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Tri(2-thienyl)arsine oxide

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Key indicators

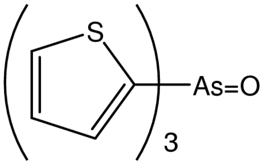
Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.089
Data-to-parameter ratio = 22.0

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

The title compound, $C_{12}H_9AsOS_3$, has a mirror plane so that one thienyl group as well as the As and O atoms lie on that plane. The As atom exists in a distorted tetrahedral geometry with a range of angles of 107.73 (8) to 112.82 (13)°, with an As═O bond distance of 1.648 (2) Å and As—C distances of 1.893 (3)–1.895 (2) Å.

Comment

The title compound, $(C_4H_3S)_3AsO$, (I), has crystallographically imposed mirror symmetry so that the arsenic and O atoms and one thienyl group lie on the plane (Fig. 1). The As atom exists in a distorted tetrahedral geometry with a range of bond angles of 107.73 (8) to 112.82 (13)°. The wider angles involve the O atom (Table 1). The pattern in geometric parameters found in (I) matches closely those found in related structures *viz.* $(C_6H_5)_3As{=}O$ (Shao *et al.*, 1982) and the triclinic and hexagonal polymorphs of $(p\text{-}ClC_6H_4)_3As{=}O$ (Belsky & Zavodnik, 1984). The dihedral angle between the thienyl ring lying on the mirror plane and the independent ring is 54.86 (9)° and that between the two symmetry-related rings is 70.28 (9)°. An analysis by *PLATON* (Spek, 2000) suggested C—H···π and C—H···O interactions. The closest C—H···π contact of 2.78 Å occurs between C6—H and the ring centroid of the thienyl ring lying on the mirror plane (symmetry operation: $1 - x, -\frac{1}{2} + y, 1 - z$), implying that this ring is involved in two such interactions; these are aligned along the *b* direction. The O atom lies in a pocket defined by three H atoms from a translationally related molecule (along *c*) so that C4—H···O1 is 2.40 Å and C8—H···O1 is 2.53 Å (twice).



(I)

Experimental

$(C_4H_3S)_3As$: To an ethereal solution of 2-thienylmagnesium bromide, C_4H_3SMgBr [prepared from Mg turnings (4.7 g, 0.19 mol) and C_4H_3SBr (31.90 g, 19.0 ml, 0.19 mol) in 300 ml ether], a solution of $AsCl_3$ (9.0 g, 0.05 mol) in Et_2O at 273 K was added over a period of 2 h (Etienne, 1949; Ramsden, 1960). The reaction mixture was stirred at room temperature for 3 h followed by refluxing for 1 h. The reactants were cooled to 273 K and treated with deoxygenated aqueous NH_4Cl solution (80–100 ml). The ether layer was separated,

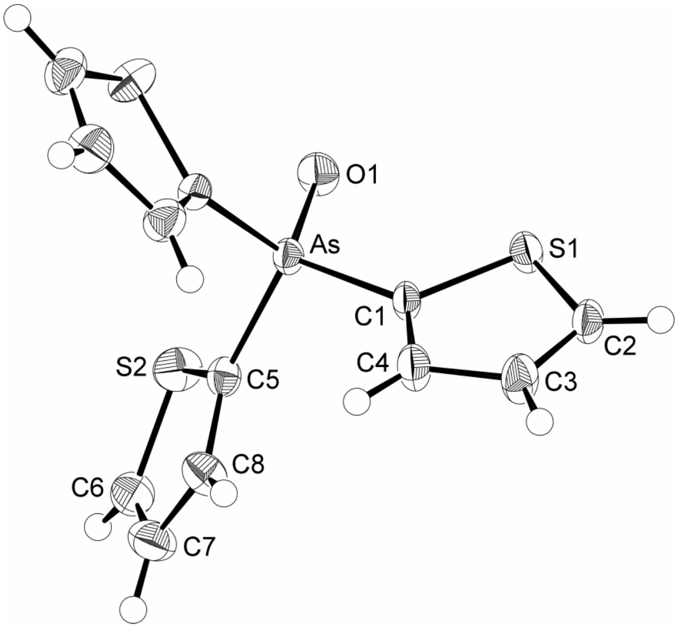


Figure 1
Molecular structure and crystallographic numbering scheme for (I); displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

dried over $CaCl_2$ and passed through a Florisil column. The solvent was evaporated *in vacuo* leaving behind a yellow liquid, which was distilled under vacuum to give a pale yellow oil in 98% yield; b.p. 423–433 K/0.4 mm Hg. Analysis for $C_{12}H_9S_3As$: Calcd: C 44.4, H 2.8%; Found C 43.8, H 2.4%. IR: 1653 (*w*), 1596 (*vw*), 1539 (*vw*), 1497 (*vw*), 1461 (*s*), 1401 (*s*), 1377 (*m*), 1330 (*m*), 1215 (*vs*), 1080 (*m*), 1050 (*w*), 969 (*vs*), 900 (*vw*), 847 (*vs*), 830 (*s*), 785 (*vw*), 743 (*s*), 703 (*vs*), 628 (*vw*), 568 (*w*), 476 (*s*), 305 (*s*), 279 (*vw*), 227 (*vw*) cm^{-1}. ^{1}H NMR in $CDCl_3$ δ: 7.24 (*dd*, 3.3, 4 Hz, H-4); 7.45 (*d*, 3.3 Hz, H-3); 7.66 (*d*, 3.8 Hz, H-5). ^{13}C{^{1}H} NMR in $CDCl_3$ δ: 127.7 [C-4]; 131.0 [C-3]; 134.3 [C-5]; 138.3 [C-2].

$(C_4H_3S)_3AsO$: To an acetone solution of $(C_4H_3S)_3As$ (520 mg, 1.60 mol), an excess of 30% H_2O_2 (2 ml) was added dropwise with continuous stirring when the pale-yellow colour of the arsine initially darkened and finally turned colourless. This was then thoroughly dried *in vacuo* to obtain $(C_4H_3S)_3AsO$ as an off-white paste which was recrystallized from CH_2Cl_2–acetone–hexane mixture to give colourless crystals of (I) (510 mg, 94%, m.p. 428 K). Analysis for $C_{12}H_9S_3AsO$: Calcd: C 42.3, H 2.6%; Found C 41.8, H 2.1%. IR: 1456 (*vs*), 1396 (*s*), 1377 (*vs*), 1331 (*s*), 1245 (*s*), 1231 (*s*), 1098 (*m*), 1083 (*m*), 1066 (*m*), 994 (*s*), 984 (*s*), 925 (*m*), 892 (*vs*), 856 (*s*), 847 (*s*), 748 (*s*), 733 (*s*), 718 (*vs*), 681 (*m*), 598 (*w*), 563 (*s*), 477 (*vs*), 398 (*vw*), 351 (*vs*), 333 (*s*), 303 (*s*), 267 (*m*), 246 (*m*), 230 (*vw*) cm^{-1}. ^{1}H NMR in $CDCl_3$ δ: 7.20 (*dd*, 3.7, 4.7 Hz, H-4); 7.60 (*dd*, 3.6, 0.9 Hz, H-3); 7.73 (*dd*, 4.8, 0.9 Hz, H-5). ^{13}C{^{1}H} NMR in $CDCl_3$ δ: 128.3 [C-4]; 132.4 [C-2]; 133.8 [C-5]; 135.8 [C-3].

Crystal data

$C_{12}H_9AsOS_3$
$M_r = 340.29$
Orthorhombic, *Pnma*
$a = 15.2840$ (4) Å
$b = 13.9364$ (4) Å
$c = 6.0585$ (2) Å
$V = 1290.48$ (7) Å^3
$Z = 4$
$D_x = 1.751$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 10 145 reflections
$\theta = 2.7$–30.0°
$\mu = 3.10$ mm^{-1}
$T = 223$ (2) K
Block, colourless
0.23 × 0.19 × 0.16 mm

Data collection

Bruker AXS SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Bruker, 2000*b*)
$T_{\min} = 0.481$, $T_{\max} = 0.609$
10145 measured reflections

1958 independent reflections
1893 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 30.0^\circ$
$h = -21 \rightarrow 21$
$k = -17 \rightarrow 19$
$l = -6 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 1.09$
1958 reflections
89 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 1.0951P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.67$ e Å^{-3}
$\Delta\rho_{\min} = -0.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

As—O1	1.648 (2)	S2—C6	1.695 (3)
As—C1	1.893 (3)	S2—C5	1.714 (2)
As—C5	1.895 (2)		
S1—C2	1.710 (3)		
S1—C1	1.716 (3)		
O1—As—C1	112.82 (13)	C4—C1—As	130.4 (2)
O1—As—C5	109.73 (8)	S1—C1—As	117.71 (17)
C1—As—C5	107.73 (8)	C8—C5—As	130.75 (17)
C5—As—C5$^{\rm i}$	109.00 (13)	S2—C5—As	117.92 (12)
C2—S1—C1	91.89 (16)		
C6—S2—C5	92.00 (12)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding-model approximation with an overall isotropic displacement parameter.

Data collection: *SMART* (Bruker, 2000*a*); cell refinement: *SAINT* (Bruker, 2000*a*); data reduction: *SHELXTL* (Bruker, 2000*a*); program(s) used to solve structure: *DIRDIF*92 *PATTY* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXTL*.

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