

5,7-Dibromo-8-methoxyquinoline

İsmail Çelik,^a Salih Ökten,^b Mehmet Akkurt,^{c*} Cem Cüneyt Ersanlı,^d Osman Çakmak^e and Rana Özbakır^a

^aDepartment of Physics, Faculty of Sciences, Cumhuriyet University, 58140 Sivas, Turkey, ^bDepartment of Maths and Science Education, Division of Science Education, Faculty of Education, Kırıkkale University, 71450, Yahşihan, Kırıkkale, Turkey, ^cDepartment of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, ^dDepartment of Physics, Faculty of Arts and Sciences, Sinop University, 57010 Sinop, Turkey, and ^eDepartment of Nutrition and Dietetics, School of Health Sciences, İstanbul Gelişim University, 34315 Avcılar, İstanbul, Turkey. *Correspondence e-mail: akkurt@erciyes.edu.tr

Received 25 April 2017

Accepted 28 April 2017

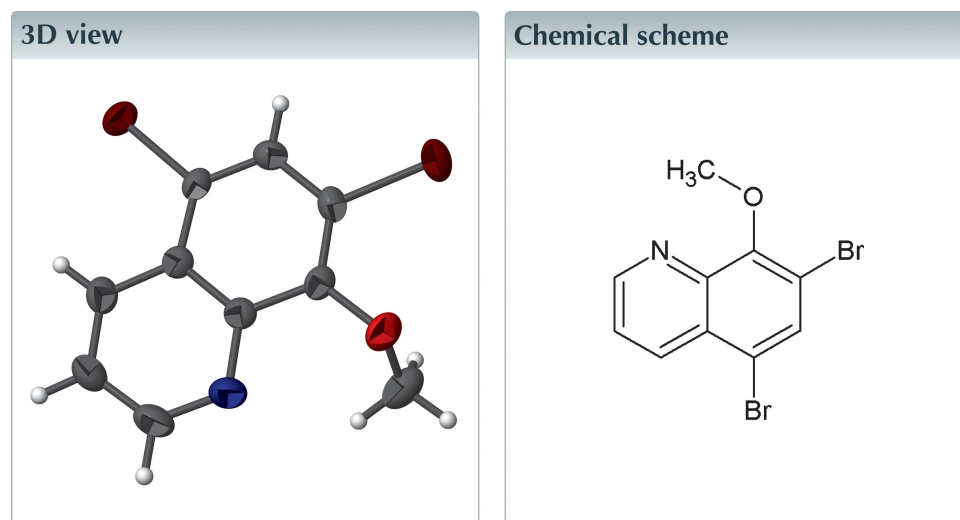
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; quinoline ring system; hydrogen bonds; π - π stacking interactions.

CCDC reference: 1546956

Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{10}H_7Br_2NO$, the methoxy C atom deviates from the quinoline ring system (r.m.s deviation = 0.003 Å) by 1.204 (4) Å. In the crystal, C—H \cdots O hydrogen bonds link the molecules into infinite chains along the *b*-axis direction. Aromatic π - π stacking interactions [centroid-to-centroid distance = 3.7659 (19) Å] are also observed.



Structure description

The treatment of several dihalogenated quinoline derivatives with NaOMe in basic solutions afforded mono methoxide analogues (Politanskaya *et al.*, 2005). Our own work has studied the bromination reactions of substituted quinolines (Ökten & Çakmak, 2015; Ökten *et al.*, 2015). The present study presents the crystal structure of 5,7-dibromo-8-hydroxyquinoline.

In the title compound (Fig. 1), the Br—C bond lengths are 1.889 (3) and 1.901 (3) Å, and the Br—C—C bond angles vary from 117.6 (2) to 120.2 (2)°. The relatively wide range of Br—C—C angles may be due to the alternation of the bond-lengths in the bromine-substituted six-membered ring, which vary from 1.357 (4) to 1.425 (4) Å.

The packing of the title compound viewed down the *b* axis is shown in Fig. 2. The crystal structure features C—H \cdots O hydrogen bonds, which lead to the formation of chains along the *b*-axis direction (Fig. 3 and Table 1). Furthermore, aromatic π - π stacking interactions [$Cg1\cdots Cg2(x, 1+y, z)$ = 3.7659 (19) Å; *Cg1* and *Cg2* are the centroids of the N1/C1—C5 pyridine and C4—C9 benzene rings, respectively] in the [010] direction are also observed.

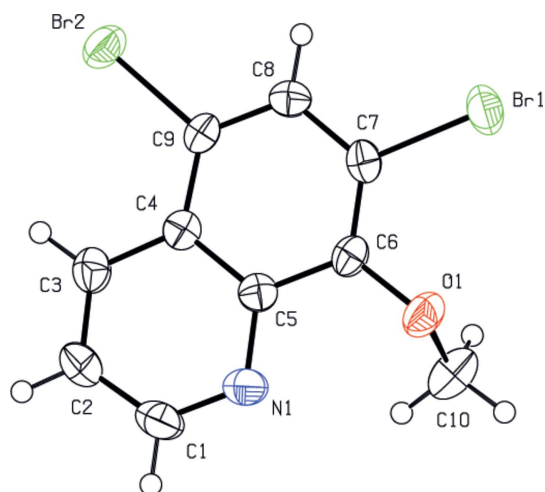


Figure 1
View of the title compound with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

Synthesis and crystallization

5,7-Dibromoquinolin-8-ol (1.0 g, 3.3 mmol) was added to a solution of NaOH (132 mg, 3.3 mmol) in distilled water (100 ml). Me_2SO_4 (416 mg, 3.3 mmol) was added dropwise to the mixture at 263 K for 1 h while being stirred. The mixture was heated to 343–353 K for 1 h. After completion of the reaction (the colour of the mixture changed, 2 h), the solid was dissolved in CHCl_3 (50 ml). The organic layer was successively washed with 10% Na_2CO_3 (2×15 ml) and 10% NaOH (2×15 ml), dried over Na_2SO_4 , and the solvent was removed under vacuum. The crude material (2.12 g) was passed through a short alumina column and eluted with EtOAc–hexane (1:6, 150 ml) to obtain the title compound (1 g, 95%) as colourless needles, m.p. 372–375 K. ^1H NMR (400 MHz, CDCl_3): (δ /p.p.m.): 9.00 (*dd*, $J_{23} = 3.2$ Hz, $J_{24} = 1.6$ Hz, 1H, H-2), 8.52 (*dd*, 1H, H-4, $J_{43} = 8$ Hz, $J_{42} = 1.6$ Hz), 8.02 (*s*, 1H, H-6) 7.58 (*dd*, 1H, H-3, $J_{34} = 8.4$ Hz, $J_{32} = 3.2$ Hz), 4.19 (*s*, 3H, OCH_3); ^{13}C NMR (100 MHz, CDCl_3) (δ /p.p.m.): 153.3, 150.9, 143.8, 136.1, 133.7, 128.3, 122.5, 116.3, 116.5, 62.1 (OCH_3); IR (ν/cm^{-1}): 2919, 2850, 1733, 1600, 1578, 1490, 1462, 1383, 1370, 1353, 1086.

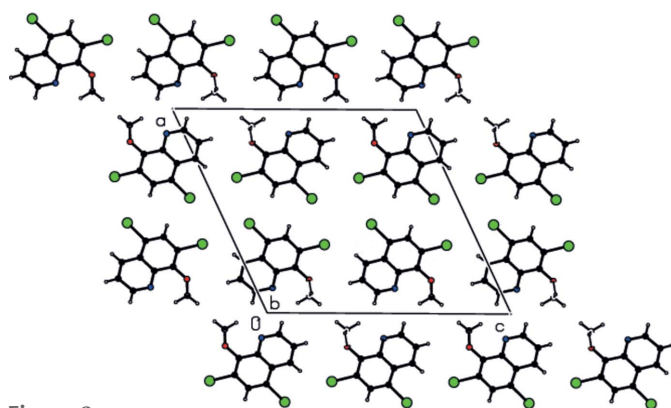


Figure 2
The packing of the title compound down the *b* axis.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

<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>
C10–H10C···O1 ⁱ	0.96	2.48	3.418 (5)	166

Symmetry code: (i) *x*, *y* – 1, *z*.

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{10}\text{H}_7\text{Br}_2\text{NO}$
M_r	316.99
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (\AA)	16.158 (3), 3.9960 (6), 17.551 (3)
β ($^\circ$)	115.316 (5)
<i>V</i> (\AA^3)	1024.4 (3)
<i>Z</i>	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.88
Crystal size (mm)	$0.11 \times 0.07 \times 0.05$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2007)
T_{min} , T_{max}	0.603, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16733, 2048, 1604
R_{int}	0.052
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.623
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.028, 0.059, 1.03
No. of reflections	2048
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.55, –0.51

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2003).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

This work is supported by the Scientific Research Project Fund of Cumhuriyet University under the project number F-513. The authors are indebted to the X-ray laboratory of

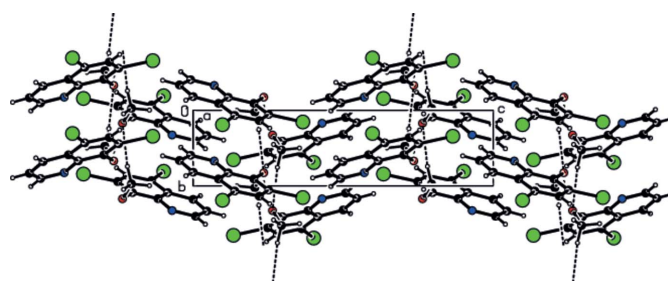


Figure 3
View of the C–H···O hydrogen bonds along the *b* axis, shown down the *a* axis.

Sinop University Scientific and Technological Applied and Research Center, Sinop, Turkey, for use of the X-ray diffractometer.

References

- Bruker (2007). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Ökten, S. & Çakmak, O. (2015). *Tetrahedron Lett.* **56**, 5337–5340.
- Ökten, S., Eyigün, D. & Çakmak, O. (2015). *Sigma J. Eng. Nat. Sci.* **33**, 8–15.
- Politanskaya, L. V., Malysheva, L. A., Beregovaya, I. V., Bagryanskaya, I. Y., Gatilov, Y. V., Malykhin, E. V. & Shteingarts, V. D. (2005). *J. Fluor. Chem.* **126**, 1502–1509.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

full crystallographic data

IUCrData (2017). **2**, x170643 [https://doi.org/10.1107/S2414314617006435]

5,7-Dibromo-8-methoxyquinoline

İsmail Çelik, Salih Ökten, Mehmet Akkurt, Cem Cüneyt Ersanlı, Osman Çakmak and Rana Özbakır

5,7-Dibromo-8-methoxyquinoline

Crystal data

$C_{10}H_7Br_2NO$

$M_r = 316.99$

Monoclinic, $P2_1/c$

$a = 16.158$ (3) Å

$b = 3.9960$ (6) Å

$c = 17.551$ (3) Å

$\beta = 115.316$ (5)°

$V = 1024.4$ (3) Å³

$Z = 4$

$F(000) = 608$

$D_x = 2.055$ Mg m⁻³

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

Cell parameters from 5051 reflections

$\theta = 3.4$ – 25.1 °

$\mu = 7.88$ mm⁻¹

$T = 296$ K

Needle, colourless

$0.11 \times 0.07 \times 0.05$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2007)

$T_{\min} = 0.603$, $T_{\max} = 0.745$

16733 measured reflections

2048 independent reflections

1604 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 26.3$ °, $\theta_{\min} = 3.4$ °

$h = -20 \rightarrow 19$

$k = -4 \rightarrow 4$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.059$

$S = 1.03$

2048 reflections

127 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 1.0875P]$

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

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

$\Delta\rho_{\max} = 0.55$ e Å⁻³

$\Delta\rho_{\min} = -0.51$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1048 (2)	0.9036 (9)	0.4918 (2)	0.0462 (9)
H1	0.049584	1.009212	0.459273	0.055*
C2	0.1639 (2)	0.8352 (9)	0.4542 (2)	0.0462 (9)
H2	0.147908	0.895425	0.398488	0.055*
C3	0.2447 (2)	0.6799 (8)	0.5000 (2)	0.0378 (8)
H3	0.284548	0.632227	0.475841	0.045*
C4	0.2681 (2)	0.5908 (7)	0.58455 (18)	0.0291 (7)
C5	0.2035 (2)	0.6703 (7)	0.61719 (19)	0.0303 (7)
C6	0.2236 (2)	0.5909 (7)	0.70229 (19)	0.0310 (7)
C7	0.3056 (2)	0.4440 (8)	0.75154 (18)	0.0319 (7)
C8	0.3698 (2)	0.3624 (7)	0.72035 (19)	0.0325 (7)
H8	0.425118	0.262233	0.755195	0.039*
C9	0.3503 (2)	0.4313 (7)	0.63871 (19)	0.0296 (7)
C10	0.0821 (3)	0.4740 (10)	0.7055 (3)	0.0544 (10)
H10A	0.043928	0.547100	0.731777	0.082*
H10B	0.049547	0.498501	0.645482	0.082*
H10C	0.098083	0.243169	0.719059	0.082*
N1	0.12264 (18)	0.8276 (7)	0.57021 (17)	0.0391 (7)
O1	0.16339 (15)	0.6720 (6)	0.73544 (14)	0.0417 (6)
BR1	0.33604 (3)	0.34441 (9)	0.86565 (2)	0.04622 (12)
BR2	0.43774 (2)	0.30825 (9)	0.59799 (2)	0.04253 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.038 (2)	0.053 (2)	0.037 (2)	0.0093 (17)	0.0060 (16)	0.0077 (17)
C2	0.044 (2)	0.059 (2)	0.0286 (18)	0.0025 (18)	0.0091 (16)	0.0056 (17)
C3	0.0425 (19)	0.0418 (19)	0.0315 (17)	-0.0029 (16)	0.0180 (15)	-0.0033 (15)
C4	0.0312 (17)	0.0264 (16)	0.0299 (16)	-0.0036 (13)	0.0133 (14)	-0.0053 (12)
C5	0.0294 (17)	0.0296 (16)	0.0303 (16)	-0.0028 (14)	0.0113 (14)	-0.0025 (13)
C6	0.0337 (17)	0.0314 (17)	0.0329 (17)	-0.0017 (13)	0.0189 (15)	-0.0057 (13)
C7	0.0399 (19)	0.0312 (17)	0.0262 (16)	-0.0016 (14)	0.0158 (14)	-0.0009 (13)
C8	0.0296 (17)	0.0302 (17)	0.0351 (18)	0.0031 (13)	0.0113 (15)	0.0015 (13)
C9	0.0310 (17)	0.0290 (16)	0.0340 (17)	-0.0020 (13)	0.0190 (14)	-0.0037 (13)
C10	0.047 (2)	0.058 (2)	0.071 (3)	-0.0053 (19)	0.038 (2)	-0.007 (2)
N1	0.0311 (15)	0.0442 (17)	0.0384 (16)	0.0068 (13)	0.0113 (13)	0.0025 (13)
O1	0.0409 (13)	0.0489 (14)	0.0437 (14)	0.0024 (11)	0.0261 (11)	-0.0078 (11)
BR1	0.0589 (2)	0.0512 (2)	0.03332 (19)	0.00706 (18)	0.02425 (17)	0.00917 (16)
BR2	0.0370 (2)	0.0521 (2)	0.0452 (2)	0.00375 (16)	0.02407 (16)	-0.00531 (16)

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

C1—N1	1.316 (4)	C6—C7	1.367 (4)
C1—C2	1.399 (5)	C6—O1	1.368 (3)
C1—H1	0.9300	C7—C8	1.403 (4)

C2—C3	1.356 (5)	C7—BR1	1.889 (3)
C2—H2	0.9300	C8—C9	1.357 (4)
C3—C4	1.411 (4)	C8—H8	0.9300
C3—H3	0.9300	C9—BR2	1.901 (3)
C4—C9	1.411 (4)	C10—O1	1.428 (4)
C4—C5	1.425 (4)	C10—H10A	0.9600
C5—N1	1.364 (4)	C10—H10B	0.9600
C5—C6	1.422 (4)	C10—H10C	0.9600
N1—C1—C2	124.0 (3)	C6—C7—C8	122.1 (3)
N1—C1—H1	118.0	C6—C7—BR1	120.2 (2)
C2—C1—H1	118.0	C8—C7—BR1	117.6 (2)
C3—C2—C1	119.2 (3)	C9—C8—C7	119.2 (3)
C3—C2—H2	120.4	C9—C8—H8	120.4
C1—C2—H2	120.4	C7—C8—H8	120.4
C2—C3—C4	119.8 (3)	C8—C9—C4	122.0 (3)
C2—C3—H3	120.1	C8—C9—BR2	118.0 (2)
C4—C3—H3	120.1	C4—C9—BR2	120.0 (2)
C3—C4—C9	125.1 (3)	O1—C10—H10A	109.5
C3—C4—C5	116.9 (3)	O1—C10—H10B	109.5
C9—C4—C5	118.0 (3)	H10A—C10—H10B	109.5
N1—C5—C6	117.8 (3)	O1—C10—H10C	109.5
N1—C5—C4	122.5 (3)	H10A—C10—H10C	109.5
C6—C5—C4	119.7 (3)	H10B—C10—H10C	109.5
C7—C6—O1	120.4 (3)	C1—N1—C5	117.6 (3)
C7—C6—C5	118.9 (3)	C6—O1—C10	114.9 (3)
O1—C6—C5	120.6 (3)		
N1—C1—C2—C3	0.3 (6)	C5—C6—C7—BR1	178.5 (2)
C1—C2—C3—C4	-0.2 (5)	C6—C7—C8—C9	0.1 (5)
C2—C3—C4—C9	-179.5 (3)	BR1—C7—C8—C9	-179.8 (2)
C2—C3—C4—C5	0.3 (5)	C7—C8—C9—C4	1.6 (5)
C3—C4—C5—N1	-0.5 (4)	C7—C8—C9—BR2	-178.6 (2)
C9—C4—C5—N1	179.3 (3)	C3—C4—C9—C8	177.8 (3)
C3—C4—C5—C6	-179.2 (3)	C5—C4—C9—C8	-1.9 (4)
C9—C4—C5—C6	0.6 (4)	C3—C4—C9—BR2	-1.9 (4)
N1—C5—C6—C7	-177.7 (3)	C5—C4—C9—BR2	178.3 (2)
C4—C5—C6—C7	1.0 (4)	C2—C1—N1—C5	-0.5 (5)
N1—C5—C6—O1	-0.3 (4)	C6—C5—N1—C1	179.3 (3)
C4—C5—C6—O1	178.5 (3)	C4—C5—N1—C1	0.6 (5)
O1—C6—C7—C8	-178.9 (3)	C7—C6—O1—C10	-110.4 (3)
C5—C6—C7—C8	-1.4 (5)	C5—C6—O1—C10	72.2 (4)
O1—C6—C7—BR1	1.0 (4)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots Br2	0.93	2.80	3.210 (3)	108

C10—H10B···N1	0.96	2.49	3.065 (6)	118
C10—H10C···O1 ⁱ	0.96	2.48	3.418 (5)	166

Symmetry code: (i) $x, y-1, z$.