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(4-Bromophenyl)arsonic acid

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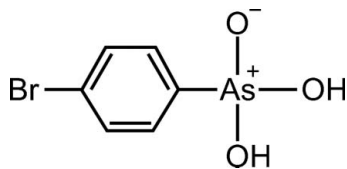
Received 3 September 2007; accepted 3 September 2007

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å;
R factor = 0.022; wR factor = 0.049; data-to-parameter ratio = 17.7.

In the title compound, $\text{C}_6\text{H}_5\text{AsBrO}_3$, the As—O bond lengths are normal. Intermolecular O—H \cdots O hydrogen bonds with O \cdots O distances of 2.600 (2) and 2.627 (2) Å link the molecules into two-dimensional layers parallel to bc plane.

Related literature

An example containing an electron-withdrawing substituent in the *para* position to the arsonic acid group is *para*-nitrophenylarsonic acid (van der Lee *et al.*, 2005). For details of synthesis and hydrogen-bonding motifs, see: Bart (1922) and Jeffrey & Saenger (1991), respectively.



Experimental

Crystal data

$\text{C}_6\text{H}_5\text{AsBrO}_3$
 $M_r = 280.94$
Monoclinic, $P2_1/c$
 $a = 9.6435$ (3) Å
 $b = 9.1107$ (3) Å
 $c = 10.2872$ (3) Å
 $\beta = 117.429$ (2)°

$V = 802.22$ (4) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 9.17$ mm⁻¹
 $T = 200$ (2) K
0.10 × 0.09 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(Otwinowski & Minor, 1997)
 $T_{\min} = 0.388$, $T_{\max} = 0.759$
12919 measured reflections
1838 independent reflections
1603 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.049$
 $S = 1.06$
1838 reflections
104 parameters
Only H-atom displacement parameters refined
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H82}\cdots\text{O1}^{\text{i}}$	0.84	1.77	2.600 (2)	171
$\text{O3}-\text{H83}\cdots\text{O1}^{\text{ii}}$	0.84	1.80	2.627 (2)	167

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

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Peter Mayer for professional support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2298).

References

- Bart, H. (1922). *Liebigs Ann. Chem.* **429**, 55–103.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, p. 34. Berlin, Heidelberg: Springer-Verlag.
Lee, A. van der, Richez, P. & Tapiero, C. (2005). *J. Mol. Struct.* **743**, 223–228.
Nonius (2004). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

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(4-Bromophenyl)arsonic acid

R. Betz, P. Klüfers and A. Walter

Comment

The title compound, C₆H₆AsBrO₃, was prepared as a starting material for attempted condensation reactions with diols.

The intramolecular atomic distances in the title compound, (I) (Fig. 1), are in the expected range (*cf.* van der Lee *et al.*, 2005, for *para*-nitrophenylarsonic acid). In particular, the bond length of the arsenic atom to the formally double-bonded oxygen atom is about 0.05 Å shorter than the bond lengths to the hydroxyl-O atoms.

The hydrophobic bromophenyl moieties and the hydrophilic arsonic-acid functions are separated in the crystal structure. Hydrophobic and hydrophilic sheets alternate along [100] (Fig. 2). A characteristic hydrogen-bond system is established in the hydrophilic sheets (Fig. 3). There are two kinds of hydrogen bonds. A pair of bonds of the first kind combine pairs of arsonic-acid molecules to dimers (the yellow bonds in Fig. 3) – a bonding motif well known from carbonic acids (Jeffrey & Saenger, 1991). One hydroxy-donor site and one of two acceptor sites of the terminally bonded oxygen atom are spent for these bonds. A second acceptor site at the same oxygen atom and the second hydroxy function connect the dimers to a two-dimensional network in the (100) plane (the green bonds in Fig. 3). Infinite cooperativity may be attributed to the latter hydrogen bonds since chains of alternating O–H and O–As vectors are running along the [010] direction. Accordingly, the As–OH bonds in the infinite chains are slightly longer than those in the dimers.

Experimental

The title compound was prepared according to standard procedures upon alkaline coupling of sodium arsenite with *para*-diazo bromobenzene in alkaline media and subsequent acidic workup (Bart, 1922). Crystals suitable for X-ray analysis were obtained upon recrystallization of the crude reaction product from boiling water.

Refinement

All H atoms were located in a difference map and refined as riding on their parent atoms, with one common isotropic displacement parameter refined to $U_{\text{iso}}(\text{H}) = 0.037(3) \text{ \AA}^2$.

Figures

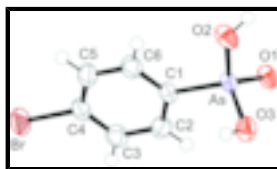


Fig. 1. The molecular structure of (I), with atom labels and displacement ellipsoids drawn at the 70% probability level.

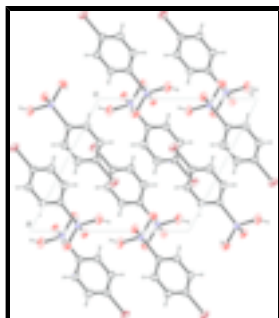


Fig. 2. The separation of hydrophilic (arsonic-acid functions) and hydrophobic (bromophenyl residues) blocks (view along [0 1 0], 50% ellipsoid probability).

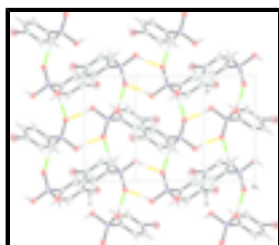


Fig. 3. The molecular packing in a hydrophilic sheet in the (100) plane of (I) (50% ellipsoid probability). Colour codes: pink As, brown Br, red O. The colours attributed to the hydrogen bonds are explained in the text.

(4-Bromophenyl)arsonic acid

Crystal data

$C_6H_6AsBrO_3$

$M_r = 280.94$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.6435$ (3) Å

$b = 9.1107$ (3) Å

$c = 10.2872$ (3) Å

$\beta = 117.429$ (2)°

$V = 802.22$ (4) Å³

$Z = 4$

$F_{000} = 536$

$D_x = 2.326$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 8505 reflections

$\theta = 3.1$ – 27.5 °

$\mu = 9.17$ mm⁻¹

$T = 200$ (2) K

Platelet, colourless

$0.10 \times 0.09 \times 0.03$ mm

Data collection

KappaCCD
diffractometer

1838 independent reflections

Radiation source: rotating anode

1603 reflections with $I > 2\sigma(I)$

Monochromator: MONTEL, graded multilayered X-ray optics

$R_{int} = 0.028$

$T = 200$ (2) K

$\theta_{max} = 27.5$ °

CCD; rotation images; thick slices scans

$\theta_{min} = 3.2$ °

Absorption correction: multi-scan
(Otwinowski & Minor, 1997)

$h = -12 \rightarrow 11$

$T_{min} = 0.388$, $T_{max} = 0.759$

$k = -11 \rightarrow 11$

12919 measured reflections

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	Only H-atom displacement parameters refined
$wR(F^2) = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1838 reflections	$(\Delta/\sigma)_{\max} = 0.001$
104 parameters	$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.63333 (3)	0.41380 (3)	0.87179 (3)	0.03591 (10)
As	0.04233 (3)	0.41520 (2)	0.21560 (2)	0.01942 (9)
O1	-0.01715 (19)	0.58148 (16)	0.14968 (16)	0.0246 (3)
O2	0.0899 (2)	0.30778 (17)	0.10672 (17)	0.0297 (4)
H82	0.0680	0.3521	0.0280	0.037 (3)*
O3	-0.11214 (19)	0.33032 (18)	0.22333 (18)	0.0281 (4)
H83	-0.0841	0.2474	0.2624	0.037 (3)*
C1	0.2162 (3)	0.4138 (2)	0.4049 (2)	0.0205 (4)
C2	0.2096 (3)	0.5001 (3)	0.5130 (2)	0.0256 (5)
H2	0.1207	0.5595	0.4914	0.037 (3)*
C3	0.3341 (3)	0.4986 (3)	0.6529 (2)	0.0268 (5)
H3	0.3311	0.5556	0.7289	0.037 (3)*
C4	0.4626 (3)	0.4130 (2)	0.6799 (2)	0.0242 (5)
C5	0.4712 (3)	0.3275 (3)	0.5733 (3)	0.0292 (5)
H5	0.5614	0.2699	0.5950	0.037 (3)*
C6	0.3459 (3)	0.3272 (3)	0.4339 (3)	0.0274 (5)
H6	0.3486	0.2684	0.3588	0.037 (3)*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.02573 (15)	0.04840 (18)	0.02244 (14)	-0.00390 (11)	0.00156 (11)	0.00221 (10)
As	0.02334 (14)	0.01677 (13)	0.01538 (13)	0.00266 (9)	0.00654 (10)	0.00137 (8)
O1	0.0337 (9)	0.0173 (8)	0.0195 (7)	0.0058 (7)	0.0094 (7)	0.0027 (6)
O2	0.0464 (11)	0.0216 (8)	0.0222 (8)	0.0109 (7)	0.0166 (8)	0.0035 (6)
O3	0.0256 (8)	0.0257 (9)	0.0292 (9)	0.0009 (7)	0.0093 (7)	0.0045 (7)
C1	0.0216 (11)	0.0201 (11)	0.0168 (10)	-0.0001 (9)	0.0063 (9)	0.0025 (8)
C2	0.0234 (12)	0.0277 (13)	0.0249 (11)	0.0017 (10)	0.0104 (10)	-0.0006 (9)
C3	0.0278 (12)	0.0289 (12)	0.0219 (11)	-0.0037 (10)	0.0101 (10)	-0.0044 (9)
C4	0.0228 (12)	0.0265 (12)	0.0184 (10)	-0.0043 (9)	0.0052 (9)	0.0040 (9)
C5	0.0259 (12)	0.0317 (13)	0.0256 (12)	0.0078 (10)	0.0082 (10)	0.0045 (10)
C6	0.0302 (12)	0.0273 (12)	0.0234 (11)	0.0062 (10)	0.0111 (10)	0.0008 (9)

Geometric parameters (\AA , $^\circ$)

Br—C4	1.901 (2)	C2—C3	1.386 (3)
As—O1	1.6509 (14)	C2—H2	0.9500
As—O2	1.7016 (15)	C3—C4	1.380 (3)
As—O3	1.7125 (16)	C3—H3	0.9500
As—C1	1.896 (2)	C4—C5	1.378 (3)
O2—H82	0.8400	C5—C6	1.386 (3)
O3—H83	0.8400	C5—H5	0.9500
C1—C2	1.387 (3)	C6—H6	0.9500
C1—C6	1.390 (3)		
O1—As—O2	113.91 (8)	C1—C2—H2	120.4
O1—As—O3	106.76 (8)	C4—C3—C2	118.8 (2)
O2—As—O3	105.95 (8)	C4—C3—H3	120.6
O1—As—C1	113.80 (8)	C2—C3—H3	120.6
O2—As—C1	107.06 (9)	C5—C4—C3	122.5 (2)
O3—As—C1	109.01 (8)	C5—C4—Br	119.18 (18)
As—O2—H82	109.5	C3—C4—Br	118.33 (17)
As—O3—H83	109.5	C4—C5—C6	118.7 (2)
C2—C1—C6	121.3 (2)	C4—C5—H5	120.6
C2—C1—As	118.31 (16)	C6—C5—H5	120.6
C6—C1—As	120.43 (16)	C5—C6—C1	119.4 (2)
C3—C2—C1	119.3 (2)	C5—C6—H6	120.3
C3—C2—H2	120.4	C1—C6—H6	120.3
O1—As—C1—C2	50.0 (2)	C1—C2—C3—C4	1.1 (3)
O2—As—C1—C2	176.79 (17)	C2—C3—C4—C5	-0.7 (4)
O3—As—C1—C2	-69.02 (19)	C2—C3—C4—Br	179.35 (17)
O1—As—C1—C6	-130.51 (18)	C3—C4—C5—C6	-0.2 (4)
O2—As—C1—C6	-3.7 (2)	Br—C4—C5—C6	179.75 (18)
O3—As—C1—C6	110.45 (19)	C4—C5—C6—C1	0.7 (4)
C6—C1—C2—C3	-0.7 (3)	C2—C1—C6—C5	-0.2 (4)
As—C1—C2—C3	178.80 (17)	As—C1—C6—C5	-179.69 (18)

Hydrogen-bond 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>
O2—H82···O1 ⁱ	0.84	1.77	2.600 (2)	171
O3—H83···O1 ⁱⁱ	0.84	1.80	2.627 (2)	167

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

Fig. 1

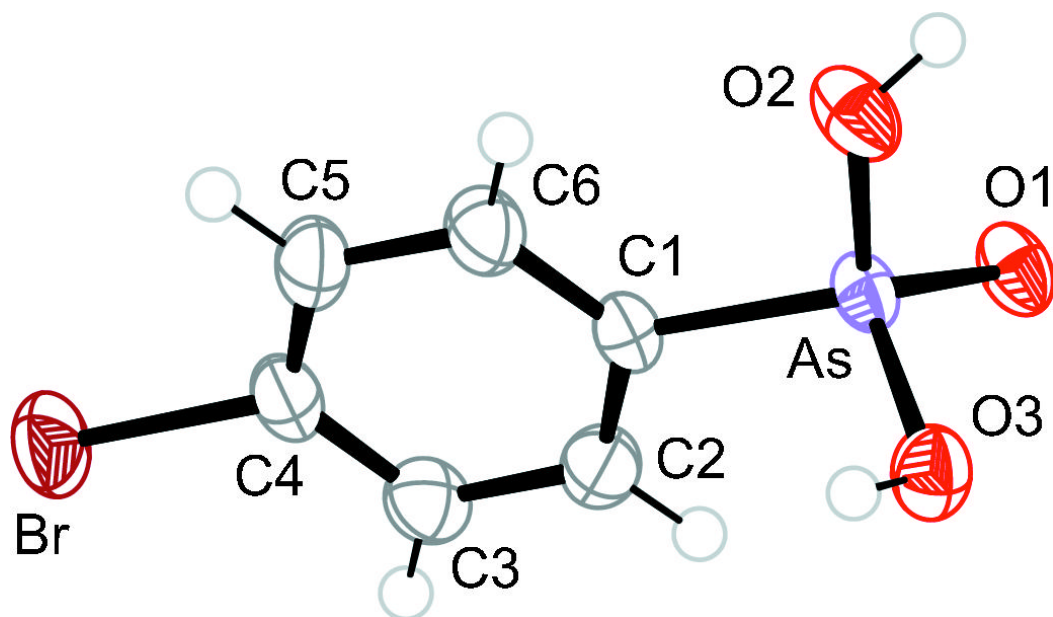


Fig. 2

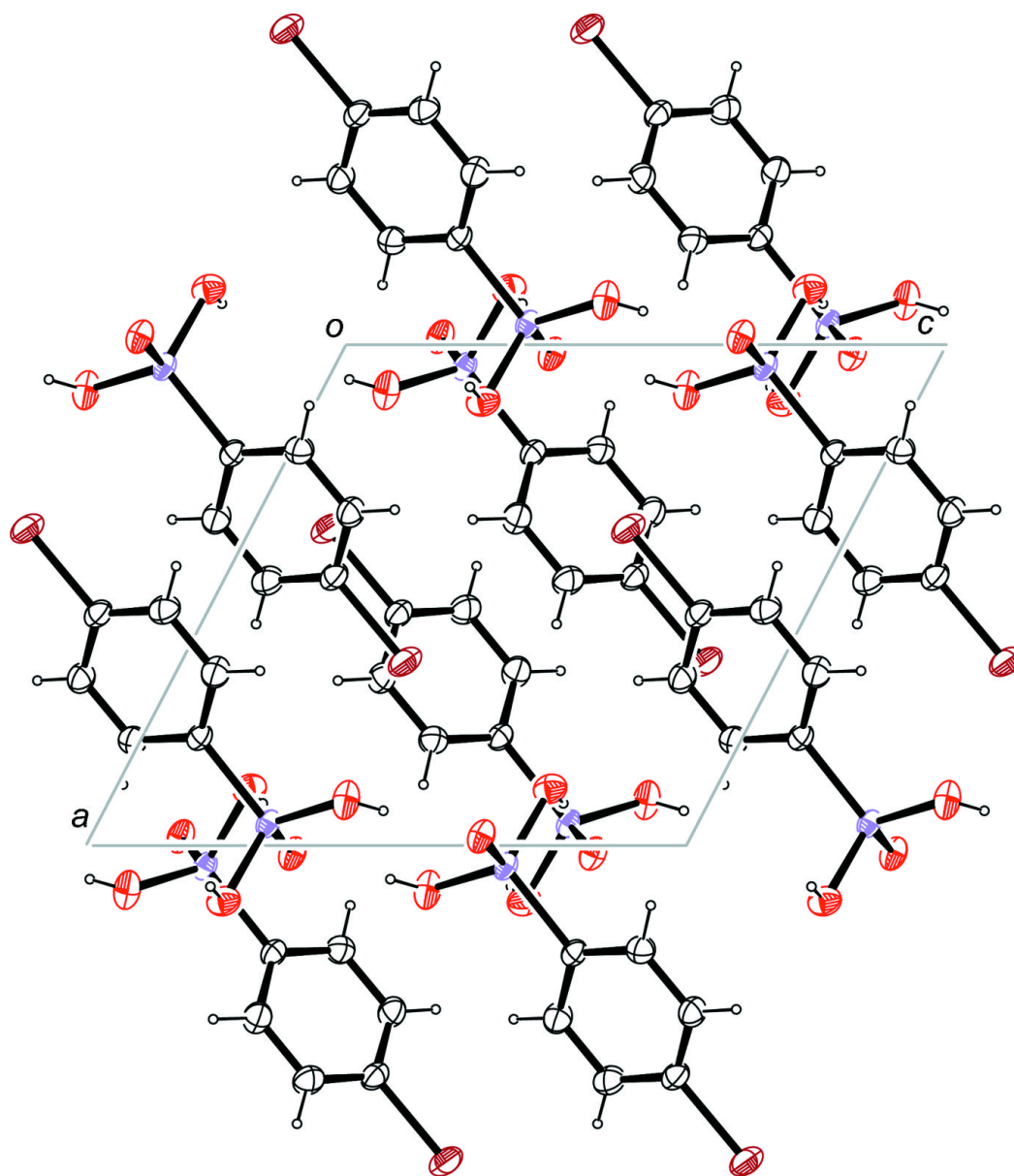


Fig. 3

