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## 2-Bromo-4-nitroaniline

 Muhammad Nadeem Arshad,<sup>a</sup> M. Nawaz Tahir,<sup>b\*</sup>  
 Islam Ullah Khan<sup>a</sup> and Muhammad Shafiq<sup>a</sup>
<sup>a</sup>Department of Chemistry, Government College University, Lahore, Pakistan, and<sup>b</sup>Department of Physics, University of Sargodha, Sargodha, Pakistan

Correspondence e-mail: dmntahir\_uos@yahoo.com

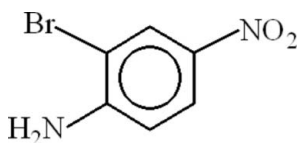
Received 1 February 2009; accepted 3 February 2009

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å;  $R$  factor = 0.039;  $wR$  factor = 0.092; data-to-parameter ratio = 15.4.

In the molecule of the title compound,  $\text{C}_6\text{H}_5\text{BrN}_2\text{O}_2$ , the dihedral angle between the nitro group and the aromatic ring is  $4.57$  ( $4$ )°. An intramolecular  $\text{N}-\text{H}\cdots\text{Br}$  interaction results in the formation of a planar five-membered ring, which is oriented with respect to the aromatic ring at a dihedral angle of  $1.64$  ( $6$ )°. In the crystal structure, intermolecular  $\text{N}-\text{H}\cdots\text{N}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules.

## Related literature

For related structures, see: Arshad *et al.* (2008, 2009); McPhail & Sim (1965); McWilliam *et al.* (2001); Krishna Mohan *et al.* (2004).



## Experimental

## Crystal data

 $\text{C}_6\text{H}_5\text{BrN}_2\text{O}_2$  $M_r = 217.03$ Orthorhombic,  $Pna2_1$  $a = 11.098$  (3) Å $b = 16.763$  (4) Å $c = 3.9540$  (9) Å $V = 735.6$  (3) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 5.53$  mm<sup>-1</sup> $T = 296$  (2) K $0.26 \times 0.12 \times 0.10$  mm

## Data collection

Bruker Kappa APEXII CCD  
diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.450$ ,  $T_{\max} = 0.578$ 

4932 measured reflections

1542 independent reflections

986 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.058$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$  $wR(F^2) = 0.092$  $S = 1.00$ 

1542 reflections

100 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.50$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.62$  e Å<sup>-3</sup>

Absolute structure: Flack (1983),

469 Friedel pairs

Flack parameter: 0.01 (2)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{N1}^i$	0.86	2.32	3.158 (7)	167.00
$\text{N1}-\text{H1B}\cdots\text{Br1}$	0.86	2.68	3.095 (5)	111.00
$\text{N1}-\text{H1B}\cdots\text{O2}^{ii}$	0.86	2.32	3.049 (7)	143.00

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2621).

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## supporting information

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## 2-Bromo-4-nitroaniline

Muhammad Nadeem Arshad, M. Nawaz Tahir, Islam Ullah Khan and Muhammad Shafiq

### S1. Comment

The title compound, (I), has been prepared as an intermediate for the synthesis of sulfonamides (Arshad *et al.*, 2009) and benzothiazines (Arshad *et al.*, 2008).

The crystal structures of 2-iodo-4-nitroaniline, (II) (McWilliam *et al.*, 2001) and 2-chloro-4-nitroaniline, (III) (McPhail & Sim, 1965) have been reported. The title compound, (I), (Fig 1) is structural isomer of (III). It is essentially planar. The dihedral angle between the nitro group (O1/O2/N2) and the aromatic ring A (C1-C6) is 4.57 (4)°. The intramolecular N-H...Br interaction (Table 1) results in the formation of a planar five-membered ring (Br1/N1/C3/C4/H1B), which is oriented with respect to ring A at a dihedral angle of 1.64 (6)°. So, they are nearly coplanar.

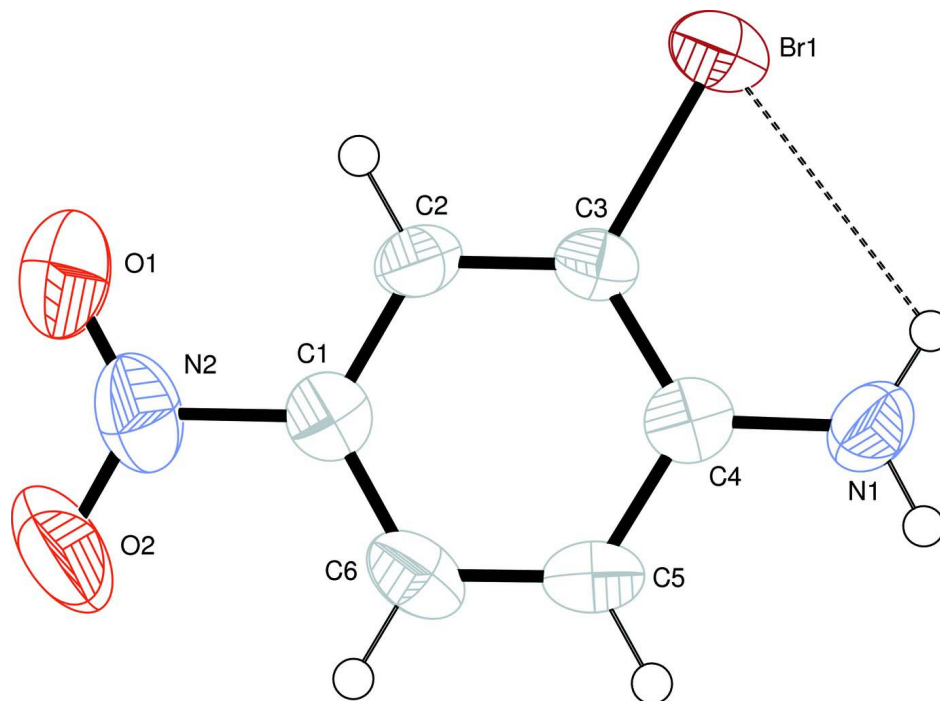
In the crystal structure, intermolecular N-H...N and N-H...O hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they may be effective in the stabilization of the structure.

### S2. Experimental

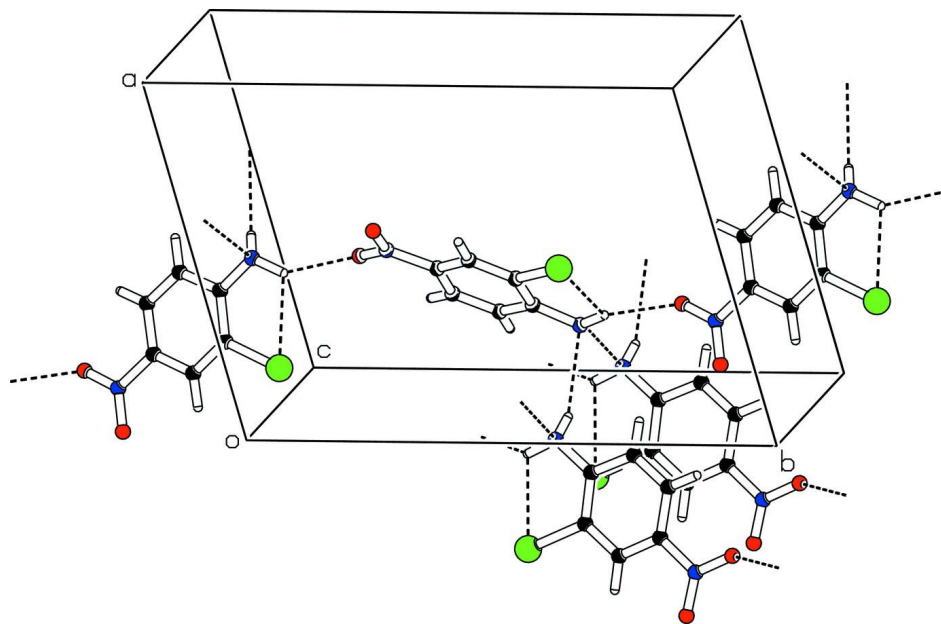
The title compound was synthesized following the method available in literature (Krishna Mohan *et al.*, 2004). 4-Nitroaniline (6 g, 0.0435 mol) and ammonium bromide (4.5 g, 0.0479 mol) were charged to a flask (50 ml) containing acetic acid (30 ml). Hydrogen peroxide (1.629 g, 0.0479 mol, 35%) was added dropwise to the mixture, and stirred at room temperature for 3 h. Then, the obtained precipitate was filtered and washed with water and recrystallized in dichloromethane and methanol.

### S3. Refinement

H-atoms were positioned geometrically, with N-H = 0.86 Å (for NH<sub>2</sub>) and C-H = 0.93 Å for aromatic H, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bond is shown as dashed line.

**Figure 2**

A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

**2-Bromo-4-nitroaniline***Crystal data*C<sub>6</sub>H<sub>5</sub>BrN<sub>2</sub>O<sub>2</sub> $M_r = 217.03$ Orthorhombic, *Pna*2<sub>1</sub>

Hall symbol: P 2c -2n

 $a = 11.098$  (3) Å $b = 16.763$  (4) Å $c = 3.9540$  (9) Å $V = 735.6$  (3) Å<sup>3</sup> $Z = 4$  $F(000) = 424$  $D_x = 1.960$  Mg m<sup>-3</sup>Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1542 reflections

 $\theta = 3.1$ – $28.6^\circ$  $\mu = 5.53$  mm<sup>-1</sup> $T = 296$  K

Needle, yellow

 $0.26 \times 0.12 \times 0.10$  mm*Data collection*

Bruker Kappa APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 7.40 pixels mm<sup>-1</sup> $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.450$ ,  $T_{\max} = 0.578$ 

4932 measured reflections

1542 independent reflections

986 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.058$  $\theta_{\max} = 28.6^\circ$ ,  $\theta_{\min} = 3.1^\circ$  $h = -13 \rightarrow 14$  $k = -22 \rightarrow 22$  $l = -3 \rightarrow 5$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$  $wR(F^2) = 0.092$  $S = 1.00$ 

1542 reflections

100 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.50$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.62$  e Å<sup>-3</sup>

Absolute structure: Flack (1983), 469 Friedel

pairs

Absolute structure parameter: 0.01 (2)

*Special details*

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**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 (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.34261 (5)	0.56438 (3)	0.7237 (2)	0.0524 (2)
O1	0.4834 (5)	0.2673 (3)	0.5214 (15)	0.088 (3)
O2	0.3637 (4)	0.1882 (2)	0.763 (3)	0.101 (2)

N1	0.1095 (4)	0.5118 (3)	1.0912 (13)	0.0510 (18)
N2	0.3960 (5)	0.2544 (3)	0.689 (2)	0.064 (2)
C1	0.3231 (4)	0.3212 (3)	0.8007 (18)	0.043 (3)
C2	0.3615 (4)	0.3974 (3)	0.730 (3)	0.0420 (17)
C3	0.2913 (5)	0.4600 (3)	0.8270 (13)	0.0347 (19)
C4	0.1833 (5)	0.4491 (3)	0.9987 (15)	0.0377 (17)
C5	0.1479 (5)	0.3705 (4)	1.0711 (16)	0.048 (2)
C6	0.2169 (5)	0.3076 (3)	0.9745 (17)	0.051 (2)
H1A	0.04332	0.50258	1.19738	0.0611*
H1B	0.12976	0.55993	1.04260	0.0611*
H2	0.43405	0.40604	0.61823	0.0502*
H5	0.07627	0.36137	1.18676	0.0576*
H6	0.19297	0.25579	1.02478	0.0605*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0557 (3)	0.0436 (3)	0.0578 (4)	-0.0094 (3)	-0.0026 (7)	0.0100 (5)
O1	0.075 (4)	0.077 (4)	0.112 (5)	0.028 (3)	0.016 (4)	-0.009 (3)
O2	0.110 (4)	0.037 (2)	0.157 (6)	0.010 (2)	0.000 (5)	-0.006 (5)
N1	0.035 (2)	0.056 (3)	0.062 (4)	0.001 (2)	0.003 (2)	-0.008 (2)
N2	0.063 (3)	0.051 (3)	0.078 (5)	0.017 (3)	-0.018 (5)	-0.007 (5)
C1	0.041 (3)	0.046 (3)	0.041 (7)	0.001 (2)	-0.010 (3)	0.000 (3)
C2	0.034 (3)	0.049 (3)	0.043 (3)	-0.001 (2)	0.005 (5)	0.009 (6)
C3	0.034 (3)	0.037 (3)	0.033 (4)	-0.007 (2)	-0.007 (2)	0.002 (2)
C4	0.038 (3)	0.049 (3)	0.026 (3)	-0.002 (3)	-0.012 (3)	0.000 (3)
C5	0.043 (3)	0.053 (4)	0.047 (4)	-0.015 (3)	0.002 (3)	0.006 (3)
C6	0.056 (4)	0.037 (3)	0.059 (5)	-0.008 (3)	-0.018 (4)	0.005 (3)

*Geometric parameters (Å, °)*

Br1—C3	1.885 (5)	C1—C2	1.375 (7)
O1—N2	1.195 (9)	C2—C3	1.362 (8)
O2—N2	1.202 (7)	C3—C4	1.390 (8)
N1—C4	1.382 (7)	C4—C5	1.404 (8)
N2—C1	1.450 (8)	C5—C6	1.358 (8)
N1—H1B	0.8600	C2—H2	0.9300
N1—H1A	0.8600	C5—H5	0.9300
C1—C6	1.383 (8)	C6—H6	0.9300
Br1...N1	3.095 (5)	C5...C1 <sup>ix</sup>	3.576 (9)
Br1...H1B	2.6800	C5...C2 <sup>ix</sup>	3.551 (11)
Br1...H2 <sup>i</sup>	2.9700	C6...C1 <sup>ix</sup>	3.480 (10)
O1...C6 <sup>ii</sup>	3.391 (8)	C6...O1 <sup>x</sup>	3.391 (8)
O2...N1 <sup>iii</sup>	3.049 (7)	C4...H1A <sup>v</sup>	2.9000
O1...H2	2.4200	H1A...H5	2.4000
O1...H5 <sup>iv</sup>	2.7300	H1A...N1 <sup>v</sup>	2.9500
O2...H6	2.4400	H1A...N1 <sup>vi</sup>	2.3200

O2...H1B <sup>iii</sup>	2.3200	H1A...C4 <sup>vi</sup>	2.9000
N1...Br1	3.095 (5)	H1A...H1A <sup>v</sup>	2.2000
N1...N1 <sup>v</sup>	3.158 (7)	H1A...H1A <sup>vi</sup>	2.2000
N1...N1 <sup>vi</sup>	3.158 (7)	H1A...H1B <sup>vi</sup>	2.5800
N1...O2 <sup>vii</sup>	3.049 (7)	H1B...Br1	2.6800
N1...H1A <sup>v</sup>	2.3200	H1B...H1A <sup>v</sup>	2.5800
N1...H1A <sup>vi</sup>	2.9500	H1B...O2 <sup>vii</sup>	2.3200
C1...C5 <sup>viii</sup>	3.576 (9)	H2...O1	2.4200
C1...C6 <sup>viii</sup>	3.480 (10)	H2...Br1 <sup>xi</sup>	2.9700
C2...C5 <sup>viii</sup>	3.551 (11)	H5...H1A	2.4000
C3...C4 <sup>viii</sup>	3.492 (8)	H5...O1 <sup>xii</sup>	2.7300
C4...C3 <sup>ix</sup>	3.492 (8)	H6...O2	2.4400
O1—N2—O2	123.0 (6)	C2—C3—C4	122.0 (5)
O1—N2—C1	118.8 (5)	N1—C4—C5	119.6 (5)
O2—N2—C1	118.2 (6)	N1—C4—C3	122.7 (5)
H1A—N1—H1B	120.00	C3—C4—C5	117.7 (5)
C4—N1—H1A	120.00	C4—C5—C6	120.9 (5)
C4—N1—H1B	120.00	C1—C6—C5	119.5 (5)
N2—C1—C6	120.0 (5)	C1—C2—H2	121.00
N2—C1—C2	118.8 (5)	C3—C2—H2	121.00
C2—C1—C6	121.2 (5)	C4—C5—H5	120.00
C1—C2—C3	118.8 (6)	C6—C5—H5	120.00
Br1—C3—C2	118.8 (4)	C1—C6—H6	120.00
Br1—C3—C4	119.2 (4)	C5—C6—H6	120.00
O1—N2—C1—C2	-4.5 (11)	C1—C2—C3—C4	0.9 (12)
O1—N2—C1—C6	175.4 (7)	Br1—C3—C4—N1	1.6 (8)
O2—N2—C1—C2	177.4 (9)	Br1—C3—C4—C5	179.9 (4)
O2—N2—C1—C6	-2.8 (11)	C2—C3—C4—N1	-178.3 (7)
N2—C1—C2—C3	178.2 (7)	C2—C3—C4—C5	0.1 (10)
C6—C1—C2—C3	-1.6 (13)	N1—C4—C5—C6	178.1 (6)
N2—C1—C6—C5	-178.5 (6)	C3—C4—C5—C6	-0.3 (9)
C2—C1—C6—C5	1.4 (11)	C4—C5—C6—C1	-0.4 (10)
C1—C2—C3—Br1	-179.0 (6)		

Symmetry codes: (i)  $-x+1, -y+1, z+1/2$ ; (ii)  $x+1/2, -y+1/2, z$ ; (iii)  $-x+1/2, y-1/2, z-1/2$ ; (iv)  $x+1/2, -y+1/2, z-1$ ; (v)  $-x, -y+1, z-1/2$ ; (vi)  $-x, -y+1, z+1/2$ ; (vii)  $-x+1/2, y+1/2, z+1/2$ ; (viii)  $x, y, z-1$ ; (ix)  $x, y, z+1$ ; (x)  $x-1/2, -y+1/2, z$ ; (xi)  $-x+1, -y+1, z-1/2$ ; (xii)  $x-1/2, -y+1/2, z+1$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A...N1 <sup>vi</sup>	0.86	2.32	3.158 (7)	167.00
N1—H1B...Br1	0.86	2.68	3.095 (5)	111.00
N1—H1B...O2 <sup>vii</sup>	0.86	2.32	3.049 (7)	143.00

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