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Quinolin-6-ol at 100 K

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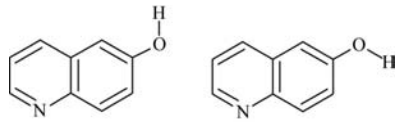
The title compound, C_9H_7NO, has two symmetry-independent molecules in the asymmetric unit, which have different conformations of the hydroxy group with respect to the quinoline ring. One of the molecules adopts a *cis* conformation, while the other shows a *trans* conformation. Each type of independent molecule links into a separate infinite O—H···N hydrogen-bonded chain with the graph-set notation $C(7)$. These chains are perpendicular in the unit cell, one extended in the *a*-axis direction and the other in the *b*-axis direction. There is also a weak C—H···O hydrogen bond with graph-set notation $D(2)$, which runs in the *c*-axis direction and joins the two separate O—H···N chains. The significance of this study lies in the comparison drawn between the experimental and calculated data of the crystal structure of the title compound and the data of several other derivatives possessing the hydroxy group or the quinoline ring. The correlation between the IR spectrum of this compound and the hydrogen-bond energy is also discussed.

Comment

Quinoline derivatives are well known for their antifungal and antibacterial activities (Bambury, 1979). On the other hand, they also have toxic, mutagenic and carcinogenic activities (Reinhardt & Britteli, 1981). Quinoline was metabolized by *Pseudomonas sp.* and several intermediate products were obtained, such as 2-hydroxyquinoline and 8-hydroxycoumarin (Shukla, 1986). Hydroxyquinolines are good substrates for glucoronidation by UDP-glucoronosyltransferase (Kanou *et al.*, 2002). Thus, the biological function of quinolin-6-ol (6-HQ) has attracted considerable interest in recent years. Quinoline and 6-HQ have been degraded into quinolones by *Brevundimonas diminuta*, *Pseudomonas diminuta* and *Bacillus circulans* (Han & Andrade, 2005; Bott & Lingens, 1991). A series of 6-HQ derivatives, *i.e.* ethyl 6-hydroxyquinoline-3-carboxylates, have important antihepatitis B virus activities *in vitro* (Liu *et al.*, 2008). The major studies on 6-HQ have focused on the excited-state proton transfers in aqueous solutions and on the photophysical properties of this compound (Yu *et al.*, 1997; Kim *et al.*, 1997, 2001; Mehata *et al.*, 2002, 2003). The vibrational frequencies of the title compound have been calculated by using Hartree–Fock and density functional methods (Arici & Köksal, 2008).



6-HQ*A* 6-HQ*B*

The objects of our research are the IR spectra of crystals with open hydrogen-bonded chains in the unit cell, measured in the frequency range of the proton and deuteron stretching vibrations of the hydrogen bridge (Flakus & Michta, 2003, 2004, 2005). Characteristic isotopic and spectroscopic effects, called the H/D isotopic self-organization effects, have been observed in this vibration frequency range (Flakus, 1989, 2003; Flakus & Bańczyk, 1999). Measurements of polarized IR spectra of diverse spatially oriented hydrogen-bond systems present in the lattices of molecular crystals allow us to estimate the polarization properties of transitions found in the excited states of the proton vibrations in the crystals. These transitions contribute to the ν_{X-H} band generation mechanisms in the crystalline spectra. Thus, for the reliable interpretation of the self-organization mechanism, the crystal structure of the hydrogen-bond system must be known. In the case of 6-HQ, a crystallographic study has not yet been reported. A search of the Cambridge Structural Database [Version 5.28 (Allen, 2002); *ConQuest*, Version 1.9 (Bruno *et al.*, 2002)] for 6-HQ derivatives yielded only 11 complex structures with different and large substituents on the quinoline ring. Among other hydroxyquinolines, only the structure of quinolin-8-ol, containing centrosymmetric hydrogen-bonded dimers in the asymmetric unit, is well known (Roychowdhury *et al.*, 1978; Banerjee & Saha, 1986; Zhang & Wu, 2005).

In this article, the results of our structural studies of the hydrogen bonds of 6-HQ are presented. 6-HQ crystallizes with

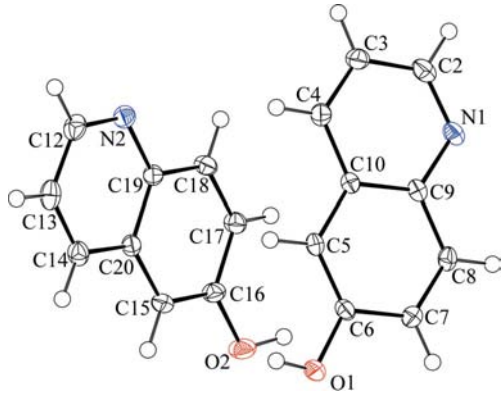


Figure 1
The two independent molecules of 6-HQ, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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two molecules in the asymmetric unit (Fig. 1), which exhibit comparable bond lengths and angles. Both six-membered rings of 6-HQ are essentially planar, with deviations from the mean plane in the range 0.0001 (9)–0.0231 (9) Å. Larger r.m.s. deviations from the quinoline plane are observed for the N1-containing molecule than for the N2-containing molecule (0.0141 *versus* 0.0027 Å, respectively). The C—O bond lengths are in the region of 1.355 Å (Table 1) and compare well with the calculated value (1.352 Å; Bach *et al.*, 1998). The C—O distances are also similar to those of related compounds, such as 8-hydroxyquinoline *N*-oxide (Desiderato *et al.*, 1971) and ethyl 4-(4-chlorophenyl)-6-hydroxyquinoline-2-carboxylate (Wu *et al.*, 2006). The hydroxy group exerts an influence on the lengths of the C5—C6 (C15—C16) and C6—C7 (C16—C17) endocyclic bonds of the adjacent benzene ring (Table 1). These bonds are elongated in comparison with the corresponding distances in quinoline, *i.e.* 1.358 (2) [1.360 (2) Å] and 1.410 (2) Å [1.405 (2) Å], respectively (Davies & Bond, 2001). This behavior is probably a consequence of some degree of conjugation between the O atom and the quinoline system, which was also observed in other quinoline derivatives (Suszko-Purzycka *et al.*, 1985).

The main difference between the two symmetry-independent molecules is the orientation of the hydroxy group with respect to the quinoline ring system. In the N1-containing molecule, the hydroxy H atom is in a *cis* position relative to atom C5 and this is the *cis* conformer of 6-HQ (6-HQ*A*). In turn, the second molecule has a *trans* conformation of the C15—C16—O2—H2O group and this is the *trans* conformer of 6-HQ (6-HQ*B*). Thus, the values of the C5—C6—O1—H1O and C7—C6 —O1—H1O torsion angles [−2.8 (9) and 177.6 (9)°, respectively] are different from those of the C15—C16—O2—H2O and C17—C16—O2—H2O angles [−162.3 (9) and 19.0 (9)°, respectively]. Similar calculated and experimental conformers with a different orientation of the hydroxy group have been found in the structure of β-naphthol (Marciniak *et al.*, 2003; Ahn *et al.*, 2003). The values of the same torsion angles were −1.39 and 178.66°, respectively, for *cis*-β-naphthol and −159.42 and 22.13° for *trans*-β-naphthol (Marciniak *et al.*, 2003). In the case of 6-HQ, as well as β-naphtol, the total energies of two rotamers in the ground state calculated by the *ab initio* self-consistent field method showed that the *cis* rotamer is more stable than the *trans* rotamer (Bach *et al.*, 1998).

In the crystal structure of 6-HQ, the two symmetry-independent molecules interact *via* O—H···N hydrogen bonds (Table 2), forming two separate extended zigzag chains (Fig. 2) with the graph-set notation $C(7)$ (Bernstein *et al.*, 1990; Grell *et al.*, 1999). The chain formed by the *cis* conformers runs in the *a*-axis direction and the second chain, formed by the *trans* conformers, runs in the *b*-axis direction. Thus, the two separate chains are perpendicular in the unit cell. There is also a weak C—H···O hydrogen bond with graph-set notation $D(2)$. This weak bond joins the two symmetry-independent chains (Fig. 3). Thus, the second-level graph-set notation gives two possible sets of hydrogen-bond motifs, *i.e.* $D_3^3(10)$ and $D_3^3(14)$.

The O···N distances in the O—H···N hydrogen bonds are in the range 2.5–3.2 Å and therefore they can be regarded as strong hydrogen bonds (Desiraju & Steiner, 1999). The

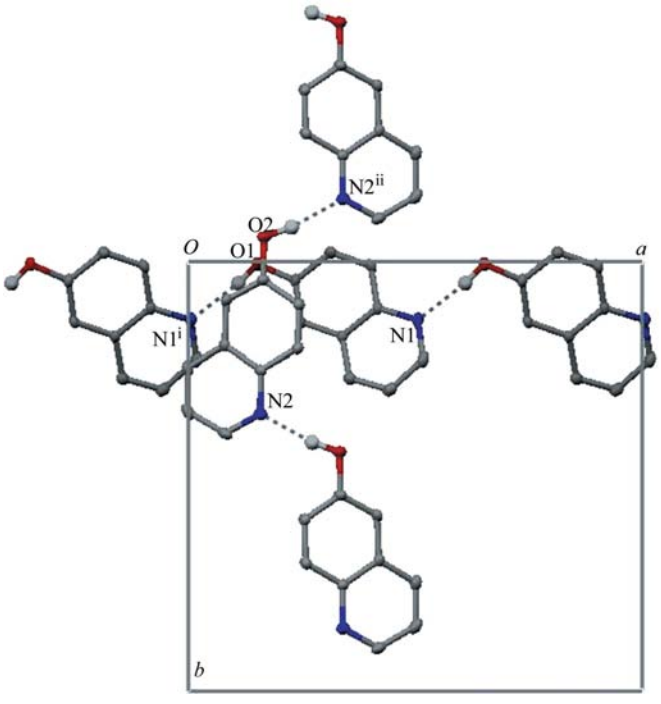

Figure 2
A view along the *c* axis of the O—H···N hydrogen-bonded chains of 6-HQ molecules. [Symmetry codes: (i) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.]

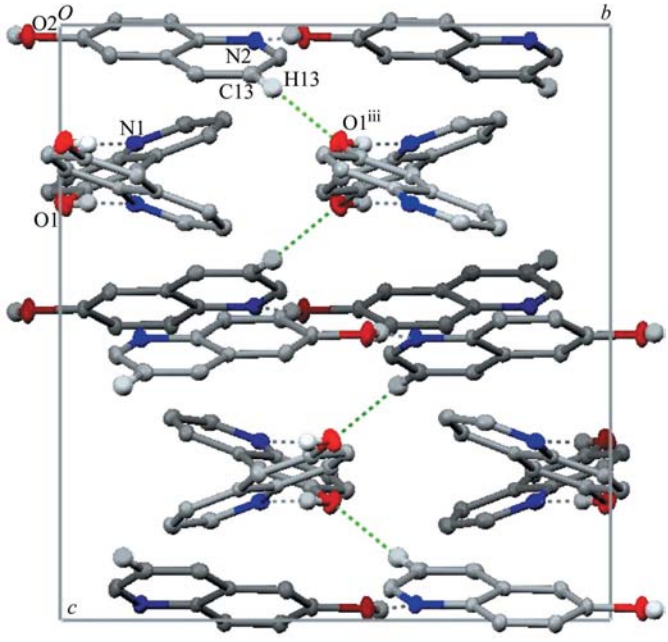

Figure 3
A view along the *a* axis, showing weak C—H···O hydrogen bonds (green in the electronic version of the paper). [Symmetry code: (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.]

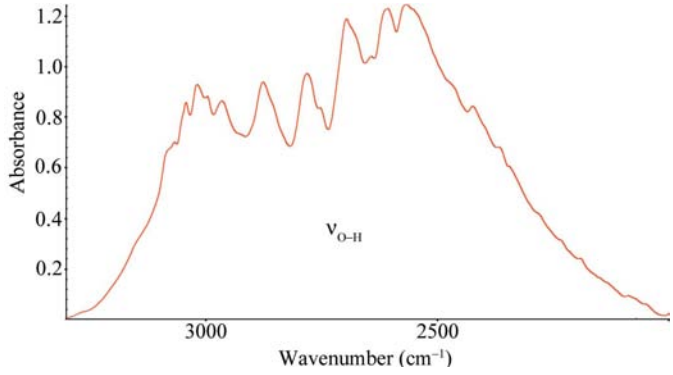

Figure 4
The IR spectrum of 6-HQ measured by the KBr pellet technique at room temperature, showing the ν_{O-H} frequency range.

strength of the hydrogen bonds in this compound was also investigated with the help of IR spectroscopy. The band of the isolated O—H stretching vibration in alcohols, ν_{O-H}, is located at a frequency of about 3600 cm^{-1} (Günzler & Gremlich, 2002). In the case of 6-HQ, we observed a wide contour of the O—H stretching vibration band in the frequency range 3100–2200 cm^{-1} (Fig. 4). This band is shifted towards the lower frequencies by *ca* 900 cm^{-1} with respect to the band frequency of the isolated O—H stretching vibration. This shift in relation to the unpeturbated value is 25% and this value lies on the border between a strong and a very strong hydrogen bond (Desiraju & Steiner, 1999).

Experimental

Powder of 6-HQ was purchased from Sigma–Aldrich and used without further purification. It took nearly four years to obtain crystals suitable for X-ray diffraction analysis. During this time, many crystal growth trials were carried out from mixtures of various solvents, such as chloroform, petroleum ether, ethyl acetate, ethanol and water. Suitable crystals were grown only by very slow evaporation at 280.0 (1) K of an acetone solution of 6-HQ, which was placed in a bottle with a very thin glass capillary inserted in the bottle stopper.

Crystal data

C_9H_7NO
M_r = 145.16
Orthorhombic, *Pbca*
a = 14.2061 (2) Å
b = 13.4440 (2) Å
c = 14.5341 (2) Å
V = 2775.82 (7) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 (2) K
0.41 × 0.18 × 0.1 mm

Data collection

Oxford Diffraction diffractometer with a Sapphire3 CCD detector
31753 measured reflections
5637 independent reflections
3361 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.102
S = 1.00
5637 reflections
208 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected bond lengths (Å).

O1—C6	1.3557 (11)	O2—C16	1.3550 (12)
C5—C6	1.3722 (14)	C15—C16	1.3746 (13)
C6—C7	1.4188 (14)	C16—C17	1.4159 (14)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N1^{i}	0.842 (13)	1.877 (13)	2.7125 (11)	171.4 (12)
O2—H2O···N2^{ii}	0.904 (12)	1.852 (13)	2.7442 (11)	168.6 (12)
C13—H13···O1^{iii}	0.958 (12)	2.518 (12)	3.4411 (13)	161.8 (10)

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

The aromatic H atoms were treated as riding on their parent atoms, with C—H distances of 0.95 Å and U_{iso}(H) values of $1.2U_{eq}$(C). H atoms involved in hydrogen bonding were located in a difference Fourier map and refined freely with isotropic displacement parameters (distances are given in Table 2).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3283). Services for accessing these data are described at the back of the journal.

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