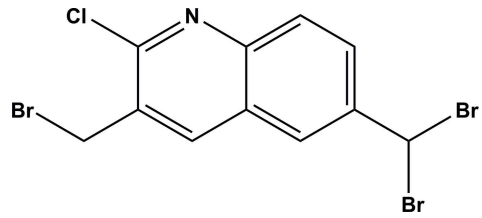
Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890



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

Kasirajan Gayathri,[a] Palathurai S. Mohan,[a]* Judith A. K. Howard[b] and Hazel A. Sparkes[b,c]

[a]Department of Chemistry, Bharathiar University, Coimbatore 641 046, Tamil Nadu, India, [b]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and [c]Univeristy of Bristol, Department of Chemistry, Cantock's Close, Bristol BS8 1TS, England. *Correspondence e-mail: psmohan59@gmail.com

Received 18 March 2015; accepted 22 April 2015

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

In the title compound, $C_{11}H_7Br_3ClN$, 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.

CCDC reference: 902598

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

$C_{11}H_7Br_3ClN$
M_r = 428.36
Monoclinic, $P2_1/n$
a = 8.9042 (5) Å
b = 9.3375 (4) Å
c = 15.5107 (7) Å
β = 104.553 (5)°
V = 1248.23 (11) Å^3
Z = 4
Mo $K\alpha$ 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 $I > 2\sigma(I)$
R_{int} = 0.029

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.143
S = 1.09
2259 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.65 e Å^{-3}
$\Delta\rho_{min}$ = −1.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*2 is the centroid of the C4–C9 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···Br1^{i}	1.00	2.92	3.709 (8)	137
C10—H10B···*Cg*2^{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

HAS is grateful to the Leverhulme Trust and Durham University for financial support.

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

References

Chauhan, P. M. S. & Srivastava, S. K. (2001). *Curr. Med. Chem.* **8**, 1535–1542.
Chen, Y. L., Fang, K. C., Sheu, J. Y., Hsu, S. L. & Tzeng, C. C. (2001). *J. Med. Chem.* **44**, 2374–2377.
Ferrarini, P. L., Mori, C., Badawneh, M., Calderone, V., Greco, R., Manera, C., Martinelli, A., Nieri, P. & Saccomanni, G. (2000). *Eur. J. Med. Chem.* **35**, 815–826.
Jones, G. (1977). *Quinolines, Part-I*. Wiley Interscience Publication, John Wiley & Sons.
Lyle, R. E., Portlock, D. E., Kane, M. J. & Bristol, J. A. (1972). *J. Org. Chem.* **37**, 3967–3968.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Sahin, A., Cakmak, O., Demirtas, I., Okten, S. & Tutar, A. (2008). *Tetrahedron*, **64**, 10068–10074.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2015). E**71**, o354–o355 [https://doi.org/10.1107/S2056989015008002]

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

Kasirajan Gayathri, Palathurai S. Mohan, Judith A. K. Howard and Hazel A. Sparkes

S1. Synthesis and crystallization

The title compound was prepared in line with literature methods (Jones, 1977; Lyle *et al.*, 1972). 2-Chloro-3,6-dimethyl-quinoline (0.001 mole) was dissolved in CCl_4. 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 CCl_4) by filtration and washed with 20 ml of CCl_4. 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···Cl^{i} contact of 3.4904 (18) Å and a Br3···N^{ii} 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)].

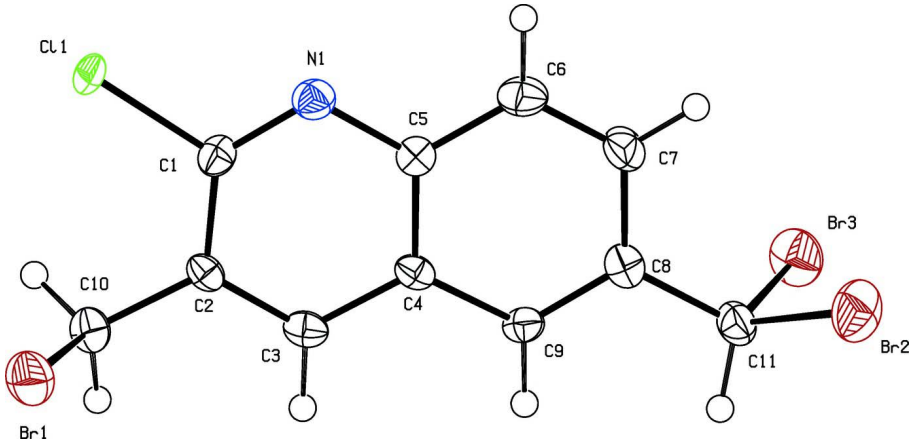


Figure 1

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

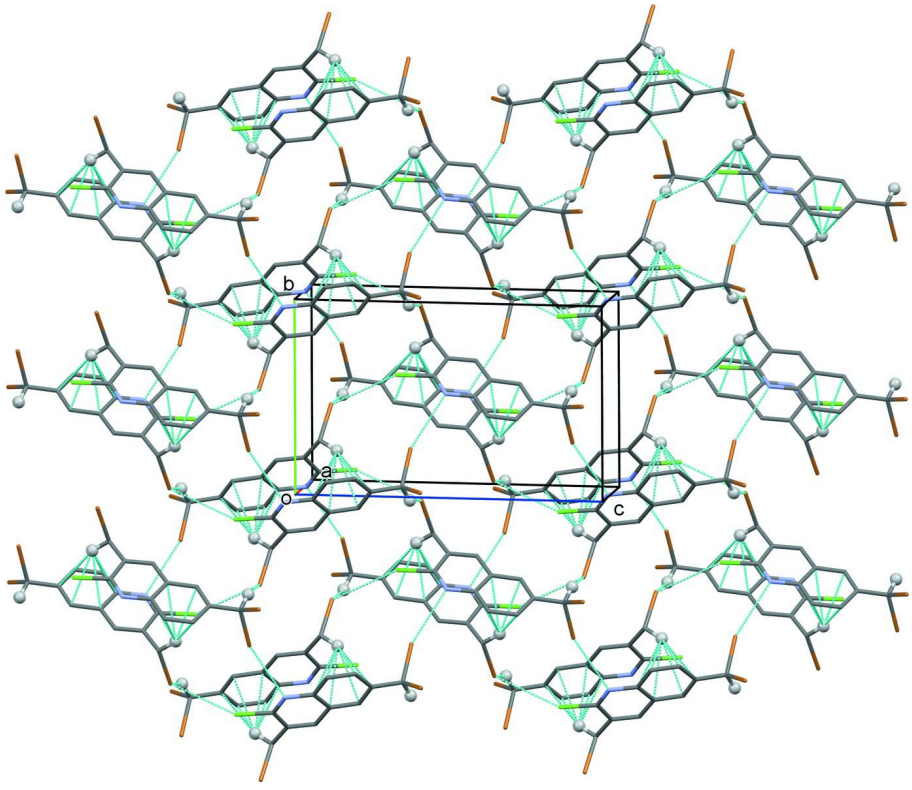


Figure 2

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

$C_{11}H_7Br_3ClN$
$M_r = 428.36$
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) Å^3
$Z = 4$
$F(000) = 808$
$D_x = 2.279$ Mg m^{-3}
Mo $K\alpha$ 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 × 0.36 × 0.30 mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 Gemini ultra diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector 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 $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.3°$, $\theta_{min} = 2.4°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 12$

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 methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 10.6242P]$ 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)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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 (Å, º)

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, º)

Cg2 is the centroid of the C4–C9 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···Br1^{i}	1.00	2.92	3.709 (8)	137

C10—H10*B*···*Cg*2^{ii}	0.99	2.70	3.438 (8)	131

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