2988 reflections
167 parameters
H atoms treated by a
  mixture of independent
  and constrained refinement

Extinction correction: none
Scattering factors from
  Stewart *et al.* (1965) (H)
  and Creagh & McAuley
  (1992) (C, O)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.212 (2)	O3—C4	1.358 (2)
O2—C3	1.366 (2)	O3—C9	1.442 (2)
O2—C8	1.419 (2)		
C3—O2—C8	117.5 (1)	C4—O3—C9	117.1 (1)

Table 2. *Intermolecular C—H···O interactions (Å, °)*

No s.u.'s are given for quantities involving fixed H atoms.

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O2^i	0.98	2.58	3.460 (2)	150
C6—H6···O1"	0.98	2.60	3.420 (2)	142
C12—H12···O3^i	0.98	2.79	3.405 (2)	121
C9—H9B···O1'"	0.98	2.79	3.570 (2)	137
C8—H8B···O1^{iv}	0.98	2.83	3.778 (2)	162
C8—H8A···O2^v	0.98	2.89	3.802 (2)	154

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $-x, 2 - y, 1 - z$; (iv) $x, \frac{5}{2} - y, z - \frac{1}{2}$; (v) $x, \frac{5}{2} - y, \frac{1}{2} + z$.

Table 3. *Basic first- and second-level graph-set descriptors involving interactions designated a–f in order as given in Table 2*

	a	b	c	d	e	f
a	$R_2^2(18)$	$C_2^2(18)$	$R_1^2(5)$	$C_2^3(12)$	$C_2^3(15)$	$C_1^1(12)$
b		$C(5)$	$C_3^2(17)$	$C_1^2(8)$	$R_4^2(18)$	$R_4^2(28)$
c			$R_2^2(12)$	$C_3^2(13)$	$C_2^2(18)$	$C_2^3(15)$
d				$R_2^2(18)$	$C_1^1(9)$	$C_2^2(14)$
e					$C(8)$	$C_2^3(9)$
f						$C(3)$

The aldehyde H atom (H7) was refined isotropically [C7—H7 = 1.03 (2) Å]; all other H atoms were allowed for as riding atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1220). Services for accessing these data are described at the back of the journal.

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Hydrogen bonding and C—H···O interactions in bis(4-carboxyquinolinium) sulfate monohydrate

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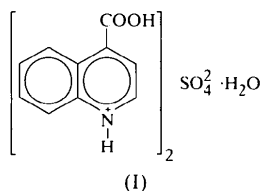
Abstract

The title substance, $2C_{10}H_8NO_2^+ \cdot SO_4^{2-} \cdot H_2O$, crystallized in the centrosymmetric space group $P\bar{1}$ with two organic cations, one sulfate ion and one water molecule in the asymmetric unit. Seven leading intermolecular hydrogen bonds are formed in this structure: two N—H···O bonds have N···O distances of 2.592 (3) and 2.650 (3) Å, while five O—H···O bonds have O···O distances ranging from 2.493 (2) to 3.072 (3) Å. All of the potential donors are involved in these bonds, but three of the potential nine acceptors are not. The H and O atoms in all these hydrogen bonds are ordered. The hydrogen bonds form a three-dimensional network. In addition, there are nine significant C—H···O interactions for which the H···O distances are less than the corresponding van der Waals radii sum. The dihedral angle between the best-fit quinoline core plane and the carboxyl group plane is 35.2 (3)° for one of the organic cations and 6.4 (4)° for the other.

Comment

Early compositional and crystallographic studies of solids obtained from aqueous solutions containing quinoline-4-carboxylic acid characterized a number of phases (Weidel, 1874; Claus & Kickelhayn, 1887; Muthmann & Nef, 1887; Muthmann, 1889; Skraup, 1880; Stuhlmann, 1888). We have previously reported structures of a monoclinic anhydrous phase (Dobson & Gerkin, 1998), of a monoclinic dihydrate (Dobson & Gerkin, 1999a), and of a triclinic trihydrate (Dobson & Gerkin, 1999b). Following addition of HCl to the parent solutions in attempts to crystallize the triclinic dihydrate phase of quinoline-4-carboxylic acid, two previously undescribed triclinic phases of 4-carboxyquinolinium chloride monohydrate were obtained and their structures determined (Dobson & Gerkin, 1999c). In a second similar attempt, H_2SO_4 was added to parent solutions and a previously undescribed phase was obtained, bis(4-carboxyquinolinium) sulfate monohydrate, (I), which is characterized here.

$$\left[\begin{array}{c} COOH \\ \text{(quinolinium ring system)} \\ N \\ H \end{array} \right]_2 SO_4^{2-} \cdot H_2O$$

(I)

Compound (I) crystallized in the centrosymmetric triclinic space group $P\bar{1}$ with two organic cations, one sulfate ion and one water molecule in the asymmetric unit. The refined asymmetric unit and the atom labeling are shown in Fig. 1. Seven leading conventional hydrogen bonds are formed. The H atoms and O atoms in all seven bonds are ordered. Geometric details of these bonds are given in Table 2. The results of hydrogen-bond graph-set analysis (Bernstein et al., 1995) for basic first- and second-level sets involving these hydrogen bonds, labeled for this purpose a–g, are presented in Table 3. The preponderance of finite graphs in the table is consistent with the very substantial involvement of the sulfate ion and the water molecule, neither possessing special symmetry, in the hydrogen bonding. The single second-level chain propagates along [001]. However, for example, there are third-level chains based on aef and aeg, both with descriptor $C_3^3(10)$ and both propagating along [100], and a fourth-level chain based on abde with descriptor $C_4^4(17)$ and propagating along [010]. These chains alone suffice to generate a three-dimensional network of hydrogen bonds. In addition, there are nine leading intermolecular C—H· · ·O interactions whose parameters fall easily within the criteria of Taylor & Kennard (1982) for significant attractive interactions and whose H· · ·O distances are less than the corresponding van der Waals (Bondi, 1964) radii sum. Geometric details of these are given in Table 2. The packing arrangement and hydrogen bonds are shown in Fig. 2.
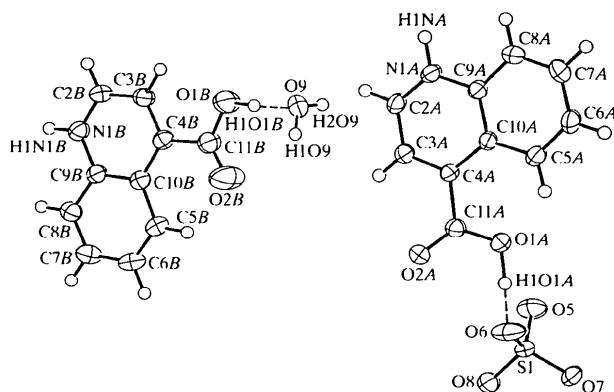

Fig. 1. ORTEPII (Johnson, 1976) drawing of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at 50% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. Dashed lines depict hydrogen bonds within the asymmetric unit.
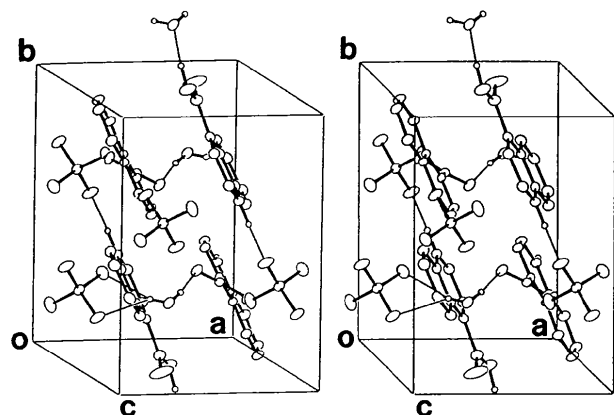

Fig. 2. ORTEPII (Johnson, 1976) packing stereodiagram of (I). Displacement ellipsoids are drawn at 20% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. For clarity, H atoms not involved in hydrogen bonding are omitted. Hydrogen bonds are depicted by the finer interatomic lines.

It may be noted that the hydrogen bond between one of the carboxyl groups and a sulfate O atom (O1A—H1O1A· · ·O6) is quite short. A comparably short hydrogen bond between a carboxyl group and a sulfate O atom has been reported for triclinic betaine hydrogen ammonium sulfate (Haussühl & Schreuer, 1996): H—O$_{carboxyl}$ = 0.90 (3), H· · ·O$_{sulfate}$ = 1.61 (3) and O$_{carboxyl}$· · ·O$_{sulfate}$ = 2.509 (2) Å, and O—H· · ·O = 176 (3)°. Moreover, although in (I) the H atom in this short hydrogen bond is farther than usual from the carboxylic O atom, it is yet too far from the sulfate O atom to support interpretation of this interaction as a carboxylate–bisulfate hydrogen bond. In bis(betaine)–sulfuric acid (Ratajczak et al., 1994), for example, the carboxylate group of the betaine I zwitterion is hydrogen-bonded by a bisulfate ion with parameters as follows: H· · ·O$_{carboxylate}$ = 1.42 (2), H—O$_{bisulfate}$ = 1.16 (2) and O$_{carboxylate}$· · ·O$_{bisulfate}$ = 2.566 (6) Å, and O· · ·H—O = 168 (2)°. [In contrast, the betaine II moiety

in the latter example exists in protonated form and is a hydrogen-bond donor to a 'bare' O atom of the bisulfate ion: H—$O_{carboxyl}$ = 0.88 (2), H$\cdots O_{bisulfate}$ = 1.68 (2) and $O_{carboxyl}\cdots O_{bisulfate}$ = 2.532 (3) Å, and O—H$\cdots$O = 166 (1)°.]

The heterocyclic and carbocyclic rings of quinoline cores *A* and *B* are, separately, nearly planar: the maximum deviations of an atom from the best-fit planes describing the rings are 0.008 (3) and 0.011 (3) Å, respectively, for *A*, and 0.013 (3) and 0.005 (3) Å for *B*. Since the dihedral angle between the planes of these rings is 2.4 (1)° in the *A* molecule and 1.4 (1)° in the *B* molecule, the quinoline cores as a whole are nearly planar. The maximum deviation of a core atom from the best-fit core plane is 0.037 (3) Å for *A* and 0.022 (3) Å for *B*. The dihedral angle between the plane of the carboxyl group and that of the ring to which it is attached is 35.2 (3)° in the *A* molecule and 6.4 (4)° in the *B* molecule. The dihedral angle between the *A* core plane and the *B* core plane is only 0.7 (1)°, so all the core planes are strictly or virtually parallel to one another, as can be seen in Fig. 2.

Corresponding (non-H) bond lengths for the *A* and *B* quinoline cores are in very good agreement. The greatest difference between members of 11 pairs of corresponding bond lengths, whose individual s.u.'s are 0.003–0.004 Å, is 0.011 Å, while the average difference is 0.005 Å. With respect to quinoline core angles, the agreement is also very good: for 12 corresponding core angles, whose s.u.'s are 0.2–0.3°, the greatest difference is 0.8°, while the average difference is less than 0.4°. The C—O single-bond distances in the carboxyl groups of *A* and *B* are also in good agreement: 1.298 (3) *versus* 1.291 (3) Å; the C=O double-bond distances are, however, not in quite such good agreement: 1.211 (3) *versus* 1.182 (2) Å. Nonetheless, a single and a double C—O bond are clearly present in both carboxyl groups and the carboxylic H atoms are ordered. The difference in the C=O double-bond distances is most likely a consequence of the notably larger thermal displacement of O2*B*, which in turn is most likely a consequence of the fact that O2*A* is the acceptor of a substantial hydrogen bond and of the strongest C—H$\cdots$O interaction, whereas O2*B* is the only O atom in the structure without a significant interaction of either type. An alternative explanation would invoke disordering of O2*B* which, however, would apparently not involve the remaining atoms of the *B* carboxyl group and thus appears implausible. A low-temperature study would, of course, be useful for resolving this issue. Finally, it may be noted that the largest *U* component of O2*B* is only approximately twice as large as the corresponding *U* component of O8, even though the latter is involved in a hydrogen bond.
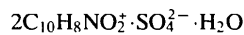
Selected bond distances and angles of (I) are given in Table 1. All distances and angles fall within normal limits. The closest intermolecular approaches, excluding pairs of atoms involved in the tabulated hydrogen-

bonding groups or C—H$\cdots$O interactions, are between O5 and C2 $(-x, 1-y, 1-z)$, and fall short of the corresponding van der Waals (Bondi, 1964) radii sum by 0.12 Å.

Experimental

Crystal data

$2C_{10}H_8NO_2^+ \cdot SO_4^{2-} \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 462.43$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 7.811\,(1)$ Å	$\theta = 13.9–17.5°$
$b = 11.1324\,(8)$ Å	$\mu = 0.227$ mm^{-1}
$c = 11.831\,(1)$ Å	$T = 296$ K
$\alpha = 87.508\,(7)°$	Cut column
$\beta = 71.538\,(8)°$	$0.40 \times 0.23 \times 0.15$ mm
$\gamma = 87.198\,(9)°$	Colorless
$V = 974.3\,(2)$ Å^3	
$Z = 2$	
$D_x = 1.576$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5S diffractometer	$\theta_{max} = 27.55°$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: none	$k = -14 \rightarrow 0$
4742 measured reflections	$l = -15 \rightarrow 15$
4508 independent reflections	6 standard reflections
2882 reflections with	every 150 reflections
$I > 2\sigma(I)$	intensity decay: $\pm$ 3.4%
$R_{int} = 0.052$	(average maximum
	relative intensity)

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F) = 0.056$	$\Delta\rho_{max} = 0.60$ e Å^{-3}
$wR(F^2) = 0.098$	$\Delta\rho_{min} = -0.63$ e Å^{-3}
$S = 1.61$	Extinction correction: none
4505 reflections	Scattering factors from
313 parameters	Stewart *et al.* (1965) (H)
H atoms: see below	and Creagh & McAuley
$w = 1/[\sigma_{cs}^2 + (0.011I)^2]$	(1992) (C, N, O, S)

Table 1. *Selected geometric parameters (Å, °)*

S1—O5	1.447 (2)	O1A—C11A	1.298 (3)
S1—O6	1.470 (2)	O2A—C11A	1.211 (3)
S1—O7	1.476 (2)	O1B—C11B	1.291 (3)
S1—O8	1.466 (2)	O2B—C11B	1.182 (3)
O5—S1—O6	109.9 (1)	O1A—C11A—O2A	125.2 (2)
O5—S1—O7	109.9 (1)	O1A—C11A—C4A	114.5 (2)
O5—S1—O8	112.2 (1)	O2A—C11A—C4A	120.2 (2)
O6—S1—O7	107.8 (1)	O1B—C11B—O2B	123.5 (3)
O6—S1—O8	109.6 (1)	O1B—C11B—C4B	112.9 (3)
O7—S1—O8	107.3 (1)	O2B—C11B—C4B	123.6 (3)
H1O9—O9—H2O9	112 (3)		

Table 2. *Geometry of hydrogen bonds and leading inter-molecular C—H···O interactions in (I) (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1O1A···O6	1.16 (4)	1.34 (4)	2.493 (2)	172 (3)
O1B—H1O1B···O9	0.96 (4)	1.62 (4)	2.572 (3)	172 (4)
N1A—H1N1A···O7^i	1.01 (3)	1.61 (3)	2.592 (3)	163 (3)
N1B—H1N1B···O8^{ii}	1.00 (3)	1.66 (3)	2.650 (3)	169 (3)
O9—H1O9···O2A^{iii}	0.93 (4)	1.92 (4)	2.846 (3)	170 (4)
O9—H2O9···O5^{iv}	0.77 (4)	2.16 (4)	2.892 (3)	159 (4)
O9—H2O9···O7^{iv}	0.77 (4)	2.45 (3)	3.072 (3)	139 (3)
C3A—H3A···O2A^{iii}	0.98	2.34	3.255 (3)	154
C2B—H2B···O9^v	0.98	2.46	3.293 (4)	142
C2B—H2B···O6^{vi}	0.98	2.47	3.210 (3)	133
C8A—H8A···O7^i	0.98	2.50	3.191 (3)	127
C8B—H8B···O5^{ii}	0.98	2.52	3.435 (4)	155
C7B—H7B···O5^{vii}	0.98	2.57	3.290 (3)	130
C6A—H6A···O1A^{viii}	0.98	2.57	3.514 (3)	163
C7A—H7A···O7^{viii}	0.98	2.61	3.461 (3)	146
C2A—H2A···O9	0.98	2.67	3.498 (4)	142

Symmetry codes: (i) $x, y, 1+z$; (ii) $1-x, -y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1-y, 1-z$; (v) $1-x, -y, 2-z$; (vi) $x, y-1, 1+z$; (vii) $1+x, y-1, z$; (viii) $-x, 2-y, 1-z$.

Table 3. *Basic first- and second-level graph set descriptors involving conventional hydrogen bonds which are designated a–g in the order given in Table 2*

	a	b	c	d	e	f	g
a	D	—	$C_2^2(11)$	$D_2^2(7)$	$D_2^2(7)$	$D_2^2(7)$	$D_2^2(7)$
b		D	—	$D_2^2(10)$	$D_2^2(5)$	$D_2^2(5)$	$D_2^2(5)$
c			D	$D_2^2(7)$	$D_2^2(10)$	$D_2^2(7)$	$D_2^1(5)$
d				D	—	$D_2^2(7)$	$D_2^2(7)$
e					D	$D_2^2(5)$	$D_2^2(5)$
f						D	$R_1^2(4)$
g							D

H(—C) atoms were allowed for as riding atoms; coordinates for H atoms on N and O atoms were determined from difference maps and refined isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1225). Services for accessing these data are described at the back of the journal.

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Dicyclohexylammonium trifluoroacetate

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Abstract

Two hydrogen bonds [N···O = 2.785 (2) and 2.794 (2) Å] link the cations and anions of dicyclohexylammonium trifluoroacetate, $C_{12}H_{24}N^+·C_2F_3O_2^-$, into a zigzag chain.