

2-Bromo-4-nitroaniline

Muhammad Nadeem Arshad,^a M. Nawaz Tahir,^{b*}
Islam Ullah Khan^a and Muhammad Shafiq^a

^aDepartment of Chemistry, Government College University, Lahore, Pakistan, and

^bDepartment of Physics, University of Sargodha, Sargodha, Pakistan

Correspondence e-mail: dmntahir_uos@yahoo.com

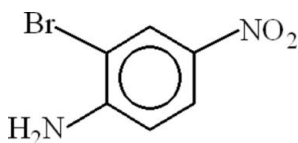
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.039; wR factor = 0.092; data-to-parameter ratio = 15.4.

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) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 5.53$ mm⁻¹

$T = 296$ (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⁻³

$\Delta\rho_{\text{min}} = -0.62$ e Å⁻³

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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supplementary materials

Acta Cryst. (2009). E65, o480 [doi:10.1107/S1600536809004073]

2-Bromo-4-nitroaniline

M. N. Arshad, M. N. Tahir, I. U. Khan and M. Shafiq

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.

Experimental

The title compound was synthesized following the method available in literature (Krishna Mohan *et al.*, 2004). 4-Nitro aniline (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.

Refinement

H-atoms were positioned geometrically, with N-H = 0.86 Å (for NH₂) and C-H = 0.93 Å for aromatic H, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Figures

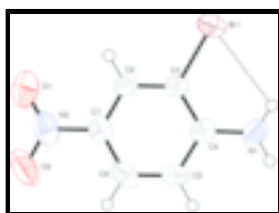


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bond is shown as dashed line.

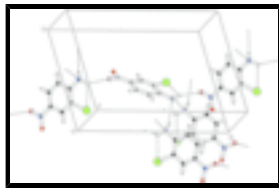


Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

2-Bromo-4-nitroaniline

Crystal data

$C_6H_5BrN_2O_2$

$M_r = 217.03$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 11.098$ (3) Å

$b = 16.763$ (4) Å

$c = 3.9540$ (9) Å

$V = 735.6$ (3) Å³

$Z = 4$

$F_{000} = 424$

$D_x = 1.960$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1542 reflections

$\theta = 3.1$ – 28.6°

$\mu = 5.53$ mm⁻¹

$T = 296$ 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

Monochromator: graphite

Detector resolution: 7.40 pixels mm⁻¹

$T = 296$ K

ω 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

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⁻³

$\Delta\rho_{\min} = -0.62$ e Å⁻³

Extinction correction: none

Absolute structure: Flack (1983), 469 Friedel pairs

Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 Flack 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 (\AA^2)

	<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 (\AA^2)

	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)

supplementary materials

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 ^{ix}	3.576 (9)
Br1…H1B	2.6800	C5…C2 ^{ix}	3.551 (11)
Br1…H2 ⁱ	2.9700	C6…C1 ^{ix}	3.480 (10)
O1…C6 ⁱⁱ	3.391 (8)	C6…O1 ^x	3.391 (8)
O2…N1 ⁱⁱⁱ	3.049 (7)	C4…H1A ^v	2.9000
O1…H2	2.4200	H1A…H5	2.4000
O1…H5 ^{iv}	2.7300	H1A…N1 ^v	2.9500
O2…H6	2.4400	H1A…N1 ^{vi}	2.3200
O2…H1B ⁱⁱⁱ	2.3200	H1A…C4 ^{vi}	2.9000
N1…Br1	3.095 (5)	H1A…H1A ^v	2.2000
N1…N1 ^v	3.158 (7)	H1A…H1A ^{vi}	2.2000
N1…N1 ^{vi}	3.158 (7)	H1A…H1B ^{vi}	2.5800
N1…O2 ^{vii}	3.049 (7)	H1B…Br1	2.6800
N1…H1A ^v	2.3200	H1B…H1A ^v	2.5800
N1…H1A ^{vi}	2.9500	H1B…O2 ^{vii}	2.3200
C1…C5 ^{viii}	3.576 (9)	H2…O1	2.4200
C1…C6 ^{viii}	3.480 (10)	H2…Br1 ^{xi}	2.9700
C2…C5 ^{viii}	3.551 (11)	H5…H1A	2.4000
C3…C4 ^{viii}	3.492 (8)	H5…O1 ^{xiii}	2.7300
C4…C3 ^{ix}	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 ($\text{\AA}, ^\circ$)

<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—H1A \cdots N1 ^{vi}	0.86	2.32	3.158 (7)	167.00
N1—H1B \cdots Br1	0.86	2.68	3.095 (5)	111.00
N1—H1B \cdots O2 ^{vii}	0.86	2.32	3.049 (7)	143.00

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

Fig. 1

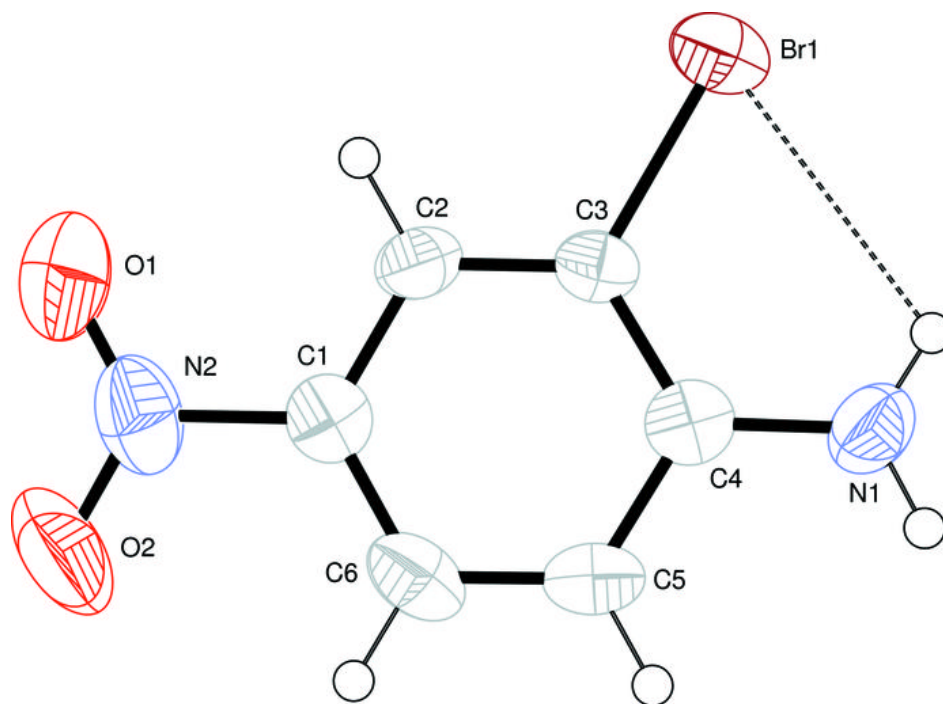


Fig. 2

