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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1205). Services for accessing these data are described at the back of the journal.

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Hydrogen bonding in quinolinium-4-carboxylate trihydrate

ALLISON J. DOBSON AND ROGER E. GERKIN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

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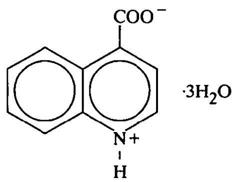
Abstract

The previously undescribed title substance, $C_{10}H_7NO_2\cdot3H_2O$, crystallized in the centrosymmetric space group $P\bar{1}$ with one zwitterionic organic molecule and three water molecules in the asymmetric unit. One N—H···O and six O—H···O hydrogen bonds are present in this structure, with donor–acceptor distances ranging from 2.607 (2) to 2.931 (3) Å. The H atoms in these hydrogen bonds are ordered. The hydrogen bonds generate a two-dimensional network. Structural comparisons are made with quinolinium-4-carboxylate dihydrate.

Comment

Early compositional and crystallographic studies of solid phases 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). These solids include two anhydrous phases, one monoclinic and one not determined crystallographically, a monohydrate, not crystallographically determined, and triclinic and monoclinic dihydrates. We have reported previously structures of the monoclinic anhydrous phase (Dobson & Gerkin, 1998) and of a monoclinic dihydrate (hereafter Q4CD; Dobson & Gerkin, 1999).

Rather curiously, one of the phases appearing commonly in our various growths from aqueous solutions containing quinoline-4-carboxylic acid is a triclinic trihydrate, quinolinium-4-carboxylate trihydrate, (I), which is not mentioned by any of the early investigators. While the stability of exposed crystals of this phase depends sensitively on the ambient humidity, it appears



(I)

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surprising that this phase either did not occur or was not recognized and characterized in the early extensive investigations of the crystallization behavior of quinoline-4-carboxylic acid.

Compound (I) crystallized in the centrosymmetric triclinic space group $P\bar{1}$ with one zwitterionic organic molecule and three water molecules in the asymmetric unit. The refined asymmetric unit and the numbering scheme are shown in Fig. 1. Seven strong conventional hydrogen bonds, which involve each of the seven possible donor H atoms and each of the five O atoms as acceptors, are formed in this structure. The H atoms in all these hydrogen 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 seven bonds, designated for this purpose *a*–*g*, are presented in Table 3. The most notable feature of this analysis is the great preponderance of finite graphs, which is consistent with the very substantial contribution by waters of hydration to the hydrogen bonding. The sole chain which appears in this table propagates along [100]. However, a chain (*bcdef*) with descriptor $C_5^4(10)$ and propagating along [010] arises at the fifth level of graph sets. Thus, a two-dimensional hydrogen-bonded network is formed. The packing diagram (Fig. 2) shows portions of both these chains and also illustrates the layering of the structure along the *c* axis, with the O atoms of the water molecules lying almost in the *ab* planes bounding the unit cell and the acid molecules lying between the water layers. Geometric details of the two leading intermolecular C—H···O interactions, whose H···O distances are less or just greater than the corresponding Bondi (1964) van der Waals radius sum, are given in Table 2. It may be noted that including these interactions with the conventional hydrogen bonds does not lead to a three-dimensional interaction network.

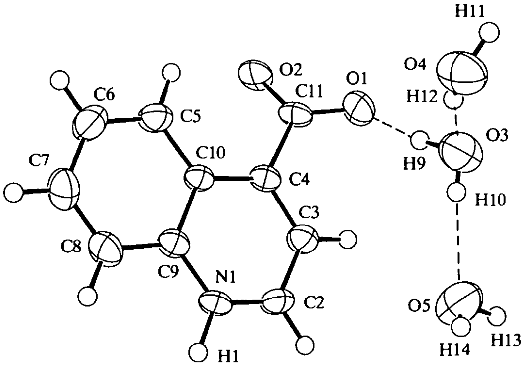

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms, while spheres of arbitrary small radius depict H atoms. Dashed lines depict hydrogen bonds within the asymmetric unit.

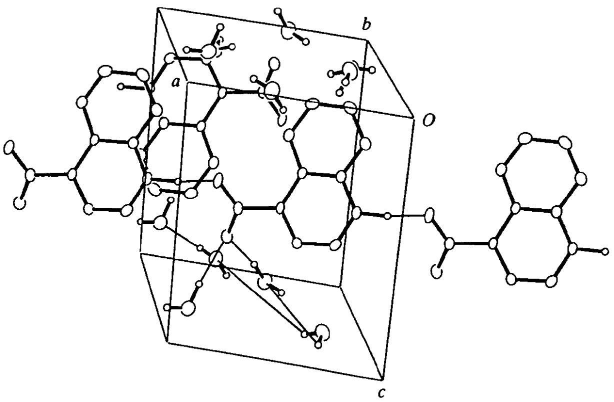

Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 20% probability for all non-H atoms, while spheres of arbitrary small radius depict H atoms. Hydrogen bonds are depicted by the finer interatomic lines.

The heterocyclic and carbocyclic rings of the quinoline core are, separately, very nearly planar; the maximum deviations of an atom from the best-fit planes describing the rings are 0.005 (2) and 0.010 (2) Å, respectively. Since the dihedral angle between the planes of these rings is only 1.2 (1)°, the quinoline core as a whole is nearly planar; the maximum deviation of a core atom from the best-fit core plane is 0.020 (2) Å. The corresponding deviation in the comparison structure, Q4CD, is 0.045 (1) Å. Whereas in Q4CD, the core planes of the organic molecules are either strictly parallel or nearly perpendicular, in (I), they are all parallel, a situation very similar to that in the monoclinic phase of the anhydrous acid. The dihedral angle between the core plane and the plane of the carboxylate group in (I) is 33.4 (1)°; in Q4CD, it is 65.2 (3)°. This difference appears readily ascribable to the different disposition of the waters of hydration.

Corresponding (non-H) bond lengths for the quinoline cores of Q4CD and (I) are in very good agreement. The greatest difference between the 11 corresponding bond lengths, whose s.u.'s are 0.003 Å, is 0.009 Å, while the average difference is 0.004 Å. With respect to the quinoline core angles, the agreement is also very good; for 12 corresponding core angles, whose s.u.'s are 0.2°, the greatest difference is 0.7°, while the average difference is 0.3°. Thus, particularly with respect to core angles involving the protonated N atom, compounds (I) and Q4CD are in substantially better agreement than is either one with the anhydrous acid, in which the N atom is not protonated. The C—O bond distances in the carboxylate group of (I), 1.242 (2) and 1.248 (2) Å, are, as expected, not significantly different; in Q4CD, the corresponding distances are not so nearly equal.

Bond distances and angles in (I) of particular interest are given in Table 1. All distances and angles fall within normal limits. The closest intermolecular approaches, excluding pairs of atoms involved in hydrogen-bonding groups or in the tabulated C—H···O interactions, are between O2 and C9^{vi} [symmetry code: (vi) $1-x$, $1-y$, $1-z$], and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.05 Å.

Experimental

Quinoline-4-carboxylic acid was obtained from the Aldrich Chemical Company as a tan powder of stated purity 97%. It was dissolved in water as received, and the solution was either just filtered or treated with decolorizing carbon and filtered. Evaporation of such solutions at room temperature produced a variable number of phases, including the triclinic trihydrate phase reported here. Unit-cell determinations on a number of samples from such growths established that the triclinic trihydrate phase of interest grew as polyhedra, irregular hexagonal columns and plates, with hues ranging from pale amber to colorless. The data reported here were collected from a colorless plate. Since this phase is quite sensitive to the ambient humidity, the sample was mounted in a sealed glass capillary.

Crystal data

$C_{10}H_7NO_2{\cdot}3H_2O$
$M_r = 227.22$
Triclinic
$P\bar{1}$
$a = 7.547\ (2)$ Å
$b = 8.035\ (1)$ Å
$c = 10.240\ (1)$ Å
$\alpha = 77.78\ (1)°$
$\beta = 86.62\ (1)°$
$\gamma = 65.46\ (1)°$
$V = 551.8\ (2)$ Å^3
$Z = 2$
$D_x = 1.367$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.0–17.4°$
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Plate
0.54 × 0.27 × 0.12 mm
Colorless

Data collection

AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2736 measured reflections
2542 independent reflections
1270 reflections with $I > 2\sigma_I$
$R_{\rm int} = 0.024$

$\theta_{\rm max} = 27.56°$
$h = 0 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = -13 \rightarrow 13$
6 standard reflections every 150 reflections intensity decay: 1.33%

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.078$
$S = 1.27$
2539 reflections
173 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2_{\rm cs} + (0.003I)^2]$
$(\Delta/\sigma)_{\rm max} = 0.0002$
$\Delta\rho_{\rm max} = 0.43$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, N, O)

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

O1—C11	1.242 (2)	N1—C2	1.311 (3)
O2—C11	1.248 (2)	N1—C9	1.369 (2)
H9—O3—H10	101 (3)	O1—C11—O2	126.0 (2)
H11—O4—H12	116 (3)	O1—C11—C4	117.3 (2)
H13—O5—H14	109 (3)	O2—C11—C4	116.8 (2)
C2—N1—C9	122.8 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °) and leading intermolecular C—H···O interactions*

Note that no s.u.'s are given for quantities involving H atoms H2 and H8 since they are fixed.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^i	1.03 (2)	1.58 (2)	2.607 (2)	172 (2)
O3—H9···O1	0.97 (3)	1.79 (3)	2.753 (3)	170 (3)
O3—H10···O5	0.74 (4)	2.06 (4)	2.794 (3)	172 (4)
O4—H11···O3^{ii}	0.87 (3)	2.10 (3)	2.931 (3)	161 (3)
O4—H12···O3	0.84 (3)	1.97 (3)	2.796 (3)	165 (3)
O5—H13···O1^{iii}	0.92 (3)	1.92 (3)	2.837 (3)	170 (3)
O5—H14···O4^{iv}	0.75 (3)	2.09 (3)	2.834 (3)	174 (4)
C2—H2···O4^v	0.98	2.58	3.300 (3)	131
C8—H8···O2^i	0.98	2.72	3.390 (3)	126

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

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

	a	*b*	*c*	*d*	*e*	*f*	*g*
a	$C(7)$	$D_2^2(7)$	–	–	–	$D_2{}^2(7)$	–
b		D	$D_2^2(5)$	$D_2^2(5)$	$D_2^2(5)$	$D_2^1(5)$	–
c			D	$D_2^2(5)$	$D_2^2(5)$	$D_2^2(5)$	$D_2^2(5)$
d				D	$R_4^4(8)$	–	$D_2^2(5)$
e					D	–	$D_2^2(5)$
f						D	$D_2^2(5)$
g							D

Scan widths were $(1.50 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. A linear decay correction was applied. The Laue group assignment and the centrosymmetry indicated by the intensity statistics led to assignment of the space group as $P\bar{1}$ (No. 2); since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions. Then, all H atoms were refined; the six C—H distances ranged from 0.92 (2) to 1.02 (2) Å, with a mean value of 0.98 (4) Å. Subsequently, these six H atoms were made canonical with C—H = 0.98 Å and $B_{\rm iso} = 1.2B_{\rm eq}$ of the attached C atom. Refined N—H and O—H distances are given in Table 2. In the late stages of refinement, the extinction coefficient was predicted to be negative and was hence not included in the model. However, three intense low-angle reflections (001, 021 and 022) appeared to be substantially affected by extinction and were excluded from further refinement. The maximum peak in the final difference map occurred ∼0.8 Å from O1 and the maximum negative peak occurred ∼1.3 Å from N1.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1203). Services for accessing these data are described at the back of the journal.

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