Acta Cryst. (1998). C**54**, 1883–1885

Quinoline-4-carboxylic Acid

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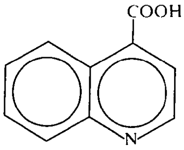
(*Received 26 May 1998; accepted 14 July 1998*)

Abstract

The title acid, $C_{10}H_7NO_2$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. There is a single hydrogen bond, O—H···N, with a donor–acceptor distance of 2.596 (1) Å. The carboxylic H atom is ordered. The dihedral angle between the best-fit quinoline core plane and the carboxyl plane is 45.9 (1)°. Structural comparisons are made with the closely related molecule 2-phenylquinoline-4-carboxylic acid.

Comment

This study of quinoline-4-carboxylic acid, (I), is one of a series on hydrogen bonding in heterocyclic aromatic carboxylic acids, which includes 4-aminoquinoline-2-carboxylic acid (Burd *et al.*, 1997) and 3-aminopyrazine-2-carboxylic acid, 2-aminonicotinic acid and 3-aminopyrazole-4-carboxylic acid (Dobson & Gerkin, 1996, 1997, 1998). The title acid crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The refined molecule and the numbering scheme are shown in Fig. 1. The carboxyl group has an ordered H atom, and participates in a hydrogen bond to the N atom of a second molecule rather than forming a cyclic dimer with a second carboxyl group. The geometric parameters of the hydrogen bond are given in Table 2. The first-level hydrogen-bond graph (Bernstein *et al.*, 1995) is a chain with descriptor $C(7)$, and there are no higher-level graphs. The chain propagates along the b direction, as illustrated in Fig. 2, and links molecules of a single space-group symmetry type. Thus, there are four sets of chains in the structure and each propagates along **b**. Interconnections between these sets of chains are made by C—H···O interactions, the four leading ones being specified in Table 2.



(I)

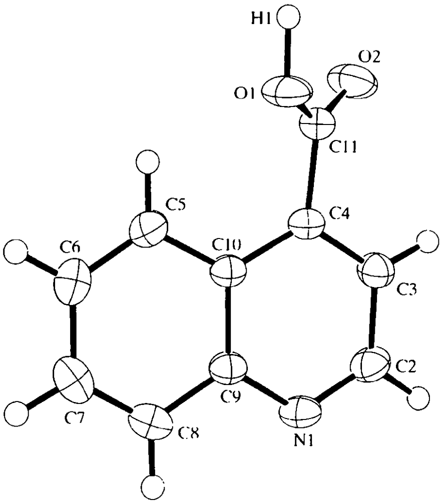


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H, which are shown as small spheres of an arbitrary radius.

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 0.014 (1) and 0.009 (1) Å, respectively. Since the dihedral angle between the planes of these rings is only 2.1 (1)°, the quinoline core as a whole is nearly planar: the maximum deviation of a core atom from the best-fit core plane is 0.029 (1) Å. The di-

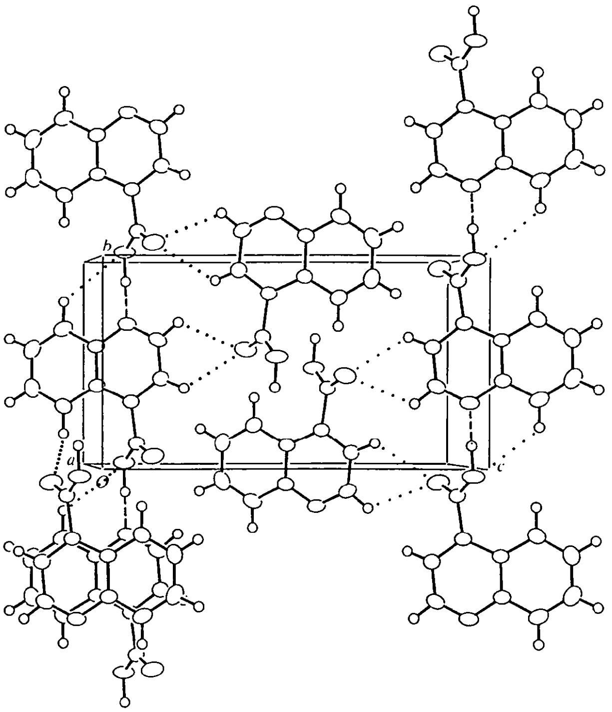


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 50% probability for all atoms except H, which are shown as small spheres of an arbitrary radius. Hydrogen bonds are shown as dashed lines and C—H···O interactions as dotted lines.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998

hedral angle between the core plane and the plane of the carboxyl group is 45.9 (1)°. The dihedral angle between the quinoline core planes not required to be parallel by symmetry is 14.6 (1)°. Hence, the core planes of all the molecules are either strictly or approximately parallel, as is apparent in Fig. 2.

Numerous comparisons with the structure of (I) are afforded by the structure of the closely related molecule, 2-phenylquinoline-4-carboxylic acid (hereafter, PQ4CA) (Blackburn *et al.*, 1996). As does (I), PQ4CA has a single hydrogen bond, and it is also an O—H···N bond rather than a cyclic dimer. The quinoline core of PQ4CA is comparably planar to that of (I), the maximum deviation of a core atom from its best-fit core plane being 0.040 (3) Å. The dihedral angle between the core plane and the plane of the carboxyl group in PQ4CA, 53.6 (1)°, is also quite similar to that given above for (I). Moreover, corresponding individual (non-H) bond lengths and angles for the core and the carboxyl group in PQ4CA and (I) are in generally excellent agreement. The greatest differences between bonds involve C2, the ring atom which is phenyl-substituted going from (I) to QP4CA, and are 0.015 and 0.016 Å; the average difference for the remaining twelve bonds is less than 0.004 Å. The maximum difference in 19 corresponding angles is 1.4°, while the average difference is less than 0.7°. Thus, apart from alteration of the molecular packing, the introduction of the phenyl group has almost no effect on structural parameters in this case.

Intramolecular distances and angles of (I) which are of particular interest are given in Table 1. All distances and angles fall within normal limits.

Given that the hydrogen bond as described above occurs in (I), there are close approaches between H1 of the donor molecule and C2, C8 and C9 of the acceptor molecule which are dictated by the molecular geometry. Otherwise, the closest intermolecular approaches are between H3 and O2^{ii} [(ii) = $-x, \frac{1}{2}+y, \frac{1}{2}-z$], which occur in one of the tabulated C—H···O interactions, and which fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.06 Å. No other approach falls short of its corresponding Bondi sum.

Experimental

Quinoline-4-carboxylic acid was obtained from the Aldrich Chemical Company as a tan powder of 97% stated purity. It was dissolved in water as received, and the solution was filtered. Evaporation at room temperature produced the anhydrous phase reported here as pale amber multifaceted columns. One of these was cut to provide the experimental sample.

Crystal data

$C_{10}H_7NO_2$
$M_r = 173.17$
Monoclinic
$P2_1/c$
$a = 7.6299$ (8) Å
$b = 7.5234$ (9) Å
$c = 13.6917$ (8) Å
$\beta = 93.280$ (7)°
$V = 784.7$ (1) Å^3
$Z = 4$
$D_x = 1.466$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.2$–17.3°
$\mu = 0.097$ mm^{-1}
$T = 296$ K
Column
0.38 × 0.35 × 0.31 mm
Pale amber

Data collection

AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2086 measured reflections
1804 independent reflections
1384 reflections with $I > 2\sigma(I)$
$R_{int} = 0.007$
$\theta_{max} = 27.56°$

$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 17$
6 standard reflections every 150 reflections intensity variation: ±1.2% (average maximum relative intensity)

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.085$
$S = 1.86$
1804 reflections
147 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 1.3 (3) × 10^{-6}
Scattering factors from Stewart *et al.* (1965) for H and Creagh & McAuley (1992) for C, N, O

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

O1—C11	1.306 (2)	N1—C2	1.312 (2)
O2—C11	1.205 (1)	N1—C9	1.370 (1)
O1—C11—O2	125.3 (1)	O2—C11—C4	121.3 (1)
O1—C11—C4	113.3 (1)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1^i	1.08 (2)	1.52 (2)	2.596 (1)	174 (2)
C3—H3···O2^{ii}	0.95 (1)	2.64 (1)	3.314 (2)	128 (1)
C5—H5···O2^{iii}	0.99 (1)	2.74 (1)	3.528 (2)	137 (1)
C2—H2···O2^{ii}	0.97 (1)	2.76 (1)	3.357 (2)	120 (1)
C8—H8···O1^{iv}	0.97 (1)	2.82 (1)	3.496 (2)	127 (1)

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

H-atom positions were assigned from a difference Fourier map and were refined isotropically; C—H distances range from 0.95 (1) to 0.99 (1) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/FC 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*.

We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1498). Services for accessing these data are described at the back of the journal.

References

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

Blackburn, A. C., Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 409–411.

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

Burd, C. J., Dobson, A. J. & Gerkin, R. E. (1997). *Acta Cryst.* C**53**, 602–605.

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

Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 1512–1514.

Dobson, A. J. & Gerkin, R. E. (1997). *Acta Cryst.* C**53**, 1427–1429.

Dobson, A. J. & Gerkin, R. E. (1998). *Acta Cryst.* C**54**, 253–256.

Johnson, C. K. (1976). *ORTEP*II. 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 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

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

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1998). C**54**, 1885–1887

1-(*o*-Tolylmethyl)naphthalene-2-carboxylic Acid

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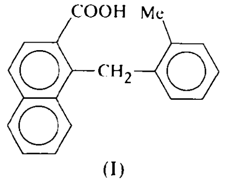
(*Received 20 March 1998; accepted 7 July 1998*)

Abstract

The title acid, $C_{19}H_{16}O_2$, crystallized in space group $P\bar{1}$. In this structure, a hydrogen bond of the 'cyclic dimer' type is formed about a center of symmetry. The $O_{donor}\cdots O_{acceptor}$ distance is 2.647 (1) Å. The carboxylic H and O atoms are ordered. The dihedral angle between the best-fit naphthalene plane and the carboxylic acid group plane is 11.1 (2)°.

Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids. 1-(*o*-Tolylmethyl)naphthalene-2-carboxylic acid, (I), crystallized in space group $P\bar{1}$. The refined molecule is shown in Fig. 1, which also presents the numbering scheme. The single type of hydrogen bond forms a cyclic dimer about a center of symmetry, as shown in Fig. 2. Geometric details of the hydrogen bond are given in Table 1. The first-level graph-set descriptor (Bernstein *et al.*, 1995) is $R^2_2(8)$ and there are no higher-level graph sets.



(I)

The ten C atoms of the naphthalene core and the six C atoms of the benzene ring lie very nearly in planes, the maximum deviations of an atom from the best-fit planes through them being 0.016 (1) and 0.003 (1) Å, respectively, while the average deviations are 0.010 (4) and 0.002 (1) Å, respectively. The dihedral angle between the naphthalene plane and the benzene plane is 79.76 (5)°. The dihedral angle between the naphthalene plane and the plane of the carboxy group is 11.1 (2)°; this value may be compared with that of 1.4 (5)° for naphthalene-2-carboxylic acid (Fitzgerald & Gerkin, 1993).

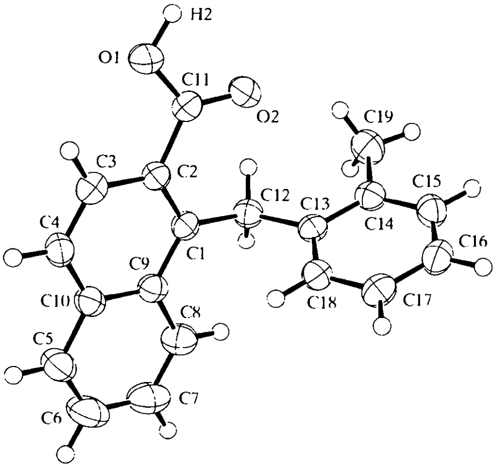


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of 1-(*o*-tolylmethyl)-naphthalene-2-carboxylic acid, showing the molecular numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

Distances and angles of special interest are given in Table 1. All intramolecular distances and angles fall within normal ranges. Whereas in naphthalene-2-carboxylic acid, the carboxylic H atom is disordered to