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Bis(triphenylsilyl)phenylarsenite, $PhAs(OSiPh_3)_2$

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The geometry at the As atom in the title compound, $[As(C_6H_5)(C_{18}H_{15}OSi)_2]$, is trigonal pyramidal, with C—As—O angles of 94.9 (2) and 99.9 (2)°, an O—As—O angle of 95.12 (19)°, As—O distances of 1.759 (4) and 1.786 (4) Å, and an As—C distance of 1.932 (5) Å. Four of the six independent phenyl rings in the two $SiPh_3$ groups are disordered.

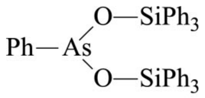
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.010 Å
Disorder in main residue
R factor = 0.060
wR factor = 0.185
Data-to-parameter ratio = 14.7

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

Comment

The structural study of organoarsenosilicate compounds has received only limited attention (Baier *et al.*, 1992, 1993*a*,*b*; Ferguson *et al.*, 1995, 1996, 2003). Of the compounds reported, five structures contain As^{III} (Ferguson *et al.*, 1995, 1996, 2003) and the other four contain As^V bonded to trimethylsiloxy groups (Baier *et al.*, 1992, 1993*a*,*b*). In this paper, the structure of bis(triphenylsilyl)phenylarsenite, $PhAs(OSiPh_3)_2$, (I), is compared with the structures of triphenylsilylarsenite compounds $As(OSiPh_3)_3$, (II) (Ferguson *et al.*, 1996), $[OCMe_2CH_2C(H)MeO]AsOSiPh_3$, (III) (Ferguson *et al.*, 2003), and the related ring and cage derivatives $(PhAsO)_2(^tBu_2SiO)_2$, (IV) (Ferguson *et al.*, 2003), and $As(OSiPh_2O)_3As$, (V) (Ferguson *et al.*, 1995). Structural data obtained for a fifth silylarsenite, *viz*. $^tBuSi\{OAs(Ph)O\}_3Si^tBu$, (VI) (Ferguson *et al.*, 2003), are also available but are unreliable because of disorder.



(I)

Compound (I) contains a trigonal pyramidal arsenic-centred AsO_2C_{Ph} unit bound through the O atoms to two $SiPh_3$ groups (Fig. 1). The analysis revealed that four of the six phenyl rings of the $SiPh_3$ groups are disordered. The Si—O distances (Table 1) fall within the range of values reported in other related compounds (Ferguson *et al.*, 1995, 1996; Ph_3SiOH, Puff *et al.*, 1991).

The As—O distances in (I) are unequal (Table 1) and may be compared with the previously reported shortest and longest As—O bonds in triphenylsilylarsenite species (II) and (III) of 1.728 (2) and 1.769 (5) Å, respectively. Large variations in $As—O_{Si}$ bond distances have been reported previously in As^{III} compounds [*e.g.* from 1.728 (2) Å in (II) to 1.889 (4) Å in the ring compound $(PhAsO)_2(^tBu_2SiO)_2$, (IV)]. The O—As—O angle in (I) (Table 1) is smaller than the angles found in $As(OSiPh_3)_3$, (II) (Ferguson *et al.*, 1996), for which a mean

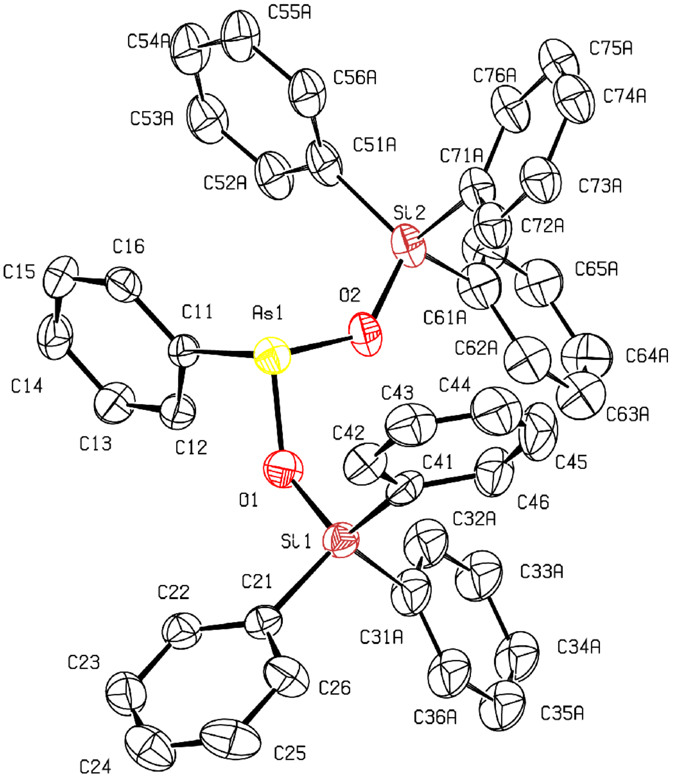


Figure 1
A view of (I) with the atomic numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level. Only one orientation is shown for each of the four disordered phenyl rings. H atoms have been omitted for clarity.

value of 98.13 (8)° was reported, with the range of values from 96.70 (8) to 99.42 (9)°.

The two As—O—Si angles in (I) (Table 1) are in the range of reported As—O—Si angles in the triphenylsilylarsenite compounds (II) and (III) [133.15 (10)–146.94 (11)°, both the maximum and the minimum occurring in (II)]. A similarly large range was reported in the ring compound $(PhAsO)_2$-$(^tBu_2SiO)_2$, (IV) [123.4 (2)–136.7 (2)°], but the range was much narrower in the cage species $As(OSiPh_2O)_3As$, (V) [136.4 (2)–140.4 (2)°].

The As—C distance in (I) (Table 1) is in accord with As—C_{Ph} distances of 1.950 (3) Å in (IV) and 1.942 (6) and 1.953 (6) Å in diphenylarsenic(III) iodide (Begley *et al.*, 1995). A mean value of 1.956 Å has been reported for As—C_{ar} bonds, where the arsenic is three-coordinate and the attached C atom is part of an aromatic system (Allen *et al.*, 1987).

Experimental

Compound (I) was originally synthesized in 78% yield from the reaction between $Na[OSiPh_3]$ and $PhAsI_2$ in benzene solution (Chamberland & MacDiarmid, 1961). In the present work, phenylarsine oxide (0.341 g, 2.03 mmol) and triphenylsilanol (1.121 g, 4.06 mmol) were refluxed in toluene (35 ml) for 20 h in a Dean–Stark apparatus. Removal of solvent on a rotary evaporator gave a viscous liquid, which formed a white solid after pumping under vacuum. Crystallization from dichloromethane–cyclohexane (1:3) afforded (I) as rectangular crystals [1.185 g, 83.1%; m.p. 391–393 K, literature 392–393 K (Chamberland & MacDiarmid, 1961)]. Analysis found: C 72.0, H 5.1%; $C_{42}H_{35}AsO_2Si_2$ requires: C 71.8, H 5.0%. FT–IR (KBr disc, cm^{-1}): ν_{max} 1428 (*s*), 1116 (*s*), 956 (*s*), 881 (*vs*), 713 (*vs*), 699 (*vs*), 516 (*s*), 506 (*s*). ^1H NMR (270 MHz, $CDCl_3$, p.p.m.): 7.44–6.98 (*m*, C_6H_5As and C_6H_5Si). ^{13}C NMR ($CDCl_3$, p.p.m.): 150.73, 136.60, 135.65, 130.99, 130.18, 129.38, 128.46, 127.65 (C_6H_5As and C_6H_5Si). EIMS *m*/*z*: 702 [M^+], 625 [M^+ − Ph], 548 [M^+ − 2Ph].

Crystal data

$[As(C_6H_5)(C_{18}H_{15}OSi)_2]$
$M_r = 702.80$
Monoclinic, $P2_1/n$
$a = 9.8563$ (14) Å
$b = 11.3662$ (15) Å
$c = 32.868$ (3) Å
$\beta = 91.124$ (13)°
$V = 3681.4$ (8) Å^3
$Z = 4$
$D_x = 1.268$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.1$–17.6°
$\mu = 1.02$ mm^{-1}
$T = 294$ (1) K
Block, colourless
0.35 × 0.35 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.640$, $T_{max} = 0.750$
8126 measured reflections
7995 independent reflections
2602 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 27°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 41$
3 standard reflections frequency: 120 min intensity decay: 2.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.185$
$S = 0.88$
7995 reflections
545 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0874P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

As1—O1	1.759 (4)	Si1—O1	1.635 (4)
As1—O2	1.786 (4)	Si2—O2	1.638 (4)
As1—C11	1.932 (5)		
O1—As1—O2	95.12 (19)	Si1—O1—As1	134.7 (2)
O1—As1—C11	94.9 (2)	Si2—O2—As1	133.8 (3)
O2—As1—C11	99.2 (2)		

Molecule (I) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. The crystals did not diffract well (presumably because of the phenyl-ring disorder) and only 33% of the data were measured as 'observed'. During the anisotropic refinement, four of six phenyl rings (C*i*1–C*i*6, *i* = 3, 5, 6, 7) on the Si atoms showed marked anisotropy, indicative of there being at least two adjacent orientations for each of these rings. This was successfully modelled by replacing the atoms of each markedly anisotropic ring by two rigid planar hexagons, with C—C = 1.39 Å. Because of the disorder, all Si—C(aromatic) distances were restrained; full details are in the _refinement_special_details section of the CIF. All H atoms were allowed for as riding atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Examination of the structure with *PLATON* (Spek, 2003) before modelling the phenyl-ring disorder showed that there were small voids adjacent to these rings; after the disorder was modelled there were no significant voids in the crystal lattice.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*; data

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reduction: *DATRD*2 in *NRCVAX*94 (Gabe *et al.*, 1989); program(s) used to solve structure: *SOLVER* in *NRCVAX*94; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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