

6-Bromo-*N*-methylnaphthalen-2-amine

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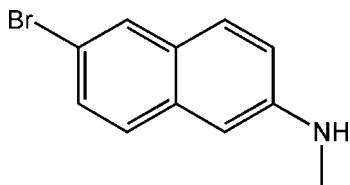
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.023; wR factor = 0.059; data-to-parameter ratio = 18.7.

In the structure of the title compound, $\text{C}_{11}\text{H}_{10}\text{BrN}$, all the atoms are coplanar, with the exception of two methyl H atoms, and the geometric parameters around the N atom are consistent with an sp^2 -hybridized atom.

Related literature

For related literature, see: Bienko *et al.* (2003); Brady *et al.* (1982); Chanh *et al.* (1973, 1976); Gao *et al.* (2005); Jameson & Penfold (1965); McCarthy & Huffman (1984); Sigouin *et al.* (2007).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{10}\text{BrN}$

$M_r = 236.11$

Orthorhombic, $P2_12_12_1$

$a = 6.1511$ (10) Å

$b = 11.4414$ (18) Å

$c = 13.593$ (2) Å

$V = 956.6$ (3) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 4.25$ mm⁻¹

$T = 200$ (2) K

$0.03 \times 0.03 \times 0.02$ mm

Data collection

Bruker SMART APEXII CCD diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)

$T_{\min} = 0.883$, $T_{\max} = 0.920$

11718 measured reflections

2296 independent reflections

2131 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.059$

$S = 1.08$

2296 reflections

123 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.51$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Absolute structure: Flack (1983),

940 Friedel pairs

Flack parameter: 0.013 (11)

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); 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: OM2168).

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supplementary materials

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Comment

The use of boronic acids as fluorescent anion or saccharide detectors generates a lot of interest in the scientific community. In the course of our study on the fluorescence of coordinated boronic acids (Sigouin *et al.*, 2007), the synthesis of the previously reported precursor 6-(*N*-methyl)-2-bromonaphthalene, (**1**), has been carried out. (Gao *et al.*, 2005) The C—Br distance observed for **1** (1.904 (2) Å) is similar to the average distance observed (1.897 Å) in the analogue 2,6-dibromonaphthalene, (**2**). (Chanh *et al.*, 1976) The average C—C distance in **1** (1.397 Å) is within the range attributed for aromatic C—C bonds in bromine containing naphthalene products (Bienko *et al.*, 2003; Brady *et al.*, 1982; Chanh *et al.*, 1973; Jameson & Penfold, 1965; and McCarthy & Huffman, 1984) and compares to the average C—C distance observed for **2** (1.403 Å). The nitrogen atom in the molecule is strongly sp^2 hybridized with a small sp^3 contribution. Indeed, the N—H bond distance of 0.80 (3) Å and the sum of the angles around the nitrogen atom was found to be 357°. Furthermore, C—N bond distances of 1.366 (3) Å and 1.410 (4) Å were observed for the aromatic and methyl carbons, respectively. This results in a high level of planarity in the molecule, all non-hydrogen atoms being in the same plane with an average deviation of 0.019 Å. The amine hydrogen was found to be slightly out of the plane, with a deviation of 0.20 (3) Å.

Experimental

In a digestion bomb, a suspension of sodium metabisulfite (4.868 g; 25.6 mmol) in water (12.0 ml; 673 mmol) was added to 6-bromo-2-naphthol. Methylamine (40%; 6.0 ml; 69.7 mmol) and a magnetic bar were added to the reaction mixture upon which the bomb was sealed and put in a 140°C sand bath. The reaction was allowed to proceed with stirring for 4 days. The bomb was then cooled down to room temperature and 150 ml of dichloromethane was added. The resulting solution was washed with 5% sodium bicarbonate (3 x 100 ml). The combined organic layers were dried on sodium sulfate, filtered, and the solvent was removed under vacuum. The resulting crude solid was dissolved in a 50/50 dichloromethane/hexane solution and filtered upon which the filtrate was placed in a -78°C freezer overnight to afford yellow crystals of quality for X-ray determination (1.87 g; 59% yield). See (Gao *et al.*, 2005) for complete characterization of **1**.

Refinement

All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions with C—H = 0.93 Å and refined using a riding model. The N—H hydrogen was found in the Fourier map and freely refined.

Figures

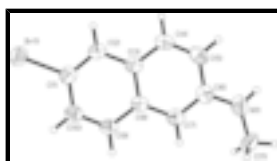


Fig. 1. ORTEP view of **1** showing the numbering scheme adopted. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Amide hydrogen atom is represented by a sphere of arbitrary size.

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Crystal data

$C_{11}H_{10}BrN$	$F_{000} = 472$
$M_r = 236.11$	$D_x = 1.639 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
Hall symbol: P2ac2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 6.1511 (10) \text{ \AA}$	Cell parameters from 6010 reflections
$b = 11.4414 (18) \text{ \AA}$	$\theta = 2.3\text{--}27.9^\circ$
$c = 13.593 (2) \text{ \AA}$	$\mu = 4.25 \text{ mm}^{-1}$
$V = 956.6 (3) \text{ \AA}^3$	$T = 200 (2) \text{ K}$
$Z = 4$	Block, yellow
	$0.03 \times 0.03 \times 0.02 \text{ mm}$

Data collection

Bruker SMART APEXII CCD diffractometer	2296 independent reflections
Radiation source: fine-focus sealed tube	2131 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.022$
$T = 200(2) \text{ K}$	$\theta_{\text{max}} = 28.1^\circ$
ω scans	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.883$, $T_{\text{max}} = 0.920$	$k = -15 \rightarrow 15$
11718 measured reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.023$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.1339P]$
$wR(F^2) = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2296 reflections	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
123 parameters	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983)
	Flack parameter: 0.013 (11)

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 $F^2 > 2\sigma(F^2)$ 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	0.02701 (4)	0.07982 (2)	0.219138 (17)	0.04903 (9)
N1	0.4568 (4)	0.61887 (18)	0.57589 (17)	0.0505 (5)
H1	0.404 (6)	0.627 (3)	0.629 (2)	0.065 (10)*
C1	0.1627 (4)	0.20347 (18)	0.29007 (15)	0.0367 (4)
C2	0.0600 (3)	0.25158 (17)	0.36901 (14)	0.0346 (4)
H2	-0.0752	0.2235	0.3886	0.042*
C3	0.1590 (4)	0.34425 (18)	0.42120 (15)	0.0333 (4)
C4	0.0647 (4)	0.39478 (18)	0.50625 (15)	0.0378 (5)
H4	-0.0688	0.3673	0.5285	0.045*
C5	0.1639 (4)	0.4816 (2)	0.55557 (17)	0.0424 (5)
H5	0.0977	0.5122	0.6114	0.051*
C6	0.3677 (4)	0.52793 (18)	0.52452 (16)	0.0385 (5)
C7	0.4655 (4)	0.47950 (17)	0.44267 (14)	0.0363 (4)
H7	0.5990	0.5082	0.4215	0.044*
C8	0.3662 (4)	0.38702 (16)	0.39064 (14)	0.0321 (4)
C9	0.4653 (4)	0.33294 (19)	0.30813 (14)	0.0370 (4)
H9	0.5999	0.3597	0.2866	0.044*
C10	0.3683 (4)	0.2428 (2)	0.25961 (14)	0.0394 (5)
H10	0.4379	0.2075	0.2066	0.047*
C11	0.6590 (5)	0.6708 (2)	0.5542 (2)	0.0579 (7)
H11A	0.7725	0.6140	0.5620	0.087*
H11B	0.6839	0.7351	0.5982	0.087*
H11C	0.6582	0.6987	0.4876	0.087*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.05551 (14)	0.04969 (14)	0.04188 (12)	-0.01171 (11)	-0.00164 (10)	-0.00494 (10)
N1	0.0664 (14)	0.0419 (10)	0.0433 (11)	-0.0044 (10)	0.0010 (11)	-0.0046 (8)
C1	0.0403 (11)	0.0379 (10)	0.0319 (9)	-0.0031 (8)	-0.0042 (9)	0.0046 (9)
C2	0.0303 (10)	0.0379 (10)	0.0357 (10)	-0.0005 (9)	-0.0016 (8)	0.0074 (8)
C3	0.0328 (12)	0.0356 (10)	0.0314 (10)	0.0042 (9)	0.0014 (8)	0.0081 (8)

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C4	0.0338 (11)	0.0392 (11)	0.0404 (11)	0.0047 (9)	0.0071 (9)	0.0078 (8)
C5	0.0461 (14)	0.0424 (12)	0.0388 (11)	0.0108 (11)	0.0067 (10)	0.0027 (9)
C6	0.0489 (13)	0.0302 (10)	0.0364 (11)	0.0069 (10)	-0.0021 (10)	0.0061 (8)
C7	0.0368 (11)	0.0362 (10)	0.0360 (10)	0.0001 (10)	0.0008 (9)	0.0078 (8)
C8	0.0311 (10)	0.0326 (10)	0.0325 (9)	0.0032 (8)	0.0003 (8)	0.0076 (7)
C9	0.0325 (10)	0.0442 (11)	0.0343 (9)	-0.0015 (9)	0.0046 (8)	0.0043 (8)
C10	0.0402 (11)	0.0452 (12)	0.0328 (10)	0.0001 (10)	0.0035 (8)	0.0016 (8)
C11	0.0426 (16)	0.0514 (15)	0.0797 (19)	-0.0058 (12)	-0.0090 (14)	-0.0209 (14)

Geometric parameters (Å, °)

Br1—C1	1.905 (2)	C9—C10	1.362 (3)
C2—C1	1.361 (3)	C9—C8	1.419 (3)
C2—C3	1.414 (3)	C9—H9	0.9300
C2—H2	0.9300	C6—N1	1.368 (3)
C1—C10	1.405 (3)	C6—C5	1.425 (3)
C3—C4	1.417 (3)	C5—H5	0.9300
C3—C8	1.427 (3)	C10—H10	0.9300
C4—C5	1.344 (3)	C11—N1	1.410 (4)
C4—H4	0.9300	C11—H11A	0.9600
C7—C6	1.381 (3)	C11—H11B	0.9600
C7—C8	1.412 (3)	C11—H11C	0.9600
C7—H7	0.9300	N1—H1	0.80 (3)
C1—C2—C3	119.93 (19)	C7—C6—C5	118.2 (2)
C1—C2—H2	120.0	C4—C5—C6	121.8 (2)
C3—C2—H2	120.0	C4—C5—H5	119.1
C2—C1—C10	121.4 (2)	C6—C5—H5	119.1
C2—C1—Br1	119.74 (16)	C7—C8—C9	122.5 (2)
C10—C1—Br1	118.90 (17)	C7—C8—C3	119.9 (2)
C2—C3—C4	122.64 (19)	C9—C8—C3	117.67 (19)
C2—C3—C8	119.73 (19)	C9—C10—C1	119.6 (2)
C4—C3—C8	117.6 (2)	C9—C10—H10	120.2
C5—C4—C3	121.5 (2)	C1—C10—H10	120.2
C5—C4—H4	119.2	N1—C11—H11A	109.5
C3—C4—H4	119.2	N1—C11—H11B	109.5
C6—C7—C8	121.0 (2)	H11A—C11—H11B	109.5
C6—C7—H7	119.5	N1—C11—H11C	109.5
C8—C7—H7	119.5	H11A—C11—H11C	109.5
C10—C9—C8	121.7 (2)	H11B—C11—H11C	109.5
C10—C9—H9	119.2	C6—N1—C11	124.6 (2)
C8—C9—H9	119.2	C6—N1—H1	113 (2)
N1—C6—C7	122.8 (2)	C11—N1—H1	120 (2)
N1—C6—C5	119.0 (2)		
C3—C2—C1—C10	1.0 (3)	C6—C7—C8—C3	1.5 (3)
C3—C2—C1—Br1	-179.29 (15)	C10—C9—C8—C7	179.12 (19)
C1—C2—C3—C4	-177.36 (19)	C10—C9—C8—C3	-0.4 (3)
C1—C2—C3—C8	0.1 (3)	C2—C3—C8—C7	-179.94 (18)
C2—C3—C4—C5	178.9 (2)	C4—C3—C8—C7	-2.3 (3)
C8—C3—C4—C5	1.3 (3)	C2—C3—C8—C9	-0.4 (3)

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C8—C7—C6—N1	-178.84 (19)	C4—C3—C8—C9	177.21 (18)
C8—C7—C6—C5	0.4 (3)	C8—C9—C10—C1	1.5 (3)
C3—C4—C5—C6	0.5 (3)	C2—C1—C10—C9	-1.8 (3)
N1—C6—C5—C4	177.8 (2)	Br1—C1—C10—C9	178.48 (16)
C7—C6—C5—C4	-1.4 (3)	C7—C6—N1—C11	-2.2 (4)
C6—C7—C8—C9	-178.03 (18)	C5—C6—N1—C11	178.6 (2)

Fig. 1

