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The arsenic(V) compound PhAs(O)(OH)(OSiPh$_3$)

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The structure of the arsenosilicate compound, hydroxooxo(phenyl)(triphenylsiloxy)arsenic(V), PhAs(O)(OH)(OSiPh$_3$) or [As(C$_6$H$_5$)(C$_{18}$H$_{15}$OSi)O(OH)], is dimeric with the monomers joined by two As—O—H$\cdots$O═As hydrogen-bonding sequences about an inversion centre, with O$\cdots$O = 2.528 (3) Å. The monomer unit has a tetrahedral AsO$_3$C$_{Ph}$ entity. The As—O—Si angle [140.79 (12)°] is larger than any previously reported As^{V}—O—Si angle in a molecular species. The three independent As—O bond lengths are 1.6551 (18), 1.6740 (18) and 1.7086 (17) Å, respectively, for the As═O, As—OH and As—OSiPh$_3$ bonds.

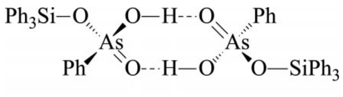
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
R factor = 0.035
wR factor = 0.079
Data-to-parameter ratio = 18.0

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

Comment

The small number of molecular silylarsenates, *i.e.* arsenic(V) silicates, which have been structurally characterized all contain terminal As^{V}–OSiMe$_3$ units (Baier *et al.*, 1992, 1993*a*,*b*). The compounds are the silylated aminoarsenates (Me$_3$SiO)$_2$(PhNH)AsO, (I), and (Me$_3$SiO)$_3$AsO(Me$_3$SiO)$_3$-AsNMe, (II), a triarsa(V)azene compound, [(Me$_3$SiO)$_2$AsN]$_3$, (III), and a diarsenate(V) compound, (Me$_3$SiO)$_8$As$_4$O$_6$, (IV). Compounds (I) and (III) contain four-coordinate arsenic, (II) has five-coordinate arsenic and (IV) contains arsenic in both four- and six-coordination. Only in (Me$_3$SiO)$_2$(PhNH)-AsO, (I), is there an As═O bond present (Baier *et al.*, 1993*b*). In an attempt to prepare PhAs(O)(OSiPh$_3$)$_2$ *via* a dehydration reaction, phenylarsonic acid was reacted with triphenylsilanol in a 1:2 molar ratio (O'Leary, 1998). The reaction did not proceed as anticipated and successive crystallizations from a dichloromethane-ether-cyclohexane (1:1:4) solution afforded what we subsequently established to be the title compound PhAs(O)(OH)(OSiPh$_3$), (V), and Ph$_3$SiOSiPh$_3$. When the reaction was repeated using a 1:1 molar ratio of phenylarsonic acid to triphenylsilanol, compound (V) was the only product obtained.



(V)

A search of the December 2003 release of the Cambridge Structural Database (Allen, 2002) shows that compound (V) is indeed a novel species and is the first structurally characterized silylarsenate containing both As—OSi and As—OH units. In the solid state, the structure is dimeric as shown in (V) with the monomers joined by two As—O—H$\cdots$O═As hydrogen-bonding sequences about an inversion centre

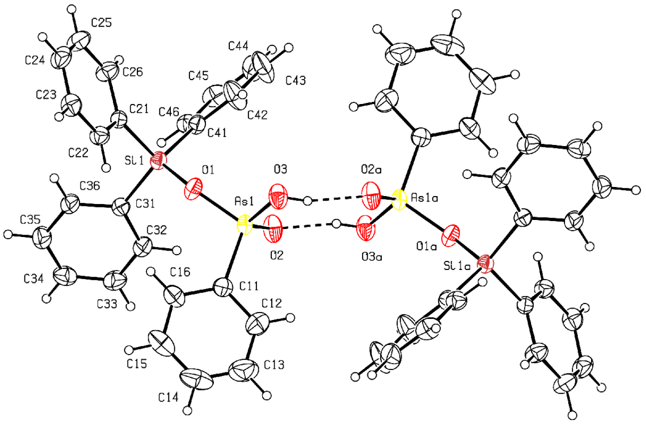


Figure 1
A view of the dimer of (V) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atom labels with suffix 'a' represent the equivalent position $(1 - x, 1 - y, 1 - z)$.

(Fig. 1). The monomers contain a central tetrahedral AsO_3C_{Ph} unit bound through one of the O atoms to a tetrahedral $-SiPh_3$ group. Principal bond-length and angle data for (V) are given in Table 1.

The As—O—Si angle in (V) [140.79 (12)°] is larger than any previously reported As^V—O—Si angles, which range from 128.5 (4) to 136.0 (3)° (Baier *et al.*, 1992, 1993*a*,*b*). The As^V—O_{Si} distance in (V) [1.7086 (17) Å] lies within the range of the corresponding distances in the previously reported As^V-containing compounds (I)–(IV) [1.680 (3)–1.780 (2) Å]. The As^{III}—O_{Si} distances in $PhAs(OSiPh_3)_2$, (VI) (Ferguson *et al.*, 2004), are 1.758 (3) and 1.786 (3) Å, and are significantly longer than the As^V—O_{Si} distance in (V).

As expected, the As—OH bond in (V) [1.6740 (18) Å] is significantly shorter than the As—O_{Si} bond [1.7086 (17) Å]. The As═O double bond in (V) [1.6551 (18) Å] is close to the value of the As—OH single bond and longer than the As═O distance of 1.626 (3) Å in the N—H···O hydrogen-bonded system $(Me_3SiO)_2(PhNH)AsO$, (I) (Baier *et al.*, 1993*b*). A mean value of 1.661 Å has been suggested for the As═O distance (Allen *et al.*, 1987).

The Si—O_{As} distance in (V) [1.6585 (18) Å] is not unusual. Comparable distances in $(Me_3SiO)_3AsO(Me_3SiO)_3AsNMe$, (II), and $[(Me_3SiO)_2AsN]_3$, (III), range from 1.646 (2) to 1.732 (6) Å. The Si—O_{As} distances in $PhAs(OSiPh_3)_2$, (VI) (Ferguson *et al.*, 2004), are 1.635 (3) and 1.641 (4) Å, and are shorter than the Si—O_{As} distance in (V). The As—C_{Ph} bond length in (V) [1.891 (3) Å] is relatively short, since a mean value of 1.922 Å has been suggested for As—C_{ar} bonds in general, where the As atom is four-coordinate and C_{ar} is a C atom in an aromatic system (Allen *et al.*, 1987). The As—C_{ar} distance in $PhAs(OSiPh_3)_2$, (VI) (Ferguson *et al.*, 2004), of 1.936 (5) Å is significantly greater than the distance of 1.891 (3) Å in (V). The Si—C and C—C distances in the $SiPh_3$ units of (V) are normal.

The two O—As═O angles in (V), *viz.* O1—As1—O2 and O2—As1—O3 in Fig. 1, are 110.76 (10) and 114.05 (10)°, and do not agree within 3 s.u.; the O1—As1—O3 angle is notably smaller at 103.11 (10)°. The three O—Si—C angles in (V) lie between 103.41 (11) and 110.96 (11)°, whilst the range for the three C—Si—C angles is 110.40 (12)–111.37 (12)°.

The AsO—H···O═As hydrogen-bond data for (V) (Table 2) indicate the presence of moderately strong hydrogen bonding (Jeffrey, 1997). The hydrogen-bonding pattern is similar to that in (I), $(Me_3SiO)_2(PhNH)AsO$. Like (V), the structure of (I) is dimeric, with the monomers connected *via* two AsN—H···O═As hydrogen bonds, but unlike (V), the monomers in (I) are not symmetry-related (Baier *et al.*, 1993*b*). As expected, all phenyl rings take part in C—H···π interactions (Table 2) with phenyl rings of adjacent molecules to generate a three-dimensional network.

Experimental

For the synthesis of $PhAs(O)(OH)(OSiPh_3)$, (V), phenylarsonic acid (2.009 g, 9.94 mmol) and triphenylsilanol (2.747 g, 9.94 mmol) were added to 50 ml toluene in a Dean–Stark apparatus. The solution was heated at reflux for 10 h. Removal of toluene afforded a colourless solid which was crystallized from dichloromethane–heptane (1:3) to give crystals of (V) (3.625 g, 79.2%; m.p. 436–438 K). Found: C 62.9, H 4.9%; $C_{24}H_{21}AsO_3Si$ requires: C 62.6, H 4.6%. FT–IR (KBr disc), ν_{max} cm^{-1}: 1428 (*s*), 1119 (*s*), 956 (*s*), 910 (*vs*), 714 (*s*), 699 (*s*), 508 (*vs*). ^1H NMR (270 MHz, $CDCl_3$, p.p.m.): 8.95 (*s*, 2H, OH), 7.49–7.03 (*m*, 40H, C_6H_5As and C_6H_5Si). ^{13}C NMR ($CDCl_3$, p.p.m.): 151.05; 136.22, 135.41, 131.00, 129.99, 129.27, 128.49, 127.49 (SiC_6H_5 and AsC_6H_5). EIMS *m*/*z* [*M* = monomeric unit $[PhAs(O)(OH)(OSiPh_3)]$: 460 [*M*], 383 [*M* − Ph], 306 [*M* − 2Ph], 275 [Ph_3SiO].

Crystal data

$[As(C_6H_5)(C_{18}H_{15}OSi)O(OH)]$
$M_r = 460.42$
Triclinic, $P\bar{1}$
$a = 8.3350 (9)$ Å
$b = 9.8193 (8)$ Å
$c = 14.8736 (14)$ Å
$\alpha = 89.948 (6)°$
$\beta = 74.391 (9)°$
$\gamma = 68.276 (5)°$
$V = 1082.51 (18)$ Å^3

$Z = 2$
$D_x = 1.413$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.6$–$21.6°$
$\mu = 1.65$ mm^{-1}
$T = 294 (1)$ K
Lath, colourless
0.42 × 0.38 × 0.22 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.549$, $T_{max} = 0.702$
4751 measured reflections
4751 independent reflections

3281 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.0°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -18 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.080$
$S = 1.01$
4751 reflections
264 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.0624P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (9)

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Table 1
Selected geometric parameters (Å, °).

As1—O1	1.7086 (17)	Si1—O1	1.6585 (18)
As1—O2	1.6551 (18)	Si1—C21	1.860 (3)
As1—O3	1.6740 (18)	Si1—C31	1.857 (3)
As1—C11	1.891 (3)	Si1—C41	1.862 (3)
O2—As1—O3	114.05 (10)	O1—Si1—C21	103.41 (11)
O2—As1—O1	110.76 (10)	C31—Si1—C21	111.04 (11)
O3—As1—O1	103.12 (10)	O1—Si1—C41	110.96 (11)
O2—As1—C11	111.69 (12)	C31—Si1—C41	110.40 (12)
O3—As1—C11	110.74 (12)	C21—Si1—C41	111.37 (12)
O1—As1—C11	105.85 (11)	Si1—O1—As1	140.79 (12)
O1—Si1—C31	109.47 (11)		

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O2$^{\rm i}$	0.82	1.73	2.528 (3)	164
C15—H15$\cdots Cg2^{\rm ii}$	0.93	2.85	3.536	132
C24—H24$\cdots Cg4^{\rm iii}$	0.93	3.04	3.932	160
C33—H33$\cdots Cg4^{\rm ii}$	0.93	2.96	3.784	149
C35—H35$\cdots Cg2^{\rm iv}$	0.93	3.01	3.824	147
C42—H42$\cdots Cg1^{\rm v}$	0.93	3.14	3.946	146

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-1, y, z$; (iii) $x, 1+y, z$; (iv) $1-x, 2-y, -z$; (v) $1+x, y, z$. $Cg1$ to $Cg4$ are the centroids of the phenyl rings Cn1–Cn6 (n = 1–4), respectively.

Peaks consistent with the H atoms were visible in difference maps and all H atoms were subsequently included as riding atoms, with O—H = 0.82 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O), and C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992); data reduction: *DATRD*2 in *NRCVAX*94 (Gabe *et al.*, 1989); program(s) used to solve structure: *NRCVAX*94 *via* Patterson heavy-atom method; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *WinGX* (Farrugia, 1999); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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