ORGANIC COMPOUNDS

Hydrogen bonding in quinolinium-4-carboxylate dihydrate

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
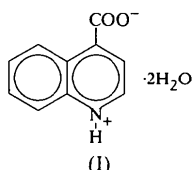
Abstract

The title acid, $C_{10}H_7NO_2 \cdot 2H_2O$, crystallized in the non-centrosymmetric space group Cc with one zwitterionic organic molecule and two water molecules in the asymmetric unit. One N—H···O and four O—H···O hydrogen bonds are present in this structure, with donor–acceptor distances ranging from 2.688 (2) to 2.852 (3) Å. These hydrogen bonds generate a three-dimensional network. Structural comparisons are made with anhydrous quinoline-4-carboxylic acid.

Comment

This study of quinolinium-4-carboxylate dihydrate, (I), is one of a series on hydrogen bonding in heterocyclic aromatic carboxylic acids, which includes most recently the parent molecule, quinoline-4-carboxylic acid (Dobson & Gerkin, 1998). The earliest report of a crystallographic investigation of a hydrate of quinoline-4-carboxylic acid is that of Weidel (1874), who presents Ditscheiner's determination of axial ratios and the β angle of a monoclinic dihydrate. Later, Muthmann & Nef (1887) reported a triclinic dihydrate and asserted that Ditscheiner's results must be misascribed, and should be withdrawn. Almost immediately thereafter, however, Claus & Kickelhayn (1887) demonstrated that both studies are valid. This system is thus among the very earliest, if not the earliest, in which dimorphism of an organic hydrate was demonstrated (since such a possibility was clearly not seriously considered by Muthmann & Nef).

COO⁻

·2H₂O

N⁺
H

(I)

(I) crystallized in the non-centrosymmetric, monoclinic space group Cc with one zwitterionic organic molecule and two water molecules in the asymmetric

unit. The refined asymmetric unit and the numbering scheme are shown in Fig. 1. Five strong conventional hydrogen bonds, which involve each of the five possible donor H atoms and acceptor atoms O1, O2 and O4, are formed in this structure. Geometric details of these bonds are given in Table 2. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) for first- and basic second-level sets involving these five bonds, labeled for this purpose a–e, are presented in Table 3. A notable feature is the preponderance of finite graphs, which is consistent with the substantial contribution by waters of hydration to the hydrogen bonding. There are also three chains which, in their order of appearance in the table, propagate along [101], [101] and [001]. In the packing diagram, Fig. 2, three additional patterns are prominent: third-level rings (abc) with descriptor $R_5^4(17)$, fourth-level rings ($bcde$) with descriptor $R_4^{12}(36)$ and fourth-level chains ($bcde$) with descriptor $C_{10}^9(28)$, which propagate along [011], [110] and [112]. The sets of chains taken together form a three-dimensional hydrogen-bonded network. It is of interest that O3, which does not participate as an acceptor in conventional hydrogen bonding, is involved in two intermolecular C—H···O interactions for which the H···O distances are the shortest occurring in the C—H···O interactions in this structure, and are significantly less than the corresponding Bondi (1964) van der Waals radius sum. Geometric details of these two interactions are given in Table 2.
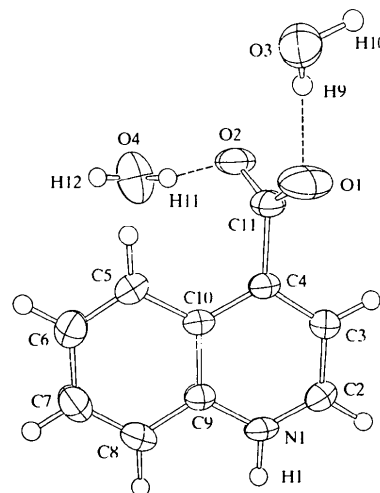

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radii depict H atoms. Hydrogen bonds are shown as dashed lines.

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
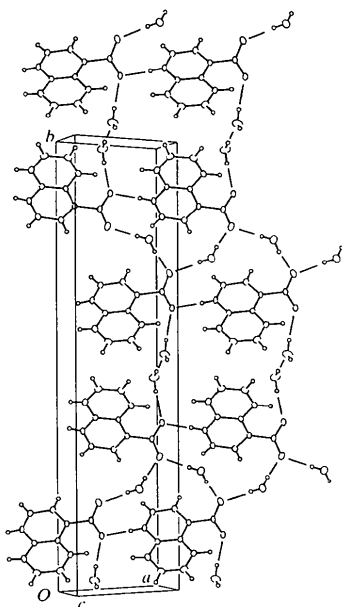
Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radii depict H atoms. Hydrogen bonds are shown as single dashes.

describing the rings are 0.017 (3) and 0.004 (3) Å, respectively. Since the dihedral angle between the planes of these rings is only 2.0 (1)°, the quinoline core as a whole is nearly planar: the maximum deviation of a core atom from the best-fit core plane is 0.045 (1) Å. The dihedral angle between the core plane and the plane of the carboxylate group is 65.2 (3)°. The dihedral angle between the quinoline core planes not required to be parallel by symmetry is 85.9 (1)°. Hence, the core planes of the organic molecules in this structure are either strictly parallel or nearly perpendicular.

Suitable comparisons with the structure of the acid moiety of (I) are afforded by the structure of anhydrous quinoline-4-carboxylic acid (hereafter, Q4CA; Dobson & Gerkin, 1998). The quinoline core of (I) is comparably planar to that of Q4CA, in which the maximum deviation of a core atom from its best-fit core plane is 0.029 (1) Å. The dihedral angle between the core plane and the plane of the carboxyl group in Q4CA, 45.9 (1)°, is somewhat different from that given above for (I). However, corresponding individual (non-H) bond lengths for the quinoline cores of Q4CA and (I) are in generally excellent agreement. The greatest difference between the 11 corresponding bond lengths is 0.010 (3) Å; the average difference is 0.005 (3) Å. With respect to quinoline core angles, the agreement is mixed: while the three pairs of angles involving the N atom differ by 3.4 (2), 2.2 (2) and 2.6 (2)°, the remaining nine corresponding pairs of angles show an average difference of 0.6 (2)°. Bond distances in the carboxylate group of (I) lie intermediate, as expected, to those in the ordered carboxyl group of Q4CA [1.306 (2)

and 1.205 (1) Å]. Finally, whereas in the title substance the quinoline core planes are strictly parallel or nearly perpendicular to each other, in Q4CA they are strictly parallel or nearly parallel to each other.

Bond distances and angles of (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 or in the tabulated C—H···O interactions, are between C11 and H10($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$), and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.20 Å.

Experimental

Quinoline-4-carboxylic acid was obtained from Aldrich Chemical Company as a tan powder of stated purity 97%. It was dissolved in water as received, and the solution was filtered. Evaporation of such solutions at room temperature produced a variable number of phases, including the monoclinic dihydrate phase reported here in the form of colorless plates. One of these was cut to provide the experimental sample.

Crystal data

C₁₀H₇NO₂·2H₂O	Mo $K\alpha$ radiation
$M_r = 209.20$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
Cc	reflections
$a = 8.438 (2)$ Å	$\theta = 15.6–17.4°$
$b = 27.496 (1)$ Å	$\mu = 0.108$ mm⁻¹
$c = 4.894 (1)$ Å	$T = 296$ K
$\beta = 117.38 (2)°$	Cut plate
$V = 1008.3 (3)$ Å³	0.46 × 0.42 × 0.19 mm
$Z = 4$	Colorless
$D_x = 1.378$ Mg m⁻³	
D_m not measured	

Data collection

AFC-5S diffractometer	$h = 0 \to 10$
ω scans	$k = 0 \to 35$
Absorption correction: none	$l = -6 \to 5$
1268 measured reflections	6 standard reflections
1239 independent reflections	every 150 reflections
1092 reflections with	intensity variation: ±1.0%
$I > 2\sigma I$	(average maximum
$R_{int} = 0.026$	relative intensity)
$\theta_{max} = 27.53°$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.0003$
$R(F) = 0.032$	$\Delta\rho_{max} = 0.22$ e Å⁻³
$wR(F^2) = 0.055$	$\Delta\rho_{min} = -0.17$ e Å⁻³
$S = 1.85$	Extinction correction:
1239 reflections	Zachariasen (1963, 1968)
155 parameters	Extinction coefficient:
H atoms treated by a	1.6 (2) × 10⁻⁶
mixture of independent	Scattering factors from
and constrained refinement	Stewart et al. (1965) for
$w = 1/\sigma^2(F^2)$, where	H and Creagh & McAuley
$\sigma^2 = \sigma_{cs}^2 + (0.002I)^2$	(1992) for C, N and O

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

O1—C11	1.225 (3)	O2—C11	1.254 (3)
C2—N1—C9	122.7 (2)	O1—C11—O2	126.4 (2)
C3—C4—C11	119.3 (2)	O1—C11—C4	117.2 (2)
C10—C4—C11	120.9 (2)	O2—C11—C4	116.4 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^i	0.93 (2)	1.76 (3)	2.688 (2)	174 (2)
O3—H9···O1	0.81 (3)	2.04 (3)	2.852 (3)	177 (3)
O3—H10···O1^{ii}	1.03 (4)	1.81 (4)	2.797 (3)	159 (3)
O4—H11···O2	0.87 (3)	1.98 (3)	2.837 (2)	169 (4)
O4—H12···O4^{iii}	0.82 (3)	1.98 (3)	2.794 (2)	173 (4)
C2—H2···O3^{iv}	0.98	2.19	3.165 (3)	171
C3—H3···O3^v	0.98	2.40	3.318 (3)	156

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

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

	a	b	c	d	e
a	C(7)	$D_3^3(14)$	$D_3^3(14)$	$D_2^1(5)$	none
b		D	$C_2^1(4)$	$D_2^2(7)$	none
c			D	$D_2^2(7)$	none
d				D	$D_3^4(7)$
e					C(2)

Scan widths were $(1.60 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and the lack of centrosymmetry indicated by the intensity statistics led to assignment of the space group as Cc (No. 9); since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions. Initially, all H atoms were refined; the six C—H distances ranged from 0.91 (2) to 1.03 (2) Å. Subsequently, these six H atoms were made canonical with C—H = 0.98 Å and $B_{iso} = 1.2 \times B_{eq}$ of the attached C atom. Refined N—H and O—H distances are given in Table 2. The maximum effect of extinction is 5.9% of F_o for 15$\bar{1}$. Assignment of the absolute configuration was not possible. The maximum peak in the final difference map occurred ~0.6 Å from C4; the maximum negative peak ~0.6 Å from C11.

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: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Claus, A. & Kickelhayn, M. (1887). *Ber. Dtsch Chem. Ges.* **20**, 1604–1606.

Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer Academic Publishers.

Dobson, A. J. & Gerkin, R. E. (1998). *Acta Cryst.* C54, 1883–1885.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Muthmann, W. & Nef, J. U. (1887). *Ber. Dtsch Chem. Ges.* **20**, 636–638.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Spek, A. L. (1990). *Acta Cryst.* A46, C-34.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.

Weidel, H. (1874). *Ann. Chem.* **173**, 76–116.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* A24, 212–216.

Network of C—H···O interactions in 1,2-naphthalenedicarboxylic anhydride

LAWRENCE J. FITZGERALD AND ROGER E. GERKIN

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

Abstract

The title substance, $C_{12}H_6O_3$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. Four significant C—H···O interactions have C···O distances ranging from 3.313 (2) to 3.453 (2) Å. They link each molecule directly to eight neighbors, generating a three-dimensional network. The anhydride group is compared with those in phthalic anhydride and 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride.

Comment

Although conventional hydrogen bonds are not possible in 1,2-naphthalenedicarboxylic anhydride, (I), it is of interest in terms of C—H···O interactions since it possesses three potential acceptors, O1–O3, and six