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Key indicators

8-Hydroxyquinolinium–dibromosuccinate–dibromosuccinic acid (2/1/2)

In the crystal of the title compound, $2C_9H_8NO^+ \cdot C_4H_2Br_2O_4{}^{2-} \cdot 2C_4H_4Br_2O_4$, the dibromosuccinate dianion and dibromosuccinic acid molecules each lie on an inversion center. They interact *via* hydrogen bonding. The hydroxyquinolinium cations are hydrogen bonded to both the dibromosuccinate anion and dibromosuccinic acid molecules. The overlapped arrangement and short face-to-face distance of 3.431 (17) Å indicate the existence of π–π stacking between hydroxyquinolinium rings in the crystal structure.

Comment

As π–π stacking between aromatic rings is correlated with the electron-transfer process in some biological systems (Deisenhofer & Michel, 1989), we have recently been interested in the nature of π–π stacking. A series of metal complexes incorporating aromatic ligands such as benzimidazole, phenanthroline and quinoline has been prepared in our laboratory, and their crystal structures yield useful information about π–π stacking (Wu *et al.*, 2003; Pan & Xu, 2004; Li *et al.*, 2005). Recently, we obtained crystals of the title hydroxyquinolinium salt, (I), while attempting to prepare an iron(II) complex with hydroxyquinoline. The crystal structure of (I) shows the existence of π–π stacking between hydroxyquinolinium rings.

(I)
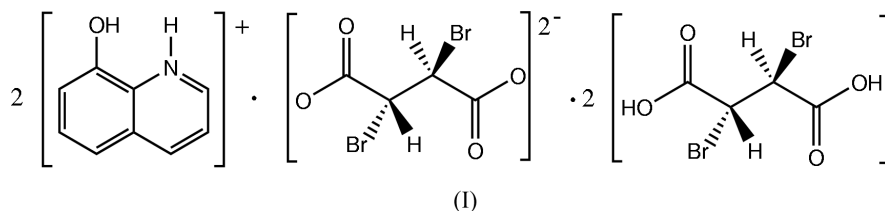
Compound (I) contains discrete 8-hydroxyquinolinium cations, dibromosuccinate (dbs) dianions and dibromosuccinic acid (H_2dbs) molecules (Fig. 1). The dbs and H_2dbs species each lie on an inversion center; thus, the carbon skeletons are planar. The carboxyl groups are not coplanar with the carbon skeletons, having dihedral angles of 23.0 (18)° for the dbs anion and 46.3 (9) and 51.4 (10)° for the two H_2dbs molecules.

The dbs and H_2dbs species are held together *via* hydrogen bonding involving the carboxyl groups, to form an extended network (Fig. 2). The hydroxyquinolinium cations link with the dbs and H_2dbs *via* O1—H1···O16^i (see Table 1 for symmetry code) and N1—H1···O11 hydrogen bonds, respectively (Table 1 and Fig. 1).

An overlapped arrangement of neighboring hydroxyquinolinum cations is observed in (I) (Fig. 3). The face-to-face distance of 3.431 (17) Å between the parallel hydroxyquinolinium rings clearly shows the existence of π–π stacking.
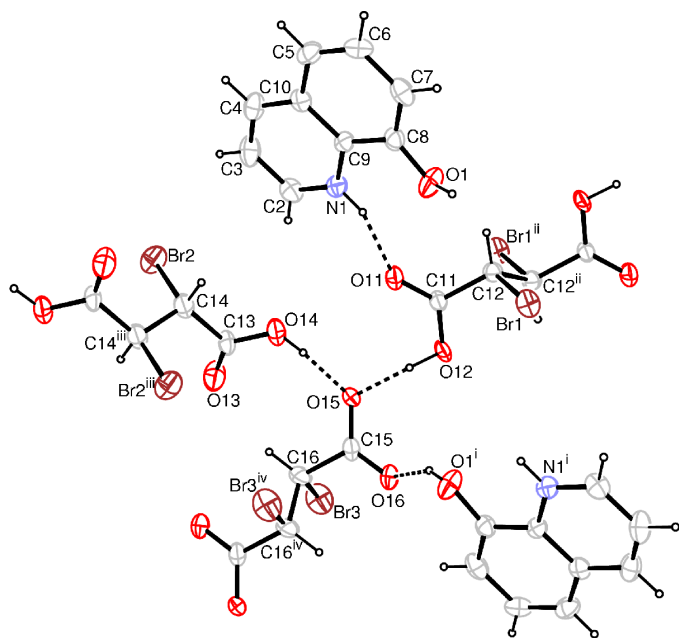
Figure 1
The structure of (I) with 40% displacement ellipsoids (arbitrary spheres for the H atoms). Dashed lines indicate hydrogen bonding [symmetry codes: (i) $2 - x$, $1 - y$, $1 - z$; (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $2 - x$, $-y$, $-z$; (iv) $2 - x$, $1 - y$, $-z$].
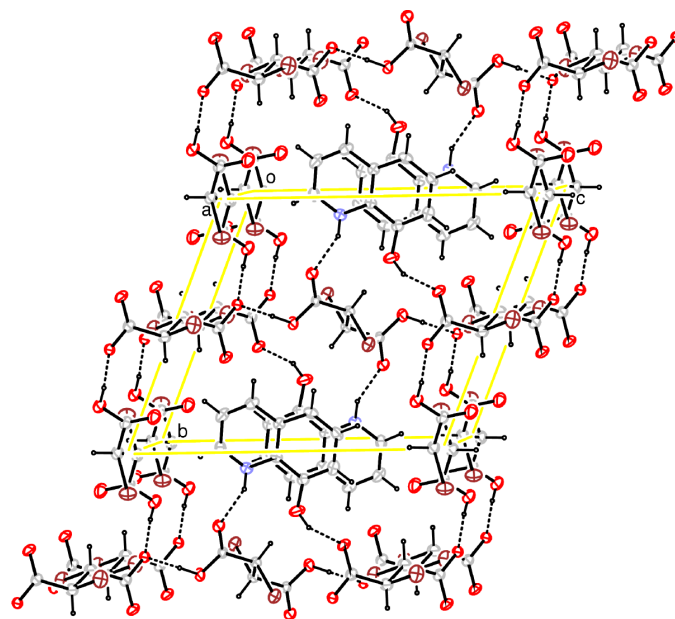

Figure 2
The packing of (I), showing the hydrogen-bond network (dashed lines).
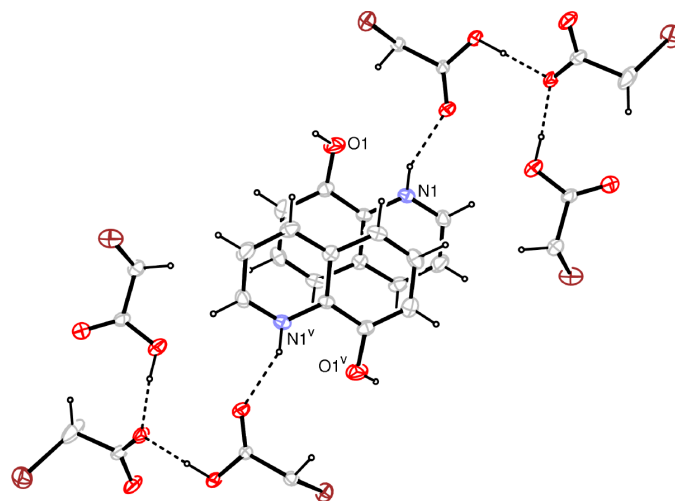

Figure 3
Detail of (I) showing π–π stacking between hydroxyquinolinium rings [symmetry code: (v) $2 - y$, $-y$, $1 - z$]. Dashed lines indicate hydrogen bonds.

Experimental

An ethanol solution (6 ml) of 8-hydroxyquinoline (0.29 g, 2 mmol) was mixed with an aqueous solution (4 ml) of dibromosuccinic acid (0.55 g, 2 mmol) at room temperature. Single crystals of (I) were obtained from the solution after 10 d.

Crystal data

$2C_9H_8NO^+\cdot C_4H_2Br_2O_4{}^{2-}\cdot$	$Z = 1$
$2C_4H_4Br_2O_4$	$D_x = 2.065$ Mg m^{-3}
$M_r = 1117.98$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 4238
$a = 6.9687$ (8) Å	reflections
$b = 11.4468$ (12) Å	$\theta = 2.0$–$24.5°$
$c = 12.6870$ (13) Å	$\mu = 6.77$ mm^{-1}
$\alpha = 110.396$ (2)°	$T = 295$ (2) K
$\beta = 100.042$ (2)°	Prism, yellow
$\gamma = 100.915$ (2)°	$0.26 \times 0.20 \times 0.18$ mm
$V = 899.10$ (17) Å^3	

Data collection

Rigaku R-AXIS RAPID	3147 independent reflections
diffractometer	2360 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.044$
Absorption correction: multi-scan	$\theta_{max} = 25.1°$
(*ABSCOR*; Higashi, 1995)	$h = -8 \rightarrow 7$
$T_{min} = 0.170$, $T_{max} = 0.292$	$k = -13 \rightarrow 13$
4687 measured reflections	$l = -11 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0697P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.064$	$+ 5.0115P]$
$wR(F^2) = 0.170$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
3147 reflections	$\Delta\rho_{max} = 0.91$ e Å^{-3}
235 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
H-atom parameters constrained	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O11	0.88	1.98	2.793 (10)	152
O1—H1A···O16^i	0.96	1.72	2.617 (9)	154
O12—H12A···O15	0.93	1.62	2.551 (9)	178
O14—H14A···O15	0.93	1.67	2.582 (10)	165

Symmetry code: (i) $2 - x$, $1 - y$, $1 - z$.

H atoms attached to C atoms were placed in calculated positions [C—H = 0.98 (methylene) or 0.93 Å (aromatic)] and were included in the final cycles of refinement using the riding model [U_{iso}(H) =

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$1.2U_{eq}(C)$]. H atoms attached to O and N atoms were located in a difference Fourier map and were included in the structure-factor calculations with a fixed isotropic displacement parameter of 0.05 Å^2 and fixed positional parameters. The large displacement parameters for atom C16 probably reflect unresolved disorder in the dbs dianion, which results in a long C16—Br3 bond distance of 2.144 (17) Å. Attempts to model the disorder were not successful.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR-92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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