



Crystal structure of 2-bromo-4,6-dinitroaniline

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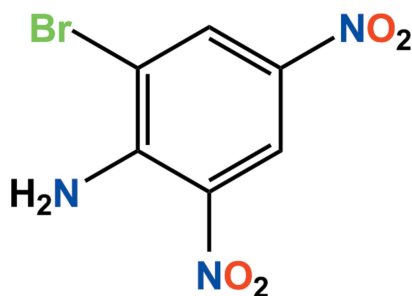
In the title compound, C₆H₄BrN₃O₄, the dihedral angles between the nitro groups and the aniline ring are 2.04 (3) and 1.18 (4)°, respectively. In the crystal, N—H···O and C—H···O hydrogen bonds and weak side-on C—Br···π interactions [3.5024 (12) Å] link adjacent molecules, forming a three-dimensional network. A close O···Br contact [3.259 (2) Å] may also add additional stability.

Keywords: crystal structure; aniline derivative; hydrogen bonding; C—Br···π interactions.

CCDC reference: 1427403

1. Related literature

For information on the title compound, see: Yadav & Sharma (2010). For a related crystal structure, see: Glidewell *et al.* (2002).



2. Experimental

2.1. Crystal data

C ₆ H ₄ BrN ₃ O ₄	$V = 832.03 (4) \text{ \AA}^3$
$M_r = 262.03$	$Z = 4$
Monoclinic $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.6955 (2) \text{ \AA}$	$\mu = 4.93 \text{ mm}^{-1}$
$b = 7.7720 (2) \text{ \AA}$	$T = 173 \text{ K}$
$c = 16.0608 (4) \text{ \AA}$	$0.20 \times 0.15 \times 0.08 \text{ mm}$
$\beta = 95.4182 (14)^\circ$	

2.2. Data collection

Bruker APEXII CCD diffractometer	12322 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2013)	1892 independent reflections
$T_{\min} = 0.534$, $T_{\max} = 0.746$	1648 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	127 parameters
$wR(F^2) = 0.083$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$
1892 reflections	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···O2 ⁱ	0.88	2.16	2.893 (3)	141
N1—H1B···O4 ⁱⁱ	0.88	2.36	3.139 (4)	148
C5—H5···O1 ⁱⁱⁱ	0.95	2.55	3.209 (4)	127

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

Data collection: APEX2 (Bruker, 2013); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 2010); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SJ5477).

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supporting information

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Crystal structure of 2-bromo-4,6-dinitroaniline

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S1. Comment

The title compound, $C_6H_4BrN_3O_4$, is an aniline derivative with additional bromine and nitro substituents. Aniline is the simplest of the primary aromatic amines an organic base used, as are its derivatives, to make dyes, drugs, explosives, plastics and chemicals for the rubber industry (Yadav & Sharma, 2010). Its crystal structure is reported herein. In this compound (Fig. 1), the dihedral angles between the nitro groups and the aniline ring are $2.04(3)$ and $1.18(4)^\circ$, respectively. All bond lengths and bond angles are normal and comparable to those observed in the crystal structure of a similar compound (Glidewell *et al.*, 2002).

The crystal structure (Fig. 2) is stabilized by N—H \cdots O and C—H \cdots O hydrogen bonds (Table 1), as well as an intermolecular side-on C2—Br1 \cdots Cg1^{iv} interaction [Br1 \cdots Cg = 3.5024(12) Å, C2—Br1 \cdots Cg = 96.90(9) °] (Cg1 is the centroid of the C1—C6 ring) [symmetry code: (iv), -x, -y + 1, -z + 2]. A close O3 \cdots Br1^{iv} contact, 3.259(2) Å may also contribute, iv = -1/2+x, 1.5-y, -1/2+z. These contacts result in a three-dimensional network.

S2. Experimental

The title compound was supplied by the Kyung In Synthetic Corporation. Slow evaporation of a solution in CH_2Cl_2 gave single crystals suitable for X-ray analysis.

S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with $d(N—H) = 0.88$ Å, $U_{iso} = 1.2U_{eq}(C)$ for amine group, $d(C—H) = 0.95$ Å, $U_{iso} = 1.2U_{eq}(C)$ for aromatic C—H.

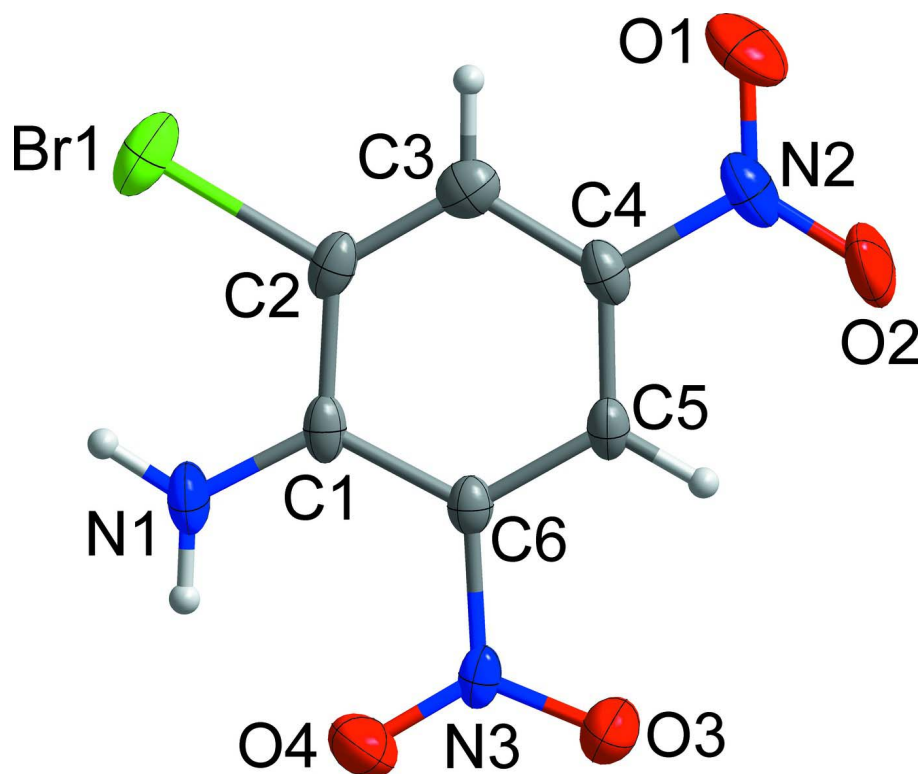


Figure 1

The asymmetric unit of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

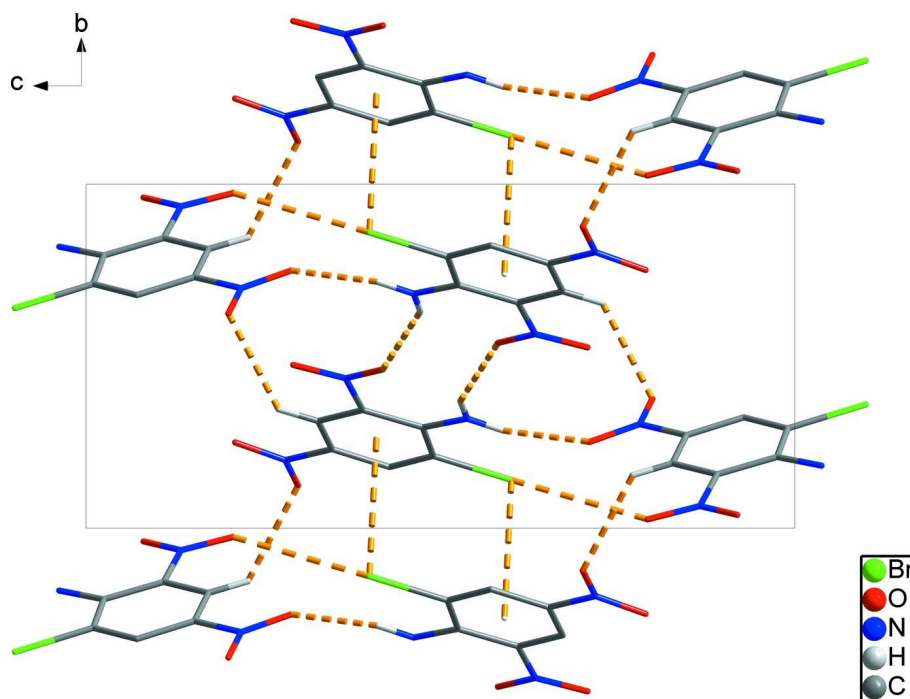


Figure 2

Crystal packing viewed along the *a* axis. The intermolecular interactions are shown as dashed lines.

2-Bromo-4,6-dinitroaniline

Crystal data

$C_6H_4BrN_3O_4$

$M_r = 262.03$

Monoclinic, $P2_1/n$

$a = 6.6955$ (2) Å

$b = 7.7720$ (2) Å

$c = 16.0608$ (4) Å

$\beta = 95.4182$ (14)°

$V = 832.03$ (4) Å³

$Z = 4$

$F(000) = 512$

$D_x = 2.092$ Mg m⁻³

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

Cell parameters from 6099 reflections

$\theta = 2.6$ – 27.1 °

$\mu = 4.93$ mm⁻¹

$T = 173$ K

Block, yellow

$0.20 \times 0.15 \times 0.08$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2013)

$T_{\min} = 0.534$, $T_{\max} = 0.746$

12322 measured reflections

1892 independent reflections

1648 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.6$ °

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.083$

$S = 1.06$

1892 reflections

127 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 1.6027P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.85$ e Å⁻³

$\Delta\rho_{\min} = -0.51$ e Å⁻³

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.19258 (6)	0.64018 (4)	1.10024 (2)	0.04116 (14)
O1	0.4575 (4)	0.6238 (3)	0.79915 (19)	0.0484 (7)
O2	0.2420 (4)	0.7493 (4)	0.71047 (15)	0.0544 (8)
O3	-0.3569 (3)	0.9745 (3)	0.79238 (13)	0.0379 (5)
O4	-0.4360 (3)	0.9614 (3)	0.91874 (15)	0.0397 (6)
N1	-0.1949 (4)	0.8183 (4)	1.03776 (15)	0.0327 (6)
H1A	-0.1531	0.7837	1.0886	0.039*
H1B	-0.3120	0.8696	1.0282	0.039*

N2	0.2978 (4)	0.6977 (4)	0.78113 (17)	0.0348 (6)
N3	-0.3276 (3)	0.9358 (3)	0.86609 (13)	0.0212 (5)
C1	-0.0806 (4)	0.7930 (4)	0.97511 (16)	0.0230 (6)
C2	0.1093 (4)	0.7101 (4)	0.98987 (17)	0.0256 (6)
C3	0.2302 (4)	0.6777 (4)	0.92827 (19)	0.0277 (6)
H3	0.3551	0.6208	0.9404	0.033*
C4	0.1671 (4)	0.7299 (4)	0.84695 (18)	0.0263 (6)
C5	-0.0114 (4)	0.8115 (4)	0.82743 (17)	0.0233 (6)
H5	-0.0513	0.8456	0.7715	0.028*
C6	-0.1333 (4)	0.8435 (3)	0.89051 (16)	0.0214 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0571 (2)	0.0375 (2)	0.02593 (18)	-0.01145 (16)	-0.01191 (14)	0.00718 (13)
O1	0.0422 (14)	0.0411 (14)	0.0655 (18)	0.0096 (11)	0.0239 (13)	-0.0063 (12)
O2	0.0471 (15)	0.094 (2)	0.0241 (12)	-0.0027 (15)	0.0165 (11)	-0.0089 (13)
O3	0.0415 (13)	0.0450 (14)	0.0268 (11)	0.0051 (11)	0.0004 (10)	0.0036 (10)
O4	0.0329 (12)	0.0438 (14)	0.0437 (14)	0.0057 (10)	0.0111 (11)	0.0000 (11)
N1	0.0409 (15)	0.0416 (15)	0.0168 (11)	-0.0026 (12)	0.0096 (11)	-0.0002 (11)
N2	0.0351 (15)	0.0381 (15)	0.0340 (15)	-0.0082 (12)	0.0174 (12)	-0.0124 (12)
N3	0.0269 (12)	0.0220 (11)	0.0147 (10)	-0.0105 (9)	0.0011 (9)	0.0003 (9)
C1	0.0323 (15)	0.0214 (13)	0.0156 (12)	-0.0095 (11)	0.0051 (11)	-0.0032 (10)
C2	0.0339 (15)	0.0246 (14)	0.0175 (13)	-0.0095 (12)	-0.0025 (11)	0.0019 (11)
C3	0.0274 (14)	0.0242 (14)	0.0308 (15)	-0.0045 (11)	-0.0010 (12)	-0.0003 (12)
C4	0.0290 (15)	0.0289 (15)	0.0224 (13)	-0.0054 (12)	0.0100 (12)	-0.0058 (11)
C5	0.0276 (14)	0.0274 (14)	0.0153 (12)	-0.0069 (11)	0.0046 (11)	-0.0009 (10)
C6	0.0257 (13)	0.0218 (13)	0.0170 (12)	-0.0045 (11)	0.0031 (10)	-0.0019 (10)

Geometric parameters (Å, °)

Br1—C2	1.887 (3)	N3—C6	1.505 (4)
O1—N2	1.224 (4)	C1—C2	1.425 (4)
O2—N2	1.228 (4)	C1—C6	1.426 (4)
O3—N3	1.219 (3)	C2—C3	1.360 (4)
O4—N3	1.182 (3)	C3—C4	1.395 (4)
N1—C1	1.335 (4)	C3—H3	0.9500
N1—H1A	0.8800	C4—C5	1.363 (4)
N1—H1B	0.8800	C5—C6	1.382 (4)
N2—C4	1.456 (4)	C5—H5	0.9500
C1—N1—H1A	120.0	C1—C2—Br1	117.8 (2)
C1—N1—H1B	120.0	C2—C3—C4	118.6 (3)
H1A—N1—H1B	120.0	C2—C3—H3	120.7
O1—N2—O2	123.7 (3)	C4—C3—H3	120.7
O1—N2—C4	118.7 (3)	C5—C4—C3	122.2 (3)
O2—N2—C4	117.6 (3)	C5—C4—N2	119.1 (3)
O4—N3—O3	126.8 (3)	C3—C4—N2	118.7 (3)

O4—N3—C6	117.9 (2)	C4—C5—C6	118.7 (3)
O3—N3—C6	115.3 (2)	C4—C5—H5	120.6
N1—C1—C2	120.5 (3)	C6—C5—H5	120.6
N1—C1—C6	124.7 (3)	C5—C6—C1	122.6 (3)
C2—C1—C6	114.8 (2)	C5—C6—N3	116.8 (2)
C3—C2—C1	123.1 (3)	C1—C6—N3	120.6 (2)
C3—C2—Br1	119.1 (2)		
N1—C1—C2—C3	178.6 (3)	C3—C4—C5—C6	0.1 (4)
C6—C1—C2—C3	-1.3 (4)	N2—C4—C5—C6	-179.2 (3)
N1—C1—C2—Br1	-0.5 (4)	C4—C5—C6—C1	-0.7 (4)
C6—C1—C2—Br1	179.52 (19)	C4—C5—C6—N3	179.3 (2)
C1—C2—C3—C4	0.9 (4)	N1—C1—C6—C5	-178.7 (3)
Br1—C2—C3—C4	180.0 (2)	C2—C1—C6—C5	1.3 (4)
C2—C3—C4—C5	-0.2 (4)	N1—C1—C6—N3	1.3 (4)
C2—C3—C4—N2	179.1 (3)	C2—C1—C6—N3	-178.7 (2)
O1—N2—C4—C5	-179.7 (3)	O4—N3—C6—C5	178.5 (3)
O2—N2—C4—C5	1.4 (4)	O3—N3—C6—C5	-0.6 (3)
O1—N2—C4—C3	1.0 (4)	O4—N3—C6—C1	-1.5 (4)
O2—N2—C4—C3	-177.9 (3)	O3—N3—C6—C1	179.4 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 <i>A</i> \cdots O2 ⁱ	0.88	2.16	2.893 (3)	141
N1—H1 <i>B</i> \cdots O4 ⁱⁱ	0.88	2.36	3.139 (4)	148
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