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8-Bromo-2-methylquinoline

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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.071; wR factor = 0.195; data-to-parameter ratio = 16.0.

In the crystal structure of the title compound, $\text{C}_{10}\text{H}_8\text{BrN}$, the dihedral angle between the two six-membered rings of the quinoline system is $0.49(16)^\circ$. The molecules are packed in a face-to-face arrangement fashion, with a centroid-centroid distance of 3.76 Å between the benzene and pyridine rings of adjacent molecules. No hydrogen bonding is found in the crystal structure.

Related literature

The title compound is an important intermediate in the pharmaceutical industry, see: Shen & Hartwig (2006); Ranu *et al.* (2000); Lee & Hartwig (2005). For related structures, see: Amini *et al.* (2008); Fazaeli *et al.* (2008); Sattarzadeh *et al.* (2009).



Experimental

Crystal data

$\text{C}_{10}\text{H}_8\text{BrN}$

$M_r = 222.08$

Monoclinic, $P2_1/c$
 $a = 5.0440(17)$ Å
 $b = 13.467(4)$ Å
 $c = 13.391(4)$ Å
 $\beta = 97.678(4)^\circ$
 $V = 901.4(5)$ Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 4.50$ mm⁻¹
 $T = 291$ K
 $0.36 \times 0.31 \times 0.28$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.235$, $T_{\max} = 0.286$

4668 measured reflections
 1765 independent reflections
 1039 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.156$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.195$
 $S = 1.01$
 1765 reflections

110 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.88$ e Å⁻³
 $\Delta\rho_{\min} = -0.91$ e Å⁻³

Data collection: SMART (Bruker, 2003); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; 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); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2533).

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supplementary materials

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8-Bromo-2-methylquinoline

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Comment

The title compound, 8-bromo-2-methylquinoline, is an important intermediate of medicine industry (Shen & Hartwig, 2006; Ranu *et al.*, 2000; Lee & Hartwig, 2005). The unit-cell of the title compound contains four molecules, and the corresponding bond lengths and angles of these molecules are agree with each other. The molecules are stabilized by π - π stacking (centroids distance is 3.76 Å). Herein we report the synthesis and crystal structure of 8-bromo-2-methylquinoline. For more related structures, see: Amini *et al.*(2008), Fazaeli *et al.* (2008), Sattarzadeh *et al.* (2009).

Experimental

A solution of 2-bromoaniline (0.05 mol), boric acid (3.10 g) and 18% HCl (50 ml) was heated to reflux. Then a mixture of crotonaldehyde (0.06 mol) and 2-bromonitrobenzene (0.01 mol) was slowly added with stirring in 1 h. The reaction mixture was subsequently stirred at 373 K for another 2.5 h, and then an equimolar amount of anhydrous ZnCl₂ was added with vigorous stirring for 0.5 h. After the reaction was completed, the reaction solution was cooled in an ice bath and the crude brown solid was filtered, washed with 2-propanol, dissolved in the water, and neutralized with concentrated NH₃.H₂O solution to pH of 8. After cool immersed, filtrated and air dried, the product was obtained as a grey solid. Yield: 52.0%. m.p. 342–343 K. Crystals suitable for X-ray structure determination were obtained by slow evaporation of an ethanol solution at room temperature.

Refinement

The H-atoms were positioned geometrically, with C—H = 0.93 Å for aromatic, 0.96 Å for methyl, and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5 U_{\text{eq}}(\text{C})$.

Figures

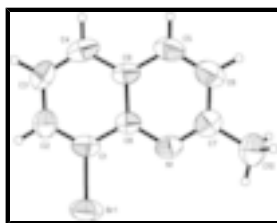


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids.

8-bromo-2-methylquinoline

Crystal data

C₁₀H₈BrN

$F_{000} = 440$

supplementary materials

$M_r = 222.08$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.0440$ (17) Å

$b = 13.467$ (4) Å

$c = 13.391$ (4) Å

$\beta = 97.678$ (4)°

$V = 901.4$ (5) Å³

$Z = 4$

$D_x = 1.636$ Mg m⁻³

Melting point: 343 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1765 reflections

$\theta = 2.2$ – 26.0 °

$\mu = 4.50$ mm⁻¹

$T = 291$ K

Block, colourless

$0.36 \times 0.31 \times 0.28$ mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291$ K

φ and ω scans

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

$T_{\min} = 0.235$, $T_{\max} = 0.286$

4668 measured reflections

1765 independent reflections

1039 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.156$

$\theta_{\max} = 26.0$ °

$\theta_{\min} = 2.2$ °

$h = -6$ → 6

$k = -13$ → 16

$l = -15$ → 16

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.071$

$wR(F^2) = 0.195$

$S = 1.01$

1765 reflections

110 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0989P)^2]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.88$ e Å⁻³

$\Delta\rho_{\min} = -0.91$ e Å⁻³

Extinction correction: none

Special details

Experimental. ¹H NMR (CDCl₃, 400 MHz) δ : 2.82 (s, 3H, CH₃), 7.33(m, 2H, quinoline 3,6-H), 7.73 (dd, J=8.0 Hz, J=1.2 Hz, 1H, quinoline 7-H), 8.02 (m, 2H, quinoline 4,5-H).

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	1.04425 (17)	0.41478 (5)	0.40291 (5)	0.0783 (4)
N1	0.6713 (11)	0.2556 (3)	0.2991 (3)	0.0507 (12)
C1	0.9974 (14)	0.3782 (4)	0.2655 (4)	0.0536 (16)
C8	0.8122 (12)	0.3021 (4)	0.2325 (4)	0.0429 (13)
C9	0.7845 (13)	0.2775 (4)	0.1287 (4)	0.0517 (15)
C7	0.5039 (14)	0.1846 (4)	0.2646 (5)	0.0568 (16)
C2	1.1397 (14)	0.4256 (4)	0.2022 (6)	0.0586 (16)
H2	1.2578	0.4757	0.2266	0.070*
C5	0.6014 (14)	0.2003 (5)	0.0957 (5)	0.0643 (18)
H5	0.5778	0.1807	0.0285	0.077*
C3	1.1122 (15)	0.4004 (5)	0.0989 (5)	0.0621 (18)
H3	1.2156	0.4321	0.0561	0.074*
C6	0.4624 (16)	0.1559 (5)	0.1622 (5)	0.070 (2)
H6	0.3394	0.1064	0.1408	0.084*
C4	0.9318 (15)	0.3287 (5)	0.0624 (5)	0.068 (2)
H4	0.9066	0.3138	-0.0061	0.082*
C10	0.3468 (14)	0.1364 (5)	0.3370 (6)	0.0694 (19)
H10A	0.3969	0.0677	0.3444	0.104*
H10B	0.1596	0.1412	0.3123	0.104*
H10C	0.3821	0.1690	0.4011	0.104*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1139 (9)	0.0735 (6)	0.0436 (4)	-0.0082 (4)	-0.0042 (4)	-0.0114 (3)
N1	0.059 (3)	0.050 (3)	0.042 (3)	0.011 (3)	0.004 (2)	0.005 (2)
C1	0.074 (5)	0.044 (3)	0.040 (3)	0.005 (3)	-0.001 (3)	-0.001 (2)
C8	0.037 (3)	0.050 (3)	0.040 (3)	0.012 (3)	0.001 (2)	-0.001 (2)
C9	0.054 (4)	0.063 (3)	0.037 (3)	0.009 (3)	0.002 (3)	-0.001 (3)
C7	0.059 (4)	0.053 (3)	0.059 (4)	0.011 (3)	0.009 (3)	0.007 (3)
C2	0.051 (4)	0.055 (3)	0.070 (4)	0.002 (3)	0.010 (3)	0.004 (3)
C5	0.057 (5)	0.083 (4)	0.050 (4)	0.003 (4)	-0.006 (3)	-0.015 (3)
C3	0.054 (5)	0.073 (4)	0.063 (4)	0.004 (4)	0.021 (3)	0.013 (3)
C6	0.080 (6)	0.063 (4)	0.062 (4)	-0.002 (4)	-0.008 (4)	-0.007 (3)
C4	0.081 (6)	0.085 (5)	0.039 (3)	0.013 (4)	0.012 (3)	0.004 (3)
C10	0.054 (4)	0.068 (4)	0.088 (5)	0.002 (4)	0.015 (4)	0.007 (4)

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

Br1—C1	1.889 (6)	C2—H2	0.9300
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N1—C7	1.318 (8)	C5—C6	1.344 (10)
N1—C8	1.365 (7)	C5—H5	0.9300
C1—C2	1.344 (9)	C3—C4	1.371 (10)
C1—C8	1.416 (8)	C3—H3	0.9300
C8—C9	1.418 (7)	C6—H6	0.9300
C9—C4	1.411 (9)	C4—H4	0.9300
C9—C5	1.422 (9)	C10—H10A	0.9600
C7—C6	1.414 (8)	C10—H10B	0.9600
C7—C10	1.481 (9)	C10—H10C	0.9600
C2—C3	1.412 (10)		
C7—N1—C8	118.0 (5)	C6—C5—H5	120.2
C2—C1—C8	122.1 (6)	C9—C5—H5	120.2
C2—C1—Br1	118.9 (5)	C4—C3—C2	119.5 (6)
C8—C1—Br1	119.0 (4)	C4—C3—H3	120.2
N1—C8—C1	120.5 (5)	C2—C3—H3	120.2
N1—C8—C9	122.8 (5)	C5—C6—C7	119.9 (7)
C1—C8—C9	116.7 (5)	C5—C6—H6	120.1
C4—C9—C8	120.8 (6)	C7—C6—H6	120.1
C4—C9—C5	122.4 (6)	C3—C4—C9	119.9 (6)
C8—C9—C5	116.8 (5)	C3—C4—H4	120.1
N1—C7—C6	122.9 (6)	C9—C4—H4	120.1
N1—C7—C10	117.6 (6)	C7—C10—H10A	109.5
C6—C7—C10	119.5 (7)	C7—C10—H10B	109.5
C1—C2—C3	120.9 (6)	H10A—C10—H10B	109.5
C1—C2—H2	119.6	C7—C10—H10C	109.5
C3—C2—H2	119.6	H10A—C10—H10C	109.5
C6—C5—C9	119.6 (6)	H10B—C10—H10C	109.5

Fig. 1

