



Crystal structure of 3-bromomethyl-2-chloro-6-(dibromomethyl)quinoline

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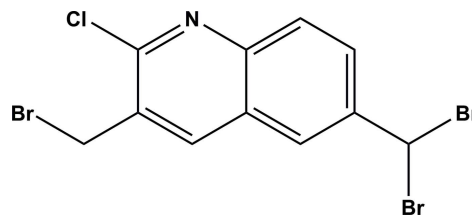
In the title compound, C₁₁H₇Br₃ClN, the quinoline ring system is approximately planar (r.m.s. = 0.011 Å). In the crystal, molecules are linked by C—H...Br interactions forming chains along [10 $\bar{1}$]. The chains are linked by C—H... π and π — π interactions involving inversion-related pyridine rings [intercentroid distance = 3.608 (4) Å], forming sheets parallel to (10 $\bar{1}$). Within the sheets, there are two significant short interactions involving a Br...Cl contact of 3.4904 (18) Å and a Br...N contact of 3.187 (6) Å, both of which are significantly shorter than the sum of their van der Waals radii.

Keywords: crystal structure; quinoline; bromoquinolines; halogen—halogen contacts; Br...Cl contacts; Br...N contacts; C—H...Br hydrogen bonds; π — π interactions.

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1. Related literature

The title compound is an important intermediate in the manufacture of materials such as organic light-emitting devices. For the synthesis of the title compound, see: Jones (1977); Lyle *et al.* (1972). For the biological activity of quinoline derivatives, see: Chauhan & Srivastava (2001); Ferrarini *et al.* (2000); Chen *et al.* (2001); Sahin *et al.* (2008).



2. Experimental

2.1. Crystal data

C₁₁H₇Br₃ClN
M_r = 428.36
Monoclinic, *P*2₁/*n*
a = 8.9042 (5) Å
b = 9.3375 (4) Å
c = 15.5107 (7) Å
 β = 104.553 (5)°

V = 1248.23 (11) Å³
Z = 4
Mo *K*α radiation
 μ = 9.88 mm^{−1}
T = 120 K
0.42 × 0.36 × 0.30 mm

2.2. Data collection

Oxford Diffraction Xcalibur
Sapphire3 Gemini ultra
diffractometer
Absorption correction: analytical
(*CrysAlis PRO*; Oxford)

Diffraction, 2010)
*T*_{min} = 0.056, *T*_{max} = 0.153
8597 measured reflections
2259 independent reflections
1889 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029

2.3. Refinement

R [*F*² > 2σ(*F*²)] = 0.051
wR (*F*²) = 0.143
S = 1.09
2259 reflections

145 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}}$ = 1.65 e Å^{−3}
 $\Delta\rho_{\text{min}}$ = −1.19 e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

Cg2 is the centroid of the C4–C9 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C11—H11...Br1 ⁱ	1.00	2.92	3.709 (8)	137
C10—H10B...Cg2 ⁱⁱ	0.99	2.70	3.438 (8)	131

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* and *PLATON*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5096).

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supporting information

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S1. Synthesis and crystallization

The title compound was prepared in line with literature methods (Jones, 1977; Lyle *et al.*, 1972). 2-Chloro-3,6-dimethylquinoline (0.001 mole) was dissolved in CCl₄. To this benzoyl peroxide (50 mg) was added and the mixture was stirred under ice-cold conditions. To this mixture *N*-bromosuccinimide (0.005 mole) was added portion wise. The whole mixture was further stirred under ice-cold condition for 1 h. The reaction mixture was then refluxed for about 10 hours. After completion of the reaction, the succinimide was removed (it was insoluble in CCl₄) by filtration and washed with 20 ml of CCl₄. The contents of the filtrate were reduced to half, and the residue was chromatographed on silica gel using petroleum ether and ethyl acetate as eluent (99:1), which gave the titled product (yield: 52%). The white solid obtained was then recrystallized using acetone yielding colourless block-like crystals.

S2. Refinement

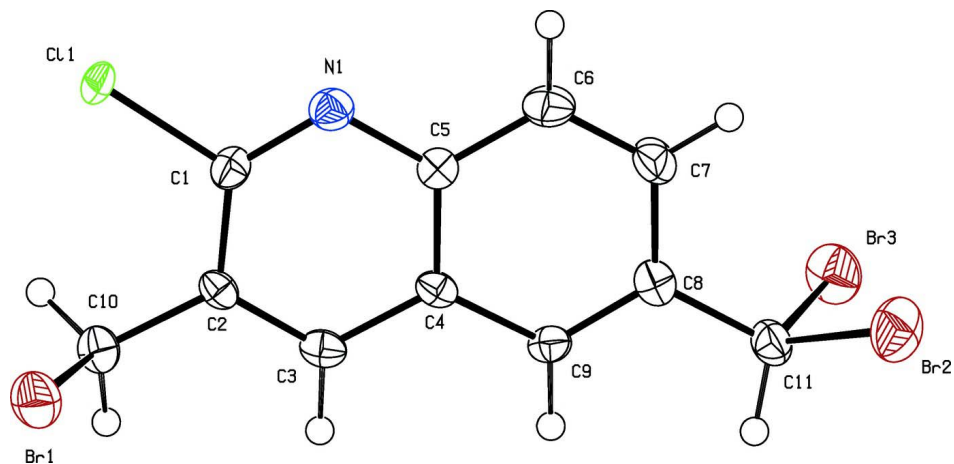
Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were included in calculated positions and refined using a riding model: C—H = 0.95 - 1.0 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak in the final difference Fourier map (1.654 eÅ⁻³) is close to atom Cl1. Attempts to split this atom were unsuccessful.

S3. Structural commentary

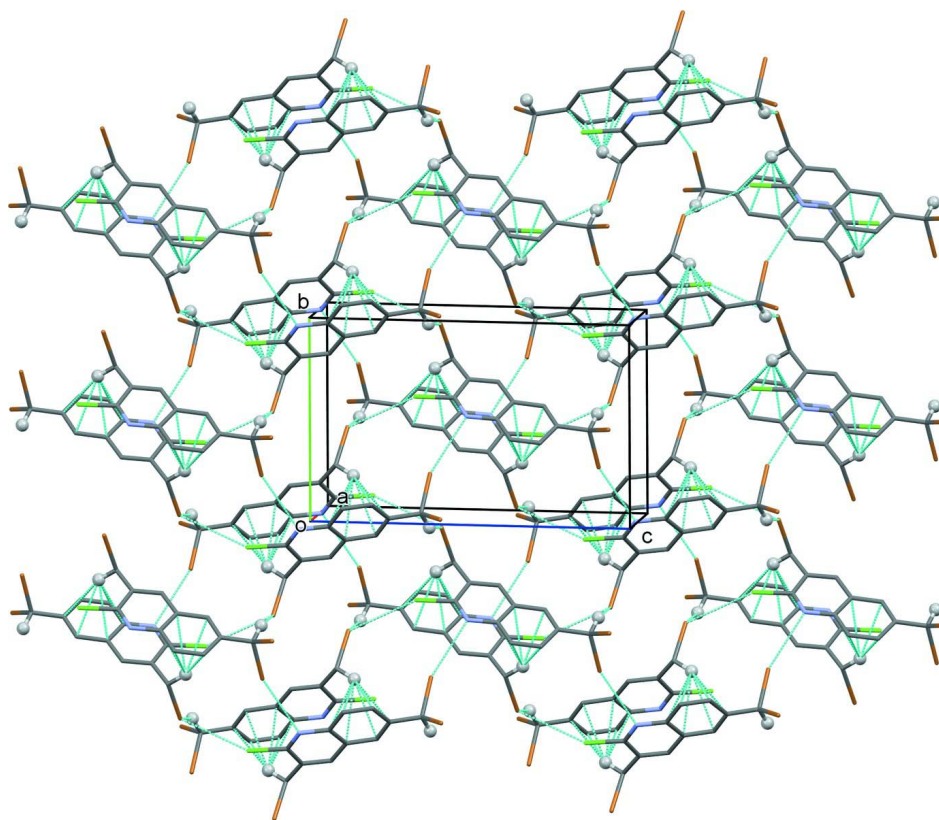
The presence of the quinoline skeleton in the frameworks of pharmacologically active compounds and natural products has spurred on the development of different strategies for their synthesis (Chauhan *et al.*, 2001; Ferrarini *et al.*, 2000; Chen *et al.*, 2001). Bromoquinolines have been of interest for chemists as precursors for heterocyclic compounds with multifunctionality, giving accessibility to a wide variety of compounds. These building blocks have been used in medicinal chemistry as starting materials for numerous compounds with pharmacological activity (Sahin *et al.*, 2008).

The molecular structure of the title compound is shown in Fig. 1. The quinoline ring is planar (r.m.s. = 0.011 Å).

In the crystal, molecules are linked by C—H...Br interactions forming chains along [10 $\bar{1}$]; Table 1 and Fig. 2. The chains are linked by C—H... π (Table 1), and π - π interactions involving inversion related pyridine rings (N1/C1—C5) with an inter-centroid distance of 3.608 (4) Å, forming sheets parallel to (10 $\bar{1}$). Within the sheets, there are two significant short interactions: A Br1...Clⁱ contact of 3.4904 (18) Å and a Br3...Nⁱⁱ contact of 3.187 (6) Å [symmetry codes: (i) -x+3/2, y-1/2, -z+3/2; (ii) x-1/2, -y+3/2, z-1/2], both are significantly shorter than the sum of their van der Waals radii [1.85 Å for Br; 1.75 Å for Cl; 1.55 Å for N; PLATON (Spek, 2009)].

**Figure 1**

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A view along the *a* axis of the crystal packing of the title compound. The C—H...Br hydrogen bonds, C—H... π interactions (Table 1) and the Br...Cl and Br...N short contacts are shown as dashed lines.

3-Bromomethyl-2-chloro-6-(dibromomethyl)quinoline*Crystal data*C₁₁H₇Br₃ClN $M_r = 428.36$ Monoclinic, $P2_1/n$ $a = 8.9042$ (5) Å $b = 9.3375$ (4) Å $c = 15.5107$ (7) Å $\beta = 104.553$ (5)° $V = 1248.23$ (11) Å³ $Z = 4$ $F(000) = 808$ $D_x = 2.279$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4382 reflections

 $\theta = 2.6$ – 29.0 ° $\mu = 9.88$ mm⁻¹ $T = 120$ K

Block, colourless

 $0.42 \times 0.36 \times 0.30$ mm*Data collection*Oxford Diffraction Xcalibur Sapphire3 Gemini
ultra
diffractometerRadiation source: Enhance (Mo) X-ray Source
Graphite monochromatorDetector resolution: 16.1511 pixels mm⁻¹ ω scans

Absorption correction: analytical

(CrysAlis PRO; Oxford Diffraction, 2010)

 $T_{\min} = 0.056$, $T_{\max} = 0.153$

8597 measured reflections

2259 independent reflections

1889 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.029$ $\theta_{\max} = 25.3$ °, $\theta_{\min} = 2.4$ ° $h = -10 \rightarrow 10$ $k = -11 \rightarrow 11$ $l = -18 \rightarrow 12$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.051$ $wR(F^2) = 0.143$ $S = 1.09$

2259 reflections

145 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 10.6242P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 1.65$ e Å⁻³ $\Delta\rho_{\min} = -1.19$ e Å⁻³*Special details*

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.63474 (10)	0.04489 (9)	0.60991 (6)	0.0370 (3)
Br3	0.45280 (10)	0.74291 (9)	0.12751 (6)	0.0381 (3)
Br2	0.70035 (11)	0.53886 (11)	0.08299 (6)	0.0429 (3)
Cl1	0.8069 (2)	0.38929 (19)	0.67965 (10)	0.0226 (4)
N1	0.7951 (7)	0.4817 (7)	0.5207 (4)	0.0242 (13)
C1	0.7245 (8)	0.3973 (8)	0.5630 (4)	0.0215 (15)
C2	0.5903 (8)	0.3156 (7)	0.5249 (4)	0.0179 (14)
C3	0.5309 (8)	0.3292 (7)	0.4361 (5)	0.0201 (14)

H3	0.4411	0.2763	0.4074	0.024*
C4	0.6012 (8)	0.4213 (7)	0.3857 (4)	0.0175 (14)
C5	0.7359 (8)	0.4957 (8)	0.4305 (5)	0.0197 (14)
C6	0.8084 (8)	0.5892 (9)	0.3828 (5)	0.0274 (17)
H6	0.8991	0.6397	0.4129	0.033*
C7	0.7505 (9)	0.6079 (9)	0.2946 (5)	0.0279 (17)
H7	0.8002	0.6722	0.2631	0.034*
C8	0.6160 (8)	0.5326 (8)	0.2483 (5)	0.0217 (15)
C9	0.5450 (8)	0.4423 (7)	0.2927 (4)	0.0201 (14)
H9	0.4555	0.3916	0.2612	0.024*
C10	0.5174 (9)	0.2212 (8)	0.5792 (5)	0.0234 (15)
H10A	0.4102	0.1981	0.5456	0.028*
H10B	0.5120	0.2718	0.6344	0.028*
C11	0.5499 (9)	0.5552 (8)	0.1511 (5)	0.0250 (16)
H11	0.4683	0.4809	0.1295	0.030*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0423 (5)	0.0311 (5)	0.0363 (5)	0.0018 (4)	0.0073 (4)	0.0085 (3)
Br3	0.0415 (5)	0.0292 (5)	0.0416 (5)	0.0098 (4)	0.0068 (4)	0.0091 (3)
Br2	0.0437 (5)	0.0546 (6)	0.0369 (5)	0.0031 (4)	0.0225 (4)	−0.0033 (4)
Cl1	0.0252 (9)	0.0296 (9)	0.0114 (7)	−0.0033 (7)	0.0013 (6)	0.0017 (6)
N1	0.022 (3)	0.025 (3)	0.024 (3)	−0.001 (3)	0.003 (2)	0.000 (3)
C1	0.020 (4)	0.026 (4)	0.018 (3)	0.001 (3)	0.005 (3)	−0.001 (3)
C2	0.019 (3)	0.012 (3)	0.023 (3)	0.002 (3)	0.007 (3)	0.002 (3)
C3	0.020 (3)	0.012 (3)	0.027 (4)	0.003 (3)	0.004 (3)	−0.001 (3)
C4	0.017 (3)	0.013 (3)	0.024 (3)	0.001 (3)	0.008 (3)	−0.002 (3)
C5	0.019 (3)	0.020 (3)	0.021 (3)	0.002 (3)	0.005 (3)	0.000 (3)
C6	0.018 (4)	0.030 (4)	0.031 (4)	−0.003 (3)	0.000 (3)	−0.002 (3)
C7	0.023 (4)	0.033 (4)	0.029 (4)	−0.007 (3)	0.008 (3)	0.004 (3)
C8	0.022 (4)	0.018 (4)	0.026 (4)	0.005 (3)	0.010 (3)	0.002 (3)
C9	0.021 (4)	0.016 (3)	0.020 (3)	0.001 (3)	−0.001 (3)	0.000 (3)
C10	0.024 (4)	0.023 (4)	0.025 (4)	0.003 (3)	0.008 (3)	0.003 (3)
C11	0.030 (4)	0.021 (4)	0.026 (4)	−0.001 (3)	0.009 (3)	0.004 (3)

Geometric parameters ($\text{\AA}$, $^\circ$)

Br1—C10	1.944 (7)	C4—C9	1.417 (9)
Br3—C11	1.948 (7)	C5—C6	1.404 (11)
Br2—C11	1.910 (8)	C6—C7	1.345 (10)
Cl1—C1	1.776 (7)	C6—H6	0.9500
N1—C1	1.286 (10)	C7—C8	1.419 (10)
N1—C5	1.371 (9)	C7—H7	0.9500
C1—C2	1.416 (10)	C8—C9	1.343 (10)
C2—C3	1.352 (10)	C8—C11	1.489 (10)
C2—C10	1.478 (10)	C9—H9	0.9500
C3—C4	1.409 (10)	C10—H10A	0.9900

C3—H3	0.9500	C10—H10B	0.9900
C4—C5	1.409 (10)	C11—H11	1.0000
C1—N1—C5	117.8 (6)	C6—C7—H7	119.7
N1—C1—C2	126.0 (6)	C8—C7—H7	119.7
N1—C1—Cl1	114.6 (5)	C9—C8—C7	119.9 (7)
C2—C1—Cl1	119.5 (5)	C9—C8—C11	119.4 (7)
C3—C2—C1	116.6 (6)	C7—C8—C11	120.7 (7)
C3—C2—C10	121.5 (6)	C8—C9—C4	121.2 (6)
C1—C2—C10	121.9 (6)	C8—C9—H9	119.4
C2—C3—C4	120.5 (6)	C4—C9—H9	119.4
C2—C3—H3	119.8	C2—C10—Br1	111.0 (5)
C4—C3—H3	119.8	C2—C10—H10A	109.4
C5—C4—C3	118.0 (6)	Br1—C10—H10A	109.4
C5—C4—C9	118.2 (6)	C2—C10—H10B	109.4
C3—C4—C9	123.8 (6)	Br1—C10—H10B	109.4
N1—C5—C6	119.2 (6)	H10A—C10—H10B	108.0
N1—C5—C4	121.2 (6)	C8—C11—Br2	113.3 (5)
C6—C5—C4	119.6 (6)	C8—C11—Br3	111.2 (5)
C7—C6—C5	120.5 (7)	Br2—C11—Br3	107.9 (3)
C7—C6—H6	119.8	C8—C11—H11	108.1
C5—C6—H6	119.8	Br2—C11—H11	108.1
C6—C7—C8	120.6 (7)	Br3—C11—H11	108.1
C5—N1—C1—C2	0.4 (11)	N1—C5—C6—C7	−178.3 (7)
C5—N1—C1—Cl1	−178.6 (5)	C4—C5—C6—C7	−0.2 (11)
N1—C1—C2—C3	−0.7 (11)	C5—C6—C7—C8	−0.5 (12)
Cl1—C1—C2—C3	178.3 (5)	C6—C7—C8—C9	0.4 (12)
N1—C1—C2—C10	180.0 (7)	C6—C7—C8—C11	178.8 (7)
Cl1—C1—C2—C10	−1.0 (9)	C7—C8—C9—C4	0.5 (11)
C1—C2—C3—C4	−0.2 (10)	C11—C8—C9—C4	−177.9 (6)
C10—C2—C3—C4	179.1 (6)	C5—C4—C9—C8	−1.2 (10)
C2—C3—C4—C5	1.2 (10)	C3—C4—C9—C8	179.4 (7)
C2—C3—C4—C9	−179.4 (7)	C3—C2—C10—Br1	103.9 (7)
C1—N1—C5—C6	178.7 (7)	C1—C2—C10—Br1	−76.8 (8)
C1—N1—C5—C4	0.7 (10)	C9—C8—C11—Br2	−131.1 (6)
C3—C4—C5—N1	−1.5 (10)	C7—C8—C11—Br2	50.5 (8)
C9—C4—C5—N1	179.1 (6)	C9—C8—C11—Br3	107.2 (7)
C3—C4—C5—C6	−179.5 (7)	C7—C8—C11—Br3	−71.3 (8)
C9—C4—C5—C6	1.0 (10)		

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C4—C9 ring.

<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>
C11—H11 $\cdots$ Br1 ⁱ	1.00	2.92	3.709 (8)	137

C10—H10B $\cdots$ Cg2 ⁱⁱ	0.99	2.70	3.438 (8)	131
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