Electronic Supplementary Information

From a molecular precursor to twin-free single crystals of metallic bismuth

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Content

I. Materials and Methods

All of the manipulations were carried out in a dry, oxygen-free, argon atmosphere by employing standard ampule and Schlenk techniques. Bismuth(II) trifluoroacetate was prepared as bulk orange crystalline product based on the reported synthetic procedure.[1] Its purity was confirmed by ^{1}H and ^{19}F NMR spectroscopy. Sublimation and decomposition processes of bismuth(II) trifluoroacetate were broadly investigated under variable experimental settings (Table S1). The optimal conditions to grow high quality single crystals of metallic bismuth were identified.

Crystallization of Bi-I: Orange crystals of bismuth(II) trifluoroacetate (16 mg, 0.036 mmol) were sealed under vacuum in a 6.5 cm glass ampule. The ampule was placed in an electric furnace at 265 °C and kept at that temperature for 25 hours (a temperature gradient was set approximately at 5 °C). The furnace was then slowly cooled to room temperature over 4 days. White solid (Bi(III) trifluoroacetate) was deposited in the "cold" end of the glass ampule. Metallic-silver block-shaped bismuth crystals were observed in the middle part of the ampule (Figures S1 and S2). Yield: 2.1 mg (81.9%).

Table S1. Experimental Conditions Used to Grow Bi Crystals and Visual Observations

Decomposition temperature	Ampule length	Time	Visual observations
130 °C	6 cm	19 hours	Cold zone: melting of the starting reagent Hot zone: deposition of a gray film
160 °C	10.5 cm	1 hour	Cold zone: melting of the starting reagent Hot zone: deposition of a gray powder
194 °C	7.5 cm	8 hours	Cold zone: melting of the starting reagent Hot zone: deposition of a gray film
220 °C	8.5 cm	18 hours	Cold zone: melting and decomposition of the starting reagent Hot zone: deposition of a metallic-grey thin film.
240 °C	6 cm	48 hours	Cold zone: formation of a white solid with a small amount of residual yellow melt Hot zone: deposition of a grey crystalline material
250 °C	5 cm	26 hours	Cold zone: formation of a white solid Hot zone: some grey crystals of Bi of low quality
250 °C	5.5 cm	34 hours	Cold zone: a white solid Hot zone: a few metallic-grey crystals of Bi
250 °C	6 cm	24 hours	Cold zone: a white solid

			Hot zone: crystals of Bi metal of low quality.
250 °C	7 cm	24 hours	Cold zone: a white solid Hot zone: crystals of Bi metal of low quality
250 °C	8 cm	44 hours	Cold zone: a white solid Hot zone: grey Bi crystals of low quality
250 °C	8.5 cm	46 hours	Cold zone: a white solid Middle zone: grey Bi crystals of low quality
260 °C	7.5 cm	43 hours	Cold zone: a white solid Hot/middle zone: a grey crystalline film, no single crystals.
265 °C	8 cm	48 hours	Cold zone: a white solid Hot zone: a grey crystalline material with some low quality crystals.
265 °C	6.5 cm	25 hours	Cold zone: a white solid Middle zone: good quality metallic grey block-shaped Bi crystals. X-ray data were collected

Note: Melting temperature of bismuth is 271.5° C.

II. Crystal Structure Solution and Refinement

A single crystal of bismuth was selected and mounted on a 20 μm MiTeGen Dual Thickness MicroMounts and Oxford Instruments Cryojet cryostat was applied to cool the single crystal to 100 K. At room temperature, Oxford Instruments Cryojet cryostat was applied to maintain the single crystal temperature at 298 K with the protection of dry nitrogen flow. The single crystal diffraction data were measured on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS detector equipped with a Mo-target fine-focus sealed X-ray tube (λ = 0.71073 Å). Data were collected using both ω and ϕ scans. Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).[2] Data were corrected for absorption effects using the face-indexed absorption correction methods as implemented in SADABS (version 2016/2).[3] The structures were solved by SHELXT (version 2018/2)[4] and refined by full-matrix least-squares procedures using SHELXTL (version 2018/3).[5] Bismuth atoms were refined anisotropically. Reflections (-1 1 1) and (0 2 1) were omitted since they are truncated by the beamstop. Extinction correction was performed against the data, and the extinction parameter was refined to 0.0060(3) for 100 K structure and to 0.0081(4) for 298 K structure. Crystallographic data, details of the data collection and structure refinement for the above structures are listed in Table S2. Bond distances and angles are shown in Table S3.

Table S2. Crystallographic Data for Bismuth at 100 K and 298 K

Empirical formula	Bi	
Formula weight	208.98	208.98
Temperature (K)	100(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Trigonal	Trigonal
Space group	*R*-3*m*	*R*-3*m*
a (Å)	4.5392(4)	4.5481(5)
b (Å)	4.5392(4)	4.5481(5)
c (Å)	11.8347(11)	11.8600(12)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	120.00	120.00
V (Å^3)	211.18(4)	212.46(5)
Z	6	6
ρ_{calcd} (g·cm^{-3})	9.860	9.800
μ (mm^{-1})	124.45	123.694
F(000)	498	498
Crystal size (mm)	0.12 × 0.11 × 0.06	0.12 × 0.11 × 0.06
θ range for data collection (°)	5.2–33.1	5.2–36.3
Reflections collected	3525	4485
Independent reflections	118 [R_{int} = 0.049]	150 [R_{int} = 0.042]
Transmission factors (min/max)	0.004/0.042	0.005/0.050
Data/restraints/params.	118/0/5	150/0/5
*R*1,[a] *wR*2[b] (*I* > 2σ(*I*))	0.0104, 0.0258	0.0120, 0.0286
*R*1,[a] *wR*2[b] (all data)	0.0104, 0.0258	0.0122, 0.0287
Quality-of-fit[c]	1.227	1.429
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.23, -1.85	1.41, -1.43

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.
[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data

Table S3. Bond Distances (Å) and Angles (°) in the Structure of Metallic Bismuth

	100 K	298 K
Bi1–Bi1^{i}	3.0674(3)	3.0723(4)
Bi1–Bi1^{ii}	3.0674(3)	3.0723(4)
Bi1–Bi1^{iii}	3.0674(3)	3.0723(4)
Bi1–Bi1^{iv}	3.5207(4)	3.5294(4)
Bi1–Bi1^{v}	3.5207(4)	3.5294(4)
Bi1–Bi1^{vi}	3.5207(4)	3.5294(4)
Bi1^{i}–Bi1–Bi1^{ii}	95.448(12)	95.493(11)
Bi1^{i}–Bi1–Bi1^{iii}	95.448(12)	95.493(11)
Bi1^{ii}–Bi1–Bi1^{iii}	95.447(12)	95.492(11)
Bi1^{i}–Bi1–Bi1^{iv}	91.663(5)	91.660(6)
Bi1^{ii}–Bi1–Bi1^{iv}	169.415(15)	169.348(13)
Bi1^{iii}–Bi1–Bi1^{iv}	91.663(5)	91.660(6)
Bi1^{i}–Bi1–Bi1^{v}	169.415(15)	169.348(13)
Bi1^{ii}–Bi1–Bi1^{v}	91.662(5)	91.659(7)
Bi1^{iii}–Bi1–Bi1^{v}	91.662(6)	91.659(7)
Bi1^{iv}–Bi1–Bi1^{v}	80.279(11)	80.228(11)
Bi1^{i}–Bi1–Bi1^{vi}	91.663(5)	91.660(6)
Bi1^{ii}–Bi1–Bi1^{vi}	91.663(5)	91.660(6)
Bi1^{iii}–Bi1–Bi1^{vi}	169.415(15)	169.348(13)
Bi1^{iv}–Bi1–Bi1^{vi}	80.279(11)	80.228(11)
Bi1^{v}–Bi1–Bi1^{vi}	80.279(11)	80.228(11)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*, -*z*+1; (iii) -*x*+2, -*y*+1, -*z*+1; (iv) -*x*+5/3, -*y*+4/3, -*z*+4/3; (v) -*x*+5/3, -*y*+1/3, -*z*+4/3; (vi) -*x*+2/3, -*y*+1/3, -*z*+4/3.

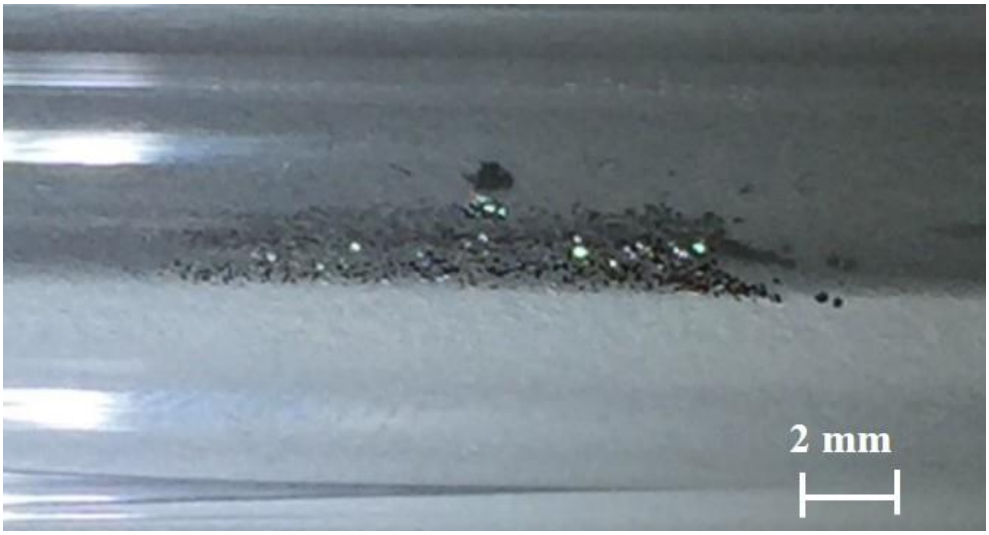

Figure S1. Single crystals of bismuth deposited on the wall of glass ampule.

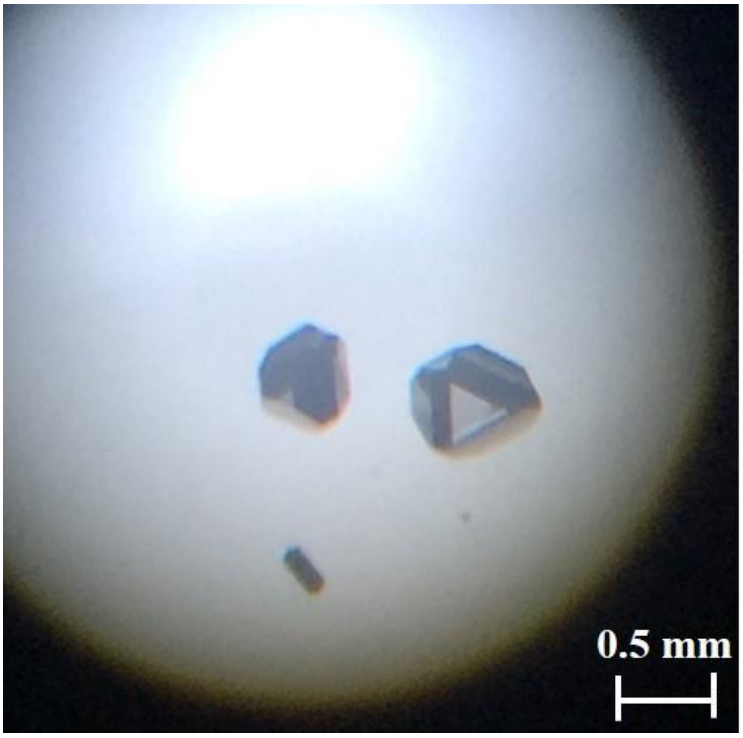

Figure S2. Single crystals of bismuth observed under a microscope.

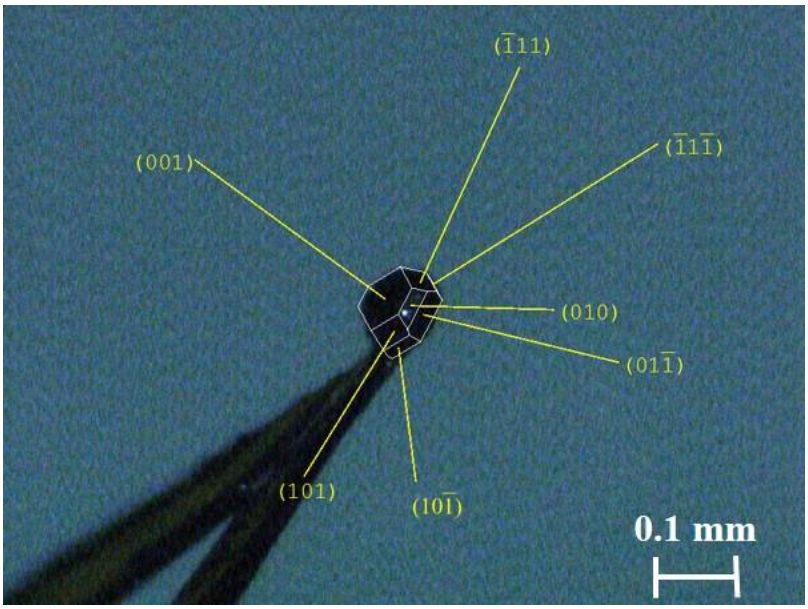

Figure S3. Face indexing of bismuth single crystal used for data collection.

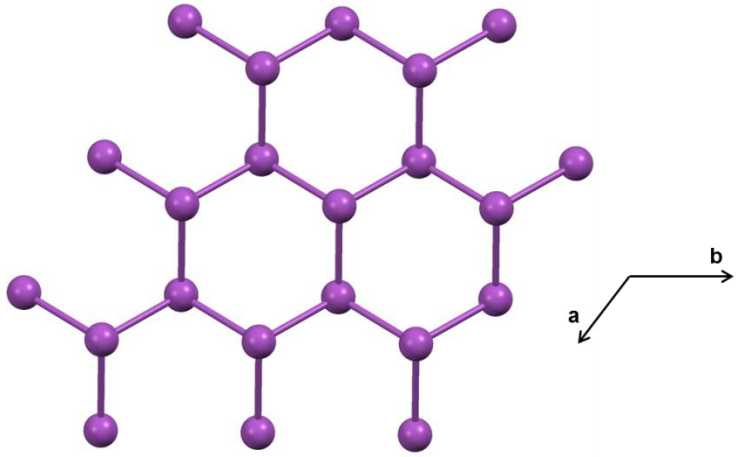

Figure S4. A fragment of a layer in the crystal structure of bismuth viewed along the *c*-axis.

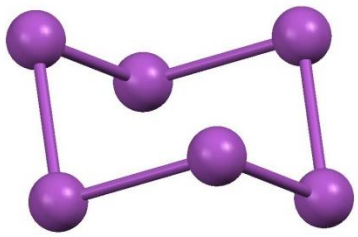

Figure S5. "Bi_6" ring in a classic chair conformation.

III. Nelson-Riley Correction of the Unit Cell Parameters

Data collections with the same single crystal were performed at both 100 K and 298 K to correct the virtual shift of reflections due to strong absorption. Reflections in the θ angle ranges of 0-20°, 20-30°, 30-40°, 40-50°, and 50-60° were collected separately. Unit cell parameters were derived from each shell using SAINT (V8.38A) program. Intensities of reflections with θ angle higher than 60° were too weak (even with long exposure time) to be used in reliable determination of the unit cell parameters. Nelson-Riley analysis[6] was performed for both 100 K and 298 K data sets. Unit cell parameters *a* and *c* derived from different θ angle shells were plotted *vs.* Nelson-Riley function separately. The plots for angular dependence of the unit cell parameters under different temperatures are shown in Figures S6–S9. In all cases, a linear relation has been observed. The line that fits best in each case was calculated and drawn by the program Origin (V.2018C). The corrected values for the unit cell parameters were applied in refinement of the structure model. The results of these structural refinements are presented in Tables S4 and S5 against our original data. The bond distances and angles for original and corrected data are compared in Tables S6 and S7.

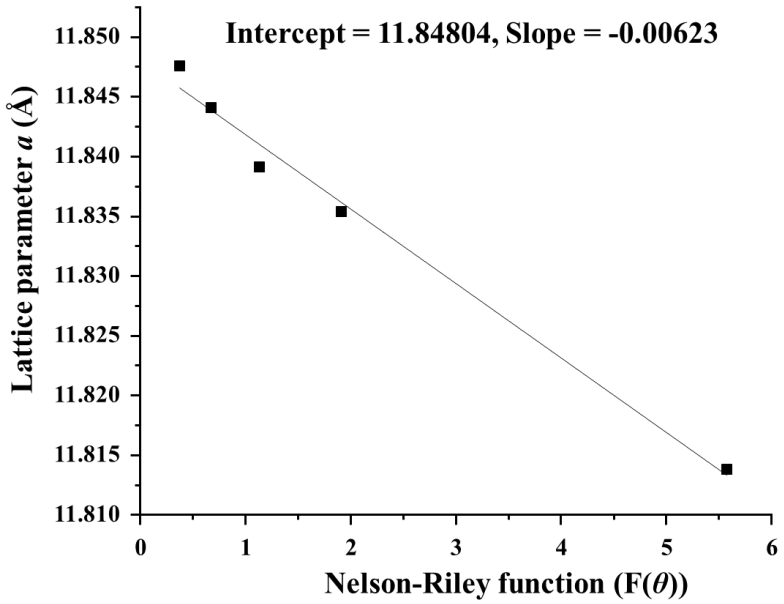

Figure S6. Determination of the lattice constant *c* at 100 K by Nelson-Riley analysis.

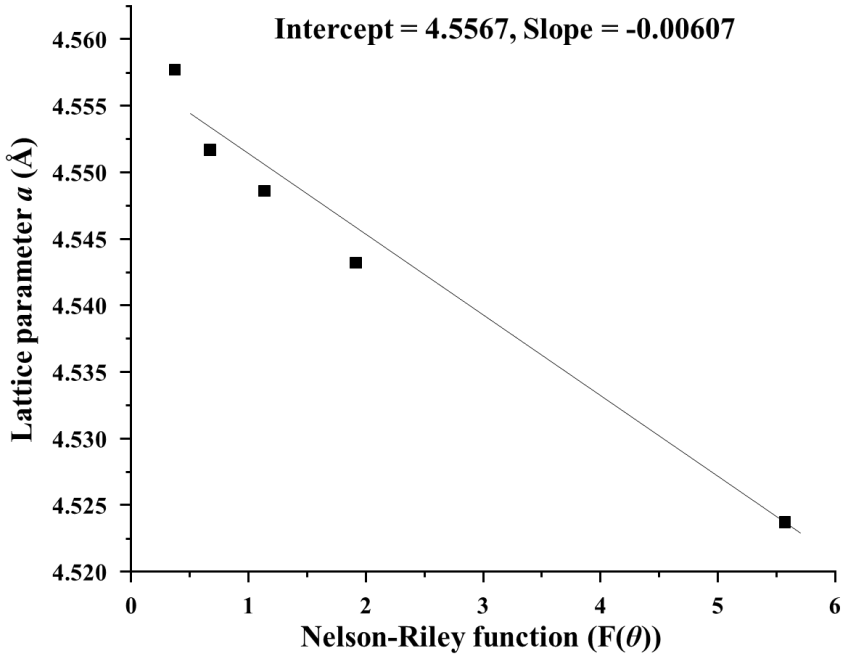

Figure S7. Determination of the lattice constant *a* at 100 K by Nelson-Riley analysis.

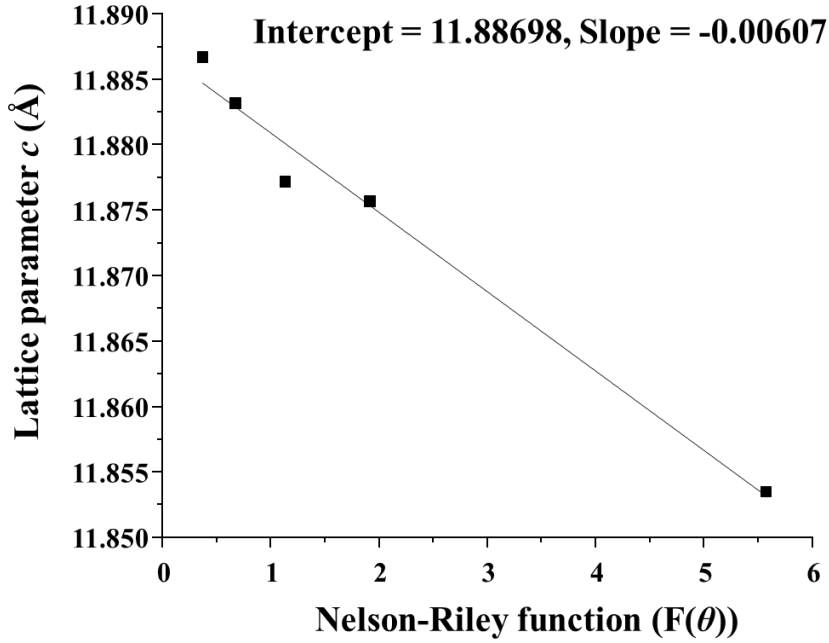

Figure S8. Determination of the lattice constant *c* at 298 K by Nelson-Riley analysis.

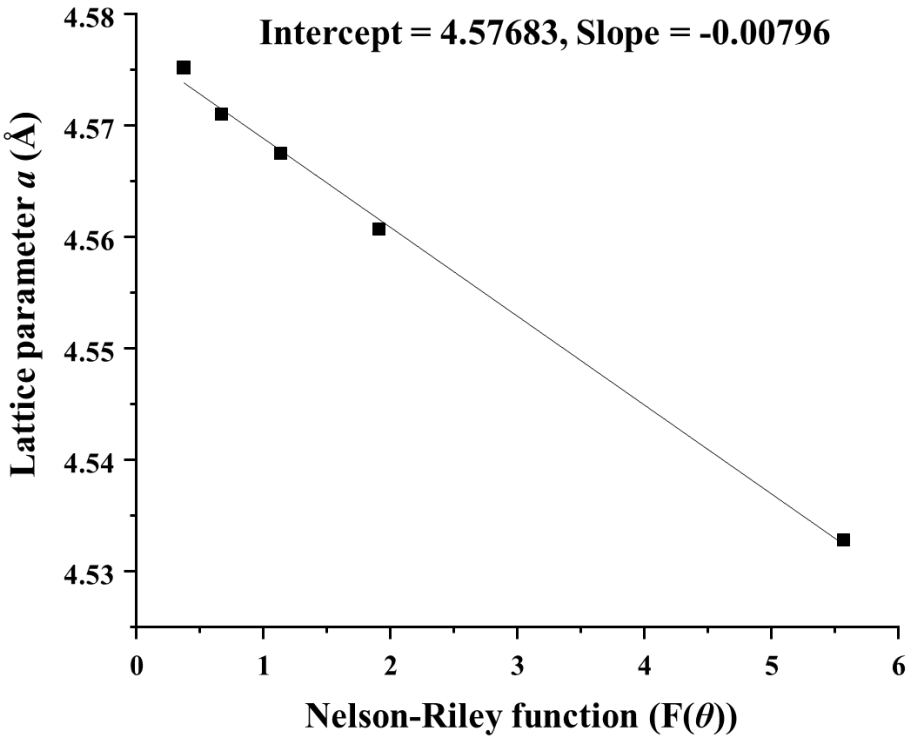

Figure S9. Determination of the lattice constant *a* at 298 K by Nelson-Riley analysis.

Table S4. Crystallographic Data Comparison for the Structure of Metallic Bismuth at 100 K

	Original Data	Nelson-Riley Analysis
a (Å)	4.5392(4)	4.5567(4)
c (Å)	11.8347(11)	11.8480(11)
V (Å^3)	211.18(4)	213.05(4)
ρ_{calcd} (g·cm^{-3})	9.860	9.773
μ (mm^{-1})	124.45	123.353
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0104, 0.0258	0.0104, 0.0259
$R1$,[a] $wR2$[b] (all data)	0.0104, 0.0258	0.0104, 0.0259
Quality-of-fit[c]	1.227	1.220
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e·Å^{-3})	1.23, -1.85	1.22, -1.83

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.
[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data

Table S5. Crystallographic Data Comparison for the Structure of Metallic Bismuth at 298 K

	Original Data	Nelson-Riley Analysis
a (Å)	4.5481(5)	4.5768(5)
c (Å)	11.8600(12)	11.8870(12)
V (Å^3)	212.46(5)	215.64(5)
ρ_{calcd} (g·cm^{-3})	9.800	9.656
μ (mm^{-1})	123.69	121.871
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0120, 0.0286	0.0121, 0.0288
$R1$,[a] $wR2$[b] (all data)	0.0122, 0.0287	0.0123, 0.0289
Quality-of-fit[c]	1.429	1.426
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.41, -1.43	1.42, -1.41

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.
[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data

Table S6. Bond Distances (Å) and Angles (°) in the Structure of Metallic Bismuth at 100 K

	Original Data	Nelson-Riley Analysis
Bi1–Bi1^{i}	3.0674(3)	3.0770(3)
Bi1–Bi1^{iv}	3.5207(4)	3.5299(4)
Bi1^{i}–Bi1–Bi1^{ii}	95.448(12)	95.540(12)
Bi1^{i}–Bi1–Bi1^{iv}	91.663(5)	91.558(5)
Bi1^{ii}–Bi1–Bi1^{iv}	169.415(15)	169.424(15)
Bi1^{iv}–Bi1–Bi1^{v}	80.279(11)	80.397(11)

Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) -x+1, -y, -z+1; (iii) -x+2, -y+1, -z+1; (iv) -x+5/3, -y+4/3, -z+4/3; (v) -x+5/3, -y+1/3, -z+4/3; (vi) -x+2/3, -y+1/3, -z+4/3.

Table S7. Bond Distances (Å) and Angles (°) in the Structure of Metallic Bismuth at 298 K

	Original Data	Nelson-Riley Analysis
Bi1–Bi1^{i}	3.0723(4)	3.0884(4)
Bi1–Bi1^{iv}	3.5294(4)	3.5453(4)
Bi1^{i}–Bi1–Bi1^{ii}	95.493(11)	95.629(12)
Bi1^{i}–Bi1–Bi1^{iv}	91.660(6)	91.505(6)
Bi1^{ii}–Bi1–Bi1^{iv}	169.348(13)	169.361(13)
Bi1^{iv}–Bi1–Bi1^{v}	80.228(11)	80.401(11)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*, -*z*+1; (iii) -*x*+2, -*y*+1, -*z*+1; (iv) -*x*+5/3, -*y*+4/3, -*z*+4/3; (v) -*x*+5/3, -*y*+1/3, -*z*+4/3; (vi) -*x*+2/3, -*y*+1/3, -*z*+4/3.

IV. References.

1. E. V. Dikarev and B. Li, *Inorg. Chem.*, 2004, **43**, 3461−3466.

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3. SADABS; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017.

4. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3−8.

5. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3−8.

6. B. Nelson, D. P. Riley, *Proc. Phys. Soc.*, 1945, **57**, 160−177.