
T = 294 (1) K
 Rectangular, colourless
 0.41 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 6674 measured reflections
 6349 independent reflections
 2874 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.010

θ_{\max} = 25.0°
 h = –10 → 11
 k = 0 → 12
 l = –22 → 22
 3 standard reflections every 250 reflections
 intensity decay: 3.2%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.052
 wR (*F*²) = 0.143
S = 0.95
 6349 reflections
 433 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P1–O3	1.453 (3)	Si1–C31	1.852 (4)
P1–O2	1.546 (3)	Si1–C21	1.856 (4)
P1–O1	1.566 (3)	Si2–O2	1.651 (3)
P1–C11	1.777 (4)	Si2–C71	1.849 (4)
Si1–O1	1.661 (3)	Si2–C61	1.855 (4)
Si1–C41	1.845 (4)	Si2–C51	1.858 (4)
O3–P1–O2	114.22 (17)	C41–Si1–C21	111.33 (18)
O3–P1–O1	114.45 (16)	C31–Si1–C21	110.66 (19)
O2–P1–O1	103.26 (14)	O2–Si2–C71	110.47 (16)
O3–P1–C11	112.45 (17)	O2–Si2–C61	108.17 (17)
O2–P1–C11	105.74 (16)	C71–Si2–C61	111.96 (18)
O1–P1–C11	105.79 (17)	O2–Si2–C51	104.43 (15)
O1–Si1–C41	106.78 (17)	C71–Si2–C51	109.75 (18)
O1–Si1–C31	104.26 (16)	C61–Si2–C51	111.79 (18)
C41–Si1–C31	112.47 (18)	P1–O1–Si1	141.59 (16)
O1–Si1–C21	111.07 (16)	P1–O2–Si2	152.38 (18)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C22–H22...O3	0.93	2.58	3.324 (6)	137
C33–H33...O3 ⁱ	0.93	2.39	3.243 (6)	152
C13–H13...Cg1 ⁱⁱ	0.93	2.78	3.631 (6)	153
C15–H15...Cg2 ⁱⁱⁱ	0.93	2.99	3.897 (6)	165
C34–H34...Cg3 ⁱ	0.93	2.93	3.709 (7)	142

Symmetry codes: (i) *x* – 1, *y*, *z*; (ii) *x*, 1 + *y*, *z*; (iii) 1 – *x*, 1 – *y*, –*z*. Cg1, Cg2 and Cg3 are the centroids of the phenyl rings C61–C66, C51–C56 and C41–C46, respectively

All H atoms were visible in difference maps and included as riding atoms, with C–H = 0.93 Å and *U*_{iso} = 1.2*U*_{eq}(C).

Data collection: *DIFRAC* with profile analysis (Gabe & White, 1993); cell refinement: *DIFRAC*; data reduction: *DATRD2* in

NRCVAX94 (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Version 1.70.01; Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

References

Borisov, S. N., Voronkov, M. G. & Lukevits, E. Ya. (1971). *Organosilicon Derivatives of Phosphorus and Sulfur*. New York: Plenum Press.

Chamberlain, M. M., Kern, G., Jabs, G. A., Germanas, D., Greene, A., Brain, K. & Wayland, B. (1960). *US Department. Com. Office Tech. Serv.* PB Report 152, pp. 086–110.

Chernyshev, E. A. & Bugerenko, E. F. (1968). *Organomet. Chem. Rev. A*, **3**, 469–496.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Gabe, E. J. & White, P. S. (1993). *DIFRAC*. Pittsburgh meeting. Abstract PA104.

Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.