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# 7-Bromoquinolin-8-ol

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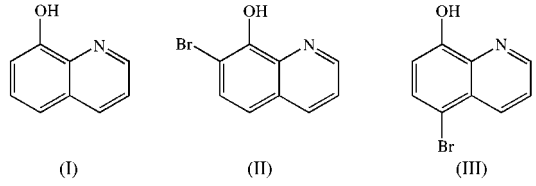
Structure analysis of the title compound, $C_9H_6BrNO$, has established that bromination of an 8-hydroxyquinoline derivative occurred in the 7-position. Intermolecular and weak intramolecular O—H···N hydrogen bonds are present, the former causing the molecules to pack as hydrogen-bonded dimers in the solid state.

## Comment

Because of our interest in synthesizing a variety of 7-substituted 8-hydroxyquinoline ligands, studies into the electrophilic aromatic halogenation of 8-hydroxyquinoline, (I), were considered. The literature presents four key papers that describe the synthesis of 7-bromo-8-hydroxyquinoline, (II), *via* two different routes. The earliest procedure (Claus & Giwartovsky, 1896), which was later optimized by Gershon *et al.* (1969), brominated 8-hydroxyquinoline-5-sulfonic acid and subjected this material to acid hydrolysis to afford a product concluded to be (II) (m.p. 411 and 412–413 K, respectively). Alternatively, low-temperature base-induced bromination of (I) (Pearson *et al.*, 1967; Schmitz & Pagenkopf, 1985) gave a product also concluded to be (II) because it had a similar melting point (410–411 K). Unfortunately, no detailed spectral information was provided with these experimental procedures to substantiate the incorporation of the Br atom *ortho* to the phenol hydroxy group.




(I) (II) (III)

On further investigation of the literature, it became apparent that there has been some contention regarding the regioselective halogenation of 8-hydroxyquinoline derivatives and the assignment of the products (Prasad *et al.*, 1965; Gershon *et al.*, 1969). To add to this uncertainty, it has been reported that the acid hydrolysis of 7-bromo-8-hydroxyquinoline-5-sulfonic acid results in the facile migration of the Br atom, thus affording the 5-bromo-8-hydroxyquinoline isomer, (III) (Suzuki *et al.*, 1980). Recently, the NMR assignment for the structure of 7-iodo-8-hydroxyquinoline (Clarke *et al.*, 1998) has been revised on the basis of X-ray crystallographic data (Gershon *et al.*, 1997). A search of the Cambridge Structural Database (Allen, 2002), in which dimerized quinolines at the 7-position were ignored, revealed six reported 7-substituted 8-hydroxyquinoline structures (Boeyens, 1976; Rericha *et al.*, 1989, 1990; Faizi *et al.*, 1997; Gershon *et al.*, 1997; Albrecht *et al.*, 1999), one of which was the related 7-iodo-8-hydroxyquinoline of Gershon *et al.* (1997). Because of the limited amount of reported information and the conflicting literature reports, we decided that it was prudent to perform an X-ray crystal structure analysis of the monobromide product obtained using the procedures of Gershon *et al.* (1969) and Pearson *et al.* (1967).

The structure of (II) (Fig. 1) was solved in space group *C*2/*c*, and this solution confirms that bromination has occurred in the 7-position. The fused ring system is planar, with an r.m.s. deviation from planarity of 0.0181 (12) Å. Both the phenol O atom and the bromo substituent lie essentially in this plane [the out-of-plane distances for atoms O1 and Br1 are 0.090 (6) and 0.060 (2) Å, respectively]. Weak intramolecular hydrogen-bonding interactions are present between the phenol donor (located from a difference map) and the adjacent pyridine N-atom acceptor [O1···N1 = 2.768 (6) Å and O1—H1···N1 = 110°; Table 1]. Moderate intermolecular O1—H1···N1$^{i}$ hydrogen bonds are also present [O1···N1$^{i}$ = 2.736 (6) Å and O1—H1···N1$^{i}$ = 152°; symmetry code: (i) $1-x, y, \frac{1}{2}-z$]. To facilitate the intermolecular hydrogen bonding, the fused aromatic rings are twisted slightly, the angle between the ring planes being 1.6 (3)°. In addition, the mean planes of the two hydrogen-bonded molecules are at an angle of 59.6 (2)° with respect to one another, so that overall

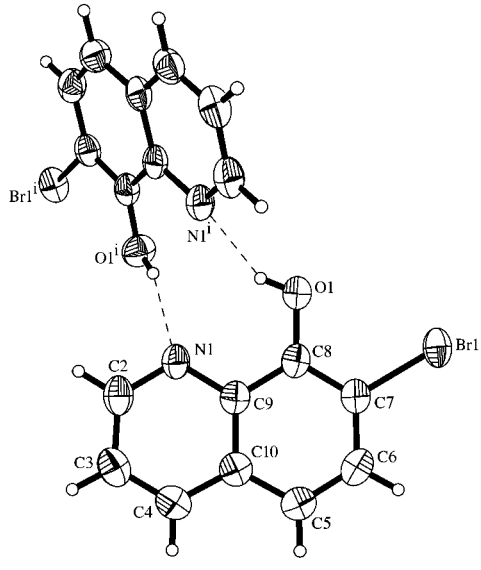



**Figure 1**
A view of the hydrogen-bonded dimer of (II), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.]

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the molecules are packed as twisted hydrogen-bonded dimers (Fig. 1).

The current crystallographic data suggest that the synthetic methods of both Gershon *et al.* (1969) and Pearson *et al.* (1967) result in the formation of (II).

## Experimental

The title compound was synthesized following the procedures described by Gershon *et al.* (1969) and Pearson *et al.* (1967), and was recrystallized to give (II) (m.p. 412–413 K). $^1$H NMR ($CDCl_3$, TMS): $\delta$ 8.80 (1H, $^1J$ = 4.2 Hz, $^3J$ = 1.5 Hz, H2), 8.15 (1H, $^1J$ = 8.4 Hz, $^3J$ = 1.5 Hz, H4), 7.62 (1H, $^1J$ = 9 Hz, H6), 7.47 (1H, $^1J_1$ = 8.4 Hz, $^1J_2$ = 4.2 Hz, H3), 7.25 (1H, $^1J$ = 9 Hz, H5). A sample of (II) was crystallized from cyclohexane, giving needle-like crystals of which a fragment was suitable for X-ray diffraction.

*Crystal data*

$C_9H_6BrNO$
$M_r$ = 224.06
Monoclinic, $C2/c$
$a$ = 26.770 (8) Å
$b$ = 4.020 (1) Å
$c$ = 16.344 (5) Å
$\beta$ = 114.077 (5)°
$V$ = 1605.9 (8) Å$^3$
$Z$ = 8
$D_x$ = 1.853 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4647 reflections
$\theta$ = 1.7–25.4°
$\mu$ = 5.06 mm$^{-1}$
$T$ = 203 (2) K
Plate, colorless
0.32 × 0.12 × 0.08 mm

*Data collection*

Bruker $P4$ CCD diffractometer
$\omega$ and $\varphi$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.20, $T_{max}$ = 0.67
4647 measured reflections
1465 independent reflections
1272 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026
$\theta_{max}$ = 25.4°
$h = -32 \rightarrow 28$
$k = -4 \rightarrow 4$
$l = -17 \rightarrow 19$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.127
$S$ = 1.11
1465 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 7.273P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.94 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.30 e Å$^{-3}$

The phenol H atom was located from a difference map, refined using a riding model and given an isotropic displacement parameter equal to 1.2 times that of atom O1. All other H atoms were placed in calculated positions, refined using a riding model and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the parent atom. There were three remaining residual peaks greater than 0.37 e Å$^{-3}$, two of which were less than 1.1 Å from atom Br1 (1.05 and 0.84 e Å$^{-3}$). The third and largest residual peak was 1.60 Å from atom C5, coplanar with the aromatic ring system but 'leaning' slightly towards atom C4 ($Q1$—C5—C4 = 111.9°). This peak has been attributed to a minor cocrystallization impurity of 5,7-dibromo-8-hydroxyquinoline (modeling resulted in a <3% occupancy factor for $Q1$ as Br). $^1$H NMR analysis of the crystal sample was consistent with this assignment.

**Table 1**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···N1 | 0.82 | 2.37 | 2.768 (6) | 110 |
| O1—H1···N1$^{i}$ | 0.82 | 1.98 | 2.736 (6) | 152 |

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1024). Services for accessing these data are described at the back of the journal.

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