

2-Bromo-3-nitrobenzaldehyde

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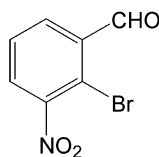
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.031; wR factor = 0.079; data-to-parameter ratio = 19.4.

The title compound, $C_7H_4BrNO_3$, was isolated as a by-product while attempting to prepare a diselenide. There is a close intramolecular $Br \cdots O$ contact [2.984 (2) Å]. The molecules form loosely associated dimers held together by weak intermolecular $Br \cdots O$ interactions with the nitro O atoms [$Br \cdots O = 3.179$ (3) Å]. As a result of these interactions, there is also a close $Br \cdots Br$ intermolecular contact [3.8714 (6) Å]. In addition, there are weak intermolecular $C-H \cdots O$ interactions. The combination of these interactions produces sheets which propagate in the (210) and ($\bar{2}10$) directions perpendicular to c .

Related literature

For the preparation and reactivity of the title compound, see: Rahman & Scrowston (1984); Sienkowska *et al.* (2000); Wirth & Fragale (1997). For bond-length data, see: Allen (2002). For intramolecular chalcogen interactions, see: Singh *et al.* (2009). For intermolecular $Br \cdots O$ interactions, see: Jones & Lozano (2004); Kruszynski (2007); Pedireddi *et al.* (1992); Xie *et al.* (2009).



Experimental

Crystal data

$C_7H_4BrNO_3$
 $M_r = 230.02$
 Monoclinic, $P2_1/c$

$a = 8.1578$ (8) Å
 $b = 6.3079$ (5) Å
 $c = 15.0537$ (11) Å

$\beta = 91.603$ (8)°
 $V = 774.34$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 5.27$ mm⁻¹
 $T = 296$ K
 $0.27 \times 0.18 \times 0.09$ mm

Data collection

Oxford Diffraction Gemini R diffractometer
 Absorption correction: multi-scan (*CrysAlisPro*; Oxford Diffraction, 2009)
 $T_{\min} = 0.330$, $T_{\max} = 0.649$

5208 measured reflections
 2120 independent reflections
 1308 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.079$
 $S = 0.97$
 2120 reflections

109 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C6-H6 \cdots O1^i$	0.93	2.55	3.354 (4)	145
$C7-H7 \cdots O3^{ii}$	0.93	2.62	3.534 (4)	168

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

Data collection: *CrysAlisPro* (Oxford Diffraction, 2009); cell refinement: *CrysAlisPro*; data reduction: *CrysAlisPro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2283).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Jones, P. G. & Lozano, V. (2004). *Acta Cryst.* **C60**, o876–o878.
 Kruszynski, R. (2007). *Acta Cryst.* **C63**, o389–o391.
 Oxford Diffraction (2009). *CrysAlisPro*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
 Pedireddi, V. R., Sarma, J. A. R. P. & Desiraju, G. R. (1992). *J. Chem. Soc. Perkin Trans. 2*, pp. 311–320.
 Rahman, L. K. A. & Scrowston, R. M. (1984). *J. Chem. Soc. Perkin Trans. 1*, pp. 385–390.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sienkowska, M., Benin, V. & Kaszynski, P. (2000). *Tetrahedron*, **56**, 165–173.
 Singh, V. P., Singh, H. B. & Butcher, R. J. (2009). In preparation.
 Wirth, T. & Fragale, G. (1997). *Chem. Eur. J.* **3**, 1894–1902.
 Xie, M., Deng, C., Zheng, J. & Zhu, Y. (2009). *Acta Cryst.* **E65**, o1980.

supplementary materials

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Comment

The structure of the title compound, (I), is shown below. Dimensions are available in the archived CIF.

The title compound 1, C₇H₄NO₃Br, was isolated as a by-product while attempting to prepare diselenide 2 by reacting 2-bromo-3-nitrobenzylalcohol with disodium diselenide (Wirth & Fragale, 1997) as shown in scheme 1. Presumably, the formation of 1 takes place during column chromatography on silica gel where the alcohol function is oxidized to the aldehyde function. The preparation (but not the structure) of the title compound by different routes has been previously reported (Rahman & Scrowston, 1984; Sienkowska *et al.*, 2000). In 1, with two withdrawing *ortho* groups present, the 2-position is highly susceptible to nucleophilic substitution by Na₂Se₂, Na₂Te₂, Na₂Se to afford a series of novel chalcogen compounds (Singh *et al.* 2009). In this paper we report the structure of the precursor.

The bond lengths and angles in the title compound are within the normal ranges for related compounds (Allen *et al.*, 2002). When chalcogens (Se, Te) are present in the 2-position in place of bromine there is an intramolecular chalcogen (Se/Te...oxygen(aldehyde/nitro)) interaction (Singh *et al.* 2009). It was of interest to see whether the bromo analog will interact intramolecularly with the nitro/aldehyde donor groups. There is a close intramolecular Br...O contact of 2.984 (2) Å. The molecules form loosely associated dimers held together by weak intermolecular Br...O interactions with the nitro O atoms (Br...O 3.179 (3) Å, see Figure 1). Similar interactions have been previously reported (Jones & Lozano, 2004; Kruszynski, 2007; Pedireddi *et al.*, 1992; Xie *et al.*, 2009). As a result of these interactions there is also a close Br...Br intermolecular contact (3.8714 (6) Å) as has been commonly observed [42 examples found in a search of the Cambridge Structural Database (Allen, 2002)]. In addition there are weak intermolecular C—H...O interactions. Of the intermolecular interactions, only that between O3 and the aldehyde H is out of plane. As a result of this out-of-plane interaction the nitro group is twisted by 43.6 (4)° from the plane of the aromatic ring. The combination of these interactions produces sheets which propagate in the (2 1 0) and (-2 1 0) directions perpendicular to c as shown in Figure 2.

Experimental

The title compound 1, C₇H₄NO₃Br, was isolated as a by-product while attempting to prepare diselenide 2 by reacting 2-bromo-3-nitrobenzylalcohol with disodium diselenide (Wirth & Fragale, 1997). Presumably, the formation of 1 takes place during column chromatography on silica gel where the alcohol function is oxidized to the aldehyde function. It has been prepared previously by a different routes (Rahman & Scrowston, 1984; Sienkowska *et al.* 2000).

Crystal suitable for X-ray diffraction were obtained from CH₂Cl₂/ethyl acetate.

Figures

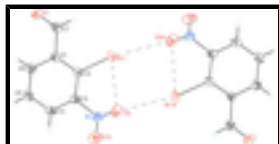


Fig. 1. The molecular structure of $C_7H_4BrNO_3$ showing the Br...O intra- and intermolecular interactions (as dashed lines) forming loosely associated dimers. The atom numbering scheme and 50% probability displacement ellipsoids.

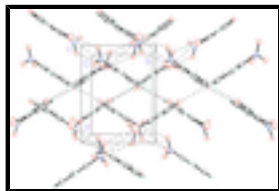


Fig. 2. The molecular packing for $C_7H_4BrNO_3$ viewed down the c axis showing the sheets of associated molecules in the (2 1 0) and (-2 1 0) directions. The secondary interactions are shown by dashed lines.

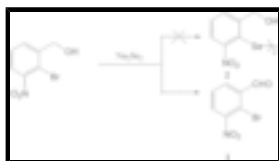


Fig. 3. The formation of the title compound.

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Crystal data

$C_7H_4BrNO_3$

$M_r = 230.02$

Monoclinic, $P2_1/c$

$a = 8.1578$ (8) Å

$b = 6.3079$ (5) Å

$c = 15.0537$ (11) Å

$\beta = 91.603$ (8)°

$V = 774.34$ (11) Å³

$Z = 4$

$F_{000} = 448$

$D_x = 1.973$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2069 reflections

$\theta = 4.7\text{--}30.5^\circ$

$\mu = 5.27$ mm⁻¹

$T = 296$ K

Rectangular plate, orange

$0.27 \times 0.18 \times 0.09$ mm

Data collection

Oxford Diffraction Gemini R diffractometer

Radiation source: Enhance (Mo) X-ray Source

Monochromator: graphite

Detector resolution: 10.5081 pixels mm⁻¹

$T = 296$ K

ω scans

Absorption correction: multi-scan (CrysAlisPro; Oxford Diffraction, 2009)

$T_{\min} = 0.330$, $T_{\max} = 0.649$

5208 measured reflections

2120 independent reflections

1308 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 30.6^\circ$

$\theta_{\min} = 4.9^\circ$

$h = -11 \rightarrow 10$

$k = -8 \rightarrow 7$

$l = -21 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$
$S = 0.97$	where $P = (F_o^2 + 2F_c^2)/3$
2120 reflections	$(\Delta/\sigma)_{\max} < 0.001$
109 parameters	$\Delta\rho_{\max} = 0.77 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$
	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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.14664 (4)	0.22483 (5)	0.465488 (18)	0.04777 (13)
O1	0.4218 (3)	0.7906 (3)	0.39513 (14)	0.0541 (5)
O2	-0.0180 (3)	0.1829 (4)	0.63917 (17)	0.0744 (7)
O3	0.1725 (4)	0.1401 (5)	0.73881 (17)	0.0868 (8)
N1	0.1141 (4)	0.2271 (4)	0.67396 (17)	0.0505 (7)
C1	0.3125 (3)	0.6054 (4)	0.51753 (16)	0.0348 (6)
C2	0.2254 (3)	0.4311 (4)	0.54696 (16)	0.0328 (5)
C3	0.2073 (3)	0.4060 (4)	0.63756 (17)	0.0370 (6)
C4	0.2767 (3)	0.5454 (5)	0.69788 (18)	0.0470 (7)
H4	0.2653	0.5227	0.7584	0.056*
C5	0.3621 (4)	0.7169 (5)	0.6692 (2)	0.0508 (8)
H5	0.4088	0.8119	0.7098	0.061*
C6	0.3785 (4)	0.7478 (4)	0.5787 (2)	0.0434 (7)
H6	0.4348	0.8660	0.5587	0.052*
C7	0.3397 (4)	0.6456 (5)	0.42181 (18)	0.0443 (7)
H7	0.2910	0.5545	0.3803	0.053*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0561 (2)	0.04590 (19)	0.04115 (18)	-0.00979 (14)	-0.00130 (13)	-0.00726 (13)
O1	0.0632 (13)	0.0526 (13)	0.0468 (12)	-0.0092 (11)	0.0069 (10)	0.0147 (10)
O2	0.0641 (16)	0.0862 (18)	0.0735 (17)	-0.0285 (14)	0.0124 (14)	0.0052 (14)
O3	0.119 (2)	0.0817 (19)	0.0591 (15)	-0.0035 (17)	-0.0007 (15)	0.0315 (15)
N1	0.0631 (18)	0.0518 (16)	0.0375 (13)	-0.0010 (13)	0.0145 (13)	0.0043 (12)
C1	0.0361 (14)	0.0354 (14)	0.0329 (13)	0.0038 (11)	0.0010 (11)	-0.0006 (11)
C2	0.0306 (13)	0.0351 (13)	0.0325 (13)	0.0046 (11)	-0.0014 (10)	-0.0021 (11)
C3	0.0363 (14)	0.0407 (14)	0.0341 (14)	0.0034 (12)	0.0039 (11)	0.0007 (11)
C4	0.0520 (18)	0.060 (2)	0.0291 (13)	0.0078 (15)	0.0055 (13)	-0.0049 (13)
C5	0.0549 (19)	0.0558 (18)	0.0413 (16)	-0.0046 (15)	-0.0044 (14)	-0.0159 (14)
C6	0.0449 (17)	0.0392 (17)	0.0460 (16)	-0.0018 (12)	0.0017 (13)	-0.0033 (13)
C7	0.0486 (17)	0.0447 (16)	0.0394 (15)	0.0044 (14)	-0.0053 (13)	0.0003 (13)

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

Br1—C2	1.889 (2)	C1—C7	1.486 (4)
Br1—O2	2.984 (2)	C2—C3	1.385 (3)
Br1—Br1 ⁱ	3.8714 (6)	C3—C4	1.375 (4)
O1—C7	1.209 (3)	C4—C5	1.363 (4)
O2—N1	1.217 (4)	C4—H4	0.9300
O2—Br1 ⁱ	3.179 (3)	C5—C6	1.387 (4)
O3—N1	1.206 (4)	C5—H5	0.9300
N1—C3	1.475 (4)	C6—H6	0.9300
C1—C6	1.384 (4)	C7—H7	0.9300
C1—C2	1.388 (3)		
C2—Br1—O2	69.23 (9)	C4—C3—C2	121.6 (2)
C2—Br1—Br1 ⁱ	122.15 (8)	C4—C3—N1	116.8 (2)
O2—Br1—Br1 ⁱ	53.36 (5)	C2—C3—N1	121.6 (2)
N1—O2—Br1	86.66 (16)	C5—C4—C3	120.2 (3)
N1—O2—Br1 ⁱ	132.4 (2)	C5—C4—H4	119.9
Br1—O2—Br1 ⁱ	77.75 (6)	C3—C4—H4	119.9
O3—N1—O2	124.7 (3)	C4—C5—C6	119.1 (3)
O3—N1—C3	116.9 (3)	C4—C5—H5	120.4
O2—N1—C3	118.4 (3)	C6—C5—H5	120.4
C6—C1—C2	119.6 (2)	C1—C6—C5	121.1 (3)
C6—C1—C7	117.9 (2)	C1—C6—H6	119.5
C2—C1—C7	122.4 (2)	C5—C6—H6	119.5
C3—C2—C1	118.3 (2)	O1—C7—C1	123.4 (3)
C3—C2—Br1	121.12 (19)	O1—C7—H7	118.3
C1—C2—Br1	120.42 (18)	C1—C7—H7	118.3
C2—Br1—O2—N1	-37.66 (19)	Br1—C2—C3—C4	174.2 (2)
Br1 ⁱ —Br1—O2—N1	134.7 (2)	C1—C2—C3—N1	178.9 (2)
C2—Br1—O2—Br1 ⁱ	-172.41 (10)	Br1—C2—C3—N1	-5.2 (3)

Br1—O2—N1—O3	-137.5 (3)	O3—N1—C3—C4	-41.7 (4)
Br1 ⁱ —O2—N1—O3	-67.4 (4)	O2—N1—C3—C4	135.4 (3)
Br1—O2—N1—C3	45.6 (2)	O3—N1—C3—C2	137.7 (3)
Br1 ⁱ —O2—N1—C3	115.6 (3)	O2—N1—C3—C2	-45.1 (4)
C6—C1—C2—C3	0.2 (4)	C2—C3—C4—C5	1.8 (4)
C7—C1—C2—C3	179.5 (2)	N1—C3—C4—C5	-178.8 (3)
C6—C1—C2—Br1	-175.8 (2)	C3—C4—C5—C6	-0.3 (4)
C7—C1—C2—Br1	3.6 (3)	C2—C1—C6—C5	1.3 (4)
O2—Br1—C2—C3	19.93 (19)	C7—C1—C6—C5	-178.1 (3)
Br1 ⁱ —Br1—C2—C3	12.7 (2)	C4—C5—C6—C1	-1.3 (5)
O2—Br1—C2—C1	-164.3 (2)	C6—C1—C7—O1	3.1 (4)
Br1 ⁱ —Br1—C2—C1	-171.45 (16)	C2—C1—C7—O1	-176.3 (3)
C1—C2—C3—C4	-1.7 (4)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots O1 ⁱⁱ	0.93	2.55	3.354 (4)	145
C7—H7 \cdots O3 ⁱⁱⁱ	0.93	2.62	3.534 (4)	168

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

Fig. 1

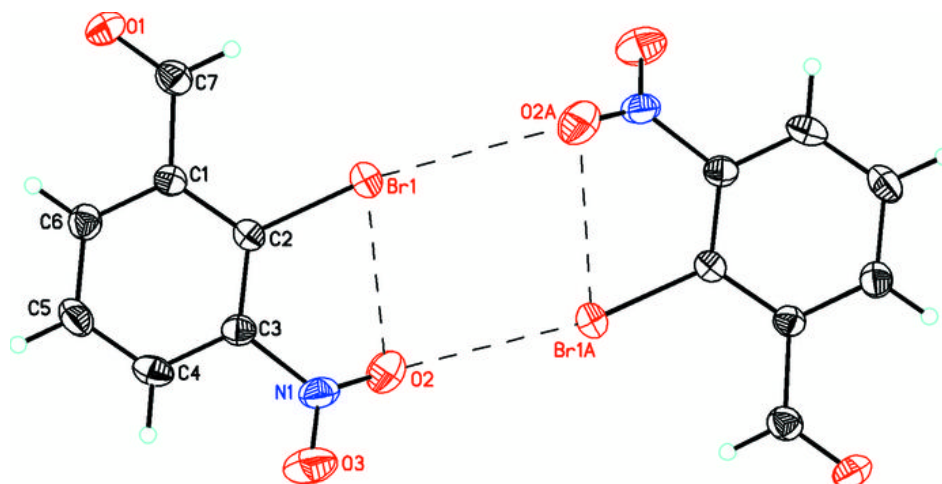


Fig. 2

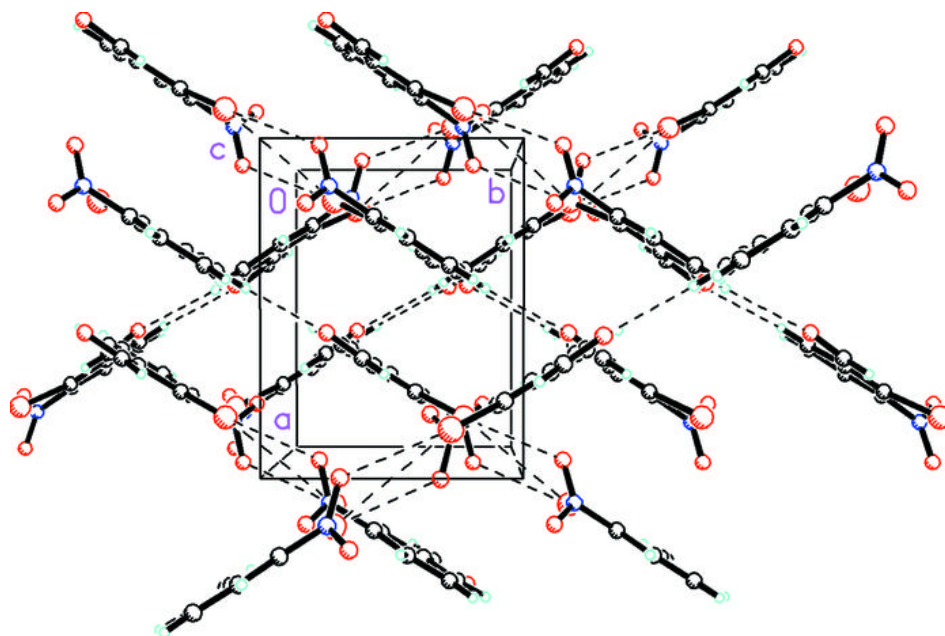


Fig. 3

