



IUCrData

ISSN 2414-3146

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

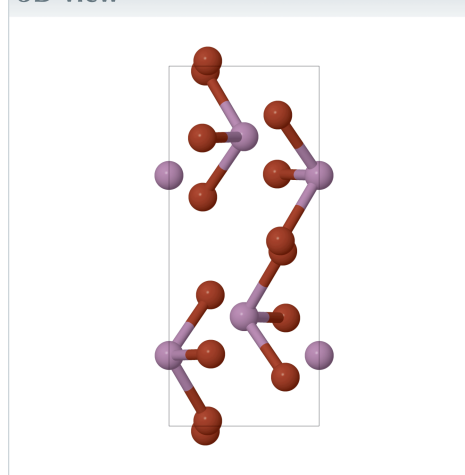
Structural data: full structural data are available from iucrdata.iucr.org

Redetermination of the crystal structure of arsenic tribromide, AsBr₃

Erik Uran,^{a,b,‡} Kristian Radan^{a,‡} and Matic Lozinšek^{a,b,*}
^aExtreme Conditions Chemistry Laboratory (ECCL K2), Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia, and ^bJožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia. *Correspondence e-mail: matic.lozinsek@ijs.si

The crystal structure of AsBr₃ 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 AsBr₃ 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, PnX₃, typically adopt a trigonal-pyramidal shape and crystallize predominantly as discrete molecular units (Galy & Enjalbert, 1982). In general, molecules of the PnX₃ 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 NBr₃ (Klapötke, 1997) has not been determined, whereas PBr₃ (Enjalbert & Galy, 1979*a*), AsBr₃ (Braekken, 1935; Singh & Swaminathan, 1964; Trotter, 1965; Singh & Swaminathan, 1967), SbBr₃ (Cushen & Hulme, 1962, 1964), and BiBr₃ (von Benda, 1980) have all been crystallographically characterized. Notably, BiBr₃ is the only member reported to crystallize in both a molecular form, composed of discrete trigonal-pyramidal BiBr₃ molecules, and a bromide-bridged polymeric form (von Benda, 1980). AsBr₃ crystallizes in the $P2_12_12_1$



OPEN ACCESS

Published under a CC BY 4.0 licence

Table 1

Comparison of the crystallographic parameters for AsBr₃ 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	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
<i>a</i> (Å)	10.15	12.148	4.33 (1)	10.244	4.20575 (8)
<i>b</i> (Å)	12.07	10.244	10.24 (0.5)	12.148	10.08102 (18)
<i>c</i> (Å)	4.31	4.34	12.20 (0.5)	4.34	12.0632 (2)
<i>V</i> (Å ³)	528.02	540.09	540.94	540.09	511.46 (2)
<i>T</i> (K)	<i>ns</i>	263	<i>ns</i>	<i>ns</i>	100
<i>R</i>	<i>ns</i>	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 AsCl₃ (Galy *et al.*, 2002) and the α -polymorph of SbBr₃ (Cushen & Hulme, 1964). Its crystal structure differs from that of AsF₃, which crystallizes in the $Pn2_1a$ space group (Enjalbert & Galy, 1979*b*), and from AsI₃, which adopts two polymorphs: the $R\bar{3}$ room-temperature form (Enjalbert & Galy, 1980) and the $P3_212$ high-temperature form (Galy & Enjalbert, 1982).

The AsBr₃ 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 AsBr₃ molecules adopting a slightly distorted C_{3v} geometry (true symmetry C_1 ; Fig. 1).

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 AsBr₃ molecules with crystallographically imposed C_{3v} symmetry, with shorter As—Br bond lengths reported for the Br₃As·C₆Et₆·AsBr₃ cocrystal [2.322 (1) Å; 98.9 (1)°; 295 K] (Schmidbaur *et al.*, 1987) and longer for the (*p*-FC₆H₄)₃P=Se·AsBr₃ cocrystal [2.379 (3) Å; 96.54 (9)°; 100 K] (Alhanash *et al.*, 2012).

The packing in the crystal structure of AsBr₃ (Fig. 2) can be described as columns of AsBr₃ molecules stacked along the *a* axis, interconnected to neighbouring columns *via* long As⋯Br

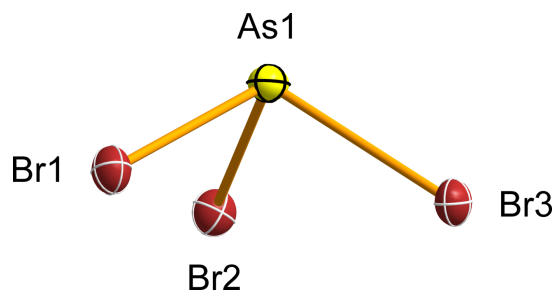


Figure 1
The molecular structure of AsBr₃ with displacement ellipsoids shown at the 50% probability level.

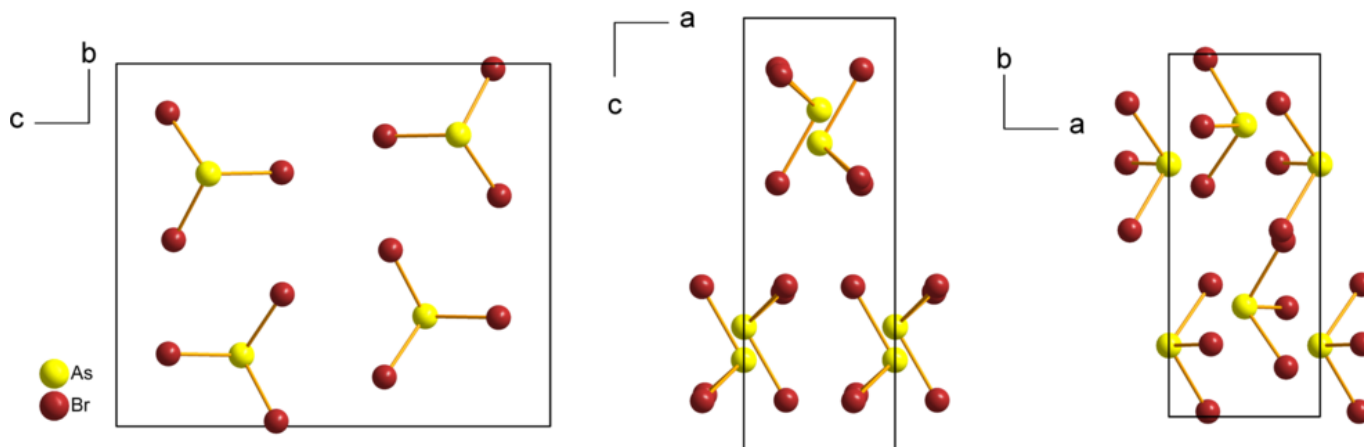


Figure 2
Unit cell and molecular packing of AsBr₃ viewed along the *a*, *b*, and *c* axes.

(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.* **A71**, 59–75.
- Braekken, H. (1935). *Forh. K. Nor. Vidensk. Selsk.* **8**, 33.
- Brammer, L., Peuronen, A. & Roseveare, T. M. (2023). *Acta Cryst.* **C79**, 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. (1979a). *Acta Cryst.* **B35**, 546–550.
- Enjalbert, R. & Galy, J. (1979b). *C. R. Acad. Sci.* **C289**, 441–443.
- Enjalbert, R. & Galy, J. (1980). *Acta Cryst.* **B36**, 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.* **B72**, 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.* **C71**, 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.* **C81**, 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, AsBr₃

Erik Uran, Kristian Radan and Matic Lozinšek

Arsenic tribromide

Crystal data

AsBr ₃	$D_x = 4.086 \text{ Mg m}^{-3}$
$M_r = 314.65$	Ag $K\alpha$ radiation, $\lambda = 0.56087 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 20011 reflections
$a = 4.20575 (8) \text{ \AA}$	$\theta = 3.1\text{--}30.0^\circ$
$b = 10.08102 (18) \text{ \AA}$	$\mu = 15.94 \text{ mm}^{-1}$
$c = 12.0632 (2) \text{ \AA}$	$T = 100 \text{ K}$
$V = 511.46 (2) \text{ \AA}^3$	Needle, clear colourless
$Z = 4$	$0.15 \times 0.06 \times 0.03 \text{ mm}$
$F(000) = 552$	

Data collection

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

Refinement

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ($\text{\AA}^2$)

	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 ($\text{\AA}$, $^\circ$)

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)		