IUCrData

ISSN 2414-3146

Redetermination of the crystal structure of arsenic tribromide, $AsBr_3$

Erik Uran,[a,b]‡ Kristian Radan[a]‡ and Matic Lozinšek[a,b]*

[a]Extreme Conditions Chemistry Laboratory (ECCL K2), Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia, and [b]Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia. *Correspondence e-mail: matic.lozinsek@ijs.si

Received 23 February 2026
Accepted 4 March 2026

Edited by M. Weil, Vienna University of Technology, Austria

‡ These authors contributed equally.

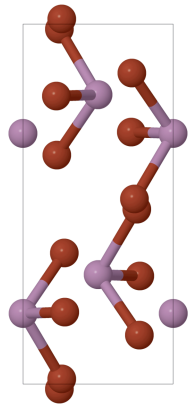
Keywords: arsenic tribromide; pnictogen bonding; crystal structure; single-crystal X-ray diffraction.

CCDC reference: 2535582

Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of $AsBr_3$ was redetermined from low-temperature single-crystal X-ray diffraction data. Arsenic tribromide crystallizes in the orthorhombic Sohncke space group $P2_12_12_1$ with $Z = 4$; the trigonal–pyramidal molecule exhibits three symmetry-independent As—Br bond lengths [2.3386 (3)–2.3481 (3) Å]. An overview of the previous structure refinements of $AsBr_3$ is provided, along with a comparison of the crystallographic parameters determined with higher precision in the current study.

3D view



Structure description

Pnictogen (Pn) elements (N, P, As, Sb, and Bi) form a wide range of halides, among which pnictogen(III) halides, PnX_3, typically adopt a trigonal–pyramidal shape and crystallize predominantly as discrete molecular units (Galy & Enjalbert, 1982). In general, molecules of the PnX_3 type are of interest owing to the presence of intermolecular Pn···X contacts in their crystal structures, which arise from σ-holes located on the Pn atom (Varadwaj *et al.*, 2022). These features render them valuable model systems for studies of noncovalent interactions, particularly pnictogen bonding (Mahmudov *et al.*, 2020; Varadwaj *et al.*, 2022; Brammer *et al.*, 2023; Resnati *et al.*, 2024), as well as for high-pressure investigations, owing to their ability to expand their coordination sphere under high pressure (Schwarz *et al.*, 2019; Cai *et al.*, 2023; Gain *et al.*, 2024; Li *et al.*, 2025).

Among pnictogen(III) bromides, only the crystal structure of NBr_3 (Klapötke, 1997) has not been determined, whereas PBr_3 (Enjalbert & Galy, 1979*a*), $AsBr_3$ (Braekken, 1935; Singh & Swaminathan, 1964; Trotter, 1965; Singh & Swaminathan, 1967), $SbBr_3$ (Cushen & Hulme, 1962, 1964), and $BiBr_3$ (von Benda, 1980) have all been crystallographically characterized. Notably, $BiBr_3$ is the only member reported to crystallize in both a molecular form, composed of discrete trigonal–pyramidal $BiBr_3$ molecules, and a bromide-bridged polymeric form (von Benda, 1980). $AsBr_3$ crystallizes in the $P2_12_12_1$

Table 1
Comparison of the crystallographic parameters for $AsBr_3$ from previous structure determinations deposited in the Inorganic Crystal Structure Database (ICSD; Zagorac *et al.*, 2019) and the Cambridge Structural Database (CSD; Groom *et al.*, 2016) and from the present work.

ICSD number/ CSD deposition number	24589/1600611	24579/1600602	26774/1602157	24915/1600922	–/2535582
Reference	Braekken (1935)	Singh & Swaminathan (1964)	Trotter (1965)	Singh & Swaminathan (1967)	This work
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.15	12.148	4.33 (1)	10.244	4.20575 (8)
b (Å)	12.07	10.244	10.24 (0.5)	12.148	10.08102 (18)
c (Å)	4.31	4.34	12.20 (0.5)	4.34	12.0632 (2)
V (Å^3)	528.02	540.09	540.94	540.09	511.46 (2)
T (K)	*ns*	263	*ns*	*ns*	100
R	*ns*	0.23	0.188	0.143	0.0161
As—Br (Å)	2.26‡	2.325‡	2.354 (15)	2.349‡	2.3386 (3)
	2.32	2.335	2.354 (15)	2.352	2.3416 (3)
	2.41	2.354	2.384 (15)	2.383	2.3481 (3)
Br—As—Br (°)	97.0‡	99.47‡	97.3 (5)	96.43‡	97.980 (11)
	98.7	100.34	97.5 (5)	96.77	98.124 (10)
	101.2	100.78	98.2 (5)	99.05	99.460 (10)

ns not specified; ‡values calculated from atom coordinates reported in the ICSD.

space group and is isostructural with $AsCl_3$ (Galy *et al.*, 2002) and the α-polymorph of $SbBr_3$ (Cushen & Hulme, 1964). Its crystal structure differs from that of AsF_3, which crystallizes in the $Pn2_1a$ space group (Enjalbert & Galy, 1979*b*), and from AsI_3, which adopts two polymorphs: the $R\overline{3}$ room-temperature form (Enjalbert & Galy, 1980) and the $P3_212$ high-temperature form (Galy & Enjalbert, 1982).

The $AsBr_3$ crystal investigated at 100 K in the present work exhibits unit-cell parameters similar to those reported previously (Braekken, 1935; Singh & Swaminathan, 1964; Trotter, 1965; Singh & Swaminathan, 1967), but with significantly improved crystallographic parameters (Table 1). It crystallizes in the Sohncke space group $P2_12_12_1$ and the unit cell contains four symmetrically equivalent $AsBr_3$ molecules adopting a slightly distorted C_{3v} geometry (true symmetry C_1; Fig. 1).

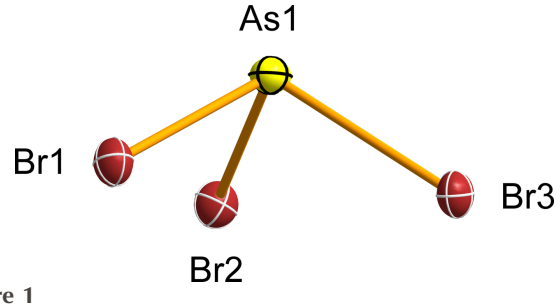


Figure 1
The molecular structure of $AsBr_3$ with displacement ellipsoids shown at the 50% probability level.

The redetermined As—Br bond lengths and Br—As—Br angles are in good agreement with previously reported values (Table 1): As1—Br1 [2.3386 (3) Å], As1—Br2 [2.3416 (3) Å], and As1—Br3 [2.3481 (3) Å]; Br1—As1—Br2 [97.980 (11)°], Br1—As1—Br3 [98.124 (10)°], and Br2—As1—Br3 [99.460 (10)°]. The arsenic atom lies 1.1345 (3) Å above the trigonal plane defined by the three bromine atoms. Similar geometry was observed for cocrystallized $AsBr_3$ molecules with crystallographically imposed C_{3v} symmetry, with shorter As—Br bond lengths reported for the $Br_3As{\cdot}C_6Et_6{\cdot}AsBr_3$ cocrystal [2.322 (1) Å; 98.9 (1)°; 295 K] (Schmidbaur *et al.*, 1987) and longer for the $(p\text{-}FC_6H_4)_3P{=}Se{\cdot}AsBr_3$ cocrystal [2.379 (3) Å; 96.54 (9)°; 100 K] (Alhanash *et al.*, 2012).

The packing in the crystal structure of $AsBr_3$ (Fig. 2) can be described as columns of $AsBr_3$ molecules stacked along the *a* axis, interconnected to neighbouring columns *via* long As···Br

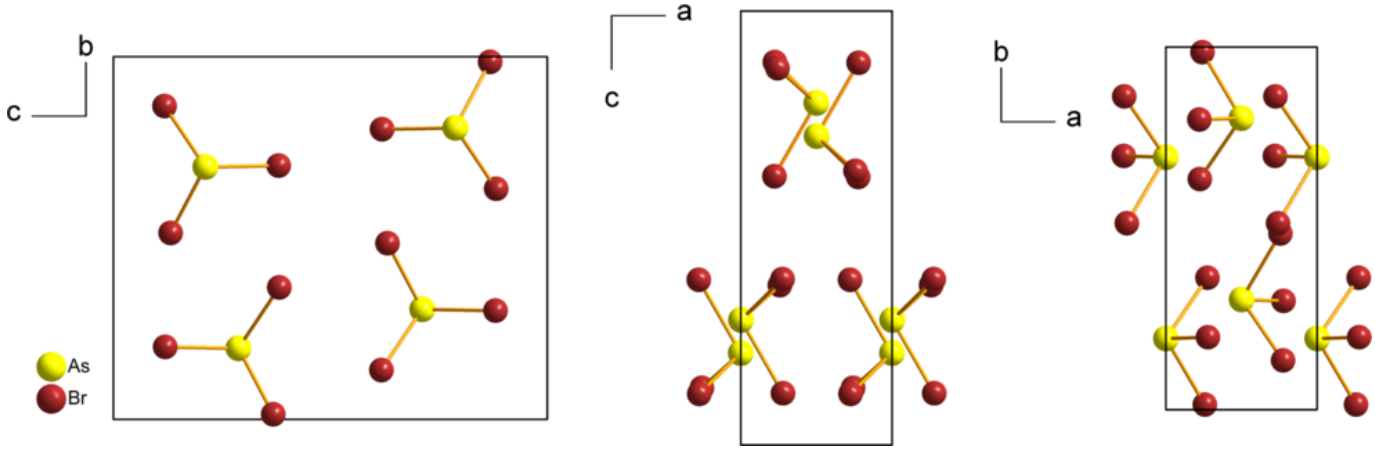


Figure 2
Unit cell and molecular packing of $AsBr_3$ viewed along the *a*, *b*, and *c* axes.

Table 2
Intermolecular As···Br and Br···Br contacts (Å, °) in the crystal structure of $AsBr_3$.

Contact	As···Br	Br—As···Br
(Br2)As1···Br3^{i}	3.6585 (3)	132.217 (9)
(Br3)As1···Br2^{i}	3.6696 (3)	132.418 (10)
(Br3)As1···Br1^{i}	3.7507 (4)	130.199 (10)
(Br1)As1···Br1^{ii}	3.8752 (3)	168.505 (9)
(Br2)As1···Br2^{iii}	4.0974 (3)	166.766 (9)
(Br3)As1···Br2^{iv}	4.1323 (4)	162.03 (1)
Contact	**Br···Br**	**As—Br···Br**
(As1)Br3···Br3^{v}	3.7044 (2)	163.822 (11)
(As1)Br1···Br3^{vi}	3.7213 (3)	140.565 (12)
(As1)Br1···Br3^{vii}	3.7236 (3)	157.885 (11)
(As1)Br2···Br1^{viii}	3.8321 (4)	150.861 (10)

Symmetry codes: (i) $-1+x, y, z$; (ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (vi) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (vii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

and Br···Br contacts (Fig. 3, Table 2). The three shortest contacts, As1···Br3^{i} [3.6585 (3) Å], As1···Br2^{i} [3.6696 (3) Å], and As1···Br1^{i} [3.7507 (4) Å], involve neighbouring $AsBr_3$ molecules stacked above one another in a columnar arrangement along the *a* axis. The corresponding Br—As···Br angles deviate substantially from linearity [130.199 (10)–132.418 (10)°]. Three additional As···Br contacts to $AsBr_3$ molecules in the adjacent columns are significantly longer than the sum of the van der Waals (vdW) radii [3.74 Å; Alvarez, 2013], and are nearly linear [3.8752 (3), 4.0974 (3), 4.1323 (4) Å; 168.505 (9), 166.766 (9), 162.03 (1)°] (Table 2). These interactions have been classified as pnictogen bonds (Varadwaj *et al.*, 2022). Br···Br contacts are likewise close to or longer than the sum of the vdW radii [3.72 Å], with only one contact being shorter [3.7044 (2) Å; Table 2]. Intermolecular Br···Br distances of 3.7 Å have also been reported for $AsBr_3$ in the liquid state (Hoge & Trotter, 1965).

Synthesis and crystallization

Reactions were performed in fluorinated ethylene propylene (FEP) vessels as previously described (Uran & Lozinšek, 2025). $AsBr_3$ formed as a side product during an attempt to synthesize $CF_3NH_3[AsF_6]$ from the reaction of BrCN with AsF_5 and anhydrous HF (aHF), using a procedure similar to that reported previously (Baxter *et al.*, 2015). A 16 mg portion of the reaction product was recrystallized from aHF (0.37 ml) by cooling the solution to 213 K at an average rate of 5 K h^{-1}. After crystallization, the volatiles were pumped off at 208 K, yielding crystals of $AsBr_3$. A suitable crystal was selected using a low-temperature crystal mounting apparatus, as described previously (Lozinšek *et al.*, 2021; Motaln *et al.*, 2024), and mounted on the tip of a MiTeGen loop using Fomblin oil (Z25, SynQuest) (Motaln *et al.*, 2025).

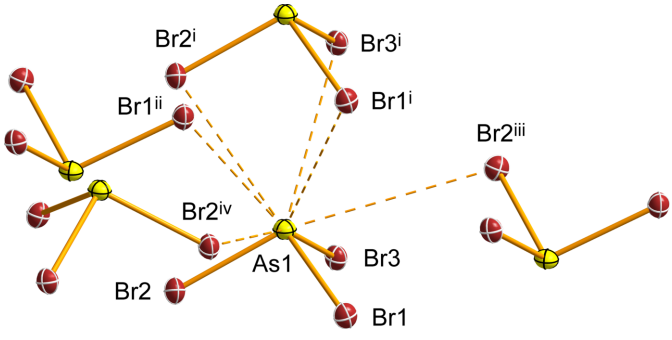


Figure 3
Intermolecular As···Br contacts in $AsBr_3$. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $-1+x, y, z$; (ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.]

Table 3
Experimental details.

Crystal data	
Chemical formula	$AsBr_3$
M_r	314.65
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, *b*, *c* (Å)	4.20575 (8), 10.08102 (18), 12.0632 (2)
V (Å^3)	511.46 (2)
Z	4
Radiation type	Ag *Kα*, λ = 0.56087 Å
μ (mm^{-1})	15.94
Crystal size (mm)	0.15 × 0.06 × 0.03
Data collection	
Diffractometer	Rigaku OD, XtaLAB Synergy-S, Dualflex, Eiger2 R CdTe 1M
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2025)
T_{min}, T_{max}	0.288, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30863, 2805, 2556
R_{int}	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.890
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.016, 0.028, 1.03
No. of reflections	2805
No. of parameters	39
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.45
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.14 (6)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2025), *OLEX2.solve* (Bourhis *et al.*, 2015), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *DIAMOND* (Brandenburg, 2022) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3.

Data availability

Data for this article are available from the Zenodo repository at https://doi.org/10.5281/zenodo.18704110.

Funding information

Funding for this research was provided by: European Research Council (ERC) Starting Grant under the European Union's Horizon 2020 Research and Innovation Programme

(grant No. 950625); Slovenian Research and Innovation Agency (grant No. J1-60022); Jožef Stefan Institute Director's Fund.

References

Alhanash, F. B., Barnes, N. A., Brisdon, A. K., Godfrey, S. M. & Pritchard, R. G. (2012). *Dalton Trans.* **41**, 10211–10218.

Alvarez, S. (2013). *Dalton Trans.* **42**, 8617–8636.

Baxter, A. F., Christe, K. O. & Haiges, R. (2015). *Angew. Chem. Int. Ed.* **54**, 14535–14538.

Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A**71**, 59–75.

Braekken, H. (1935). *Forh. K. Nor. Vidensk. Selsk.* **8**, 33.

Brammer, L., Peuronen, A. & Roseveare, T. M. (2023). *Acta Cryst.* C**79**, 204–216.

Brandenburg, K. (2022). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Cai, J., Liu, S., Lu, W., Ji, Y., Hao, K., Zhao, X., Ning, P., Liu, G., Wang, H. & Zhou, M. (2023). *Phys. Rev. B* **5**, 033164.

Cushen, D. W. & Hulme, R. (1962). *J. Chem. Soc.* pp. 2218–2222.

Cushen, D. W. & Hulme, R. (1964). *J. Chem. Soc.* pp. 4162–4166.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Enjalbert, R. & Galy, J. (1979*a*). *Acta Cryst.* B**35**, 546–550.

Enjalbert, R. & Galy, J. (1979*b*). *C. R. Acad. Sci.* C**289**, 441–443.

Enjalbert, R. & Galy, J. (1980). *Acta Cryst.* B**36**, 914–916.

Gain, P., Mondal, S. & Datta, A. (2024). *ChemPhysChem* **25**, e202400046.

Galy, J. & Enjalbert, R. (1982). *J. Solid State Chem.* **44**, 1–23.

Galy, J., Enjalbert, R., Lecante, P. & Burian, A. (2002). *Inorg. Chem.* **41**, 693–698.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hoge, R. & Trotter, J. (1965). *Can. J. Chem.* **43**, 2692–2695.

Klapötke, T. M. (1997). *Polyhedron* **16**, 2701–2704.

Li, F., Lu, W., Cai, J., Wang, H., Liu, G. & Zhou, M. (2025). *Inorg. Chem.* **64**, 13374–13381.

Lozinšek, M., Mercier, H. P. A. & Schrobilgen, G. J. (2021). *Angew. Chem. Int. Ed.* **60**, 8149–8156.

Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Resnati, G. & Pombeiro, A. J. L. (2020). *Coord. Chem. Rev.* **418**, 213381.

Motaln, K., Gurung, K., Brázda, P., Kokalj, A., Radan, K., Dragomir, M., Žemva, B., Palatinus, L. & Lozinšek, M. (2024). *ACS Cent. Sci.* **10**, 1733–1741.

Motaln, K., Uran, E., Giordano, N., Parsons, S. & Lozinšek, M. (2025). *J. Appl. Cryst.* **58**, 221–226.

Resnati, G., Bryce, D. L., Desiraju, G. R., Frontera, A., Krossing, I., Legon, A. C., Metrangolo, P., Nicotra, F., Rissanen, K., Scheiner, S. & Terraneo, G. (2024). *Pure Appl. Chem.* **96**, 135–145.

Rigaku OD (2025). *CrysAlis PRO*. Rigaku Corporation, Wrocław, Poland.

Schmidbaur, H., Bublak, W., Huber, B. & Müller, G. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 234–236.

Schwarz, U., Wosylus, A., Schmidt, M., Akselrud, L., Ormeci, A., Hanfland, M., Hermann, V. & Kuntscher, C. (2019). *Inorganics* **7**, 143.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Singh, A. K. & Swaminathan, S. (1964). *Curr. Sci.* **33**, 429–430.

Singh, A. K. & Swaminathan, S. (1967). *Z. Kristallogr.* **124**, 375–377.

Trotter, J. (1965). *Z. Kristallogr.* **124**, 3–4.

Uran, E. & Lozinšek, M. (2025). *Acta Cryst.* C**81**, 577–583.

Varadwaj, A., Varadwaj, P. R., Marques, H. M. & Yamashita, K. (2022). *Molecules* **27**, 3421.

von Benda, H. (1980). *Z. Kristallogr.* **151**, 271–285.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zagorac, D., Müller, H., Ruehl, S., Zagorac, J. & Rehme, S. (2019). *J. Appl. Cryst.* **52**, 918–925.

full crystallographic data

IUCrData (2026). **11**, x260235 [https://doi.org/10.1107/S241431462600235X]

Redetermination of the crystal structure of arsenic tribromide, $AsBr_3$

Erik Uran, Kristian Radan and Matic Lozinšek

Arsenic tribromide

Crystal data

$AsBr_3$
M_r = 314.65
Orthorhombic, $P2_12_12_1$
a = 4.20575 (8) Å
b = 10.08102 (18) Å
c = 12.0632 (2) Å
V = 511.46 (2) Å^3
Z = 4
$F(000)$ = 552
D_x = 4.086 Mg m^{-3}
Ag $K\alpha$ radiation, λ = 0.56087 Å
Cell parameters from 20011 reflections
θ = 3.1–30.0°
μ = 15.94 mm^{-1}
T = 100 K
Needle, clear colourless
0.15 × 0.06 × 0.03 mm

Data collection

Rigaku OD, XtaLAB Synergy-S, Dualflex, Eiger2 R CdTe 1M diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Ag) X-ray Source
Mirror monochromator
Detector resolution: 13.3333 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2025)
T_{min} = 0.288, T_{max} = 0.963
30863 measured reflections
2805 independent reflections
2556 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 30.0°, θ_{min} = 2.1°
h = −7→6
k = −17→16
l = −21→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.028
S = 1.03
2805 reflections
39 parameters
0 restraints
Primary atom site location: iterative
$w = 1/[\sigma^2(F_o^2) + (0.0097P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Extinction correction: SHELXL (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0013 (3)
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.14 (6)

Special details

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

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
As1	0.50086 (5)	0.30382 (2)	0.28814 (2)	0.01745 (4)
Br1	0.75779 (7)	0.48585 (2)	0.36825 (2)	0.02074 (4)
Br3	0.77836 (5)	0.30011 (2)	0.11926 (2)	0.01918 (4)
Br2	0.77521 (5)	0.13600 (2)	0.38228 (2)	0.02066 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.01404 (8)	0.02041 (8)	0.01790 (8)	−0.00019 (7)	0.00008 (7)	0.00075 (7)
Br1	0.02542 (9)	0.01809 (8)	0.01872 (8)	0.00129 (7)	−0.00113 (9)	−0.00212 (6)
Br3	0.02330 (8)	0.01976 (7)	0.01449 (7)	−0.00074 (8)	−0.00033 (7)	0.00048 (6)
Br2	0.02379 (9)	0.01909 (8)	0.01909 (8)	−0.00004 (7)	0.00067 (9)	0.00384 (6)

Geometric parameters (Å, º)

As1—Br1	2.3386 (3)	As1—Br2	2.3416 (3)
As1—Br3	2.3481 (3)		
Br1—As1—Br3	98.124 (10)	Br2—As1—Br3	99.460 (10)
Br1—As1—Br2	97.980 (11)		