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2-Bromo-4-methylbenzonitrile

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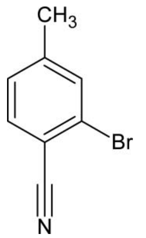
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.033; wR factor = 0.084; data-to-parameter ratio = 20.9.

The title molecule, C_8H_6BrN, is almost planar (r.m.s. deviation for the non-H atoms = 0.008 Å). In the crystal, weak π–π stacking interactions [centroid–centroid separations = 3.782 (2) and 3.919 (2) Å] generate [100] columns of molecules.

Related literature

For the synthesis, see: Johnson & Sandborn (1941). 2-Bromo-4-methylbenzonitrile derivatives are used as intermediates in the synthesis of phthalocyanine dyes. For applications of phthalocyanine dyes in photo redox reactions and photodynamic cancer therapy, see: Simon & Sirlin (1989); Simon *et al.* (1989).



Experimental

Crystal data

C_8H_6BrN
M_r = 196.05
Triclinic, $P\bar{1}$
a = 7.5168 (11) Å
b = 7.8383 (11) Å
c = 7.9428 (11) Å
α = 69.243 (7)°
β = 64.375 (8)°
γ = 87.567 (8)°
V = 391.14 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 5.17 mm^{-1}
T = 296 K
0.41 × 0.28 × 0.19 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007) T_{min} = 0.226, T_{max} = 0.440
8084 measured reflections
1921 independent reflections
1244 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.084
S = 1.01
1921 reflections
92 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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* (Farrugia, 1997) and *PLATON* (Spek, 2009); 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: HB5232).

References

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supplementary materials

Acta Cryst. (2009). E**65**, o3166   [**doi:10.1107/S1600536809048983**]

2-Bromo-4-methylbenzonitrile

M. Shahid, M. A. Munawar, S. Nadeem, W. Nasir and **M. Salim**

Comment

Synthesis of 2-bromo-4-methylbenzonitrile derivatives are important compounds due to their use as intermediates in the synthesis of phthalocyanine dyes. The substituted phthalocyanine dyes have been used for photo redox reactions (Simon & Sirlin, 1989) and photodynamic cancer therapy (Simon *et al.*. 1989).

The title compound(I) is almost planar. The cyano plane (C4/C8/N1) is oriented at a dihedral angle of 79.7 (3)° with respect to aromatic ring (C1/C2/C3/C4/C5/C6). The dihedral angle between the plane containing the methyl carbon (C1/C2/C6/C7) and aromatic ring plane is 0.22 (0.18)°. No significant intermolecular or intramolecular hydrogen bonding interaction has been observed in the molecule.

Experimental

3-Bromo-4-amino toluene (10 g, 54 mmol) (Johnson & Sandborn, 1941) was dissolved in HCl (30 ml, 17%). The mixture was cooled to 273 K in an ice-salt mixture. Over 5 min, an aqueous solution (9 ml) of $NaNO_2$ (4.3 g) was added to the above mixture. The temperature was maintained at 273-278 K. A mixture of aqueous solution (6%) of Cu(I)cyanide and KCN (40%) was heated to 333 K and added to the above cold neutralized diazonium salt solution. After work up of reaction, colourless blocks of (I) were obtained by the slow evaporation of water.

Refinement

The H atoms were geometrically placed (C—H = 0.93–0.96Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C).

Figures

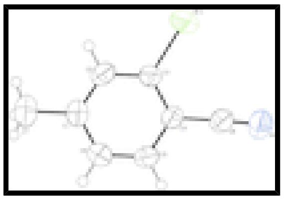

Fig. 1. The molecular structure of (I) with 50% displacement ellipsoids.

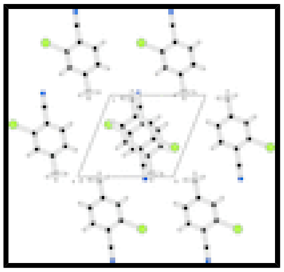
Fig. 2. Unit cell packing diagram.

2-bromo-4-methylbenzonitrile

Crystal data

C_8H_6BrN

$M_r = 196.05$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.5168 (11)$ Å

$b = 7.8383 (11)$ Å

$c = 7.9428 (11)$ Å

$\alpha = 69.243 (7)°$

$\beta = 64.375 (8)°$

$\gamma = 87.567 (8)°$

$V = 391.14 (10)$ Å^3

$Z = 2$

$F_{000} = 192$

$D_x = 1.665$ Mg m^{-3}

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

Cell parameters from 3073 reflections

$\theta = 2.2–21.2°$

$\mu = 5.17$ mm^{-1}

$T = 296$ K

Block, colourless

0.41 × 0.28 × 0.19 mm

Data collection

Bruker Kappa APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2007)

$T_{min} = 0.226$, $T_{max} = 0.440$

8084 measured reflections

1921 independent reflections

1244 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$

$\theta_{max} = 28.3°$

$\theta_{min} = 2.8°$

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.084$

$S = 1.01$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.2649P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

1921 reflections	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
92 parameters	$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.32613 (7)	0.89370 (4)	0.35907 (6)	0.07874 (19)
C1	0.2019 (4)	0.3498 (4)	0.7427 (4)	0.0525 (7)
C2	0.2395 (4)	0.5395 (4)	0.6606 (4)	0.0512 (7)
H2	0.2419	0.6033	0.7387	0.061*
C3	0.2732 (4)	0.6352 (4)	0.4660 (4)	0.0457 (6)
C4	0.2711 (4)	0.5439 (4)	0.3461 (4)	0.0445 (6)
C5	0.2349 (5)	0.3537 (4)	0.4270 (5)	0.0532 (7)
H5	0.2337	0.2899	0.3485	0.064*
C6	0.2008 (5)	0.2588 (4)	0.6222 (5)	0.0582 (8)
H6	0.1765	0.1310	0.6747	0.070*
C7	0.1639 (6)	0.2446 (5)	0.9569 (5)	0.0764 (10)
H7A	0.2191	0.3191	1.0006	0.115*
H7B	0.2253	0.1339	0.9654	0.115*
H7C	0.0231	0.2136	1.0415	0.115*
C8	0.3088 (5)	0.6413 (4)	0.1400 (5)	0.0540 (7)
N1	0.3389 (5)	0.7126 (4)	−0.0230 (5)	0.0771 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1226 (4)	0.0413 (2)	0.0893 (3)	0.01752 (18)	−0.0609 (3)	−0.02676 (18)
C1	0.0514 (18)	0.0578 (18)	0.0451 (17)	0.0061 (14)	−0.0231 (14)	−0.0136 (14)
C2	0.0571 (18)	0.0587 (18)	0.0515 (18)	0.0159 (14)	−0.0288 (15)	−0.0308 (15)
C3	0.0525 (17)	0.0403 (14)	0.0491 (17)	0.0096 (12)	−0.0251 (14)	−0.0193 (13)
C4	0.0449 (16)	0.0480 (16)	0.0410 (16)	0.0047 (12)	−0.0188 (13)	−0.0174 (13)
C5	0.0641 (19)	0.0478 (16)	0.0525 (18)	0.0029 (14)	−0.0249 (15)	−0.0249 (14)
C6	0.069 (2)	0.0437 (16)	0.056 (2)	0.0005 (14)	−0.0258 (16)	−0.0151 (15)
C7	0.086 (3)	0.085 (3)	0.050 (2)	0.007 (2)	−0.0321 (19)	−0.0132 (18)

C8	0.0586 (19)	0.0560 (18)	0.0478 (19)	−0.0003 (14)	−0.0225 (15)	−0.0205 (15)
N1	0.098 (2)	0.077 (2)	0.0512 (18)	−0.0056 (17)	−0.0332 (17)	−0.0171 (16)

Geometric parameters (Å, °)

Br1—C3	1.882 (3)	C4—C8	1.440 (4)
C1—C2	1.380 (4)	C5—C6	1.371 (4)
C1—C6	1.384 (4)	C5—H5	0.9300
C1—C7	1.503 (4)	C6—H6	0.9300
C2—C3	1.368 (4)	C7—H7A	0.9600
C2—H2	0.9300	C7—H7B	0.9600
C3—C4	1.384 (4)	C7—H7C	0.9600
C4—C5	1.383 (4)	C8—N1	1.133 (4)
C2—C1—C6	118.2 (3)	C6—C5—H5	119.9
C2—C1—C7	121.0 (3)	C4—C5—H5	119.9
C6—C1—C7	120.8 (3)	C5—C6—C1	121.2 (3)
C3—C2—C1	121.0 (3)	C5—C6—H6	119.4
C3—C2—H2	119.5	C1—C6—H6	119.4
C1—C2—H2	119.5	C1—C7—H7A	109.5
C2—C3—C4	120.8 (3)	C1—C7—H7B	109.5
C2—C3—Br1	119.6 (2)	H7A—C7—H7B	109.5
C4—C3—Br1	119.6 (2)	C1—C7—H7C	109.5
C5—C4—C3	118.6 (3)	H7A—C7—H7C	109.5
C5—C4—C8	119.6 (3)	H7B—C7—H7C	109.5
C3—C4—C8	121.8 (3)	N1—C8—C4	177.7 (3)
C6—C5—C4	120.3 (3)		

Fig. 1

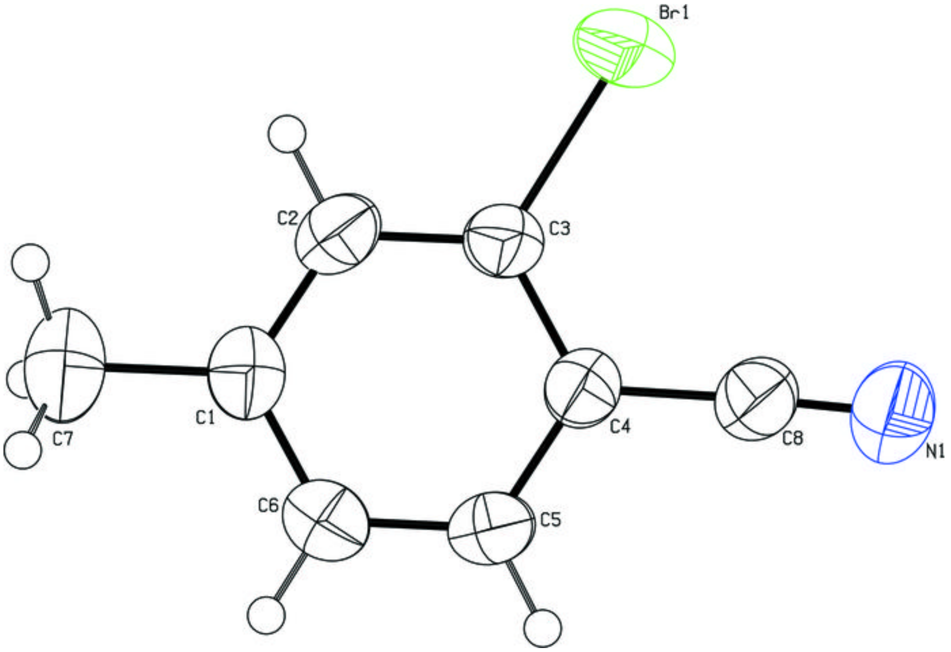

Fig. 2