C6—C7	1.518 (9)	C9a—C5a	1.500 (8)
C6′—C7	1.601 (11)	C9a′—C5a′	1.511 (10)
O5—C5a—C6	103.1 (5)	C8—C9—C9a	111.7 (5)
O5—C5a′—C6′	100.5 (6)	C8′—C9′—C9a′	112.4 (7)
C5a—C6—C7	107.8 (6)	C9—C9a—C5a	110.8 (5)
C5a′—C6′—C7	107.5 (7)	C9′—C9a′—C5a′	116.3 (6)
C6—C7—C8	108.1 (4)	C9a—C5a—C6	111.4 (5)
C6′—C7—C8′	108.6 (5)	C9a′—C5a′—C6′	114.2 (6)
C7—C8—C9	107.5 (5)	C10—C9a—C9	127.9 (6)
C7—C8′—C9′	109.2 (6)	C10—C9a′—C9′	121.1 (7)

The occupancy factors for the two enantiomers were determined by refining the occupancies of the non-overlapping atoms. The orientations of the methyl groups were refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997*a*). All H atoms were riding.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *TEXSAN* and *SHELXL*97. Molecular graphics: *ORTEP* (Johnson, 1965) and *PLATON* (Spek, 1990). Software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON*.

DHH gratefully acknowledges financial support from the American Heart Association, the Kansas Affiliate scheme (KS-96-GS-69), BioServe Space Technologies (grant NAGW-1197), and a Special Group Incentive Research Award from Kansas State University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1082). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1190–1192

2-(Isopropylthio)benzoic acid

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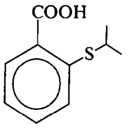
(Received 15 March 1999; accepted 20 April 1999)

Abstract

The title acid, $C_{10}H_{12}O_2S$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. There is a single hydrogen bond, in which the O and H atoms are ordered and $O_D\cdots O_A$ is 2.658 (2) Å. The hydrogen bond forms a cyclic dimer, with graph-set descriptor $R_2^2(8)$, about a center of symmetry. The dihedral angle between the best-fit planes of the benzene ring and the carboxyl group is 13.6 (1)°.

Comment

This study of the title acid, (I), is one of a series of studies of hydrogen bonding in aromatic carboxylic acids. Our previous studies of substituted benzoic acids include *ortho*-(1-naphthoyl)benzoic acid and 3-[2-(1,3-dioxolan-2-yl)ethyl]-2-methylbenzoic acid (Gerkin, 1998, 1999). (I) crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The refined molecule, with our numbering scheme, is shown in Fig. 1. In the single hydrogen bond, O1—H1$\cdots$O2$(1-x,\ 1-y,\ 2-z)$, the O and H atoms are ordered, with O—H = 0.88 (2), H$\cdots$O = 1.78 (2), $O_D\cdots O_A$ = 2.658 (2) Å, and with O—H$\cdots$O = 177 (2)°. This bond forms a cyclic dimer about a center of symmetry as shown in the packing diagram, Fig. 2. The first-level graph (Bernstein *et al.*, 1995) for the hydrogen bond is thus a ring, with descriptor $R_2^2(8)$, and there are no higher-level graphs. A single noteworthy intermolecular C—H$\cdots$O interaction, C5—H5$\cdots$O1^{ii}$(1-x,\ -\frac{1}{2}+y,\ \frac{5}{2}+z)$, occurs, for which H$\cdots$O = 2.69 (2), C$\cdots$O = 3.646 (3) Å and C—H$\cdots$O = 169 (2)°. This forms a first-level chain, with descriptor $C(6)$, which propagates along [010].



(I)

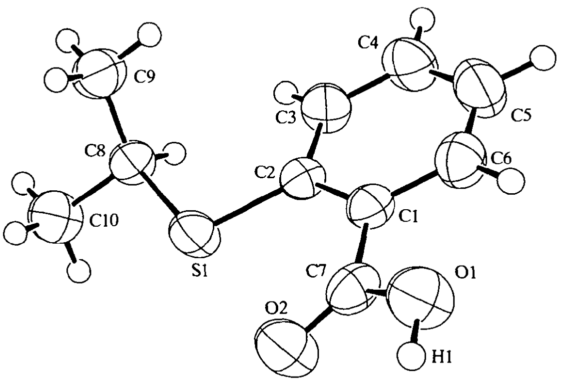


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms.

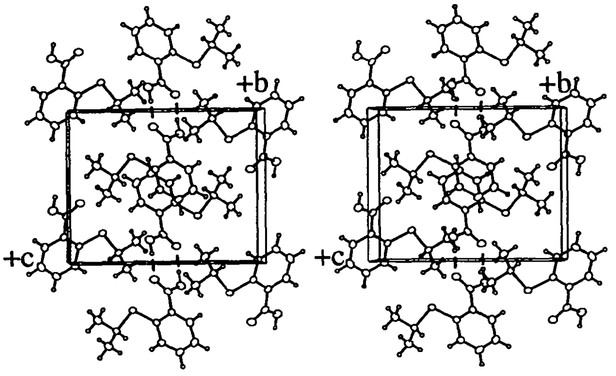


Fig. 2. *ORTEP*II (Johnson, 1976) packing stereodiagram of (I) viewed down the *a* axis. Displacement ellipsoids are drawn for 20% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. Hydrogen bonds are depicted by single dashes.

The benzene core of (I) is nearly planar, the maximum deviation of any of its atoms from the best-fit plane describing them being 0.004 (2), while the average deviation is 0.002 (2) Å. The dihedral angle between the best-fit core plane and the carboxyl group plane is 13.6 (1)°.

Selected bond distances and angles are given in Table 1. The C—O distances are consistent with an ordered carboxylic-H atom. All distances and angles fall within normal ranges. In particular, the S1—C2 distance in (I) [1.767 (2) Å] compares well with the Allen *et al.* (1987) tabulated mean value [1.773 (9) Å] for a C_{aryl}—S bond when S is bonded to a second C atom, here C8, having sp^3 hybridization. Also, the S1—C8 distance in (I) [1.824 (2) Å], compares well with the tabulated mean value for S—Csp^3 when a second C atom is bonded to S [1.819 (11) Å]. The closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups or in the C—H···O interaction cited above, are not as much as 1 s.u. less than the corresponding Bondi (1964) van der Waals radius sums.

Experimental

The title compound was obtained as off-white, somewhat coarse crystals from the chemical collection of Dr D. J. Hart. Evaporation of a solution of them in ether at room temperature produced colorless columns, one of which was cut to provide the experimental sample. A synthesis of (I) is described by Gilman & Webb (1949).

Crystal data

$C_{10}H_{12}O_2S$
$M_r = 196.26$
Monoclinic
$P2_1/c$
$a = 8.376$ (1) Å
$b = 9.7236$ (9) Å
$c = 12.325$ (1) Å
$\beta = 96.90$ (1)°
$V = 996.5$ (2) Å^3
$Z = 4$
$D_x = 1.308$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.2$–17.3°
$\mu = 0.29$ mm^{-1}
$T = 296$ K
Cut column
0.31 × 0.27 × 0.23 mm
Colorless

Data collection

AFC-5*S* diffractometer
ω scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.909$, $T_{max} = 0.935$
2609 measured reflections
2309 independent reflections

1548 reflections with $I > 2\sigma I$
$R_{int} = 0.019$
$\theta_{max} = 27.56$°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 15$
6 standard reflections every 150 reflections intensity decay: 1.29%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.068$
$S = 1.66$
2309 reflections
167 parameters
All H-atom parameters refined
$w = 1/[\sigma^2_{cs} + (0.008I)^2]$
$(\Delta/\sigma)_{max} = 0.0002$

$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 2.8 (1) × 10^{-6}
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O, S)

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

S1—C2	1.767 (2)	O1—C7	1.319 (2)
S1—C8	1.824 (2)	O2—C7	1.218 (2)
C2—S1—C8	104.93 (9)	O1—C7—O2	121.9 (2)
C2—C1—C7	122.1 (2)	O1—C7—C1	114.3 (2)
C6—C1—C7	118.4 (2)	O2—C7—C1	123.8 (2)
S1—C2—C1	121.3 (1)	S1—C8—C9	112.6 (2)
S1—C2—C3	121.3 (1)	S1—C8—C10	105.8 (2)

Refined C—H distances ranged from 0.92 (2) to 1.00 (2), with a mean value 0.97 (3) Å. The refined O1—H1 distance is 0.88 (2) Å.

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).

I acknowledge with pleasure the provision of the sample by Dr D. J. Hart and my use of the departmental X-ray crystallographic facility, which is supervised by staff crystallographer Dr J. C. Gallucci. The diffractometer system was purchased with funds provided in part by an NIH grant.

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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Acta Cryst. (1999). C**55**, 1192–1195

Hydrogen bonding in quinolinium-4-carboxylate trihydrate

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(*Received 8 March 1999; accepted 31 March 1999*)

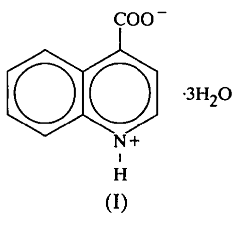
Abstract

The previously undescribed title substance, $C_{10}H_7NO_2\cdot 3H_2O$, 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)