metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.007 Å
R factor = 0.038
wR factor = 0.088
Data-to-parameter ratio = 12.1

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

(2-Acryloylaminophenyl)arsonic acid

The geometrical paramaters for the title compound, $C_9H_{10}AsNO_4$ or [As(C_9H_8NO)O(OH)$_2$], are normal. The dihedral angle between the benzene ring and the acrylamide group is 12.2 (2)°. A network of hydrogen bonds leads to a chain structure.

Comment

N-Substituted methacryloyl derivates of arsanilic acid are widely used as monomers for the synthesis of linear polymers (Percino *et al.*, 2000) with many subsequent applications in analytical chemistry (Hirsch *et al.*, 1970; Cheng *et al.*, 1982). Recently, the synthesis of low molecular weight polymers using *o*- and *p*-methacryloylaminophenylarsonic acid has been reported (Zayas *et al.*, 2000). We now report the crystal structure of the title compound, (I).

(I)
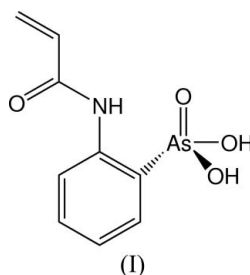
The geometrical parameters for (I) are normal and consistent with the equivalent data for similar compounds (Bel'skii,
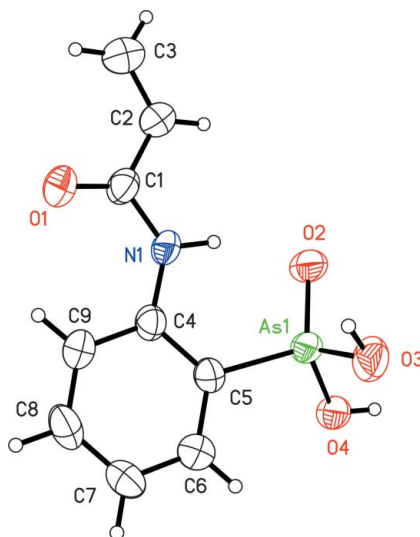

Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level for non-H atoms.
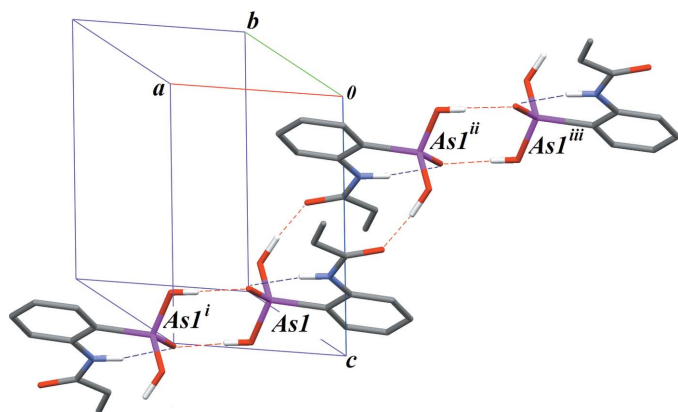
Figure 2
Part of the crystal structure of (I), showing the hydrogen-bonding scheme (dashed lines). Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $-x, -y, 1 - z$; (iii) $-1 + x, -1 + y, -1 + z$.

1982; Chatterjee, 1977). The As atom in (I) is tetrahedrally coordinated by three O atoms and one C atom of the substituted benzene ring, with the As—OH bonds being longer than the As=O bond (Table 1). The acyloyl substituent is stabilized in an s-*cis* conformation. The vinyl group is not sterically hindered, and the dihedral angle between the C4-benzene ring and the (C1/C2/C3/N1/O1) acrylamide group is 12.2 (2)°. (I) is thus a good candidate for the synthesis of polymers with high molecular weights, as this conformation allows the formation of an intramolecular hydrogen bond between the NH group of the amide functionality and the oxo O atom (Table 2).

The crystal structure of (I) is built up from classical centrosymmetric double hydrogen bonds involving the oxo and hydroxo functionalities (O2 and O4, respectively) of the arsonic acid group. These dimers are in turn connected through a hydrogen bond involving the hydroxo group O3 as donor and the carbonyl O atom of the amide functionality, O1, as acceptor. The resulting network in the crystal structure is a one-dimensional chain running along [111] (Fig. 2).

Experimental

o-Arsanilic acid (1 g, 4.61 mmol) was dissolved in 10 ml of ethanol in a 100 ml flask with mechanical stirring. The reaction flask was then cooled to 278 K in an ice bath, followed by the dropwise addition of freshly distilled acryloyl chloride (0.416 g, 4.60 mmol). The temperature of the exothermic reaction was maintained at 278 K for 8 h with stirring. The resulting mixture (colourless liquid) was precipitated with water, giving a white solid (98% yield). Finally the compound was recrystallized from ethanol/water (4:1) at 278 K. Single crystals of (I) formed almost immediately after cooling the concentrated solution at 278 K, resulting in rather small crystals for the diffraction experiment. Analysis found: C 39.89, H 3.73, N 4.22%; calculated for $C_9H_{10}AsNO_4$: C 39.87, H 3.71, N 5.16%. ^{1}H NMR (400 MHz, d_6-dimethylsulfoxide): δ 5.80 (t, J = 9.8 Hz, 1H, CH), 6.25 (m, J = 7.32, 9.8 Hz, 1H, CH_2), 6.31 (m, J = 8.32, 8.8 Hz, 1H, CH_2), 7.27 (t, J = 7.32, 7.36 Hz, 1H, Ph), 7.62 (t, J = 7.32, 8.8 Hz, 1H, Ph), 7.70 (d, J = 7.34, 6.36 Hz, 1H, Ph), 8.57 (t, J = 8.8 Hz, 1H, Ph), 11.96 (s, 1H, NH).

Crystal data

[As(C9H8NO)O(OH)2]	$Z = 2$
$M_r = 271.10$	$D_x = 1.724$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.2088$ (4) Å	Cell parameters from 1641
$b = 8.3132$ (4) Å	reflections
$c = 8.5259$ (5) Å	$\theta = 2.5$–24.0°
$\alpha = 99.432$ (1)°	$\mu = 3.25$ mm^{-1}
$\beta = 97.766$ (1)°	$T = 293$ (2) K
$\gamma = 111.390$ (1)°	Prism, colorless
$V = 522.25$ (5) Å^3	$0.14 \times 0.11 \times 0.07$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1641 independent reflections
	1322 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan	$\theta_{max} = 24.0°$
(*SADABS*; Sheldrick, 1996)	$h = -7 \rightarrow 9$
$T_{min} = 0.579$, $T_{max} = 0.800$	$k = -9 \rightarrow 9$
2862 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.94$	$(\Delta/\sigma)_{max} < 0.001$
1641 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Selected bond lengths (Å).

As1—O2	1.643 (3)	As1—O3	1.720 (3)
As1—O4	1.687 (3)	As1—C5	1.892 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2	0.93	1.93	2.814 (4)	160
O3—H3$\cdots$O1^i	1.03	1.65	2.669 (5)	172
O4—H4$\cdots$O2^{ii}	0.84	1.77	2.561 (4)	157

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z + 2$.

Data collection was limited to $\theta_{max} = 24°$ due to the small size of available single crystals. H atoms bonded to N and O atoms were located in difference maps and refined as riding in their as-found relative positions with U_{iso}(H) = 1.5U_{eq}(carrier). Other H atoms were placed in idealized positions (C—H = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL-Plus* (Bruker, 1999); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

References

Bel'skii, V. K. (1982). *Sov. Phys. Crystallogr.* **27**, 31–32.

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Bruker (1999). *SMART* (Version 5 .057), *SAINT* (Version 6.01), and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Chatterjee, (1977). *Acta Cryst.* B**33**, 164–167.

Cheng, K. L. & Ueto, I. T. (1982). *Handbook of Organic Analytical Reagents*, p. 159. Boca Raton, Florida: CRC Press Inc.

Hirsch, R. F., Gancher, E. & Russo, F. R. (1970). *Talanta*, **17**, 483-489.

Percino, M. J., Chapela, V. M., Gutiérrez, P. R. & Herrera, A. M. (2000). *Des. Monomers Polym.* **3**, 155–160.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Zayas, T., Percino, M. J., Cardoso, J. & Chapela, V. M. (2000). *Polymer*, **41**, 5505–5512.